Ruthenium-Catalyzed Reactions for Organic Synthesis

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Contents

I. Introduction

Metal-catalyzed reactions have made a great contribution to the recent growth of organic synthesis, and a variety of synthetic methods have been reported using mainly group 8 transition metal complexes in stoichiometric or catalytic amounts.[1] In particular, useful transformations bearing high chemo- and stereoselectivities have been discovered in the field of palladium chemistry.[2] Since ruthenium has $4d^75s^1$ electron configuration, it has the widest scope of oxidation states (from -2 valent in $Ru(CO)_4^{2-}$ to octavalent in RuO_4) of all elements of the periodic table,[3] and various coordination geometries in each electron configuration, which is in contrast to the narrow scope of oxidation states and simple square planar structure of palladium. For instance, in the principal lower oxidation states of 0, II, and III, ruthenium complexes normally prefer trigonal-bipyramidal and octahedral structures, respectively.[3c] Such a variety of ruthenium complexes has great potential for the exploitation of novel catalytic reactions and synthetic methods; however, as a consequence of the difficulties of matching the catalysts and substrates, ruthenium chemistry has lagged behind that of palladium by almost a quarter century. Indeed, until 1980s the reported useful synthetic methods using ruthenium reagents and catalysts were limited to a few reactions which include oxidations with RuO_4,[4] hydrogenation reactions,[5,6] and hydrogen transfer reactions.[6] As the coordination chemistry of ruthenium complexes has progressed, specific characters of ruthenium, in comparison with palladium have been made clear.

A great variety of ruthenium complexes have been prepared. The methods for preparation of representative ruthenium complexes are shown in Scheme 1. These can be roughly divided into five groups according to their supporting ligands:[3a,7] oxo, carbonyl, tertiary phosphines, cyclopentadienyl, and arenes and dienes. These ligands have proven to serve effectively as the activating factors such as in hydrogen abstraction, generation of coordinatively unsaturated species by the liberation of ligands, and stabilization of reactive intermediates. It has been understood that the precise control of coordination sites and redox sequences of the intermediacies are especially important in the case of ruthenium to design specific organic transformations, and also that ruthenium complexes have a variety of useful characteristics

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Takeshi Naota received his bachelor's degree in 1980, master's degree in 1982, and Ph.D. degree in 1988 from Osaka University. His Ph.D. studies on the development of catalytic reactions promoted by ruthenium complexes were carried out under the direction of Professor Shun-Ichi Murahashi. He joined Osaka University, Faculty of Engineering Science, as a research associate in 1983, and was promoted to associate professor of Graduate School of Engineering Science at the same university in 1995. From 1990 to 1991, he did postdoctoral work with Professor Barry M. Trost at Stanford University. He received the Chemical Society of Japan Award for Young Chemists in 1991. His current research concerns the studies on synthesis, structure, and reactivities of organometallic compounds bearing catalytic activities for various modes of carbon–carbon bond formations.

Hikaru Takaya was born in Alabama in 1969. He completed his undergraduate study and graduate study for his master's degree at Osaka University in 1993 and 1995, respectively. His Ph.D. studies on the development of catalytic reactions promoted by transition metal complexes were carried out under the direction of Professor Shun-Ichi Murahashi. He joined Osaka University, Faculty of Engineering Science, as a research associate in 1998. His research activity is focused on the development of transition metal-catalyzed carbon–carbon bond formation.

Shun-Ichi Murahashi received his bachelor's degree in 1961 and master's degree in 1963 at Osaka University, and immediately was appointed as Assistant Professor in the laboratory of the late Professor I. Moritani at the same university. He received his Ph.D. degree in 1967 under the guidance of Professor I. Moritani. Dr. Murahashi spent postdoctoral years with Professor R. Breslow at Columbia University in 1968–1970. He was promoted to associate professor in 1972 and full professor in 1979. His research interests have been mainly in the exploitation of new synthetic methodologies, particularly in the application of organometallic chemistry directed toward organic synthsis. He has discovered many practical catalytic reactions for organic synthesis. Other research interests include the relationship between structure and reactivity of reactive intermediates such as carbenes. He received the Chemical Society of Japan Award in 1995, and was the Editor in Chief of *Chemistry Letters* from 1995 to 1998.

including high electron transfer ability, high Lewis acidity, low redox potentials, and stabilities of reactive metallic species such as oxometals, metallacycles, and metal carbene complexes. Thus, a large number of novel, useful reactions have begun to be developed using both stoichiometric and catalytic amounts of ruthenium complexes.

$RuCl_3 \cdot nH_2O$ is frequently used as starting material for the preparation of most of these ruthenium complexes, and many ruthenium complexes are derived from it under ambient conditions. In addition to the higher economy of ruthenium compared to the other group 8 transition metals such as rhodium and palladium, there is a larger availability of reactive ruthenium complexes which have proven to serve as highly efficient reagents and catalysts for a variety of organic transformations. The great influence of ruthenium chemistry on organic synthesis in recent years has now elevated its importance to the same level as palladium. In this article, organic syntheses promoted by ruthenium catalysts are reviewed with an emphasis on recent progress. Although several organic reactions using ruthenium catalysts have been reviewed separately,[4,6a,22−34] comprehensive reviews of this field are rare.[35] The present article surveys a range of fields of organic syntheses which involve reduction, oxidation, isomerization, carbon−carbon bond formation, and miscellaneous nucleophilic and electrophilic reactions.

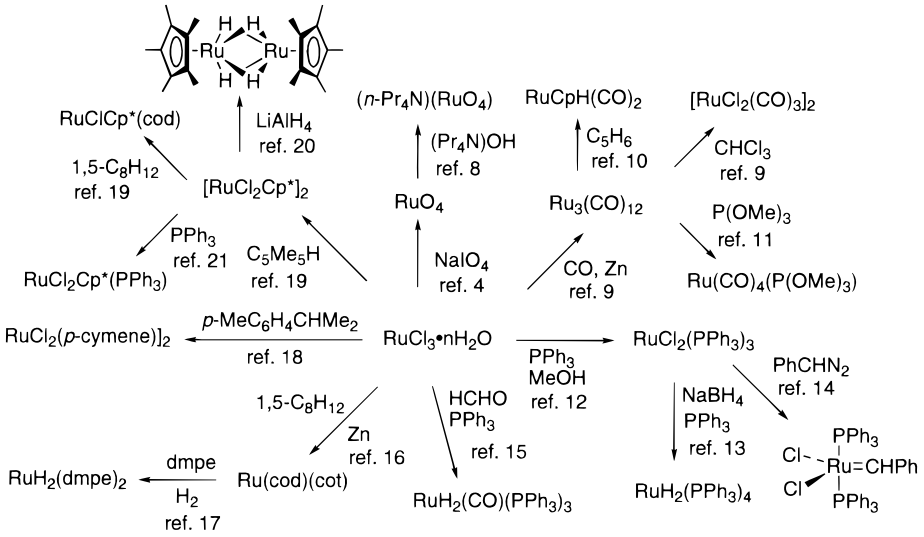
II. Hydrogenation

A. Hydrogenation with Molecular Hydrogen

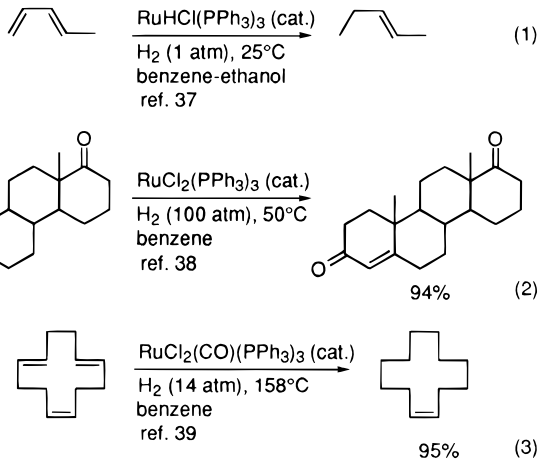
a. Chemoselective Hydrogenations

A number of homogeneous and heterogeneous ruthenium complexes catalyze hydrogenation of various substrates including functionalized olefins, aldehydes, ketones, other carbonyl compounds, and nitro compounds.[5,6] Compared to other metal complexes of rhodium, iridium, and cobalt, ruthenium complexes generally have less effective catalytic activities for hydrogenation of simple and functionalized alkenes.[36] Mild reactivities of ruthenium complex are often used for chemoselective hydrogenation of polyolefins. Terminal conjugated dienes[37] and 3-oxo-1,4-diene steroidal compounds[38] undergo selective hydrogenation with $RuHCl(PPh_3)_3$ and $RuCl_2$-

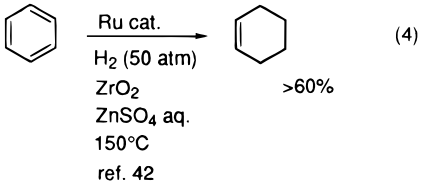
Scheme 1



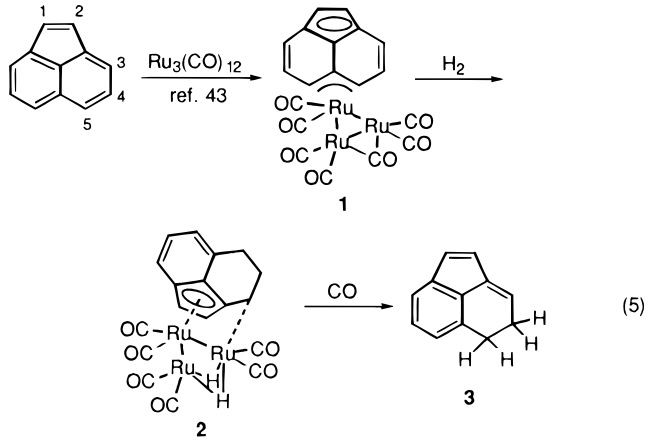
$(PPh_3)_3$ catalysts, respectively (eqs 1 and 2). Selective hydrogenation of cyclic trienes to the corresponding cyclic monoolefins have been studied using $RuCl_2(CO)(PPh_3)_3$ (eq 3),[39] $RuCl_2(PPh_3)_3$,[40] and Ru(cod)(cot)[41] catalysts.



Regioselective hydrogenation of aromatic hydrocarbons are of importance not only from industrial viewpoints but also as a potential route to a variety of fused ring systems. Conversion of benzene to cyclohexene by partial catalytic hydrogenation is of special importance from industrial aspect, since the method provides a new industrial route to cyclohexanol, an important precursor of nylons, by combination with hydration of cyclohexene. Asahi Chemical Co., Japan, developed the selective bilayer catalytic system including ruthenium metal catalyst, ZrO_2, and $ZnSO_4$ under 50 atm of H_2 pressure (eq 4). The

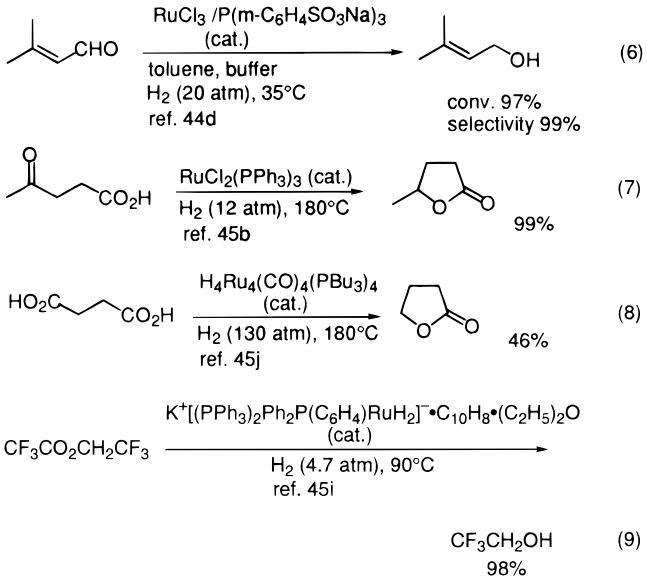


process affords the olefin with up to 60% selectivity after 90% conversion of benzene, and presently it produces 50 000 tons per year of the olefin, which are converted into 60 000 tons per year of cyclohexanol.[42] Selective hydrogenation of polycyclic aromatic compounds can be performed by multimetallic coordination of aromatic compounds to ruthenium clusters.[43] Triruthenium carbonyl cluster **1** bearing acenaphthylene as a face ligand, which was readily prepared by the reaction of acenaphthylene with $Ru_3(CO)_{12}$, was hydrogenated to give complex **2**. Treatment of **2** with CO gives 4,5-dihydroacenaphthylene (**3**) selectively (eq 5). This is quite rare regioselectivity,

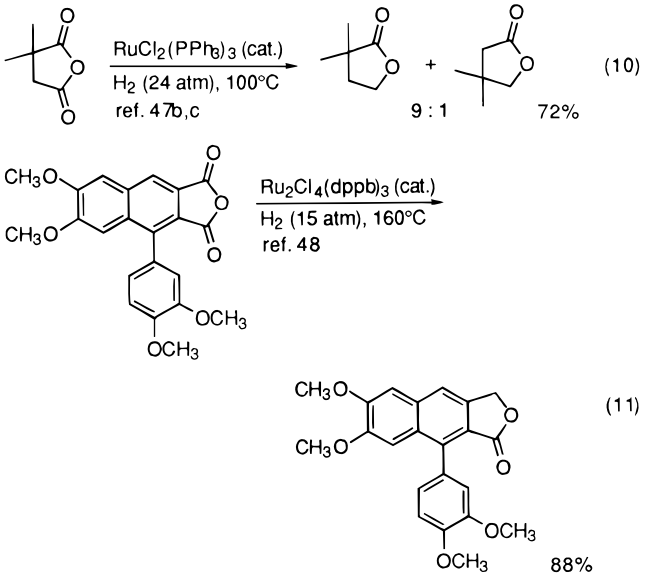


since usual hydrogenation of acenaphthylene reduces at 1,2-position and the alkali metal reduction affords 1,5-dihydroacenaphthylene.

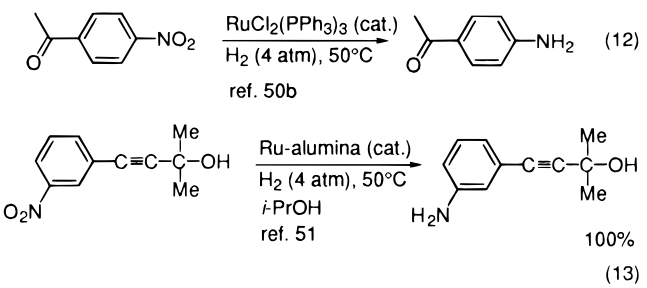
Due to the strong affinity of ruthenium toward heteroatom compounds, low-valent ruthenium complexes act as efficient catalysts for reduction of a variety of carbonyl compounds. Aldehydes,[44] ketones,[45] carboxylic acids,[45i,j] esters,[45i,46] and carboxylic anhydrides[45j,47] can be converted into the corresponding alcohols with various ruthenium complexes under hydrogen pressure (eqs 6−9). Unsymmetrical carboxylic anhydrides bearing bulky substituents are reduced with high chemoselectivity at the less hindered position (eq 10).[47b,c] The reaction can be

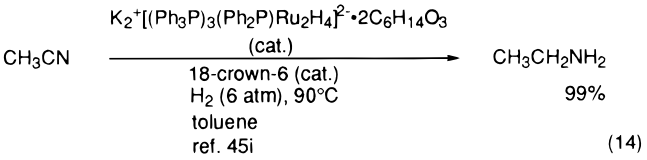


applied to the regioselective synthesis of arylnaphthalene ligands (eq 11).[48]



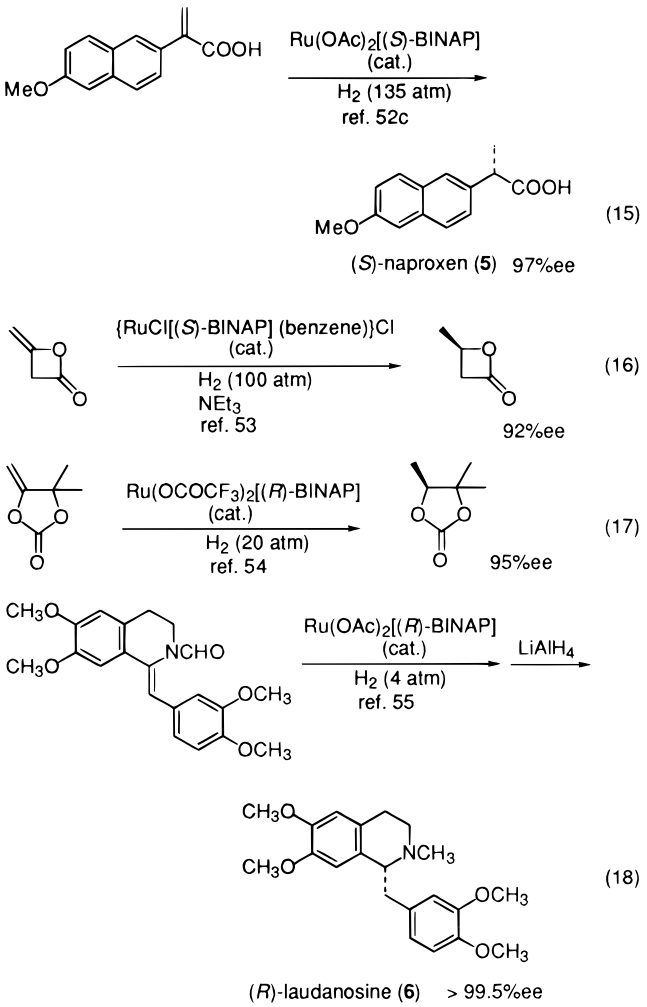
The reduction of nitro compounds to the corresponding amines is also of considerable importance from industrial viewpoints. Aliphatic[49] and aromatic[50] nitro compounds can be converted efficiently into the corresponding primary amines under H_2 pressure with ruthenium catalyst. Selective hydrogenation of aromatic nitro compounds can be performed in the presence of carbonyl[50b] and acetylene moieties[51] by using $RuCl_2(PPh_3)_3$ and Ru-alumina catalysts, respectively (eqs 12 and 13). Nitriles are reduced with ionic ruthenium hydride complex catalyst $K^+[(Ph_3P)_2Ph_2P(C_6H_4)RuH_2]^-\cdot C_{10}H_8\cdot(C_2H_5)_2O$ or $K_2^+[(Ph_3P)_3(Ph_2P)Ru_2H_4]^{2-}\cdot 2C_6H_{14}O_3$ to afford the corresponding primary amines with 99% selectivity (eq 14).[45i]





b. Enantioselective Hydrogenations

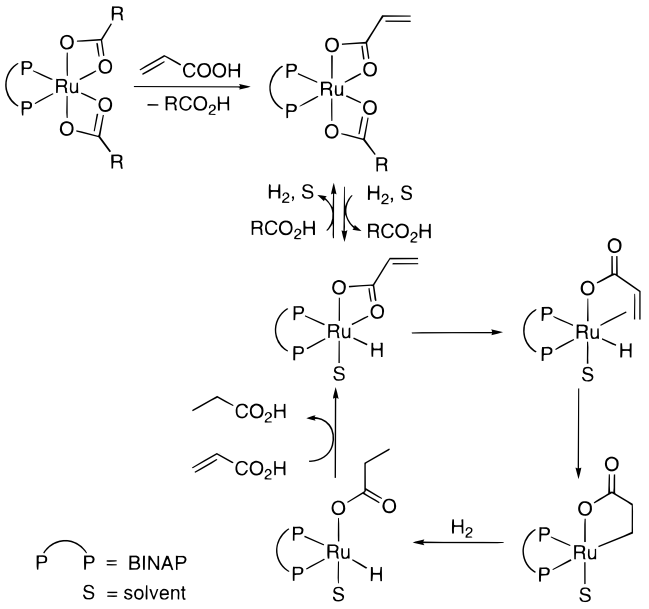
Great progress has been made on the asymmetric hydrogenations with homogeneous ruthenium complexes bearing chiral phosphine ligands. Comprehensive reviews[22] of this field are available for further exploration. By using ruthenium binaphthyl diphosphine complex bearing axial chirality [BINAP (**4**)], practical asymmetric hydrogenations have been performed from a variety of prochiral olefin substrates such as α,β-unsaturated carboxylic acids (eq 15),[52] diketene (eq 16),[53] carbonates (eq 17),[54] enamides (eq 18),[55] and allyl alcohols.[56] The reaction provides a



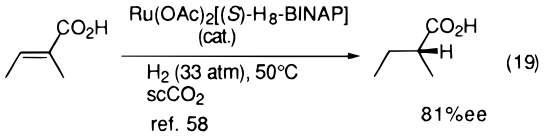
practical method for enantioselective synthesis of the biological antiinflammatory compounds, naproxen (**5**) and isoquinoline alkaloid family such as (*R*)-laudanosine (**6**).

As a result of careful study of the deuteriation of (*E*)-$CH_3CH{=}C(CH_3)CO_2H$, it was found that the deuterium at the α-position was derived from molecular deuterium, while that at the *β*-position is coming from MeOD solvent.[57] As the hydrogen pressure was increased, more of the added atom at the *β*-position was derived from molecular deuterium. These facts strongly suggest a monohydride mechanism. The proposed mechanism for the hydrogenation of α,*β*-unsaturated acids is shown in Scheme 2.

Scheme 2

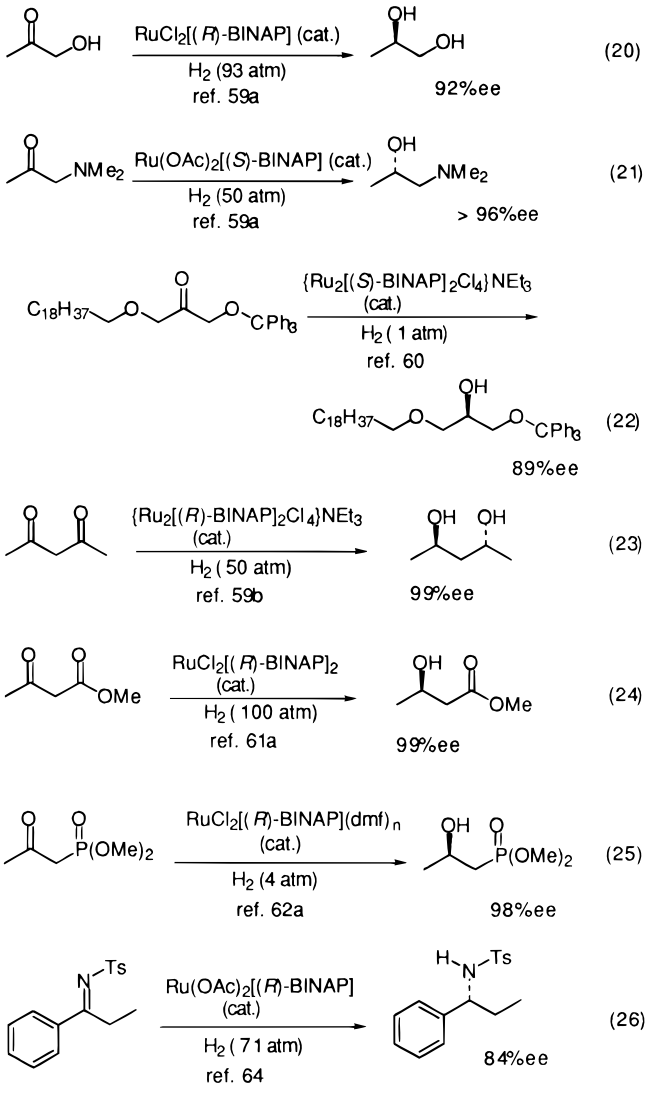


The use of supercritical CO_2 as reaction media is of importance because of its nontoxicity, nonflammability, and low cost. The BINAP-Ru-catalyzed asymmetric hydrogenation reaction of α,*β*-unsaturated carboxylic acids can be performed practically in supercritical CO_2. The enantioselectivity of the hydrogenation of tiglic acid (81% ee) is comparable with those performed in organic solvents such as methanol (82% ee) and hexane (73% ee) (eq 19).[58]

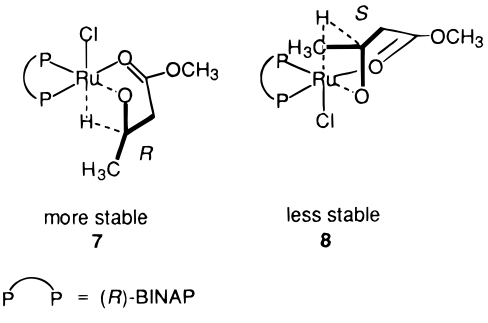


A wide range of functionalized ketones can be reduced with high enantioselectivities by using ruthenium BINAP catalysts. *β*-Hydroxy (eq 20),[59a,b] *β*-amino (eq 21),[59b] and *β*-alkoxy ketones (eq 22),[60] 1,3-diketones (eq 23),[59] *β*-keto esters (eq 24),[61] *β*-keto phosphonates (eq 25),[62] and phenylthio ketones[63] can be converted into the corresponding functionalized hydroxy compounds under similar conditions with high enantioselectivities. *N*-Tosylimines can be also reduced enantioselectively with Ru-BINAP catalyst to afford the corresponding *N*-tosylamines (eq 26).[64]

High enantioselectivities in the hydrogenation of *β*-keto esters with RuHCl[(*R*)-BINAP] catalyst can be rationalized by assuming the transition states **7** and **8**, where a *β*-keto ester acts as a bidentate *σ*-donor ligand (Scheme 3). The characteristic chiral feature of the BINAP ligand makes the difference in energetically favorableness between **7** and **8**.

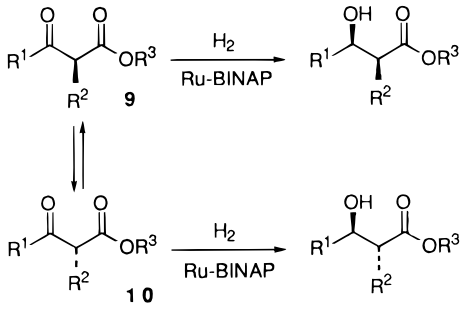


Scheme 3

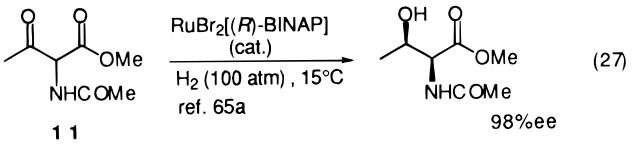


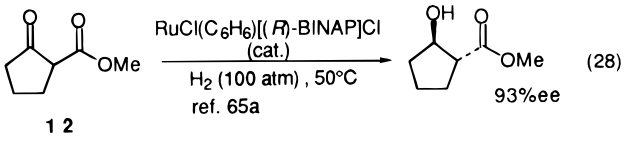
When racemic 2-substituted *β*-keto esters are employed as substrates, there exists the opportunity for dynamic kinetic resolution, if their equilibration is faster than hydrogenation (Scheme 4). Indeed, hydrogenation of equilibration system **9** and **10** with the Ru-BINAP catalyst proceeds with highly enantio- and diastereoselectivities.[65] Syn-optically active hydroxy esters can be obtained from the corresponding acyclic keto esters such as **11**, while *anti*-products

Scheme 4



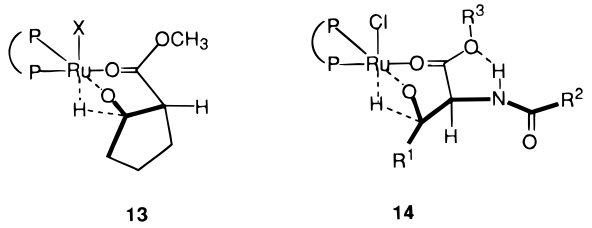
are formed by the reduction of cyclic ones such as **12** (eqs 27 and 28). The remarkable high antiselection



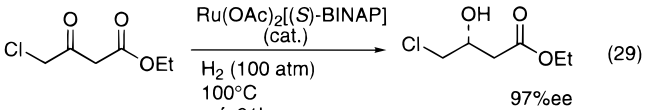


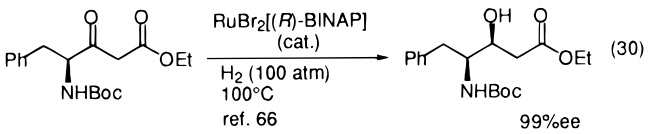
observed with **12** is rationalized in terms of the sterically constrained tricyclic transition state **13**, while syn selection directed by amide substrate **11** is arising from **14**, which is stabilized by hydrogen bonding between CONH and the ester OR (Scheme 5). This method provides a useful synthesis of

Scheme 5



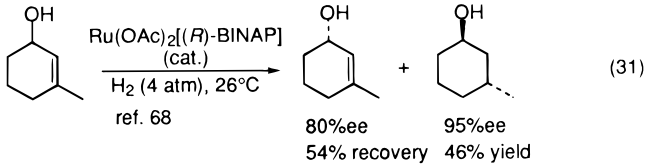
L-threonine from methyl 2-acetamido-3-oxobutanoate.[65a] Similar resolution can be observed in the reduction of 4-substituted β-keto esters such as 4-chloro[61b,h] and 4-carbamoyl ones (eqs 29 and 30).[66]



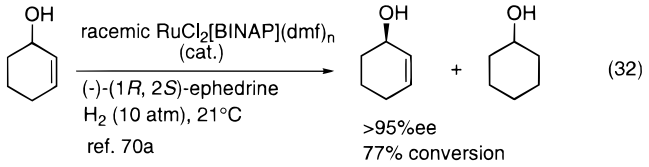


Kinetic resolution of chiral substrates with excellent enantiomer recognition can be achieved, when a combination of substrates and catalyst is matching properly. A mathematical treatment of the reaction has been described and applied to a range of case studies.[67]

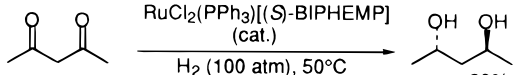
Racemic secondary alcohols can be also converted into the corresponding saturated alcohols enantioselectively along with unreacted optically active starting material.[68] When racemic 3-methyl-2-cyclohexenol is hydrogenated by using (*S*)-BINAP-Ru catalyst at 4 atm of H_2, *trans*- and *cis*-3-methylcyclohexanols are produced in a 300:1 ratio. The reaction with the (*R*)-BINAP complex affords the saturated (1*R*,3*R*) trans alcohol in 95% ee in 46% yield and unreacted *S* allylic alcohol in 80% ee with 54% recovery (eq 31).

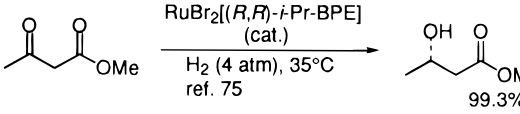


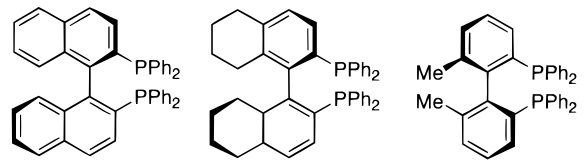
The *S* enantiomer in >99% ee was obtained at 54% conversion. Calculated k_f/k_s ratio for kinetic enantiomer selection[69] is up to 74−76. Similar kinetic resolution of racemic secondary allylic alcohols can be also performed using "chiral poisoning" where one enantiomer of racemic catalyst is deactivated by chiral amines. Using a racemic Ru-BINAP catalyst with (−)-(1*R*,2*S*)-ephedrine as a chiral poison, racemic 2-cyclohexenol is hydrogenated under 10 atm of H_2 to afford the remaining cyclohexanol and (*R*)-2-cyclohexenol in >95% ee after 77% conversion, where k_f/k_s ratio is 6.4 (eq 32).[70]

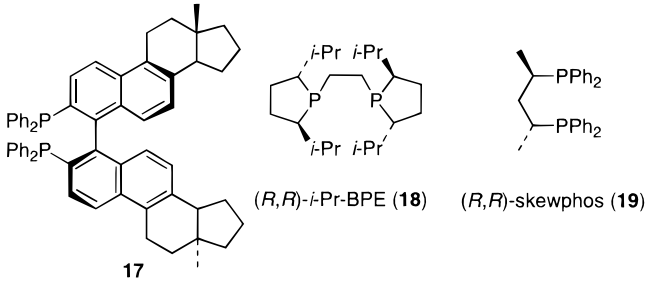


Ruthenium complexes bearing similar optically active diphosphine ligands such as H_8-BINAP (**15**),[71] 2,2′-dimethyl-6,6′-bis(diphenylphosphino)biphenyl (**16**, BIPHEMP),[56c,72,73] and bis-steroidal phosphine (**17**)[74]



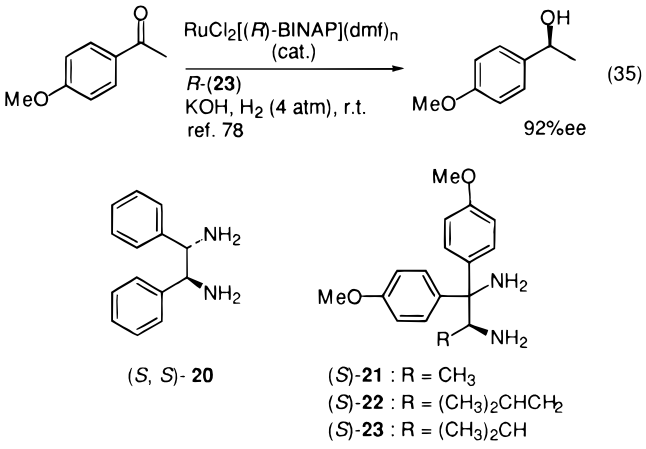




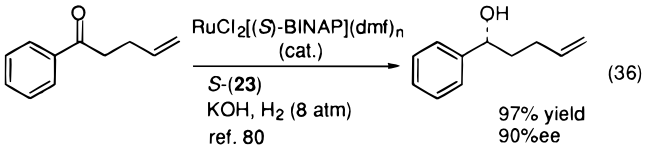


also afford practically high enantioselectivities for the catalytic hydrogenation reactions (eq 33). Electron-rich diphosphine, 1,2-bis(*trans*-2,5-diisopropylphospholano)ethane (**18**, *i*-Pr-BPE) is an effective ligand for the enantioselective hydrogenation of β-keto esters. By using $RuBr_2$[(*R*,*R*)-*i*-Pr-BPE)] catalyst practical enantioselective hydrogenation of β-keto esters can be carried out under milder reaction conditions (H_2 4 atm, 35 °C) (eq 34).[75] Simple optically active diphosphine, 1,3-dimethyl-1,3-bis(diphenylphosphino)propane (**19**, skewphos) is also effective for the hydrogenation of β-keto esters, β-keto phosphates, and phenylthio sulfides.[76]

Even some aromatic ketones can be hydrogenated with high enantioselectivity under the similar reaction conditions.[59a,77] Addition of ethylenediamine and KOH has proven to remarkably enhance the catalytic activity of ruthenium complexes.[78] Typically, in the hydrogenation of acetophenone, turnover frequency (TOF) of $RuCl_2(PPh_3)_3$ alone was less than 5, while the use of these organic and inorganic bases together led to a TOF of 6700. This catalytic system can be also applied to the diastereoselective reduction of 2-, 3-, and 4-substituted cyclohexanone affording the corresponding cis-, trans-, and cis-substituted cyclohexanol, respectively.[79] These findings led to the development of practical method for asymmetric hydrogenation of simple aromatic ketones. A variety of aromatic ketones can be hydrogenated enantioselectively with a combined use of Ru-BINAP catalyst−KOH−chiral 1,2-diamines such as **20**−**23** (eq 35).[78]



The extent of the enantioselectivity appears to be delicately influenced by the structure of the diamine auxiliaries. Use of (*S*)-BINAP and *S* diamine affords the *R*-configurated alcohol products, whereas the *R*−*R* configurational combination gives the *S*-enriched alcohols. The present Ru(II)−1,2-diamine−KOH ternary catalytic system is found to function specifically to the hydrogenation of carbonyl groups not to that of olefins. Normally, catalytic hydrogenation of olefins proceeds much faster than carbonyl compounds. In fact, a competitive reaction of heptanal and 1-octene with $RuCl_2(PPh_3)_3$ catalyst under H_2 pressure reveals that the terminal olefin is saturated 250 times faster than the aldehyde. Addition of $H_2N(CH_2)_2NH_2$ and KOH changes the reactivity drastically leading the reaction of heptanal 1500 times faster than 1-octene. This selective hydrogenation can be applied to chemo- and enantioselective hydrogenation of a variety of conjugated and unconjugated optically active enals and enones when using amines such as **23** as chiral auxiliaries (eq 36).[80]



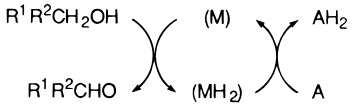
B. Hydrogen Transfer Reaction

Alternative method for hydrogenation of organic substrates is hydrogen transfer reactions from an organic hydrogen source, where the hydrogen is supplied by a donor molecule, DH_2, which itself undergoes dehydrogenation during the course of the reaction (eq 37). The basic concept of the catalytic

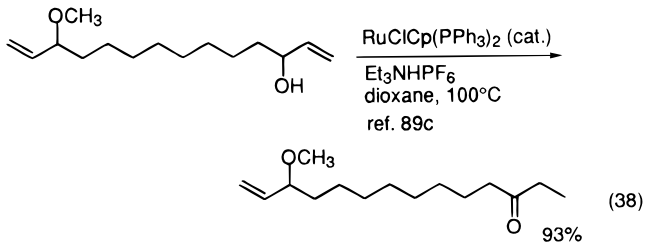
$$A + DH_2 \rightleftharpoons AH_2 + D \qquad (37)$$

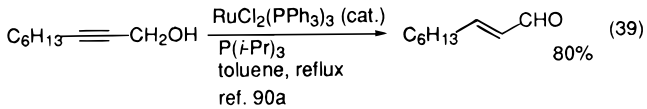
hydrogen transfer reaction from alcohols is shown in Scheme 6. Oxidative addition of alcohols to low-

Scheme 6



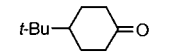
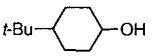
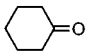
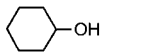
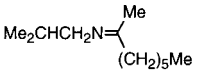
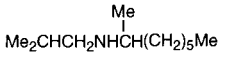
valent metal complexes and the subsequent β-hydrogen elimination gives carbonyl compounds and metal dihydrides. The metal dihydrides react with a hydrogen acceptor (A) to afford hydrogenation products (AH_2) and metal complexes to complete the catalytic cycle.[81] Low-valent ruthenium complexes are excellent catalysts for the hydrogen transfer reactions[6a] because of their low redox potential and higher affinity toward heteroatom compounds. The representative results for the hydrogen transfer reactions are listed in Table 1. A variety of substrates such as olefins,[82] α,β-unsaturated ketones,[83] aldehydes,[84] ketones,[85] imines,[86] quinolines,[87] and halogenated compounds[88] undergo hydrogen transfer from alcohols in the presence of low-valent ruthenium complex catalysts. Unsaturated alcohols such as allyl alcohols[89] and propargyl alcohols[90] undergo intramolecular hydrogen transfer reactions to afford the corresponding saturated and α,β-unsaturated carbonyl compounds, respectively (eqs 38 and 39). Formic acid





acts as an alternative hydrogen donor for hydrogen transfer reaction of α,β-unsaturated carbonyl com-

Table 1. Hydrogen Transfer Reaction

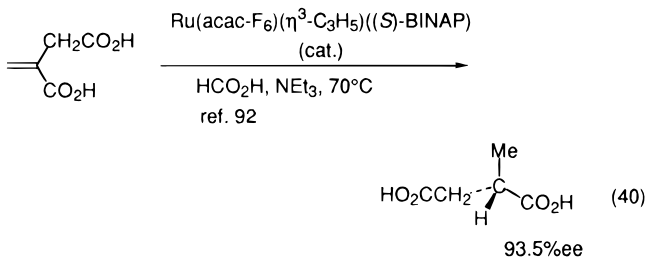
catalyst	hydrogen donor	hydrogen acceptor	T, °C	product	yield,%	ref.
$RuH_2(PPh_3)_4$	Me_2CHOH	cyclohexene	80	cyclohexane	100	82
$RuCl_2(PPh_3)_3$	$PhCH_2OH$	$4\text{-}MeOC_6H_4CH{=}CHCOCH_3$	180	$4\text{-}MeOC_6H_4CH_2CH_2COCH_3$	96	83a,c
$RuCl_2(PPh_3)_3$	MeOH		145		77	85c,d
$RuCl_2(PPh_3)_3$-NaOH	Me_2CHOH		82		89	85e
$Ru_3(CO)_{12}$	Me_2CHOH	PhCH=NPh	82	$PhCH_2NHPh$	80	86a
$RuCl_2(PPh_3)_3$-K_2CO_3	Me_2CHOH		82		54	86b
$RuCl_3$-DDAB-Na_2CO_3	$PhCH_2OH$	CCl_4	80	$CHCl_3$		
				PhCHO	93	88a,b
$RuCl_2(PPh_3)_3$	HCO_2H	$PhCH{=}CHCOCH_3$	97	$PhCH_2CH_2COCH_3$	90	83b
$RuCl_2(PPh_3)_3$	HCO_2Na-H_2O-THAHS	$PhCH{=}CHCOPh$	109	$PhCH_2CH_2COPh$	99	83d
$RuCl_2(PTA)_4$	HCO_2Na-H_2O	PhCHO	80	$PhCH_2OH$	95	84a
$RuHCl(CO)(PPh_3)_3$	HCO_2H	PhCHO	microwave (300 W)	$PhCH_2OCHO$	51	84b
				$PhCH_2OH$	47	
$RuCl_2(PPh_3)_3$	HCO_2H	$PhCOCH_3$	125	$PhCH(OH)CH_3$	54	85b
$RuCl_2(PPh_3)_3$	HCO_2H		180		76	87
	HCO_2H	$PhNO_2$	180	$PhNH_2$	94	87
$RuH_2(PPh_3)_4$		$n\text{-}C_5H_{11}CHO$	140	$n\text{-}C_6H_{13}OH$	10	85a
$RuH_2(PPh_3)_4$		$n\text{-}C_5H_{11}CHO$	140	$n\text{-}C_6H_{13}OH$	29	85a

DDAB = didecyldimethylammonium bromide PTA = 1,3,5-triaza-7-phosphaadamantane
THAHS = tetrahexylammonium hydrogensulfate

pounds,[83] aldehydes,[84] ketones,[85] nitro compounds,[87] and quinolines.[87] The reactions also initiate the formation of ruthenium hydride complex by the reaction of low-valent ruthenium complex with formic acid via elimination of carbon dioxide. Tetrahydrofuran and tetrahydronaphthalene also undergo hydrogen transfer reaction to carbonyl compounds to afford alcohols along with the corresponding aromatic compounds.[85a] The formation of dihydride ruthenium intermediate from hydrocarbon can be explained by the formation of ruthenium dihydride complex via oxidative addition of the C−H bond to ruthenium and subsequent β-hydride elimination.

Asymmetric hydrogen transfer reactions to olefins and ketones are potentially powerful alternatives to asymmetric catalytic hydrogenation with molecular hydrogen because of their simple operations; however, they have remained at a low level of synthetic practical use. Various ruthenium complex catalysts bearing optically active phosphine ligands have been investigated.[91] Recently, it has been found that practically high enantioselectivity can be achieved by using some chiral low-valent ruthenium complex catalysts.

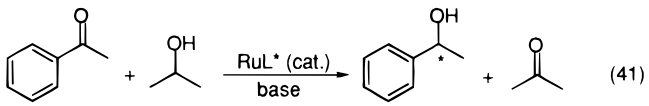
Ru-BINAP complexes serve as efficient catalysts for the asymmetric hydrogen transfer reactions of α,β-unsaturated carboxylic acids with formic acid (eq 40).[92] Combined use of ruthenium complexes with chiral amine ligands are proven to be highly effective



(40)

93.5%ee

for this purpose.[23] Simple aromatic ketones undergo enantioselective hydrogen transfer from 2-propanol (eq 41)[93a,94−101] and formic acid[93b] using a combination

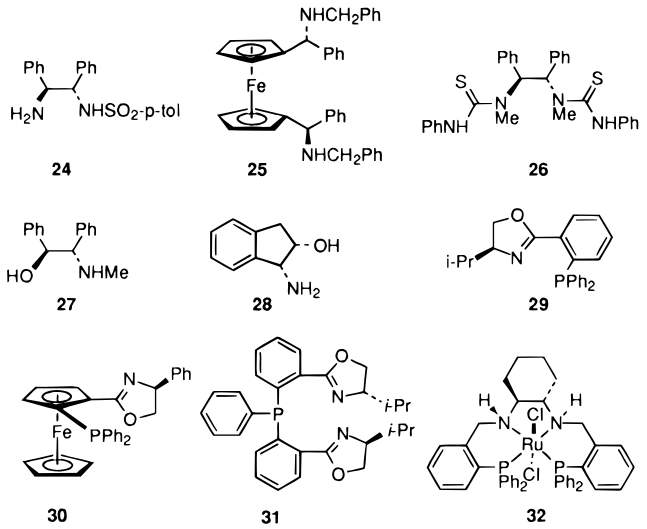


(41)

of divalent ruthenium complex catalysts with chiral ligands such as diamine **24**,[93] **25**,[94] and **26**,[95] amino alcohols **27**[96] and **28**,[97] aminophosphine **29**[98] and **30**,[99] bis(oxazolinyl) phosphine **31**,[100] or using chiral complex **32**.[101] The representative results of enantioselective transfer hydrogenation of acetophenone with 2-propanol are summarized in Table 2.

Similarly, α,β-acetylenic ketones[102] and cyclic α,β-unsaturated ketones[103] can be transformed into the corresponding optically active alcohols with high

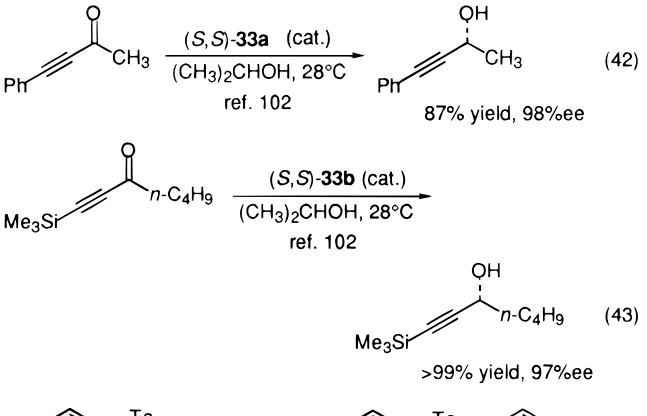
Table 2. Ruthenium-Catalyzed Enantioselective Transfer Hydrogenation of Acetophenone with 2-Propanol



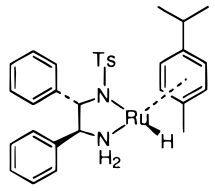
catalyst	ligand	base	conv.,[a] %	ee %	confign.	ref.
$[RuCl_2(mesitylene)]_2$	**24**	KOH	95	97	*S*	93a
$[RuCl_2(p\text{-cymene})]_2$	**25**	KOH	91	90	*R*	94
$[RuCl_2(p\text{-cymene})]_2$	**26**	*t*-BuOK	98	87	*S*	95
$[RuCl_2(\eta^6\text{-}C_6Me_6)]_2$	**27**	KOH	94	92	*S*	96
$[RuCl_2(p\text{-cymene})]_2$	**28**	KOH	70[b]	91	*S*	97
$RuCl_2(PPh_3)_3$	**29**	NaOH	24 (83)	94 (73)	*R*	98
$RuCl_2(PPh_3)_3$	**30**	*i*-PrOK	93	94	*R*	99
$[RuCl_2(C_6H_6)]_2$	**31**	NaOH	72[b]	79	*R*	100
32	–	Me_2CHOK	93	97	*R*	101

[a]Based on the starting acetophenone. [b]Isolated yield.

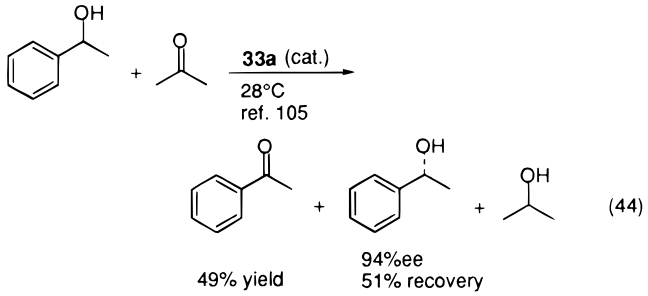
enantioselectivity using 2-propanol and chiral diamine−ruthenium complex catalysts **33** and **34** (eqs 42 and 43). As the reactive intermediate of the



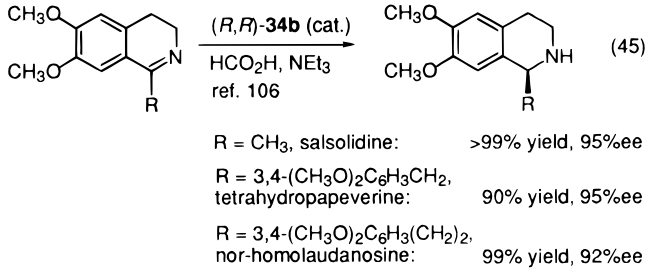
asymmetric transfer hydrogenations with a catalytic system of $[RuCl_2(arene)]_2$ and **24**, hydrido complex **35** has been isolated and the structure was confirmed by single-crystal X-ray analysis.[104]

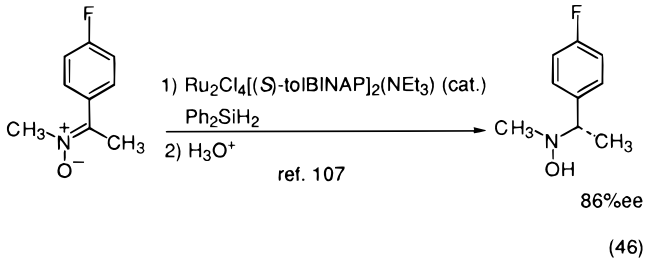


Under similar reaction conditions, kinetic resolution of racemic secondary alcohols can be performed with high enantioselectivity.[105] Typically, when a solution of racemic 1-phenylethanol in acetone containing **33a** catalyst was left at 28 °C for 30 h, a 97:3 mixture of (*R*) and (*S*) substrates (94% ee) was recovered in 51% yield in addition to the acetophenone in 49% yield, where k_f/k_s ratio is over 100 (eq 44).



The chiral diamine−ruthenium complexes also catalyze asymmetric reduction of imines with a formic acid−triethylamine mixture. This method is useful for asymmetric reduction of cyclic imines, providing a general and convenient route to a various indole alkaloids (eq 45).[106] Hydrosilylation of nitrones can be performed enantioselectively with diphenylsilane in the presence of Ru-BINAP catalyst to afford optically active hydroxylamines (eq 46).[107]





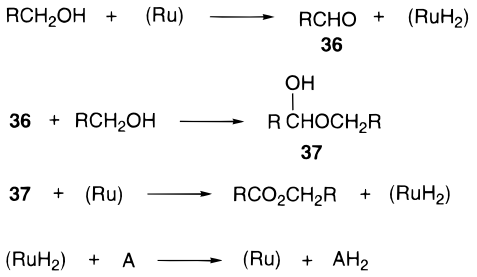
III. Oxidation

A. Hydrogen Transfer Reactions

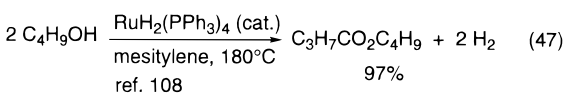
The principle of the hydrogen transfer reactions (section II.B) has been applied to a variety of oxida-

tive transformations of alcohols with low-valent ruthenium complex catalysts.[28] One of the typical reactions is the transformation of primary alcohols to the corresponding esters. The reaction is simply formulated as shown in Scheme 7. When primary

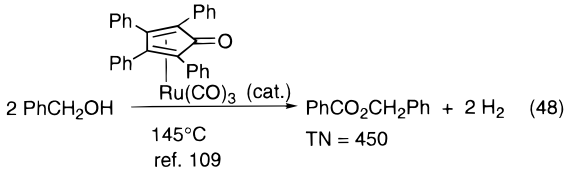
Scheme 7



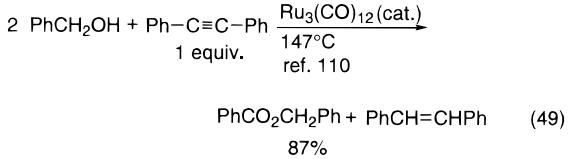
alcohols are allowed to react with low-valent ruthenium catalyst, a similar dehydrogenation reaction occurs to give aldehyde **36** and ruthenium dihydride (RuH_2). The aldehyde intermediate **36** is trapped with the second molecule of primary alcohol to give hemiacetal **37**. Further dehydrogenation of **37** with ruthenium gives the corresponding ester. The low-valent ruthenium complex is regenerated by the hydrogen transfer reaction of ruthenium dihydride to hydrogen acceptor (A) to complete the catalytic cycle. Without hydrogen acceptor, generation of molecular hydrogen occurs via reductive elimination from ruthenium dihydride. Thus, the reaction of primary alcohols with $RuH_2(PPh_3)_4$ catalyst gives the corresponding esters with evolution of molecular hydrogen (eq 47).[108] $Ru(CO)_3(\eta^4$-tetracyclone)[109] also catalyzes

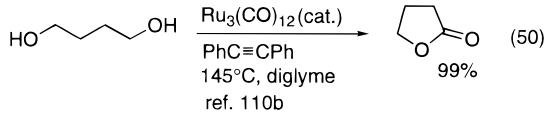


the reaction without hydrogen acceptors (eq 48),

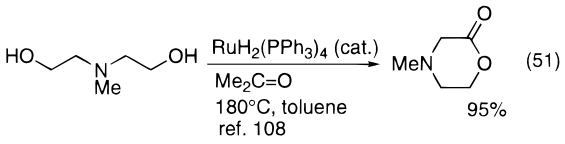


while $Ru_3(CO)_{12}$ requires a stoichiometric amount of diphenylacetylene (eq 49).[110] The reaction is applied

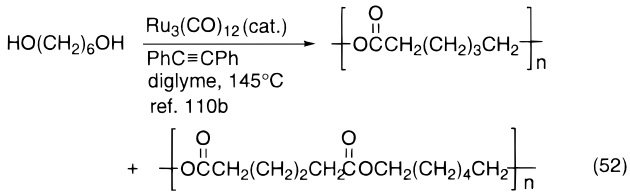




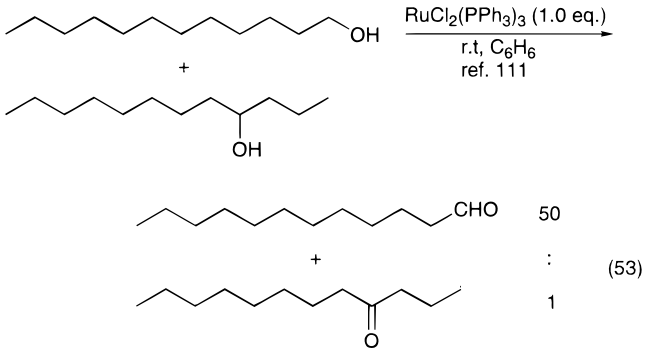
to lactone synthesis from 1,4- and 1,5-diols, where acetone,[108] benzylidenacetone,[108,109] and diphenylacetylene[108,110b] are used as an effective hydrogen acceptor for completion of the reaction (eqs 50 and 51).



Acetone was the most convenient hydrogen acceptor.[108] Similar treatment of α,ω-diols except 1,4- and 1,5-diols affords the corresponding polyesters (eq 52).[110b]

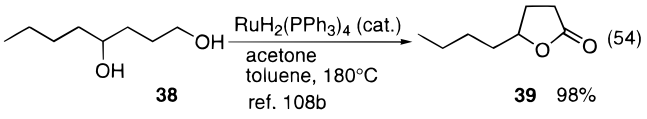


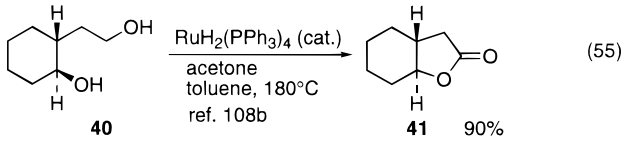
These reactions are initiated by the oxidative addition of O−H bond of alcohols to low-valent ruthenium complexes and the subsequent β-hydrogen elimination as shown in Scheme 7. Compared to the conventional oxidations with stoichiometric oxidants, which involve initial abstraction of an α-hydrogen of alcohols in a radical manner, these dehydrogenation processes are considerably affected by the steric bulkiness around the reaction sites. Thus, very rare chemoselectivity can be observed in the dehydrogenation reactions of alcohols. Whereas the conventional methods generally favor oxidation of secondary hydroxy groups rather than primary ones, primary hydroxy groups are oxidized with extremely high chemoselectivity in the present dehydrogenation processes. Stoichiometric reaction of $RuCl_2(PPh_3)_3$ with primary alcohols gives the corresponding aldehydes under mild conditions. When a mixture of 1-dodecanol and 4-dodecanol is allowed to react with a stoichiometric amount of $RuCl_2(PPh_3)_3$, 1-dodecanol is oxidized 50 times faster than 4-dodecanol to afford dodecanal chemoselectively (eq 53).[111] The above



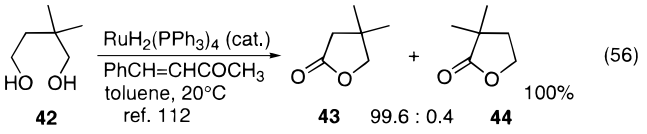
rare chemoselectivity has also been observed in the lactonization of diols. The reaction of 1,4-octanediol (**38**) and *trans*-2-(2-hydroxyethyl)cyclohexanol (**40**) with $RuH_2(PPh_3)_4$ catalyst in the presence of acetone as a hydrogen acceptor gives γ-octanolactone (**39**) and *trans*-hexahydro-2-benzofuranone (**41**), respectively without formation of the corresponding keto alcohols (eqs 54 and 55).[108]

The unsymmetrical primary, primary diols bearing bulky substituents are oxidized at the sterically less

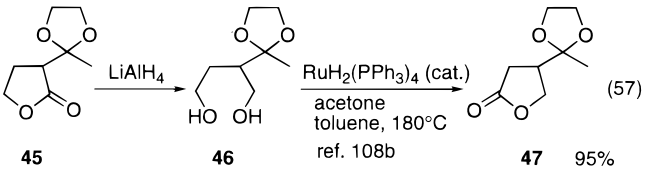




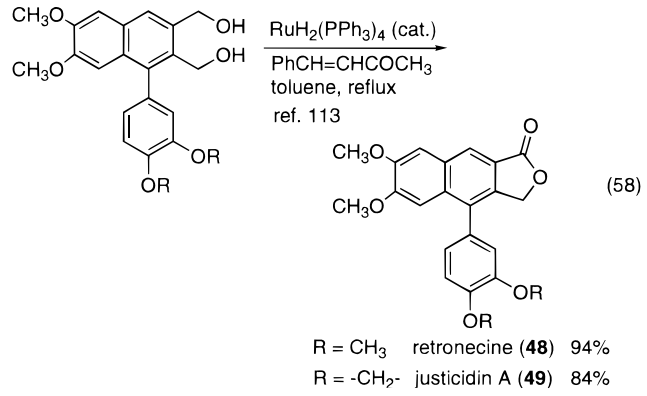
hindered position. 2,2-Dimethyl-1,4-butanediol (**42**) is converted into dihydro-4,4-dimethyl-2(3*H*)furanone (**43**) and dihydro-3,3-dimethyl-2(3*H*)-furanone (**44**) in a ratio of 99.6/0.4 in the presence of benzylideneacetone and $RuH_2(PPh_3)_4$ catalyst (eq 56).[112] Similar

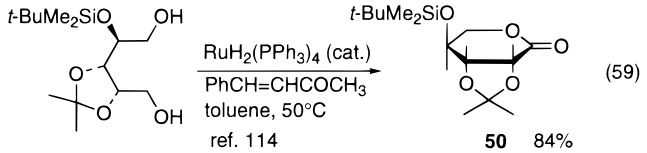


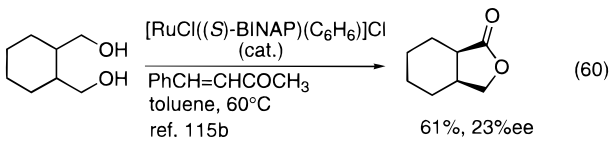
treatment of α-substituted diol **46**, derived from lactones **45**, affords lactone **47** in a ratio of 97/3 (eq 57).[108b] Since the starting unsymmetrical diols can



be readily prepared by the α-substitution of lactones followed by reduction, the present reactions provide an efficient method for the preparation of *β*-substituted *γ*-butyrolactones from α-substituted *γ*-butyrolactones. This method is applied to the regioselective synthesis of arylnaphthalene ligands such as retronecine (**48**), justicidin A (**49**) (eq 58),[113] and L-lyxose

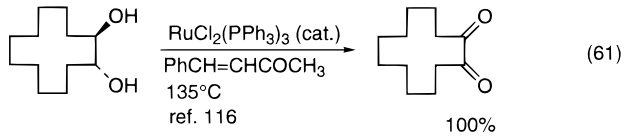


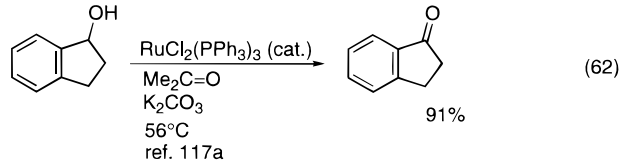


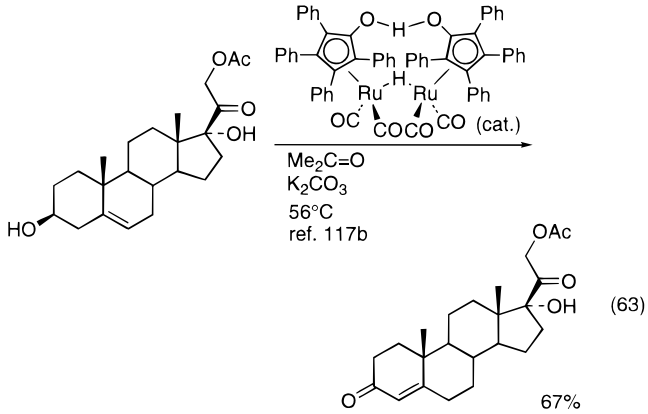


derivatives (**50**) (eq 59).[114] Asymmetric lactonization of prochiral diols has been performed with chiral phosphine complex catalysts, where enantiomer excess of the products are up to 23% ee (eq 60).[115]

The hydrogenation transfer reactions can be also applied to oxidation of alcohols to aldehydes and ketones. Various aliphatic and alicyclic secondary alcohols are converted into the corresponding ketones upon heating with low-valent ruthenium catalysts and hydrogen acceptors such as benzylideneacetone[116] and acetone (eqs 61−63).[117] The reaction proceeds under mild conditions when inorganic bases such as K_2CO_3 are used.

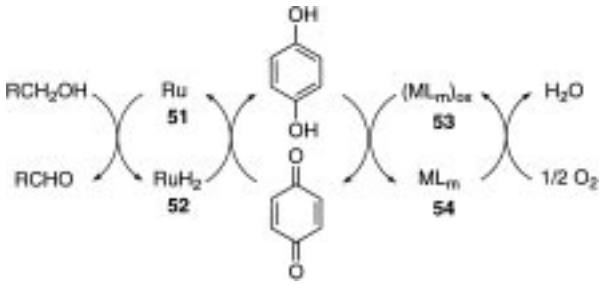






The present hydrogen transfer reaction can be extended to the aerobic oxidation of alcohols. Thus, the oxidation of alcohols can be performed with a catalytic amount of hydrogen acceptor under O_2 atmosphere by a multistep electron-transfer process. As shown in Scheme 8, ruthenium dihydrides formed

Scheme 8

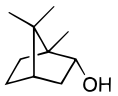


during the hydrogen transfer can be regenerated by a multistep electron-transfer process including hydroquinone, metal complexes, and molecular oxygen. Thus, low-valent ruthenium complex **51** with alcohol gives ruthenium dihydride **52**, which undergoes hydrogen transfer from quinone to give hydroquinone

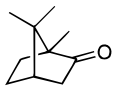
and **51**. The reaction of hydroquinone with second catalyst $(ML_m)_{ox}$ (**53**) affords quinone and ML_m (**54**) which regenerates **53** with molecular oxygen to complete catalytic cycle. On the basis of this process, aerobic oxidation of alcohols to aldehydes and ketones can be performed at ambient pressure of O_2 in the presence of ruthenium−cobalt bimetallic catalyst and hydroquinone.[118,119] Typically, benzyl alcohol is oxidized to benzaldehyde selectively at 20 °C under O_2 atmosphere with a catalytic system consisting of $RuCl(OAc)(PPh_3)_3$, Co(salophen)(PPh_3), and hydroquinone (eq 64).[118] A similar type of multistep

$$PhCH_2OH + 1/2\ O_2 \xrightarrow[\text{Co(salophen)(PPh}_3\text{) (cat.)}]{\text{RuCl(OAc)(PPh}_3\text{)}_3\text{ (cat.)}} PhCHO + H_2O \quad (64)$$

hydroquinone (cat.), CH_2Cl_2, 20°C, ref. 118; conv. 60%, >98% selectivity



$$\xrightarrow[\text{MnO}_2\text{ (1.1 eq.)}]{[(RuCl_2(p\text{-cymene})]_2\text{ (cat.)}} \quad (65)$$



2,6-di-*t*-butylbenzoquinone, K_2CO_3 (1.1 eq.), THF, 65°C, ref. 119; 87%

electron-transfer process for oxidation of alcohols can be performed in combination with $[RuCl_2(p\text{-cymene})]_2$ catalyst, MnO_2, and 2,6-di-*tert*-butylbenzoquinone in the presence of inorganic base (eq 65).[119]

Trapping the carbonyl intermediate **40** in Scheme 8 with various nucleophiles provides other catalytic oxidative transformations of alcohols. When primary or secondary amine is employed as a nucleophile, intermediate **55** undergoes nucleophilic reaction with amine to give iminium ion complex **56** along with water. Intramolecular hydride transfer of **56** gives the corresponding *N*-alkylated amine **57** with regeneration of ruthenium active species (Scheme 9, eq 66).[28] Representative results for *N*-alkylation of

Scheme 9

$$R^1R^2CHOH + (Ru) \rightleftharpoons (R^1R^2C{=}O)(Ru)(H_2)$$

55

$$\mathbf{55} + R^3R^4NH \rightleftharpoons (R^1R^2C{=}\overset{+}{N}R^3R^4)(Ru)(H)^- + H_2O$$

56

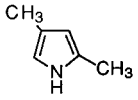
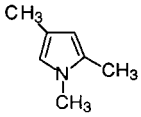
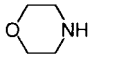
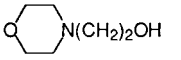
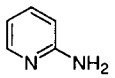
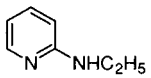
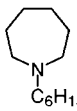
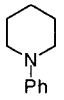
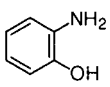
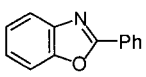
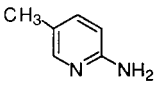
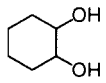
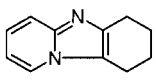
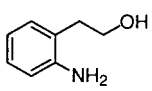
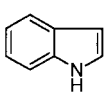
$$\mathbf{56} \rightleftharpoons R^1R^2CHNR^3R^4 + (Ru)$$

57

$$R^1R^2CHOH + R^3R^4NH \xrightarrow{\text{Ru cat.}} R^1R^2CHNR^3R^4 + H_2O \quad (66)$$

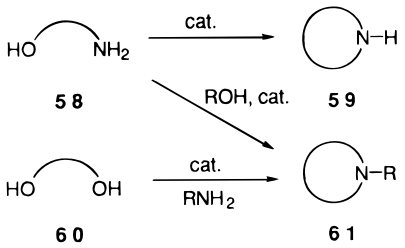
amines with alcohols are summarized in Table 3. The reaction with aliphatic amines proceeds efficiently with $RuH_2(PPh_3)_4$ catalyst (entry 1),[120] while $RuCl_2(PPh_3)_3$ (entry 2)[121,122] and $RuCl_3-PR_3$ (entries 3−5)[123] are good catalysts for the reactions with aromatic amines. Selective *N*-monoalkylation of heteroaro-

Table 3. *N*-Alkylation of Amines with Alcohols

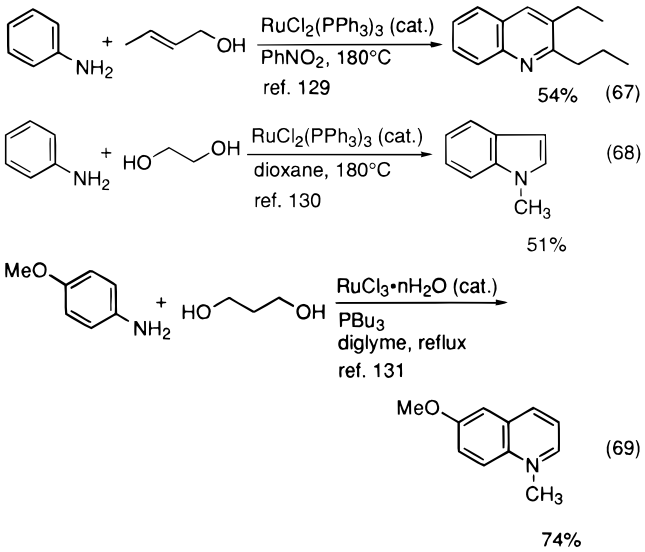
entry	catalyst	amine	alcohol	product	yield, %	ref.
1	$RuH_2(PPh_3)_4$	$C_8H_{17}NH_2$	$C_7H_{15}OH$	$C_7H_{15}NHC_8H_{17}$	92	120
2	$RuCl_2(PPh_3)_3$	$PhNH_2$	C_3H_7OH	$PhN(C_3H_7)_2$	88	121b
3	$RuCl_3{\cdot}nH_2O$-$P(OBu)_3$	$PhNH_2$	CH_3OH	$PhN(CH_3)_2$	80	123a
4	$RuCl_3{\cdot}nH_2O$-$P(OBu)_3$		CH_3OH		99	123b
5	$RuCl_3{\cdot}nH_2O$-PPh_3		$HO(CH_2)_6OH$		84	123c
6	Ru(cod)(cot)		C_2H_5OH		85	124
7	$RuH_2(PPh_3)_4$	$H_2N(CH_2)_4OH$			79	120
8	$RuH_2(PPh_3)_4$	$C_6H_{13}NH_2$	$HO(CH_2)_5OH$		87	120
9	$RuCl_2(PPh_3)_3$	$PhNH_2$	$HO(CH_2)_5OH$		89	125a
10	$RuCl_2(PPh_3)_3$		$PhCH_2OH$		80	126
11	$RuCl_2(PPh_3)_3$				74	127
12	$RuCl_2(PPh_3)_3$				100	128

matic primary amines can be performed when Ru(cod)(cot) is used as a catalyst (entry 6),[124] while similar treatment with $RuCl_2(PPh_3)_3$, or $RuCl_3$-PR_3 catalyst gives the corresponding *N*,*N*-dialkylated amines.[121a,123] Intramolecular version of this reaction provides a novel method for synthesis of cyclic amines (Scheme 10). Amino alcohols **58** undergo condensation to give secondary cyclic amines **59** (entry 7).[120] Tertiary cyclic amines **61** can be prepared either by the reaction of **58** with primary alcohols or the reaction of diols **60** with primary amines (entries 8 and 9).[120,125] It is noteworthy that seven-membered ring formation can be readily performed due to the template effect of ruthenium complexes to the difunctional substrates (entry 8).[120] 2-Aminophenols,[126] 2-aminopyridines,[127] and 2-aminophenethyl alcohols[128] undergo the *N*-alkylation reaction and the subsequent dehydrogenation reactions under the similar reaction conditions to afford benzoazoles, benzimidazoles, imidazo[1,2-*a*]pyridines, and indoles, respectively (entries 10−12).

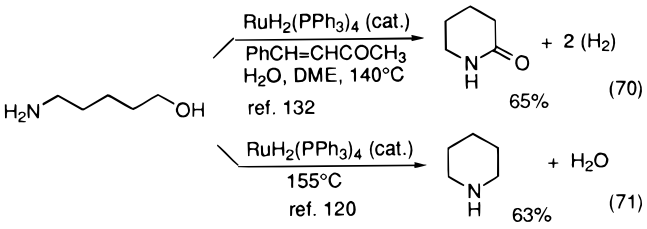
Scheme 10



N-Alkylation and subsequent aromatic ring closure can be performed when aromatic amines are allowed to react with allylic alcohols[129] and 1,2-[130] and 1,3-diols[131] under similar reaction conditions to afford the corresponding quinoline and indole derivatives (eqs 67−69).

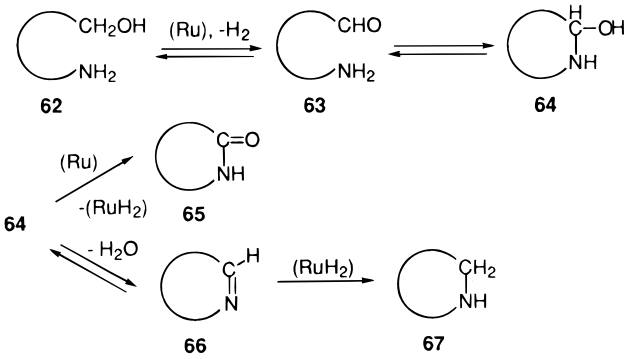


When the $RuH_2(PPh_3)_4$-catalyzed reaction of amino alcohols is carried out in the presence of a hydrogen acceptor, the dehydrogenation reaction takes place exclusively to afford the corresponding lactams (eq 70).[132] This is principally similar to the ruthenium-catalyzed lactonization of diols,[112] and contrasts with the fact that the similar cyclization reaction without a hydrogen acceptor affords cyclic amines (eq 71).[120]

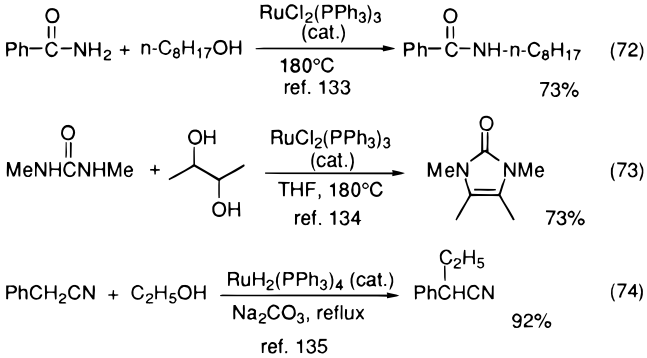


This drastic change can be rationalized by assuming the mechanism shown in Scheme 11. The oxidative addition of low-valent ruthenium complex to the O−H bond of an amino alcohol **62** followed by elimination of (RuH_2) species gives amino aldehyde **63**, which undergoes condensation to give intermediate **64**. Further dehydrogenation of **64** in the presence of a hydrogen acceptor gives lactams **65**. In contrast, the reaction without hydrogen acceptor leads to dehydration of **64**, giving imine **66** which undergoes hydrogenation with (RuH_2) to afford amine **67**.

Scheme 11



Catalytic alkylation with alcohols can be performed by using other nucleophiles. Primary amides undergo *N*-alkylation by the $RuCl_2(PPh_3)_3$-catalyzed reaction with alcohols (eq 72).[133] Similar treatment of *N*,*N*-disubstituted ureas with 1,2-diols gives 2,3-dihydroimidazol-2-ones (eq 73) via the similar alkylation reaction and subsequent dehydration reaction.[134] $RuH_2(PPh_3)_4$-catalyzed reaction of phenylacetonitrile with ethanol proceeds in the presence of inorganic base to give the corresponding α-ethylated product (eq 74).[135]



The present principle of the dehydrogenation of alcohols can be applied to catalytic transformations

of aldehydes. Esters can be obtained from the reactions of aldehydes with alcohols using $RuH_2(PPh_3)_4$ catalyst (eq 75)[112b] or a combination of $Ru_3(CO)_{12}$ catalyst and diphenylacetylene (eq 76).[114a] Cannizzaro-type reaction occurs upon treatment of aldehydes with water to give carboxylic acids and alcohols (eq 77)[136] or the corresponding esters (eq 78).[112b,114a]

$$C_3H_7CHO + C_4H_9OH \xrightarrow[\text{toluene, 180°C}]{RuH_2(PPh_3)_4\ (cat.)} C_3H_7CO_2C_4H_9 + H_2 \quad (75)$$
ref. 112b; 100%

$$PhCHO + PhCH_2OH \xrightarrow[PhC{\equiv}CPh,\ 147°C]{Ru_3(CO)_{12}\ (cat.)} PhCO_2CH_2Ph \quad (76)$$
ref. 114a; 72%

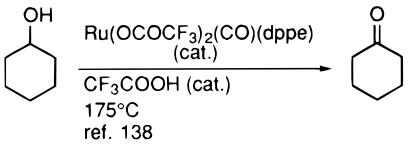
$$CH_3CHO + H_2O \xrightarrow[45°C]{[\{Ru(C_6Me_6)\}_2(OH)_3]Cl\ (cat.)} CH_3CO_2H + CH_3CH_2OH \quad (77)$$
ref. 136; TN = 2395, TN = 462

$$C_3H_7CHO + H_2O \xrightarrow[\text{toluene, 180°C}]{RuH_2(PPh_3)_4\ (cat.)} C_3H_7CO_2C_4H_9 \quad (78)$$
ref. 112b; 65%

In contrast, similar reactions in the presence of a hydrogen acceptor such as benzylideneacetone affords carboxylic acid selectively (eq 79).[112b] Similar dehydrogenative condensation of formamides with primary amines can be performed with $RuCl_2(PPh_3)_3$ catalyst to give the corresponding ureas.[137]

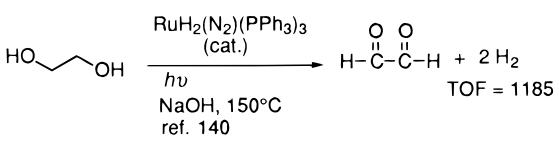
$$PhCHO + H_2O \xrightarrow[PhCH{=}CHCOCH_3,\ \text{toluene, 180°C}]{RuH_2(PPh_3)_4\ (cat.)} PhCO_2H \quad (79)$$
ref. 112b; 75%

Production of molecular hydrogen by means of the catalytic dehydrogenation of alcohols is of importance in view of its industrial aspects, and has been studied using various low-valent ruthenium complex catalysts such as $Ru(OCOCF_3)_2(CO)(dppe)$,[138] $[Ru_2(OAc)_4Cl]$-$PEtPh_2$,[139] and $RuH_2(N_2)(PPh_3)_3$[140] (eqs 80−82).



(80)

$$MeOH \xrightarrow[AcOH,\ 66°C]{Ru(OAc)Cl(PEtPh_2)_3\ (cat.)} HCHO + H_2 \quad (81)$$
ref. 139; TN = 34

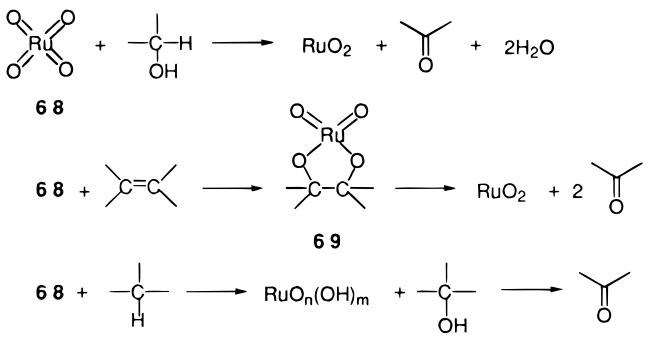


(82)

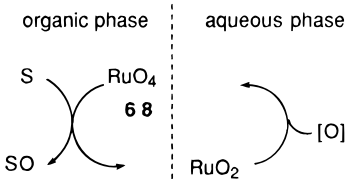
B. RuO_4-Promoted Oxidation

RuO_4 (**68**) has been widely used as a powerful oxidant for oxidative transformations of various organic compounds since the discovery by Djerassi in 1953.[4] RuO_4 shows specific power of oxygenation and hydrogen abstraction toward a variety of organic compounds. Typical reactivity of RuO_4 is shown in-

Scheme 12

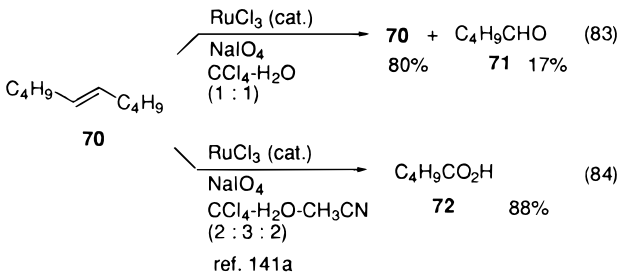


Scheme 13



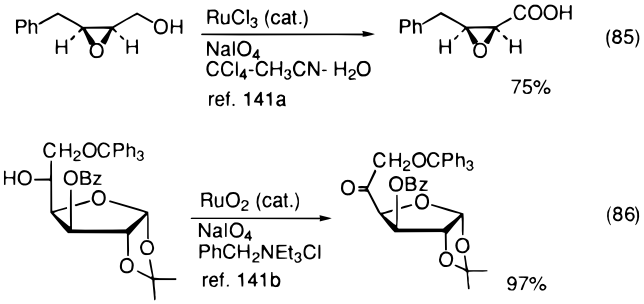
Scheme 12. Hydroxy compounds undergo abstraction of activated α-hydrogen atom followed by electron transfer to afford the corresponding carbonyl compounds and RuO_2. The reaction with olefins gives cyclic ruthenium(VI) diesters **69** which are converted into carbonyl compounds via oxidative cleavage of the carbon−carbon double bonds. Substrates bearing unactivated C−H bonds such as alkanes and amides undergo hydrogen abstraction and the subsequent oxygen rebound to afford the corresponding hydroxy compounds which are normally converted into the carbonyl compounds by second oxidation. Although a stoichiometric amount of RuO_4, prepared readily by the reaction of $RuCl_3$ or RuO_2 with $NaIO_4$, has been used for the oxidations, the reactions can be performed conveniently in a biphasic system (Scheme 13) using a catalytic amount of $RuCl_3$ or RuO_2 with a combined use of oxidants such as $NaIO_4$,[141a,b,142b−f,143a−d,146−148,149−155] HIO_4,[143f] NaOCl,[142g,h,143e,154,156] and $NaBrO_3$,[141c−e] or under electrooxidation conditions.[141f,144]

The problems such as very slow and incomplete reactions have been often encountered in the oxidations with RuO_4. These sluggish reactions are due to inactivation of ruthenium catalysts with carboxylic acids by forming low-valent ruthenium carboxylate complexes. The inactivation can be prevented by addition of CH_3CN. Thus, various oxidations with RuO_4 were remarkably improved by employing a solvent system consisting of $CCl_4-H_2O-CH_3CN$ (2:3:2).[141a] Typically, oxidative cleavage of (*E*)-5-decene (**70**) with RuO_4 in conventional CCl_4-H_2O (1:1) gave pentanal (**71**, 17%) along with 80% of recovered **70**

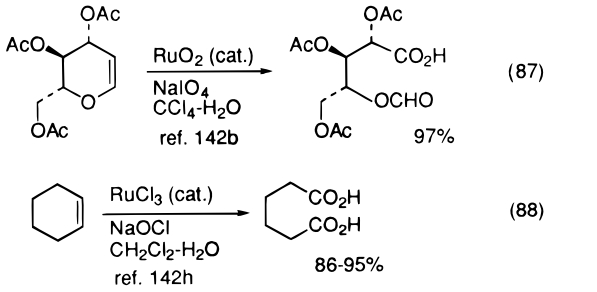


after 2 h, while pentanoic acid (**72**, 88%) can be obtained in a $CCl_4-CH_3CN-H_2O$ (2:3:2) system under similar conditions (eqs 83 and 84).

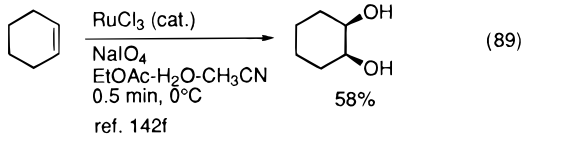
Primary and secondary alcohols are oxidized to the corresponding carboxylic acids and ketones, respectively (eqs 85 and 86).[141] Olefins undergo oxidative



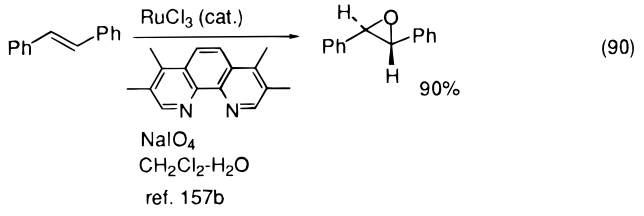
cleavage to afford the carbonyl compounds (eqs 87 and 88),[142] while *cis*-dihydroxylation occurs selec-



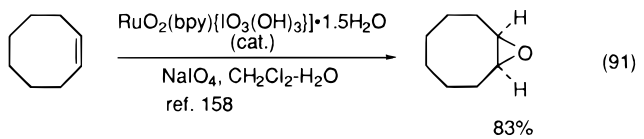
tively when the reaction is carried out in a short time (0.5 min) at 0 °C in $EtOAc-CH_3CN-H_2O$ (eq 89).[142f]



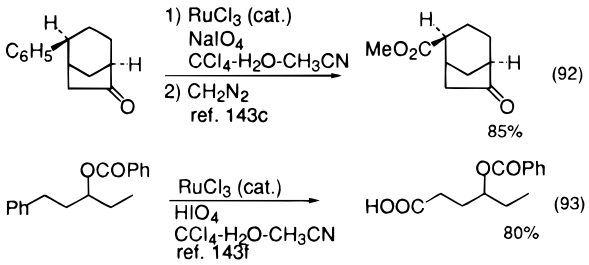
Epoxidation of olefins can be performed with RuO_4 modified by coordination of nitrogen ligands. A combination of $RuCl_3$ and nitrogen ligand such as bipyridines or phenanthroline is efficient for epoxidation of olefins with $NaIO_4$ (eq 90).[157] Dioxoruthe-



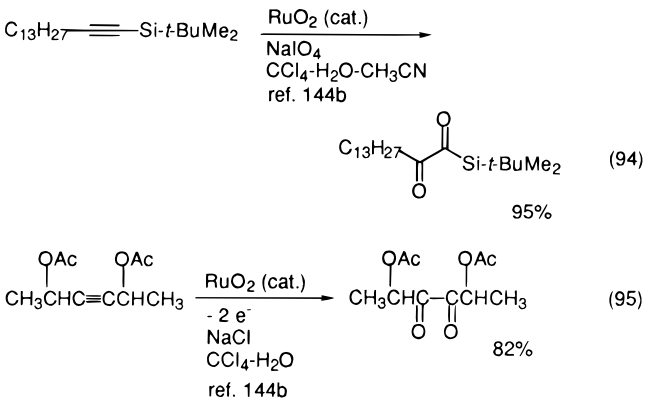
nium(IV) complex $[RuO_2(bpy)\{IO_3(OH)_3\}]\cdot 1.5H_2O$ was isolated by reaction of RuO_4 with bipyridyl in the presence of $NaIO_4$, and the complex acts as an efficient epoxidation catalyst as the three-component mixture under similar conditions (eq 91).[158]



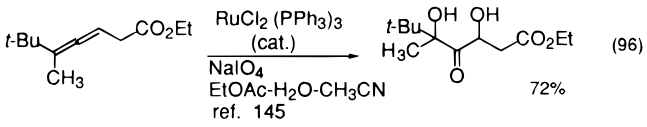
Aromatic rings are smoothly degraded to carboxylic acids (eqs 92 and 93).[143] Terminal alkynes undergo



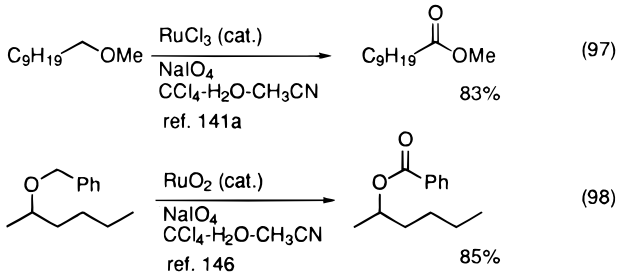
the similar oxidative cleavage to afford carboxylic acids, while internal alkynes are converted to α-diketones (eqs 94 and 95).[144] The oxidation of allenes



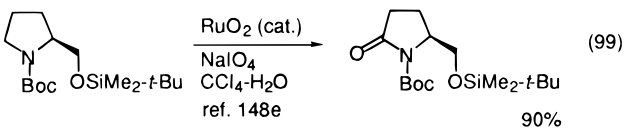
gives α,α-dihydroxy ketones (eq 96).[145]



Various heteroatom-containing compounds undergo oxidation of methylene groups at the α-position. Ethers are converted into esters and lactones (eqs 97 and 98).[141a,146] Tertiary amines[147] and amides[148]

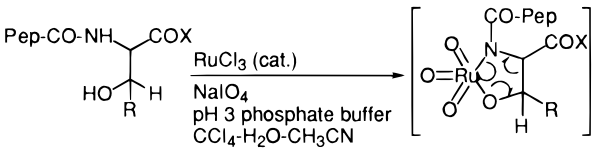


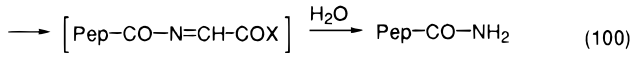
undergo similar oxygenation reactions at the α-position of nitrogen to afford the corresponding amides and imides, respectively (eq 99). The carbon−carbon



side-chain fragmentation occurs when N,C-protected serine and threonine are subjected to oxidation. The method is successfully applied to effective N−C bond

scission of peptides at serine or threonine residue (eqs 100 and 101).[149]





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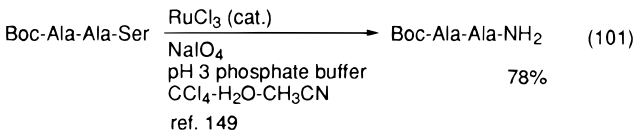
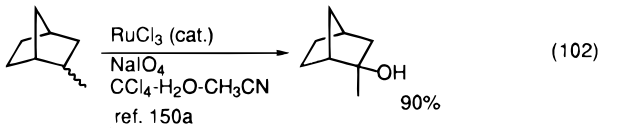


(101)

Unactivated alkanes can be also oxidized with RuO_4. Tertiary carbon−hydrogen bonds undergo chemoselective hydroxylation to afford the corresponding tertiary alcohols (eqs 102 and 103).[150]



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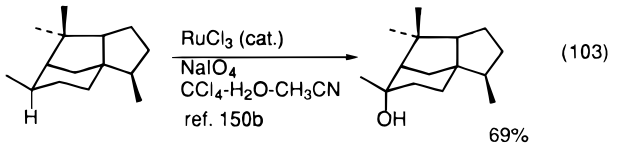
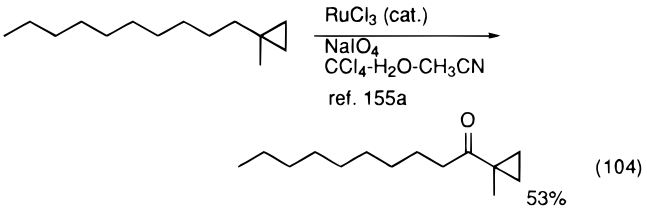


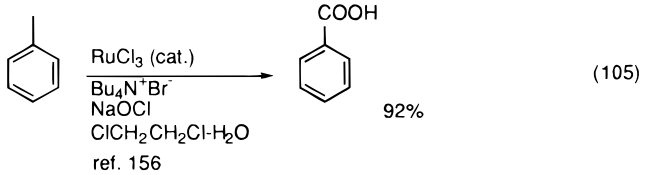
(103)

Bridgehead carbons of adamantane,[151] pinane,[152] and fused norbornanes[153] undergo selective hydroxylation under similar reaction conditions. Methylene groups of alkanes undergo hydroxylation and the subsequent oxidation to afford the corresponding ketones.[154] Methylene groups bearing a cyclopropane ring at an adjacent position undergo chemoselective oxidation to afford the corresponding cyclopropyl ketones (eq 104).[155] Generally methyl groups of alkanes do not



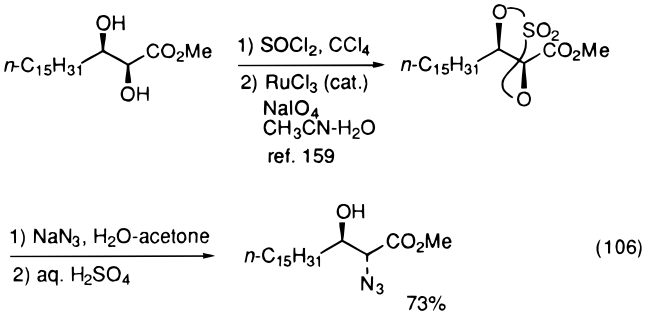
(104)

react with RuO_4, while activated methyl groups such as that in toluene can be converted into the corresponding carboxylic acids (eq 105).[156]



(105)

Cyclic sulfites, derived from *cis*-vicinal diol and $SOCl_2$, can be converted efficiently with RuO_4 to afford the corresponding cyclic sulfates. This reaction provides a versatile method for the preparation of trans-α-functionalyzed alcohols upon treatment of the sulfate with a variety of electrophiles (eq 106).[159]

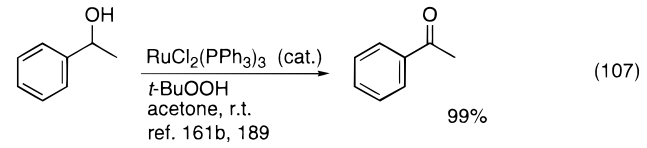


(106)

C. Oxidation with Ruthenium Complex Catalysts and Oxidants

a. Oxidation of Alcohols

Many methods for specific catalytic oxidations of various organic substrates such as alcohols, amines, amides, and hydrocarbons have been studied extensively using low-valent ruthenium complex catalysts,[25−27,160] since the systems often exhibit specific characteristics which differ from those arising from usual RuO_4 oxidations. Low-valent ruthenium complexes catalyze the oxidation of alcohols and the related hydroxy compounds in combination with various oxidants such as *t*-BuOOH (eq 107),[28a,161,189] AcOOH (eq 108),[162] H_2O_2 (eq 110),[163] $Me_3SiOOSiMe_3$ (eq 111),[164] PhIO (eq 109),[165] *N*-methylmorpholine *N*-oxide,[166] and pyridine *N*-oxide (eq 112).[167] Secondary alcohols are converted into the corresponding ketones (eqs 107−109).



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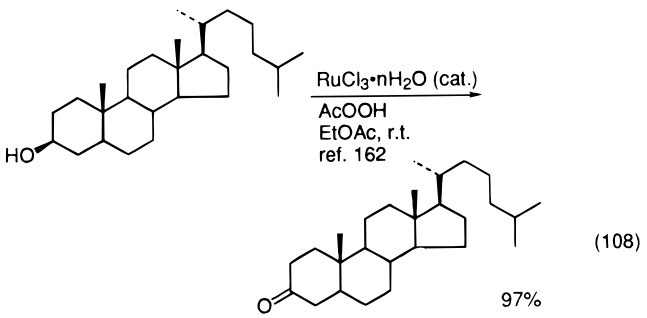

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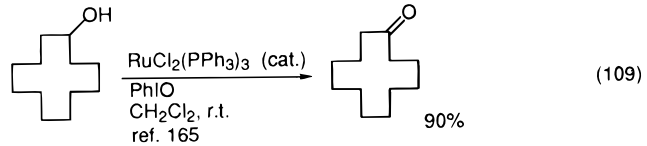
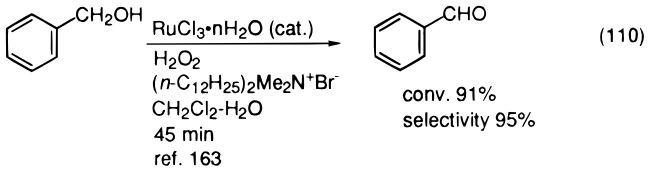


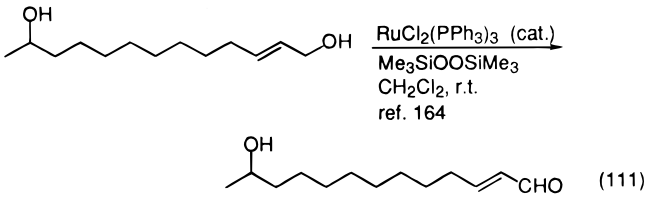
(109)

Primary alcohols are normally oxidized to carboxylic acids,[162,163] while selective oxidation of benzyl alcohols to benzaldehyde with H_2O_2 can be performed by shortening the reaction time (eq 110).[163] By using $RuCl_2(PPh_3)_3$ catalyst and $Me_3SiOOSiMe_3$, primary allyl alcohols are chemoselectively oxidized into enals



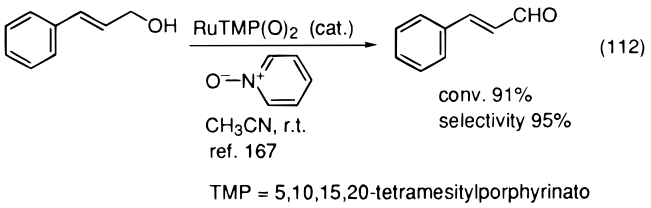
(110)

in the presence of aliphatic secondary ones (eq 111).[164] Aliphatic alcohols and aromatic allyl alcohols



(111)

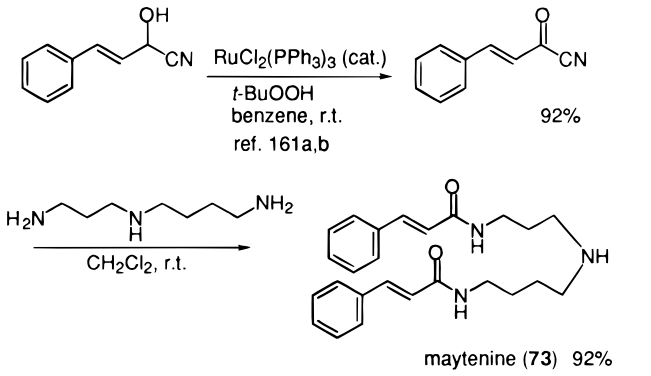
can be converted selectively into the corresponding aldehydes in the presence of ruthenium catalysts and amine *N*-oxides such as *N*-methylmorpholine *N*-oxide[166] and pyridine *N*-oxide (eq 112).[167] By using



(112)

a combination of $RuCl_2(PPh_3)_3$ catalyst with 4-(benzoyloxy)-2,2,6,6-tetramethylpiperidine-1-oxyl (4-BzOTEMPO), α-oxygenated aldehydes are obtained by the oxidation of primary alcohols and subsequent radical coupling reaction of the corresponding aldehydes with 4-BzOTEMPO.[168]

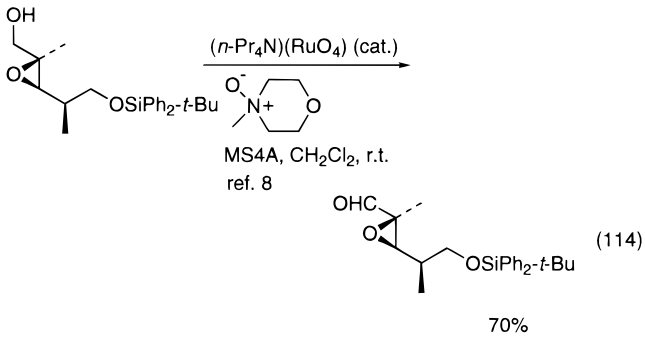
Upon treatment with $RuCl_2(PPh_3)_3$ catalyst and *t*-BuOOH, cyanohydrins can be converted into the corresponding acyl cyanides which are highly useful reagents for selective acylation of amine compounds.[161a,b] Utility of the reaction has been illustrated by the short-step synthesis of maytenine (**73**) (eq 113).[161b]



(113)

Although the catalytically active species of these reactions still remains unclear, the most plausible pathway is that of including the oxoruthenium species Ru^{n+2}═O which would be formed from the reaction of low-valent ruthenium complex Ru^n with oxidants. Abstraction of a hydrogen and subsequent electron transfer would give intermediate [R^1R^2C═OH^+ Ru(OH)], which collapses to give Ru^n, carbonyl compounds, and water to complete the catalytic cycle. The reactivity of oxoruthenium complex Ru^{IV}(trpy)(bpy)O^{2+},[169] Ru^{IV}(bpy)$_2$(py)O^{2+},[170] Ru^{IV}(TMP)$_2$(py)O^{2+},[171a] *cis*-[Ru^{IV}(Tet-Me_6)O_2]$^{2+}$,[171b] and Ru^{IV}(tpp)$(NTs)_2$[171c] toward oxidation of alcohols has been investigated.

The catalytic system of ruthenium complexes with *N*-oxides has been developed to the highly useful synthetic tool by elegant modification of catalyst. The salts of perruthenium ion $[Ru^{IV}O_4]^-$ with quarternary ammonium salts, which are soluble in a variety of organic solvents, show far milder oxidizing properties than RuO_4, and act as efficient catalysts for selective oxidation of primary alcohols with a combined use of stoichiometric amount of *N*-methylmorpholine *N*-oxide.[8,172,173] The method is widely accepted in organic synthesis, and many examples show that it has advantages over conventional practical methods for oxidative transformation of primary alcohols to aldehyde. Typical examples are shown in eqs 114−116. One of the key features of this method is its



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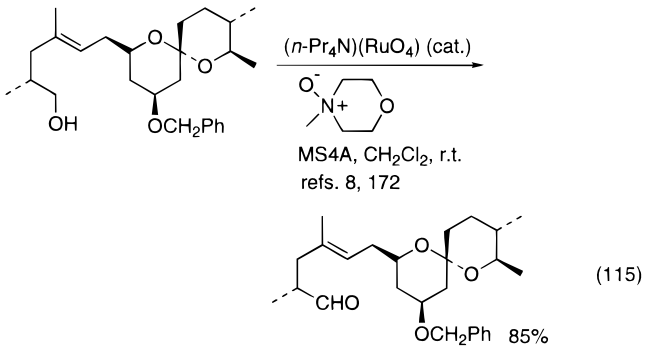

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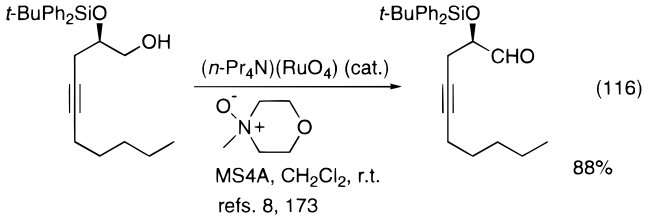
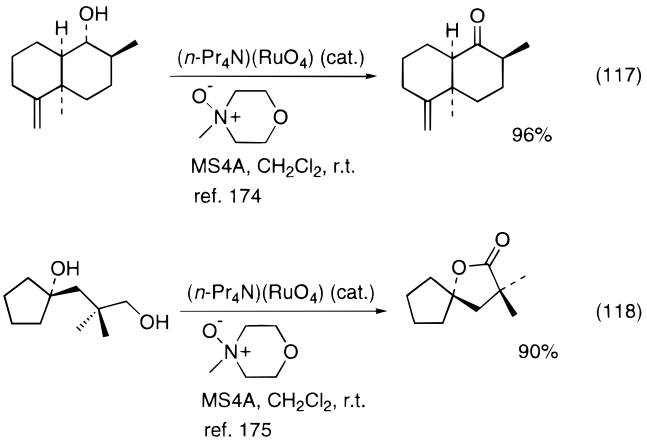


(116)

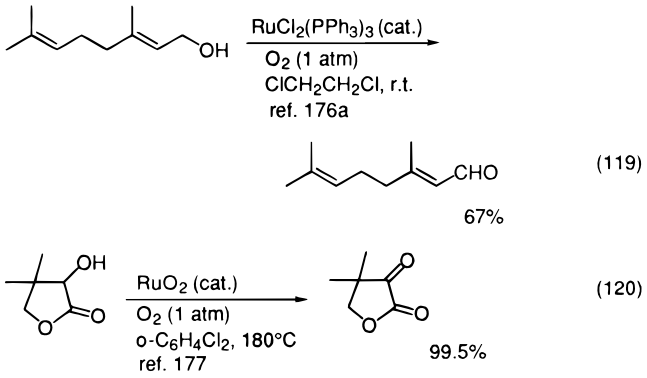
ability to tolerate other potentially reactive functional groups. For example, olefins, polyenes, enones, halides, cyclopropanes, epoxides, acetals, esters, amides, lactones, and amines remain intact during the oxidation. Protecting groups such as SEM, MOM, BOM, MEM, TEOC, THP, trityl, silyl, and benzyl are stable

to the reaction conditions. This system also provides a useful method for conversion of secondary alcohols to ketones (eq 117)[174] and diols to lactones (eq 118).[175]

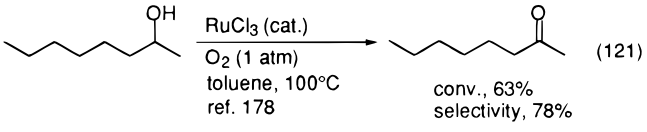


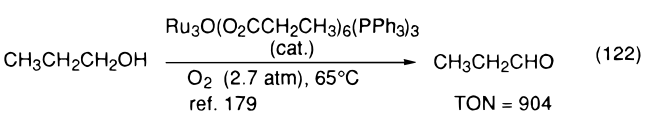
Similar selective oxidation to aldehydes can be also performed with other modified RuO_4 systems such as $[RuO_2(bipy)\{IO_3(OH)_3\}]\cdot 1.5H_2O-NaIO_4$.[158]

Aerobic oxidations of alcohols with metal catalysts is an attractive method for economical and environmental reasons. Arduous search for suitable catalysts has been continued mainly on group 8 metal complexes. By using $RuCl_3$, $RuCl_2(PPh_3)_3$, and RuO_2 catalysts, activated alcohols such as allyl alcohols (eq 119)[176] and α-ketols (eq 120)[177] can be oxidized

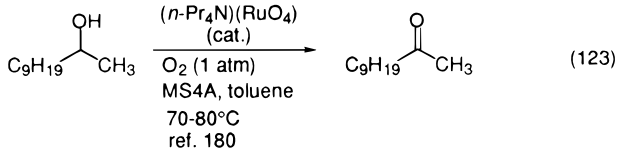


aerobically under mild and ambient conditions. Similar treatment of aliphatic alcohols also gives the aliphatic carbonyl compounds with relatively low conversions and low selectivities of the products (eq 121).[178] Trinuclear ruthenium carboxylates, $Ru_3O(O_2CR)_6L_n$ ($L = H_2O$, PPh_3) are effective catalysts for aerobic oxidation of aliphatic alcohols (eq 122).[179]

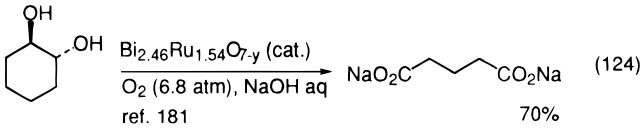




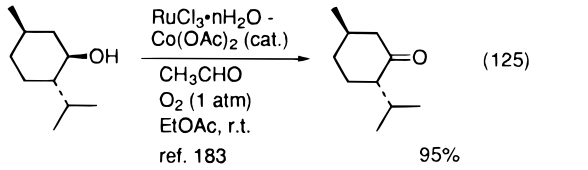
Catalytic activities of these complexes are approximately 10 times higher than those of $RuCl_3$ and $RuCl_2(PPh_3)_3$. $(n\text{-}Pr_4N)(RuO_4)$ has been used for selective oxidation of alcohols with tertiary amine *N*-oxide;[8] however, the same catalyst was found to be a highly efficient catalyst for the aerobic oxidation of alcohols.[180] A variety of primary and secondary alcohols such as aliphatic, allylic, benzylic, and keto alcohols can be oxidized at 70−80 °C under an O_2 atmosphere (eq 123). Vicinal diols undergo rare



aerobic oxidative cleavage when heated with mixed ruthenium metal oxide catalyst [$A_{2+x}Ru_{2-x}O_{7-y}$ (A = Pb, Bi; $0 < x < 1$; $0 < y \leq 0.5$)] under high pressure of O_2 (eq 124).[181]



Peracetic acid, one of the efficient oxidants for the ruthenium-catalyzed oxidations of alcohols,[162] is prepared by treatment of acetaldehyde with molecular oxygen in the presence of cobalt salts.[182] The generation of peracetic acid in situ provides an efficient method for aerobic oxidation of alcohols. The oxidation of various aliphatic and aromatic alcohols can be performed at room temperature with molecular oxygen (1 atm) in the presence of an aldehyde and $RuCl_3$-$Co(OAc)_2$ bimetallic catalyst (eq 125).[183] This



method is advantageous over the previous methods for aerobic oxidation of alcohols because of its high efficiency, mild reaction conditions, simple operation, and generality of applicable substrates. The reaction can be rationalized by assuming the following two sequential pathways: (i) formation of peracetic acid by a cobalt-mediated radical chain reaction of acetaldehyde with molecular oxygen (eqs 126−128),[182] and (ii) ruthenium-catalyzed oxidation of alcohols with peracetic acid[162] via oxoruthenium intermediates (eqs 129−131).

$$RCHO + Co(III) \longrightarrow RCO\bullet + Co(II) + H^+ \quad (126)$$

$$RCO\bullet + O_2 \longrightarrow RC(O)OO\bullet \quad (127)$$

$$RC(O)OO\bullet + RCHO \longrightarrow RC(O)OOH + RCO\bullet \quad (128)$$

$$Ru(III)L_n + RC(O)OOH \longrightarrow Ru(V)(O)L_n + RCO_2H \quad (129)$$

$$Ru(V)(O)L_n + R^1R^2CHOH \longrightarrow \left[R^1R^2C{=}OH^+\ Ru(OH)L_n\right] \quad (130)$$

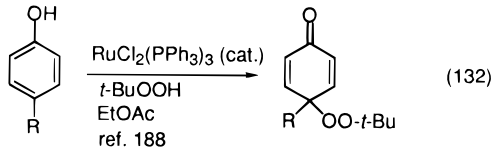
$$\left[R^1R^2C{=}OH^+\ Ru(OH)L_n\right] \longrightarrow Ru(III)L_n + R^1R^2C{=}O + H_2O \quad (131)$$

Alternative representative methods for catalytic oxidation of alcohols with the low-valent ruthenium catalysts are hydrogen transfer reactions of alcohols

with hydrogen acceptors such as olefins and ketones which we discussed previously in section III.A. As miscellaneous methods for oxidation of alcohols, oxidation with allyl methyl carbonate via π-allylruthenium[184] and electrooxidation with $[RuO(trpy)(bpy)]^{2+}$ catalyst[185] have been reported.

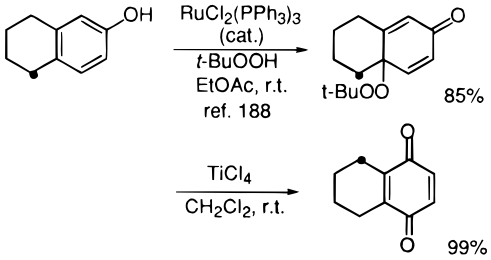
b. Oxidation of Phenols

Oxidative transformation of phenols is of importance in view of biological and synthetic aspects. However, the oxidation of phenols generally lacks selectivity because the initially formed phenoxy radical intermediate causes various unpleasant coupling reactions. Thus, metal-catalyzed oxidation of phenols generally proceeds with nonselectivity, giving a variety of side products such as radical coupling products and over oxidation products.[186,187] Due to the strong ability of electron transfer of ruthenium, various modes of radical coupling reactions of phenoxy radical intermediate have been found to be prevented when using ruthenium complex catalysts. Thus, phenols bearing para-substituents undergo selective oxidation by *t*-BuOOH in the presence of $RuCl_2(PPh_3)_3$ catalyst to afford the corresponding 4-(*tert*-butyldioxy)cyclohexadienones (eq 132) which



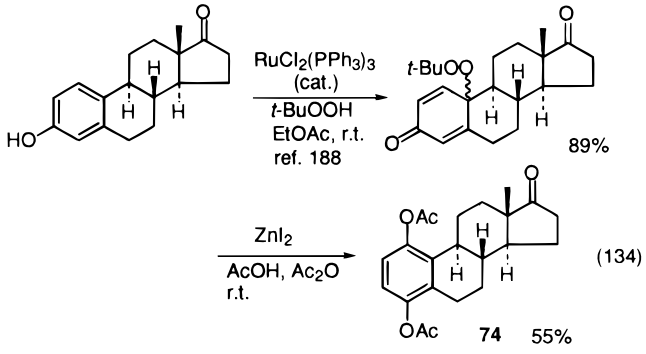
(132)

are versatile synthetic intermediates.[188] The efficiency of the reaction has been illustrated by an unusual migration reaction of the product peroxides with Lewis acid affording the corresponding 2-substituted quinones or hydroquinone derivatives (eq 133).[188] The synthetic utility of this method has been



(133)

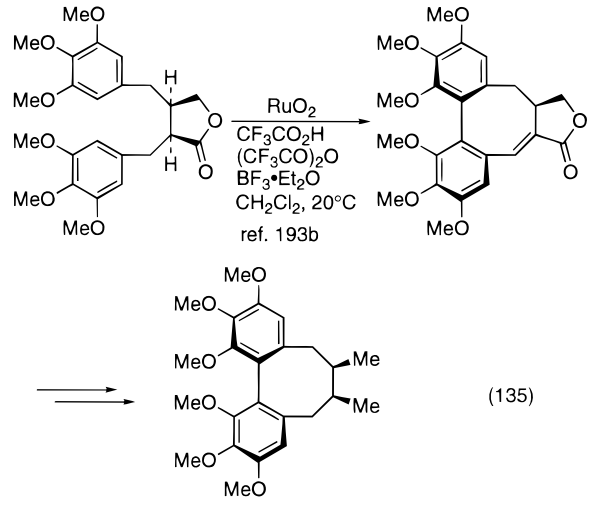
demonstrated by the preparation of rare steroid compound **74** (eq 134). Under the similar reaction



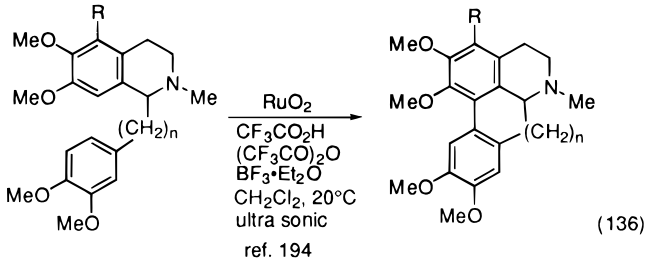
(134)

conditions catechols[189] and para-unsubstituted phenols[190] are converted into the corresponding *o*- and *p*-benzoquinones, respectively.

Oxidative coupling reactions of phenols and related compounds are useful synthetic tool for construction of carbon skeletons of various biologically active naturally occurring compounds. A combination of RuO_2 and Lewis acids in fluoro acid media has proven to be the most efficient reagents for oxidative biaryl coupling of aromatic rings, although various organometallic reagents such as vanadium(V) oxyhalides and thallium(III) tris(trifluoroacetate) have been used for this purpose.[191] Intramolecular oxidative biaryl coupling reactions of phenols[192] and aromatic rings bearing electron-donating groups[193,194] can be performed efficiently under mild conditions by a combined use of RuO_2 and $BF_3{\cdot}Et_2O$ in a mixture of trifluoroacetic acid and trifluoroacetic acid anhydride or triflic acid and triflic acid anhydride (eqs 135 and 136). The reactions provide versatile methods for the



(135)

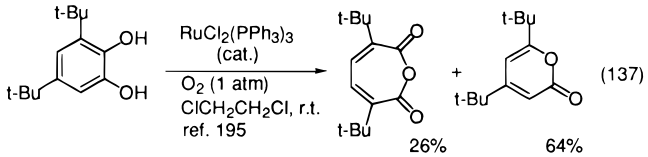


(136)

n = 1, R = H : glaucine 76%
n = 1, R = OMe : thalicsimidine 68%
n = 2, R = H : homoglaucine 60%

construction of biaryl lignans[192,193b] and isoquinoline alkaloids.[194]

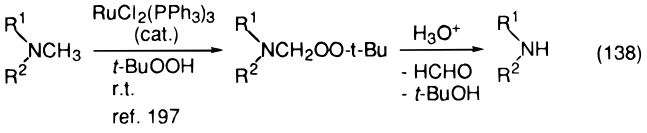
Aerobic oxidation of catechols can be performed with $RuCl_2(PPh_3)_3$ catalyst under ambient pressure of O_2 to give muconic acid anhydrides and 2*H*-pyran-2-ones (eq 137).[195]



(137)

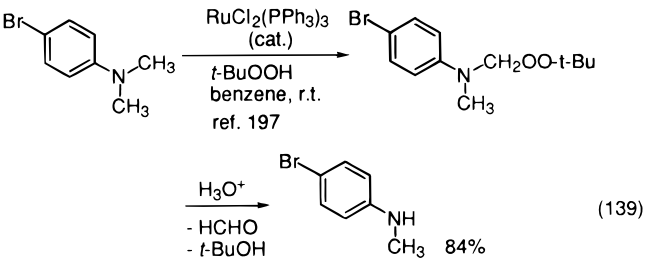
c. Oxidation of Amines and Amides

Catalytic systems of low-valent ruthenium complexes with peroxides exhibit specific reactivity toward oxidations of nitrogen compounds,[25,26,160,196] sharply differing from those with RuO_4 that simply converts amides to the corresponding imides.[148] Cytochrome P450 type oxidation of tertiary amines can be performed with a combination of non-porphyrin ruthenium complex catalysts and peroxides.[25] $RuCl_2(PPh_3)_3$-catalyzed oxidation of tertiary amines with *tert*-butyl hydroperoxide gives the corresponding α-(*tert*-butyldioxy)alkylamines efficiently (eq 138).[197]



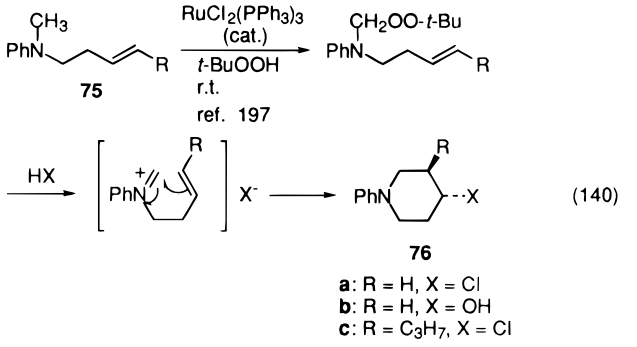
(138)

Similarly, α-methoxylation of tertiary amines can be carried out with hydrogen peroxide in the presence of $RuCl_3$ catalyst in MeOH.[198] In these reactions *N*-methyl groups are oxidized chemoselectively in the presence of other alkyl groups. Therefore, the reaction provides the first practical synthetic method for selective *N*-demethylation of tertiary methylamines by the oxidation and the subsequent hydrolysis of the peroxide with an aqueous HCl solution (eq 139). The



(139)

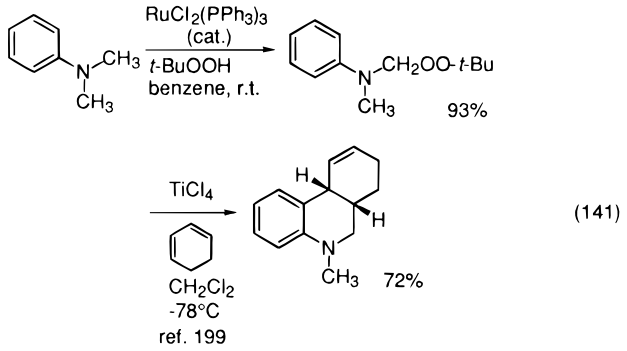
oxidation reaction also provides a novel, biomimetic construction of azacyclic skeletons, since the peroxides can be readily converted into the corresponding iminium ion intermediates (eq 140). The oxidation



(140)

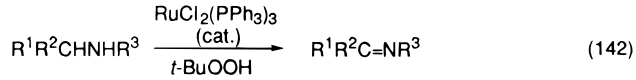
of *N*-methylhomoallylamines **75** and the subsequent treatment with acids gives substituted piperidines **76** via olefin−iminium ion cyclization.[197] Thus, the reaction of homoallylamine with 2 N HCl gives 4-chloropiperidine (**76a**), while similar treatment with aqueous CF_3CO_2H solution gives 4-hydroxypiperidine (**76b**). Cyclization of the peroxides bearing a substituted 3-butenyl group gives *trans*-3,4-disubstituted piperidines (**76c**) stereoselectively.

The iminium ion intermediate thus obtained can be trapped with external nucleophiles. Lewis acid-promoted reaction of olefins with *N*-(*tert*-butyldioxymethyl)arylamines obtained from tertiary *N*-methylarylamines gives the corresponding substituted tetrahydroquinolines (eq 141).[199]



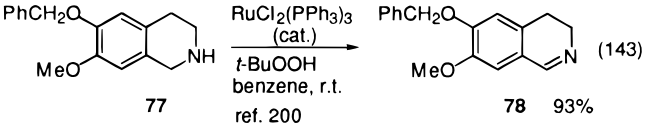
(141)

Secondary amines can be converted into the corresponding imines under the similar reaction conditions (eq 142).[200] Typically, tetrahydroisoquinoline



(142)

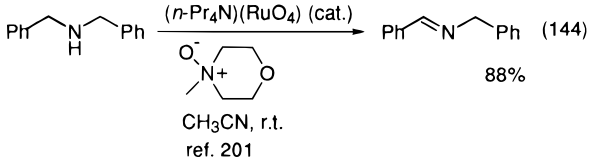
77 can be converted into the corresponding dihydroisoquinoline **78** which is a versatile synthetic intermediate for various isoquinoline alkaloids (eq 143). This is the first practical catalytic transforma-



(143)

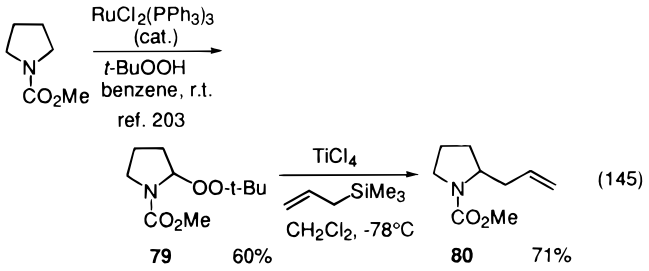
tion of secondary amines to the corresponding imines.

The catalytic system consisting of $(n\text{-}Pr_4N)(RuO_4)$ and *N*-methylmorpholine *N*-oxide[8] can be used for oxidative transformations of secondary amines to imines (eq 144)[201] and hydroxylamines to nitrones.[202]



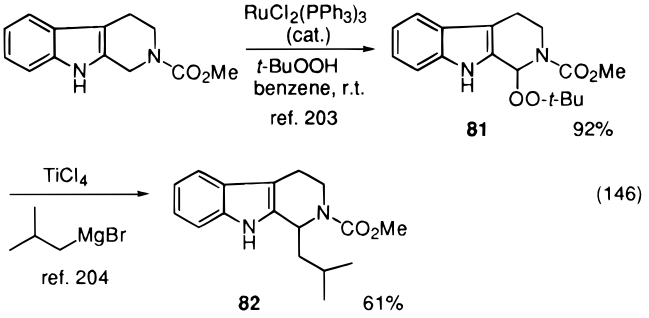
(144)

Biomimetic catalytic oxidation of amides can be performed by using a similar catalytic system, although they are very rare because of lower reactivities. The $RuCl_2(PPh_3)_3$-catalyzed oxidation of amides with *t*-BuOOH proceeds under mild conditions to give the corresponding α-(*tert*-butyldioxy)amides highly efficiently.[203] Since the Lewis acid-promoted reactions with nucleophiles give the corresponding *N*-acyl-α-substituted amines efficiently, the present reactions provide versatile methods for selective carbon−carbon bond formation at the α-position of amines.[203,204] Typically, α-*tert*-butyldioxyamide **79** derived from *N*-methoxycarbonylpyrrolidine can be converted into α-allylated compound **80** upon treatment of **79** with allyltrimethylsilane in the presence of $TiCl_4$ (eq 145).



(145)

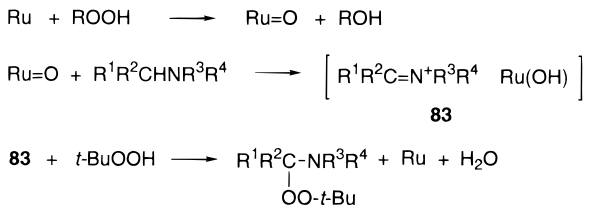
Similarly, the reaction of *tert*-butyldioxypyridoindole **81** with isobutylmagnesium bromide gave pyridoindole **82**,[204] which is a protected form of a β-carboline alkaloid isolated from *Elaeagnus commutata* (eq 146).



(146)

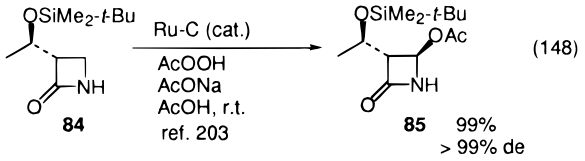
As shown in Scheme 14, these catalytic oxidation reactions can be rationalized by assuming the formation of oxoruthenium species by the reaction of low-valent ruthenium complexes with peroxides. α-Hydrogen abstraction from amines or amides and the subsequent electron transfer gives iminium ion hydroxy ruthenium complex **83**. Trapping **83** with *t*-BuOOH would afford the corresponding α-*tert*-butylhydroxyamines or amides, water, and low-valent ruthenium complexes to complete the catalytic cycle.

Scheme 14

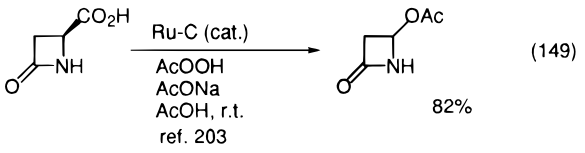


Modification of the present catalytic systems can achieve the direct acetoxylation reaction of β-lactams, which are quite difficult to oxidize because of their higher ring strains. The treatment of β-lactams with peracetic acid in acetic acid in the presence of low-valent ruthenium catalysts and sodium acetate gives the corresponding 4-acetoxy β-lactams highly efficiently (eq 147).[203,205] Importantly, (1*R*′,3*S*)-3-[1′-(*tert*-butyldimethylsilyloxy)ethyl]azetidin-2-one (**84**) can be converted with high diastereoselectivity into the corresponding 4-acetoxyazetidinone **85**, which is a versatile and key intermediate for the synthesis of thienamycin and other biologically active β-lactams (eq 148). β-Carboxy β-lactams undergo decarboxylation and subsequent acetoxylation to give β-acetoxy β-lactams (eq 149).[203] These oxidation reactions can be rationalized by the formation of highly reactive four-membered acyliminium ion intermediates through hydrogen abstraction by oxoruthenium species and the subsequent electron transfer. Trapping the intermediate by external nucleophiles of acetic acid affords the 4-acetoxy β-lactams. The nucleophilic attack of acetic acid dominates because it is much more nucleophilic than AcOOH. Acetoxylation of β-lactams can be performed with molecular oxygen (1 atm) in the presence of an aldehyde (eq 150).[206]

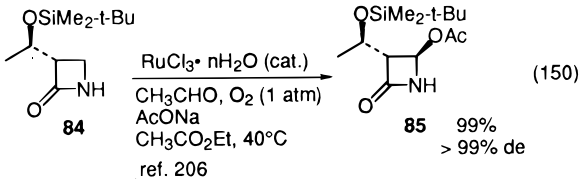
(147)



(148)



(149)



(150)

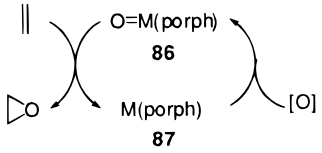
The reaction provides a powerful strategy for the preparation of optically active β-lactam **85**.

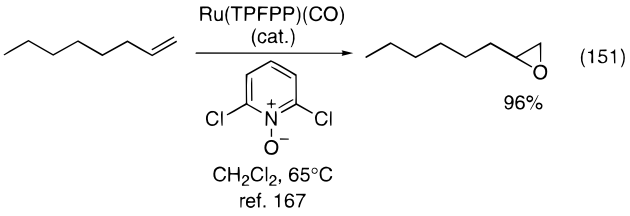
Aerobic oxidation of primary amines can be also performed with $RuCl_3$ catalyst under O_2 pressure (3 atm) at 100 °C, giving the corresponding nitriles.[178] Recently, dioxoporphyrin ruthenium Ru(TMP)$(O)_2$ (TMP = 5,10,15,20-tetramesitylporphyrinato) has proven to be an efficient catalyst for the aerobic oxidation of primary benzylic amines to the corresponding nitriles under air at 50 °C.[207]

d. Oxidation of Alkenes

Epoxidation of alkenes is one of the typical reactions of cytochrome P450. The model studies have been carried out using a variety of iron, manganese, and chromium metalloporphyrins.[208] Thus, oxometalloporphyrin complex **86** undergoes oxygen transfer to olefins to afford the corresponding epoxides along with metalloporphyrin **87**. The reaction with oxidants such as PhIO, tertiary amine *N*-oxides, and peroxides regenerates **86** to complete the catalytic cycle (Scheme 15). As well as various iron and manganese porphyrins, the reactivity of Ru(OEP)(PPh_3)Br has also been examined for the catalytic oxidation of styrene with PhIO.[209] A combination of dioxoruthenium porphyrin complexes such as Ru(TMP)$(O)_2$[167,210] and Ru($T_{2,6}$diFPP)$(O)_2$ ($T_{2,6}$diFPP = 5,10,15,20-tet-

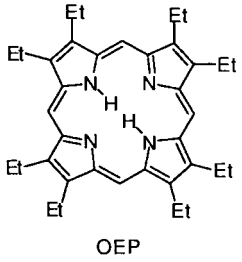
Scheme 15

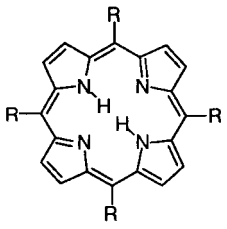


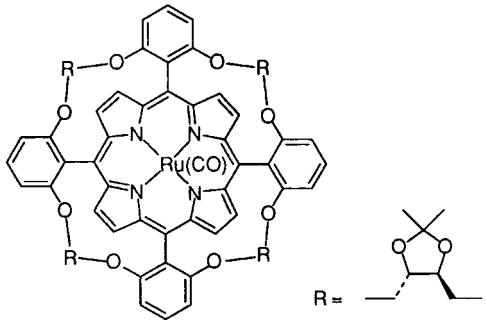


rakis(2,6-difluorophenyl)porphyrinato)[210] or Ru(TPFPP)(CO) (TPFPP = 5,10,15,20-tetrakis(pentafluorophenyl)porphyrinato)[211] with bulky amine *N*-oxide (eq 151) has proven to be a highly efficient catalytic system for the epoxidation of alkenes. Ruthenium tetrakis(4-chlorophenyl)porphyrin encapsulated in mesoporous molecular sieve MCM-41 modified with (3-aminopropyl)triethoxysilane shows high catalytic activity for epoxidation of olefins with *t*-BuOOH.[212] Table 4 summarizes the representative results for the ruthenium porphyrin catalyzed epoxidation of olefins.

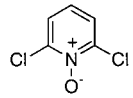
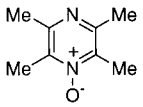
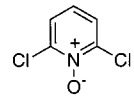
Table 4. Oxidation of Alkenes with Ruthenium Complex Catalysts





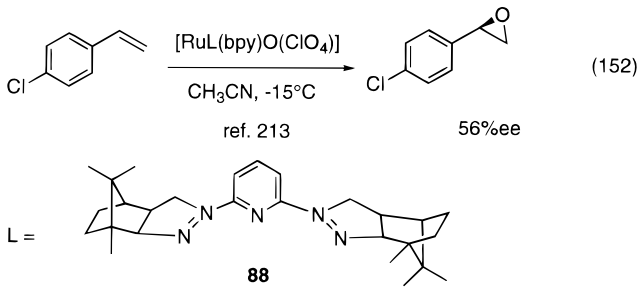


89

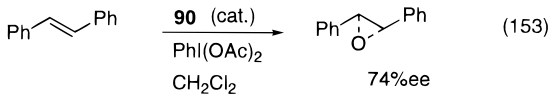
catalyst	oxidant	substrate[a]	T, °C	product	ref.
Ru(OEP)(PPh_3)Br[a]	PhIO	styrene	20	styrene oxide (21%)[g] (10)[i]	209a,b
$Ru(TMP)(O)_2$[b]		styrene	30	styrene oxide (100%)[h]	210a
$Ru(TMP)(O)_2$[b]		styrene	r.t.	styrene oxide (100%)[h]	167
Ru(TPFPP)(CO)[c]		1-octene	65	1,2-epoxyoctane (96%)[h]	211
RuL(CO)(EtOH) / MCM-41[d]	*t*-BuOOH	norbornene	r.t.	norbornene oxide (53%)[h] (9003)[i]	212
$[Ru(Me_3tacn)(O)_2(CF_3CO_2)]ClO_4$	PhIO	cyclooctene	25	cyclooctene oxide (8.5)[i]	215
$[RuCl(ppy)_2]ClO_4$[e]	PhIO	norbornene	22	norbornene oxide (6%)[h]	216
$[Ru(Me_3tacn)(O)_2(CF_3CO_2)]ClO_4$[f]	*t*-BuOOH	cyclooctene	25	cyclooctene oxide (70)[i]	215

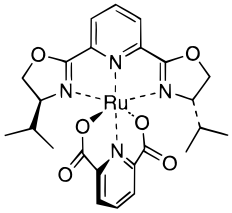
[a]OEP = octaethylporphyrinato. [b]TMP = tetramesitylporphyrinato. [c]TPFPP = tetrakis(pentafluorophenyl)porphyrinato. [d]L = tetrakis(4-chlorophenyl)porphyrinato. [e]ppy = 1-diphenylphosphino-2-(2'-pyridyl)ethane. [f]Me_3tacn = 1,4,7-trimethyl-1,4,7-triazacyclononane. [g]Yield is based on the starting alkene. [h]Yield is based on the oxidant. [i]Turnover number

The use of oxoruthenium complexes bearing optically active nitrogen ligands such as **88** provides enantioselective catalytic epoxidation of unfunctionalized olefins (eq 152).[213] Catalytic asymmetric epoxidation of styrene has been performed using a combination of chiral ruthenium porphyrin catalyst **89** with 2,6-dichloropyridine *N*-oxide to afford styrene oxide in 57% ee.[214]

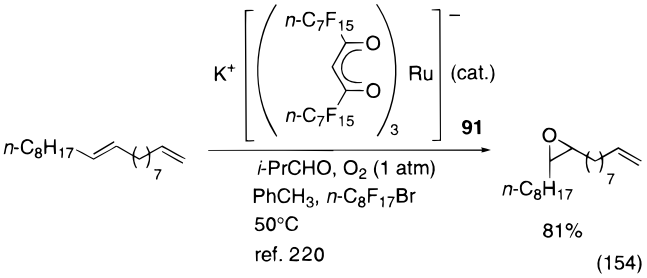


Non-porphyrin oxoruthenium complexes also act as an efficient catalyst for the epoxidation with a help of oxidants such as *t*-BuOOH[215] and PhIO.[215,216] Ruthenium complex **90** bearing chiral bis(oxazolinyl)-pyridine ligand exhibits enentioselectivity in the epoxidation of *trans*-stilbene (74% ee) in combination with [bis(acetoxy)iodo]benzene (eq 153).[217]



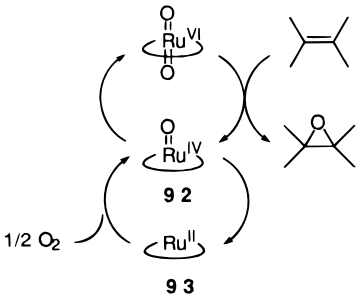


It has been found that the aerobic epoxidation of olefins can be performed efficiently with aldehydes and various transition metal catalysts.[218,219] Using a combination of ruthenium(II) perfluorinated 1,3-diketone complex catalyst **91** and perfluorinated solvents which have high solvility toward a range of gases, olefins can be epoxidized efficiently under similar conditions.[220] Only disubstituted olefins are chemoselectively converted into the corresponding epoxide (eq 154).

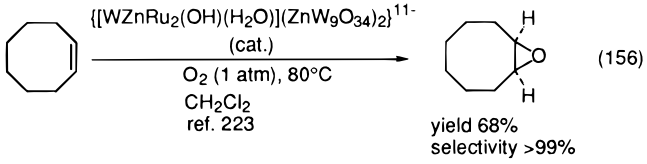


Direct aerobic epoxidation of olefins, which has never been reported using other transition metal catalysts, can be carried out at ambient pressure of O_2 using ruthenium porphyrin catalyst, such as Ru(TMP)$(O)_2$,[221] Ru(TMP)$(OH)_2$,[222] although the applicable substrate is limited to reactive olefins such as norbornene (eq 155). The reaction can be rationalized by assuming Scheme 16.[221] The active species Ru(TMP)$(O)_2$ would react with the olefin to afford oxoruthenium(IV) species **92**. Rapid disproportionation would give Ru(TMP)$(O)_2$ and ruthenium (II) complex **93**, which is reactive toward dioxygen and regenerate **92** to complete the catalytic cycle.

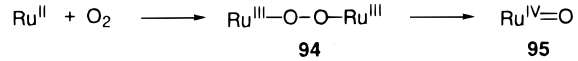
Scheme 16



Aerobic epoxidation can be also performed under O_2 with sterically hindered Ru-containing polyoxometalate $\{[WZnRu_2(OH)(H_2O)](ZnW_9O_{34})_2\}^{11-}$ (eq 156),[223] Ru(dmp)$_2$$(CH_3CN)_2$]$(PF_6)_2$,[224] and Ru$(O)_2(dmp)_2$]$(PF_6)_2$[225] (dmp = 2,9-dimethyl-1,10-phenanthroline). One of the proposed mechanisms for activation of molecular oxygen involves the formation of μ-peroxo species **94**, which undergoes the subsequent decomposition to oxoruthenium **95** (Scheme 17).[223]

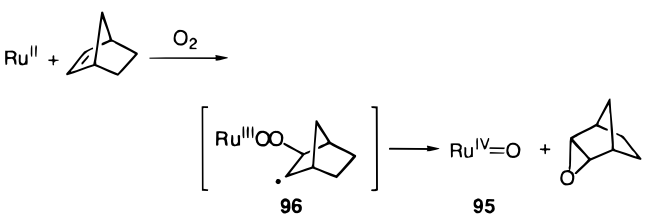


Scheme 17



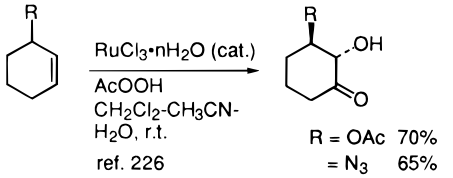
Another mechanism for the initiation of the aerobic epoxidation has been proposed as shown in Scheme 18.[224] The reaction of norbornene, dioxygen, and

Scheme 18



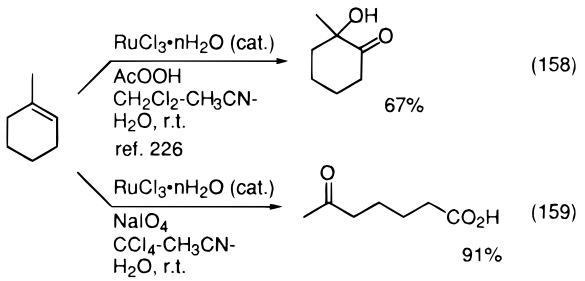
ruthenium(II) complex gives a metal peroxo norbornyl radical **96**. Decomposition of the intermediate **96** affords **95** along with norbornene oxide.

Oxidative transformation of olefins to α-ketols can be performed selectively, when the $RuCl_3$-catalyzed oxidation of alkenes with peracetic acid is carried out in an aqueous solution.[226] Typically, allylic acetates and azides are oxidized to the corresponding acetoxy and azido α-ketols with high chemo- and stereoselectivities (eq 157). The difference of the present



(157)

oxidation from that with RuO_4 has been clearly shown by the oxidation reactions of 1-cyclohexene. Thus, the $RuCl_3$-catalyzed oxidation with peracetic acid gives 2-hydroxy-2-methylcyclohexene (67%), while the oxidation of the same substrate under the conditions, in which RuO_4 is generated catalytically, gives 6-oxoheptanoic acid (91%) (eqs 158 and 159).



(158)

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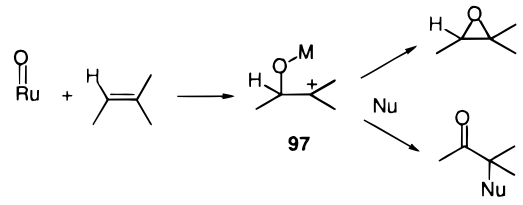
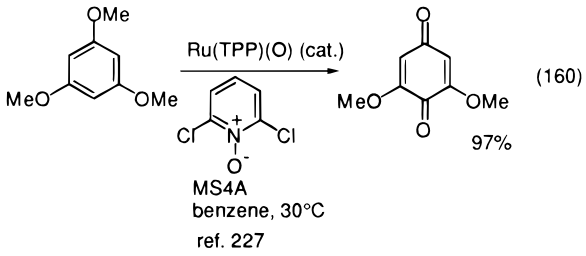
The reactions can be explained by the formation of cationic intermediate **97** by electrophilic attack of oxoruthenium species to olefins as shown in Scheme 19. Trapping the intermediate **97** with water fol-

Scheme 19



lowed by *β*-elimination of M−H species leads to α-ketols,[226] while intermediate **97** usually undergoes ring closure in the absence of nucleophiles to afford the corresponding epoxides.

Oxidation of aromatic rings is performed efficiently under the similar reaction conditions. The catalytic system including Ru(TPP)(CO) (TPP = 5,10,15,20-tetraphenylporphyrinato) and pyridine *N*-oxide can be applied to the selective oxidation of aromatic rings to the corresponding *p*-quinones (eq 160).[227] The ^{18}O-labeling experiments showed that the reaction proceeds via selective hydroxylation of the aromatic ring by oxoruthenium porphyrins to afford phenol derivatives, which undergo the subsequent oxidation to afford the corresponding quinones as shown in Scheme 20.



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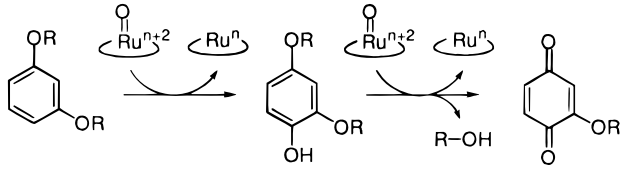
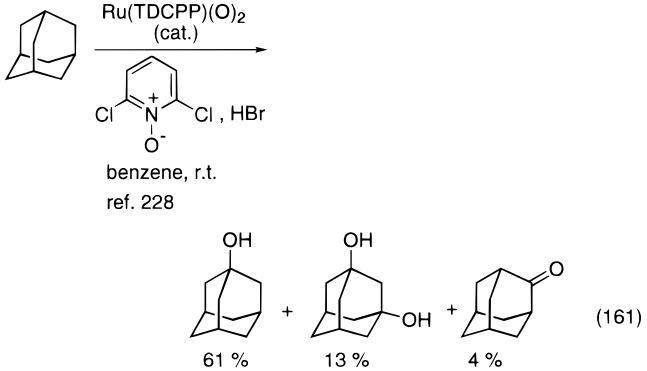
Scheme 20



e. Oxidation of Alkanes

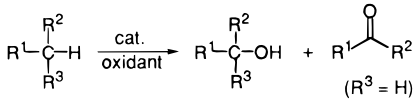
Direct oxidation of saturated hydrocarbons is one of the typical functions of cytochrome P450. Combination of metalloporphyrins with oxidants, that generates oxometal porphyrins, has proven to be highly effective for catalytic oxidation of alkanes. Aliphatic and alicyclic hydrocarbons can be converted into the corresponding alcohols and ketones with oxidants such as iodosyl benzene, amine *N*-oxides, alkyl hydroperoxides, and H_2O_2 in the presence of various iron and manganese porphyrin catalysts.[208] Ruthenium porphyrin complexes such as Ru(OEP)-(PPh_3)Br also showed the catalytic activity by combination with iodosylbenzene.[209b] Extremely high catalytic activities for alkane hydroxylation were achieved using a combination of ruthenium porphyrin catalysts and 2,4-dichloropyridine *N*-oxide. Typically, adamantane can be converted into 1-adamantanol, 1,3-adamantanediol, and 2-adamantanone in 61, 13, and 4% yield (based on the starting adamantane) upon treatment with Ru(TDCPP)$(O)_2$ catalyst [TDCPP = 5,10,15,20-tetrakis(2,6-dichlorophenyl)-porphyrinato], 2,6-dichloropyridine *N*-oxide, and HBr. The turnover numbers of 1-adamantanol reach 12 300 (eq 161).[27,228] Dichloroporphyrinruthenium derived



(161)

from dioxoporphyrin ruthenium with HX has proven to be an active species for this efficient catalytic system, although the precise mechanism must wait

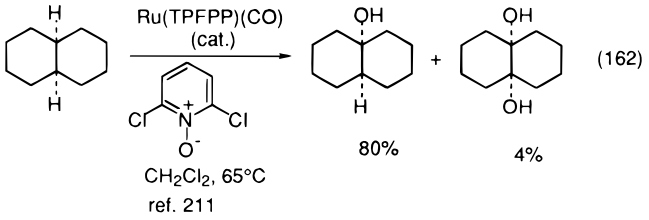
Table 5. Oxidation of Alkanes with Non-porphyrin Ruthenium Complex Catalysts



catalyst	oxidant	substrate[a]	T, °C	product[b]	ref.
$[Ru(Me_3tacn)(O)_2(CF_3CO_2)]ClO_4$[c]	PhIO	CyH	25	Cy=O (21)[h]	215
$BaRuO_3(OH)_2$-CF_3CO_2H-bpy[d]	PhIO	CyH	20	CyOH (37)[h] Cy=O (9)[h]	232
cis-$[Ru(dmp)_2(H_2O)_2](PF_6)_2$[e]	H_2O_2	AdH	75	1-AdOH (15%)[f] 2-AdOH (4%)[f] 2-Ad=O (2%)[f]	224
cis-$[Ru(dmp)_2(H_2O)_2](PF_6)_2$[e]	H_2O_2	CH_4	75	CH_3OH + HCHO (4 : 1) (125)[h]	233
$RuCl_2(PPh_3)_3$	*t*-BuOOH	CyH	20	CyOH (3%)[f] Cy=O (19%)[f]	234
cis-$[Ru(6,6\text{-}Cl_2bpy)_2(H_2O)_2](CF_3SO_2)_2$[d]	*t*-BuOOH	CyH	20	CyOH (24%)[g] Cy=O (37%)[g]	235
$[Ru(Me_3tacn)(O)_2(CF_3CO_2)]ClO_4$[c]	*t*-BuOOH	CyH	5	CyOH (18)[h] Cy=O (55)[h]	215
5% Ru/C	AcOOH	CyH	20	CyOH (1%)[f] Cy=O (42%)[f]	236
$[(C_6H_{13})_4N]_5SiRu(H_2O)W_{11}O_{39}$	$KHSO_5$	AdH	60	1-AdOH (36%)[f] 2-AdOH (2%)[f] 2-Ad=O (18%)[f]	237

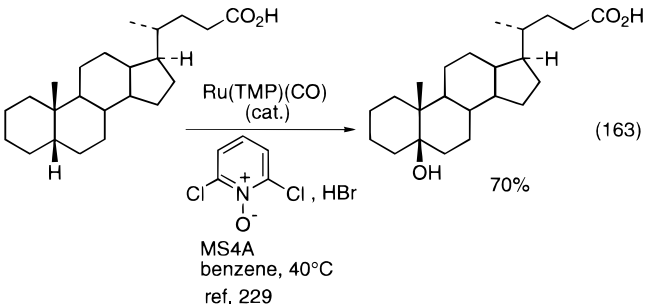
[a]CyH = cyclohexane. AdH = adamantane. [b]CyOH = cyclohexanol. Cy=O = cyclohexanone. n-AdOH = n-adamantanol. 1,3-$Ad(OH)_2$ = 1,3-adamantanediol. 2-Ad=O = 2-adamantanone. [c]Me_3tacn = 1,4,7-trimethyl1,4,7-triazacyclononane. [d]bpy = 2,2'-bipyridine. [e]dmp = 2,9-dimethyl-1,10-phenanthroline. [f]Yield is based on the starting alkane. [g]Yield is based on the oxidant. [h]Turnover number.

for further investigation. Using ruthenium pentafluorophenylporphyrin catalyst Ru(TPFPP)(CO) and 2,6-dichloropyridine *N*-oxide similar oxidation can be performed in aprotic media (eq 162) with high ef-



(162)

ficiency and high rates (64 turnovers/min).[211] This catalytic system has been applied to the regioselective oxidation of steroidal substrates (eq 163).[229]



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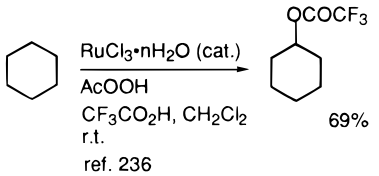
Many methods for catalytic oxidations with nonporphyrin metal catalysts have been investigated extensively because of their particular importance in view of synthetic, mechanistic, and industrial aspects.[230] As well as a family of iron-catalyzed oxidation of alkanes (Fe catalyst−pyridine and Fe catalyst−O_2−reductant) called Gif system,[231] a number of ruthenium-catalyzed reactions have been extensively investigated. The catalytic systems of low-valent ruthenium complexes with oxidants such as PhIO,[215,232] H_2O_2,[224,233] *t*-BuOOH,[25,234,235] AcOOH,[236] and $KHSO_5$[237] are effective for the oxidation of various linear and cyclic alkanes affording the corresponding alcohols and ketones. The representative results for the oxidation of alkanes with non-porphyrin ruthenium complex catalysts are summarized in Table 5.

The reactions can be applied to introduction of substituents into unactivated alkanes. Direct trifluoroacetoxylation of alkanes can be performed chemoselectively by the ruthenium-catalyzed reaction with peracetic acid in trifluoroacetic acid.[236] Typically, $RuCl_3$-catalyzed oxidation of cyclohexane with 30% peracetic acid in ethyl acetate in a mixture of trifluoroacetic acid and CH_2Cl_2 (5:1) at room temperature gave cyclohexyl trifluoroacetate in 69% yield (eq 164).

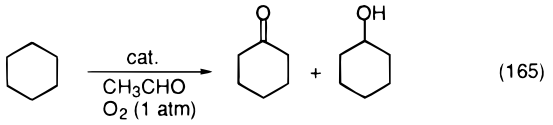


(164)

Although precise mechanistic information of these catalytic reactions remains to be explored, most of the reactions are explained by the formation of oxoruthenium intermediates $Ru^{(n+2)+}{=}O$ by the reaction of low-valent ruthenium $Ru^{n+}L_n$ with oxidants. Hydrogen abstraction from alkanes would give metal-caged radical intermediate, $[R^1R^2R^3C{\cdot}Ru^{n+}(OH)L_n]$, which undergoes one electron transfer and the subsequent hydroxy ligand transfer or direct collision

from radical intermediate to afford the corresponding alcohols and $Ru^{n+}L_n$ to complete the catalytic cycle. High reactivity of oxoruthenium species toward alkane oxidation has been confirmed in the stoichiometric reactions of various oxoruthenium complexes such as Ru(trpy)(bpy)$(O)_2^{+}$,[238a] Ru(TMC)$(O)_2^{+}$,[238b] *cis*-[Ru(Tet-Me_6)O_2]$^{2+}$,[171b] $BaRu(O)_2(OH)_3$,[232,238c] and Ru-(Me_3tacn)$(O)_2(CF_3CO_2)^{+}ClO_4^{-}$ [215] with alkanes (TMC = 1,4,8,11-tetramethyl-1,4,8,11-teraazacyclotetradecane, Tet-Me_6 = *N*,*N*,*N*′,*N*′-tetramethyl-3,6-diazaoctane-1,8-diamine). These oxidations normally show a relatively large isotope effect (k_H/k_D) for the oxidation of cyclohexane and tertiary C−H selectivities for that of adamantane. These facts have been generally interpreted to be arising from radical character of hydrogen abstraction by oxoruthenium intermediates, since stoichiometric reaction of oxometals with alkane often shows similar reactivities.

Aerobic oxidation of alkanes are a particularly important subject for the industrial process such as oxidative transformation of cyclohexane to cyclohexanone. The method employed in the oxidation of alcohols[183] and β-lactams[206] as mentioned above can be applied to aerobic oxidation of alkanes under ambient pressure of O_2 (1 atm). Thus, $RuCl_3$-[239] or Ru-(TPFPP)(CO)[240]-catalyzed reactions of alkanes with molecular oxygen (1 atm) proceed under mild conditions in the presence of acetaldehyde to give the corresponding alcohols and ketones (eq 165). Extremely

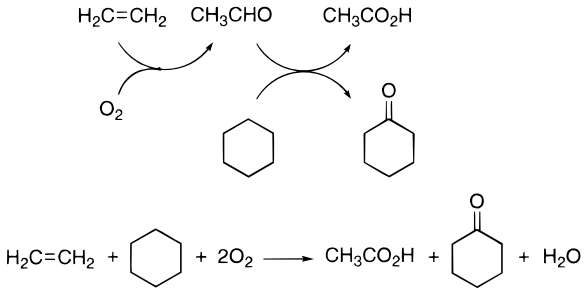


(165)

cat. = $RuCl_3$•nH_2O,[239] Ru(TPFPP)(CO)[240]

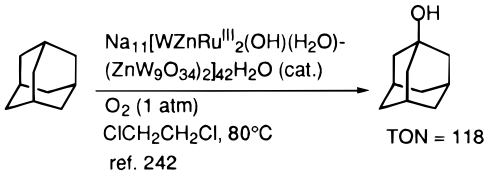
high turnover number (14 100) for the oxidation of cyclohexane can be achieved under mild reaction conditions using Ru(TPFPP)(CO) catalyst.[240] The reaction provides a powerful industrial strategy for the synthesis of cyclohexanone from cyclohexane, by combination of Wacker oxidation of ethylene with the present catalytic oxidation as shown in Scheme 21.

Scheme 21



The method is of importance as a forward-looking process that fulfills future requirements toward atom economy.

Direct use of molecular oxygen without photoexcitation or reducing agents are the most desirable methods for aerobic oxidation of alkanes. Very few methods for direct aerobic oxidation of alkanes have been reported using ruthenium cluster catalyst $[Ru_3O(OCOCF_2CF_2CF_3)_6(Et_2O)_3]^{+}$ [241] and ruthenium-substituted polyoxometalate $[WZnRu_2(OH)(H_2O)(ZnW_9O_{34})_2]^{11-}$ [242] (eq 166).

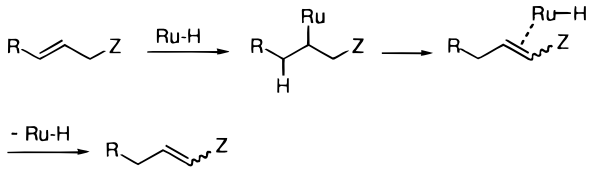


(166)

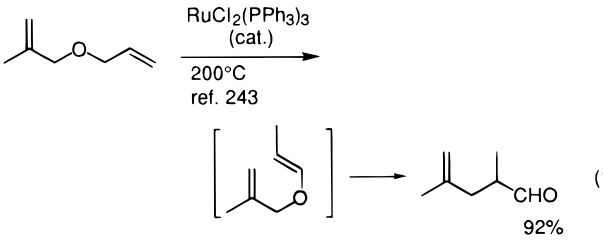
IV. Isomerization

Various low-valent ruthenium complexes act as efficient catalysts for isomerization of β,γ-unsaturated oxygen and nitrogen containing compounds, since ruthenium hydride intermediates have a strong affinity to promote hydrometalation of olefins and β-elimination of ruthenium hydride as shown in Scheme 22. The representative examples of the

Scheme 22



isomerization reaction of olefins with hydridoruthenium catalysts are shown below. Diallyl ethers are converted into allyl vinyl ethers which undergo the subsequent Claisen rearrangement to give the corresponding γ,δ-unsaturated aldehydes (eq 167).[243] Other allylic compounds such as allylbenzenes (eq 168),[244] *N*-allylamides (eq 169),[245] and allyl silyl ethers (eq 170)[246] undergo selective isomerization



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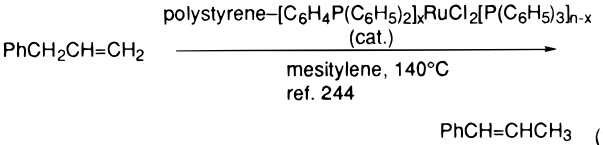

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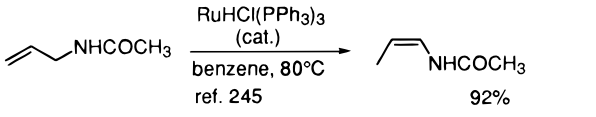

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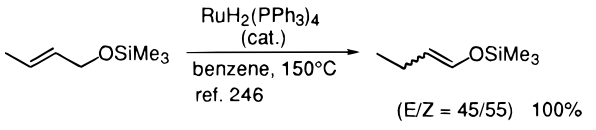
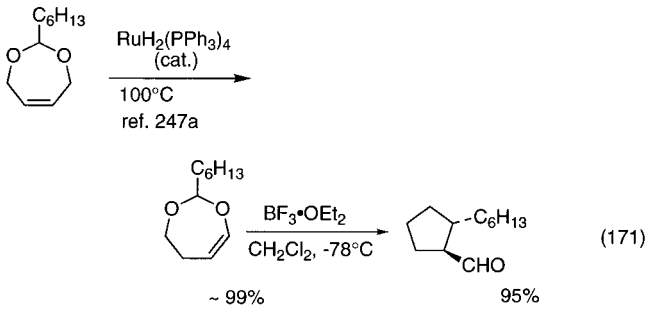
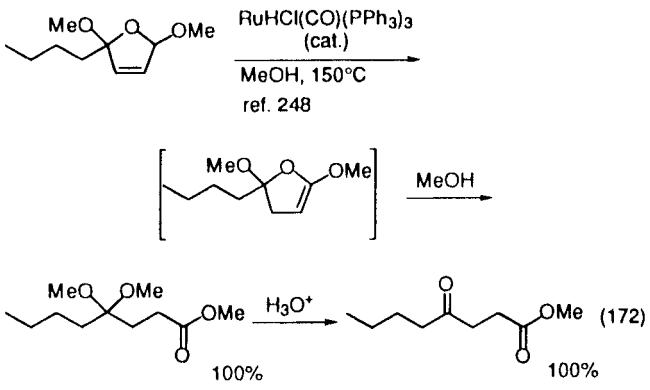


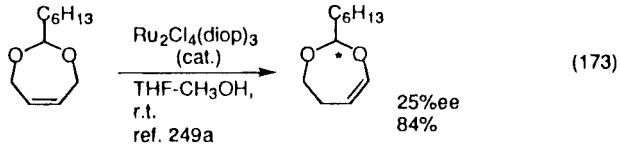
(170)

with hydridoruthenium catalysts to afford the corresponding vinylbenzenes, enamides, and silyl enol ethers, respectively. Similar treatment of alkyl allyl acetals gives the corresponding alkyl alkenyl acetals which can be converted into aldehydes[247] and

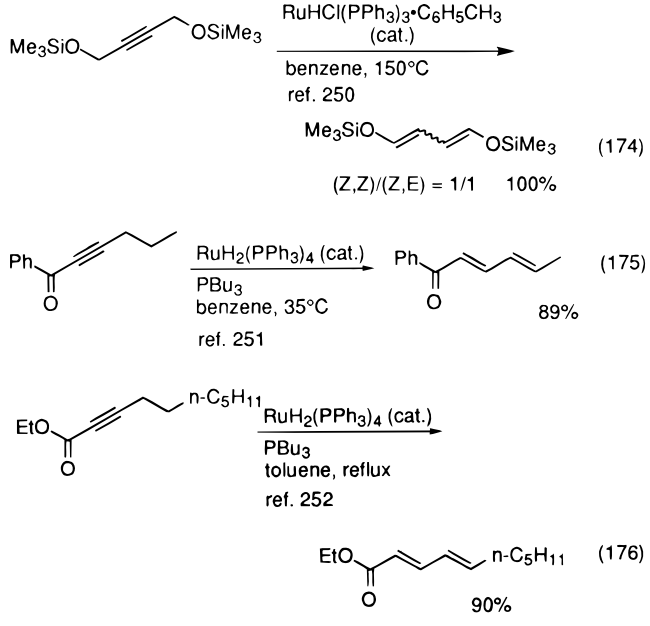
esters[248] via Lewis acid-promoted O- to C-migration (eqs 171 and 172). The reaction has been applied to the asymmetric reactions using $Ru_2Cl_4(diop)_3$ catalyst (eq 173).[249] Alkynes such as propargyl silyl ethers





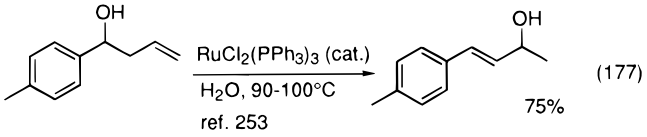


(eq 174),[250] α,β-ynones (eq 175),[251] and 2-ynoic esters (eq 176)[252] are converted into the corresponding



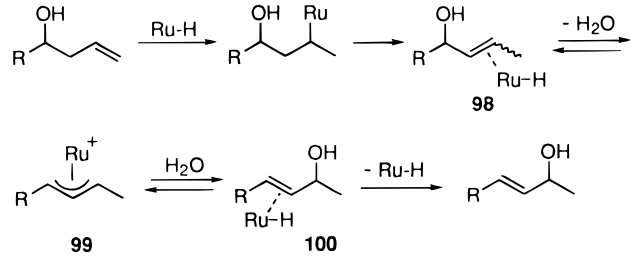
dienyl compounds. Similar treatment of unsaturated alcohols such as allyl alcohols[89] and propargyl alcohols[90] gives rise to isomerization to the corresponding carbonyl compounds via intermolecular hydrogen transfer.

When homoallyl alcohols are heated in water under the similar reaction conditions, reshuffling of both hydroxy group and the olefin occurred via the similar isomerization to afford the corresponding allyl alcohols (eq 177).[253] A possible mechanistic explanation

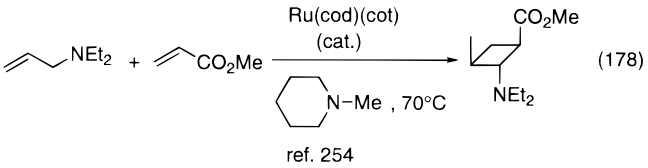


for this selective reshuffling of hydroxy group is shown in Scheme 23. Hydroruthenation and β-hydride elimination give the allyl alcohol hydrido complex **98**. π-Allyl ruthenium complex **99** is formed through carbon−oxygen bond cleavage of the allyl alcohol. Nucleophilic attack of water at less hindered side of **99** affords the stable complex **100** which gives the product and ruthenium hydride to complete the catalytic cycle.

Scheme 23



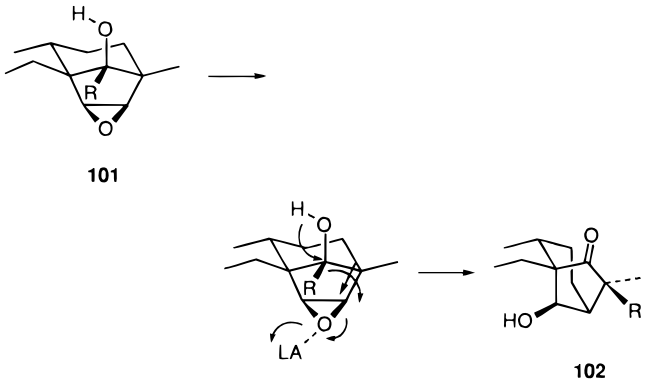
Allylamines react with acrylic compounds in the presence of Ru(cod)(cod) catalyst to give cyclobutane-β-amino acid derivatives (eq 178).[254] The reaction can



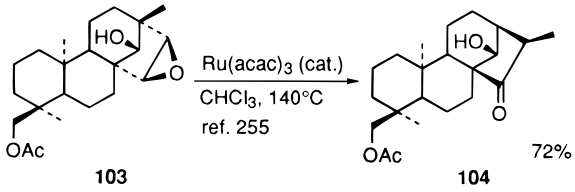
be rationalized by the formation of the enamines by the ruthenium-catalyzed isomerization and subsequent cycloaddition reaction with acrylic compounds.

Rearrangement of tetracyclic diterpenoids such as 5,16-epoxybeyeranes **101** to kaur-15-enes **102** was

Scheme 24



usually carried out by treatment with Lewis acid (Scheme 24). The moderate Lewis acidity of ruthenium complexes has proven to be suitable to perform these isomerization reactions catalytically. Typically, treatment of *ent*-18-acetoxy-15α,16α-epoxybeyerane (**103**) with $Ru(acac)_3$ catalyst at 140 °C gives *ent*-18-acetoxy-14α-hydroxy-(16*R*)-kauran-15-one (**104**) as a sole product (eq 179).[255]



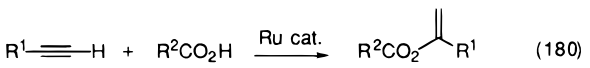
103 104 (179)

V. Nucleophilic Addition to Carbon–Carbon and Carbon–Heteroatom Multiple Bonds

Since some ruthenium complexes bearing hydrido, olefin, and arene ligands easily dissociate their ligands to generate coordinatively unsaturated species, they can activate the carbon−carbon triple bond of various alkynes and carbon−nitrogen triple bonds of nitriles upon coordination. Attack of various nucleophiles to these activated substrates provides various catalytic transformations of alkynes and nitriles.

A. Nucleophilic Addition to Alkynes

Terminal alkynes undergo regioselective nucleophilic addition of carboxylic acids upon heating with various low-valent ruthenium complex catalysts such as $RuCl_3$,[256] $Ru(cod)_2$,[257−259] $RuCl_2$(arene),[260−264] and $Ru_3(CO)_{12}$[265] to give the corresponding enols (eq 180).[29] The representative results are listed in Table



(180)

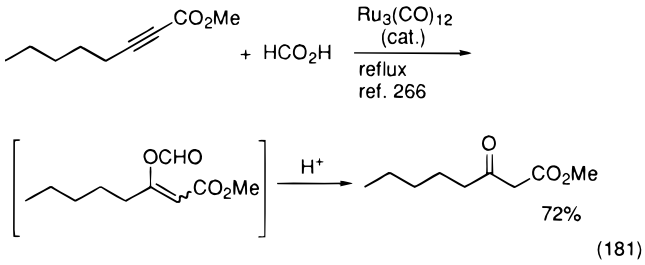
6. Generally, the nucleophilic attack of carboxylic acids occurs at the C_2 position of alkynes to afford enol esters bearing *exo*-olefins, regioselectively. When formic acid was used as a nucleophile, the corresponding saturated ketones could be obtained via

Table 6. Addition of Carboxylic Acids to Alkynes

catalyst	R^1	R^2	T, °C	yield, %	ref.
$RuCl_3$•nH_2O - PMe_3	Ph		120	73	256
$Ru(cod)_2$ - PBu_3	*n*-Pr	CH_2=C(Me)-	80	93	257
$Ru(cod)_2$ - PBu_3 -MA[a]	*n*-Bu	Me	80	99	258
$Ru(cod)_2$ - PCy_3 -MA[a]	$EtOCO_2CH_2$	Me	80	63	259
$[RuCl_2(p\text{-cymene})]_2$	EtO	$PhCH_2OCO(CH_2)_5$	40	84	260
$RuCl_2(PMe_3)(p\text{-cymene})$	Me	$BocNHCH_2$	100	76	261
$RuCl_2(PMe_3)(p\text{-cymene})$	*n*-Bu		80	94	262
$RuCl_2(PMe_3)(p\text{-cymene})$	CH_2=C(Me)		80	65	263
$RuCl_2(PPh_3)(p\text{-cymene})$	Ph	H	100	95	264
$Ru_3(CO)_{12}$	*n*-C_3H_7	Ph	145	92	265

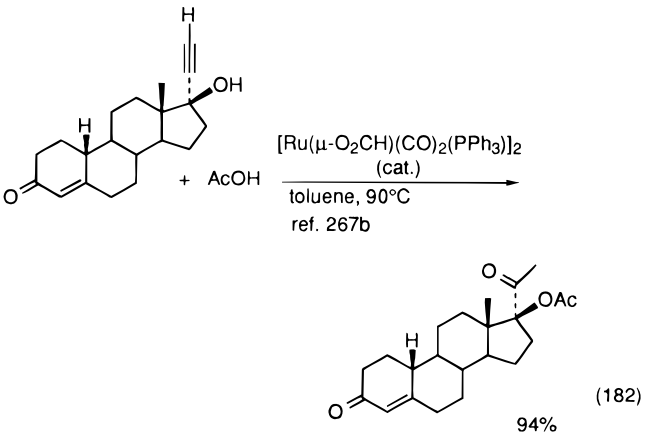
[a]MA = maleic anhydride

hydrolysis of the enol esters (eq 181).[266] Propargyl



(181)

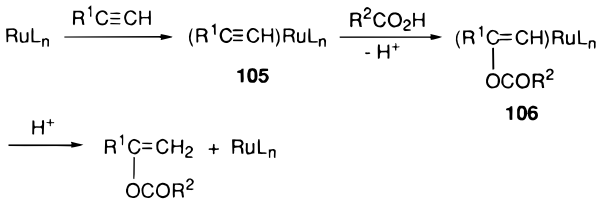
alcohols can be converted into the corresponding α-acetoxy ketones via regioselective addition of carboxylic acid and subsequent transesterification reaction with the hydroxy group (eq 182).[267]



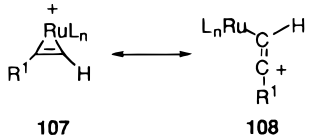
(182)

The reaction can be simply rationalized by assuming the mechanism shown in Scheme 25. Nucleo-

Scheme 25



philic attack of carboxylic acid to the coordinated alkyne of complex **105** gives acyloxyvinyl ruthenium complex **106**. Protonation of **106** produces the product enol esters and low-valent ruthenium complex to complete the catalytic cycle. To explain the regioselective attack of carboxylic acids at C_2 position of alkynes, the resonance structures **107** and **108**, which

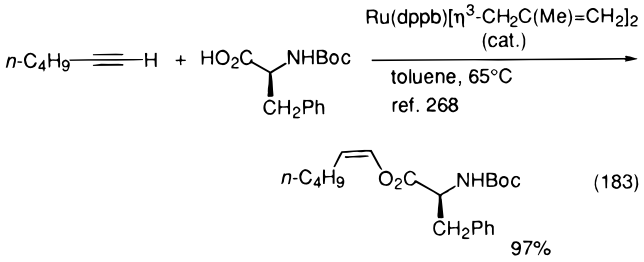


107 108

are corresponding to **105**, have been postulated as reactive intermediate.[29b,260,263] Alternatively, a mechanism involving oxidative insertion of ruthenium into the O−H bond of carboxylic acid has been postulated. The resulting hydridoacyloxy ruthenium reacts with alkynes to afford an acyloxyvinyl ruthenium complex

which undergoes reductive elimination to complete the catalytic cycle.[257]

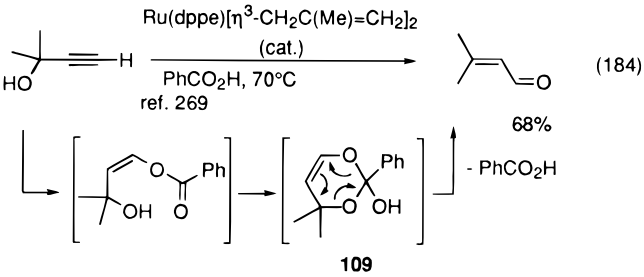
It is in contrast to the fact that some π-allyl ruthenium complexes bearing alkyldiphosphine ligands catalyze regioselective attack of carboxylic acids to C_1 position of alkynes. (*Z*)-Enol esters can be obtained with high regio- and stereoselectivities upon treatment of terminal alkynes with various carboxylic acids in the presence of Ru(dppb)(η^3-$CH_2CMe{=}CH_2$)$_2$ catalyst (eq 183).[268] Since the diphosphine ligand



(183)

bearing the longer chain such as dppb affords better chemoselectivity, steric factors rather than electronic effects could be responsible for the external attack of carboxylic acids to **107** or **108**.

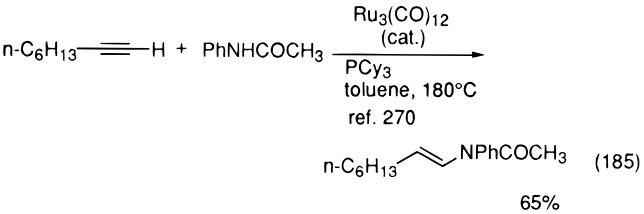
When propargylic alcohols are allowed to react with benzoic acid under the similar reaction conditions, isomerization reaction takes place selectively to afford the corresponding α,β-unsaturated aldehydes (eq 184).[269] The reaction can be explained by the forma-



(184)

tion of the corresponding enol esters and cyclic intermediate **109**. Thermal elimination of benzoic acid gives the product.

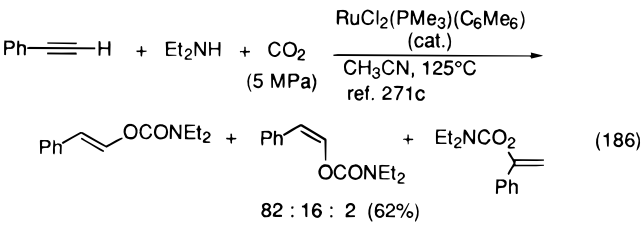
Amides also act as nucleophiles toward addition to terminal alkynes under the similar reaction conditions. $Ru_3(CO)_{12}$-catalyzed addition of *N*-aryl amides to terminal alkynes proceed regioselectively at C_1 position to afford the corresponding (*E*)-enamides (eq 185).[270] Redox mechanism including oxidative addi-



(185)

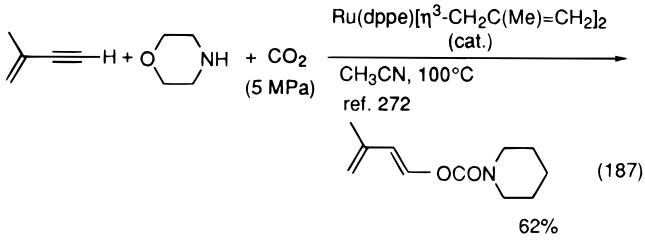
tion of N−H bond of amides to ruthenium followed by insertion of triple bond, and reductive elimination has been postulated for this reaction.

A similar type of nucleophilic addition to terminal alkynes can be performed with a combined use of secondary amines and CO_2. Thus, using ruthenium catalysts such as $RuCl_3$,[271] $RuCl_2(PR_3)$(arene) (eq 186),[271c] Ru($Ph_2P(CH_2)_nPPh_2$)(η^3-$CH_2CMe{=}CH_2$)$_2$ (eq



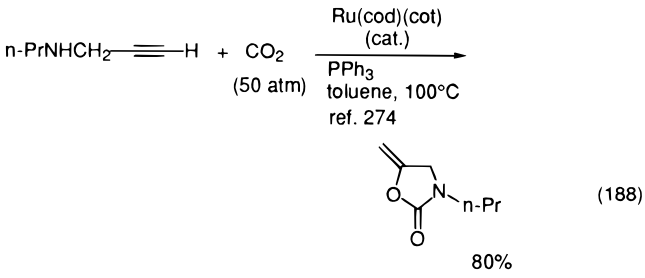
(186)

187),[272] and $Ru_3(CO)_{12}$,[271c,273] terminal alkynes can be



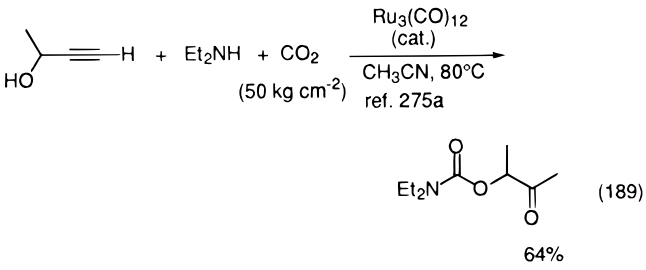
(187)

converted into the corresponding vinyl carbamates under CO_2 pressure. An intramolecular version of these reactions using propargylamines afford cyclic enol carbamates (eq 188),[274] while similar treatment



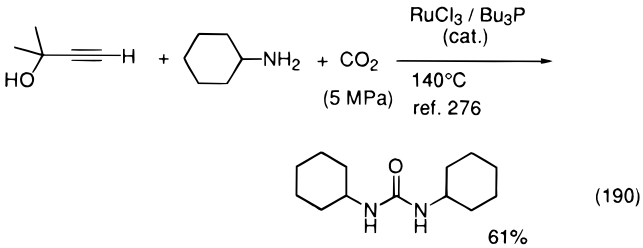
(188)

of propargyl alcohols affords the corresponding β-oxo alkylcarbamates via α-methylene cyclic carbonate and subsequent nucleophilic addition of amines (eq 189).[275] Employing primary amines instead of sec-



(189)

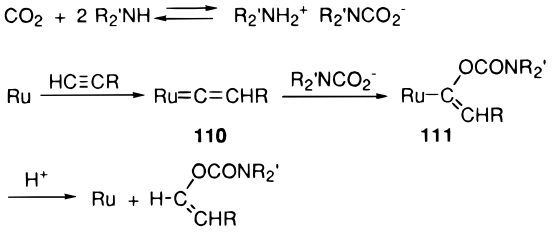
ondary ones gives rise to the subsequent nucleophilic reaction of primary amines with the product vinyl carbamates to afford the corresponding *N*,*N*′-dialkylureas (eq 190).[276] These are very rare successful



(190)

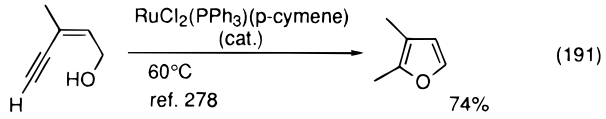
cases for utilization of CO_2 in organic synthesis. The regioselectivity of the reactions is opposite that observed for the addition of carboxylic acids to the same alkynes. Considering the opposite regioselectivity and the fact that reaction occurs only with terminal alkynes, it has been postulated that the reaction proceeds via the formation of vinylidene ruthenium intermediate **110** as shown in Scheme 26. Thus, the reaction of terminal alkynes with low-

Scheme 26

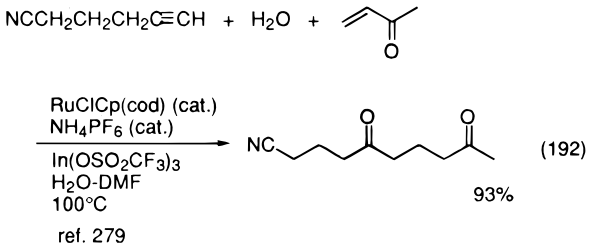


valent ruthenium complex gives **110** via 1,2-hydrogen shift.[277] The reaction of CO_2 with a secondary amine gives ammonium carbamate, which undertakes regioselective nucleophilic attack to **110** to afford complex **111**. Protonation of **111** affords products and regenerates the low-valent ruthenium complex.

Intramolecular addition of O−H to a terminal carbon−carbon bond of alkyne has been performed under the similar conditions using hydroxy enynes as a substrate.[278] Typically, the reaction of (*Z*)-3-methylpent-2-en-4-yn-1-ol with $RuCl_2(PPh_3)$(*p*-cymene) catalyst at 60 °C gives 2,3-dimethylfuran (eq 191).

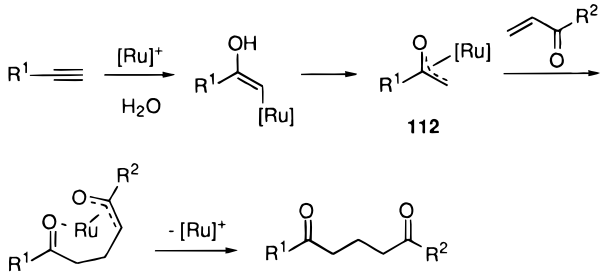


When a mixture of terminal alkynes, water, and alkyl vinyl ketones is allowed to react with a catalytic system consisting of RuClCp(cod), NH_4PF_6, and $In(OSO_2CF_3)_3$, the corresponding 1,5-diketones can be obtained selectively (eq 192).[279] Although precise

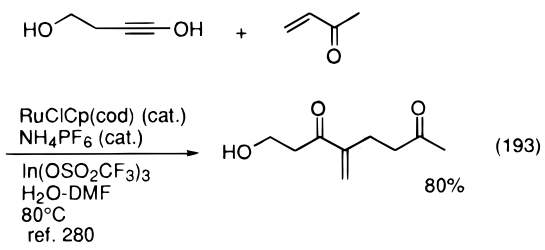


mechanism remains to be clarified, the reaction can be rationalized by assuming the ruthenium-catalyzed nucleophilic addition of water to alkynes as similar to the addition of carboxylic acids. Isomerization gives the ruthenium enolate intermediate **112**, which undergoes conjugate addition with alkyl vinyl ketones and the subsequent protonation to give the product (Scheme 27). Similar conjugate addition of propargyl alcohols to methyl vinyl ketones can be

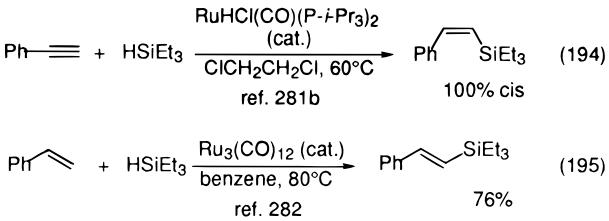
Scheme 27



performed with the same catalytic system to give the corresponding enediones (eq 193).[280]



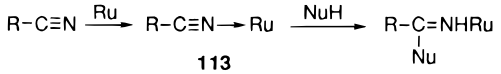
Hydrosilanes can act as nucleophiles toward alkynes and alkenes in the presence of ruthenium catalyst. The RuHCl(CO)(P-*i*-$Pr_3)_2$-catalyzed hydrosilylation of phenylacetylene affords *cis*-PhCH=CHSiEt_3 with high regio- and stereoselectivities (eq 194),[281] while reductive hydrosilylation occurs upon similar treatment with styrenes in the presence of $Ru_3(CO)_{12}$ catalyst to give the corresponding *trans*-vinylsilanes (eq 195).[282]



B. Nucleophilic Addition to CN Triple Bonds of Nitriles

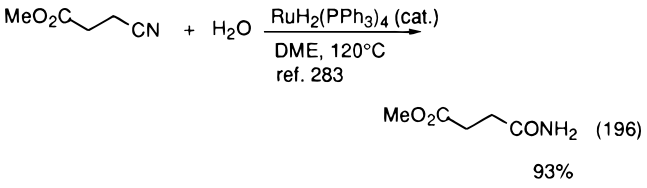
Transformations of cyano functionality with nucleophiles have been useful synthetic methods for the preparation of a variety of carbonyl compounds; however, the method often encounters the limitation of acidic conditions that are required to activate rather stable CN triple bonds. Low-valent ruthenium complexes have proven to show remarkable Lewis acidity, and high efficiency for the activation of CN triple bond of nitriles. Capture of intermediate **113** with nucleophiles provides a variety of catalytic transformations of nitriles under neutral conditions (Scheme 28).[30,31]

Scheme 28



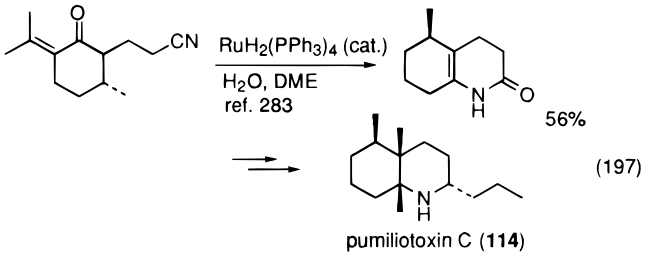
When only 1−2 equiv of water are used as nucleophile, hydration of nitriles proceeds smoothly upon

treatment with $RuH_2(PPh_3)_4$ catalyst under neutral conditions to give the corresponding amides (eq 196).[283] Similar treatment with δ-ketonitriles, ob-



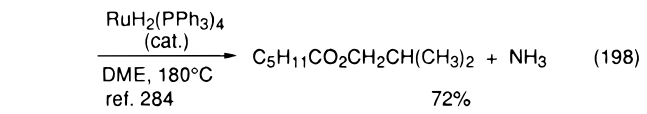
(196)

tained readily by cyanoethylation of ketones, proceeds efficiently to give the corresponding enelactams, which are versatile synthetic intermediates for various nitrogen-containing biologically active compounds such as (−)-pumiliotoxin C (**114**), an interesting toxic skin alkaloid produced by Central American frogs (eq 197).[283] By carrying out the



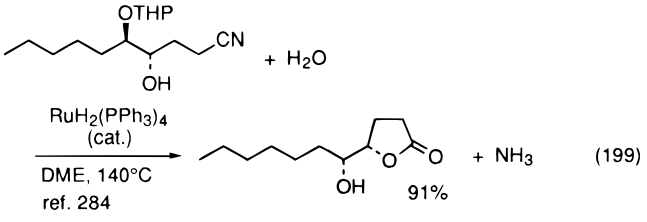
(197)

nucleophilic attack with alcohols instead of water, the catalytic condensation of nitriles with alcohols can be performed under neutral conditions to give the corresponding esters with evolution of ammonia gas (eq 198).[284] The intramolecular version of the present



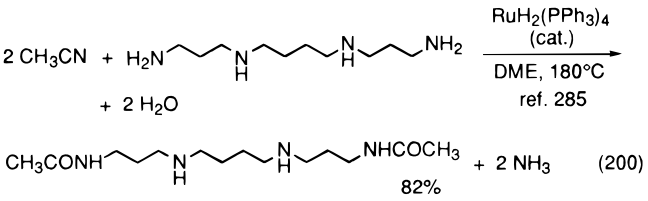
(198)

reaction provides an efficient method for synthesis of lactones (eq 199). When employing primary or



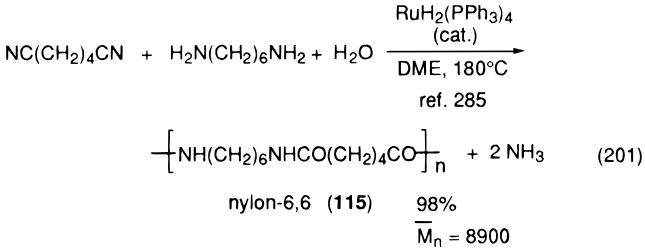
(199)

secondary amines as a nucleophile, a novel synthesis of amides from nitriles under neutral conditions has been performed with $RuH_2(PPh_3)_4$ catalyst.[285] The primary amino groups of polyamines are acylated chemoselectively with nitriles in the presence of secondary amino groups (eq 200). The present cata-



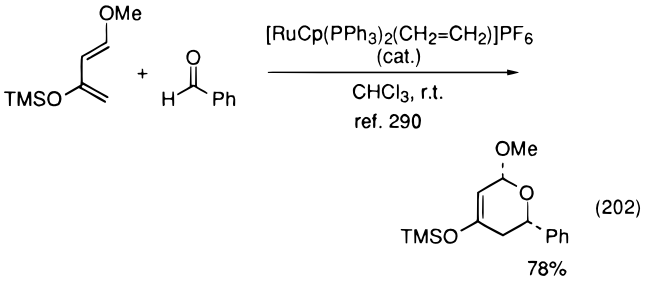
(200)

lytic condensation can be applied to industrially important polyamide synthesis from either dinitriles and diamines or aminonitrile.[285] Typically, the reaction of adiponitrile with hexamethylenediamine and 2 equiv of water affords nylon-6,6 (**115**) under neutral conditions with practical molecular weight (eq 201).



(201)

Moderate Lewis acidity of ruthenium complexes has been used for catalytic reactions of other Lewis acid-promoted reactions. Asymmetric aldol reaction of *p*-nitrobenzaldehyde with acetone has been performed with a combination of $RuCl_3$ catalyst and L-tyrosine ethyl ester to afford the corresponding optically active β-hydroxy ketone.[286] The ruthenium salen complex *trans*-$[Ru(salen)(NO)(H_2O)]SbF_6$ shows catalytic activity for Diels−Alder reactions.[287] Ruthenium complexes also act as catalysts for tetrahydropyranylation of alcohols[288] and acetalization of aldehydes.[289] Hetero Diels−Alder cycloaddition of benzaldehyde to 1-methoxy-3-[(trimethylsilyl)oxy]-1,3-butadiene can be carried out at room temperature in the presence of the cationic ruthenium catalyst $[RuCp(PPh_3)_2(CH_2{=}CH_2)]PF_6$ (eq 202).[290] The asym-



(202)

metric reaction has been performed with chiral ruthenium complex catalysts such as $[RuCp((S,S)\text{-chiraphos})(CH_2{=}CH_2)]PF_6$,[290] $RuCl(L)(\eta^6\text{-}1,3,5\text{-trimethylbenzene})]^+$ (L = 4-isopropyl-2-(2-pyridyl)-1,3-oxazoline),[291] and (R_{Ru},S_{Ru})-$[(\eta^6\text{-}p\text{-}$ cymene)$Ru(PN)(H_2O)](SbF_6)_2$ {PN = (3a*S*,8a*R*)-2-[2-(diphenylphosphino)-phenyl]-3a,8a-dihydroindan[1,2-*d*]oxazole}.[292]

VI. Carbon–Carbon Bond Formation

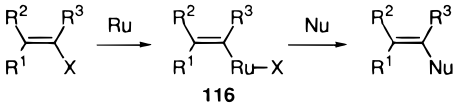
A. Carbon–Carbon Bond Formation Initiated by Oxidative Addition to Low-Valent Ruthenium Complexes

a. Reactions via Oxidative Addition of C–X Bonds

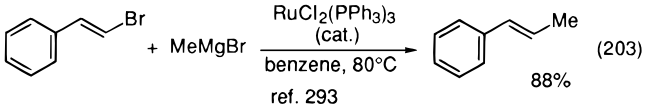
The ability of ruthenium complexes to form low-valent coordinatively unsaturated species leads to a variety of catalytic transformations initiated by oxidative addition of carbon−halogen and carbon−

hydrogen bonds. As well as zerovalent palladium complexes[2,293] low-valent ruthenium complexes readily insert into sp^2-carbon−halogen bonds of vinyl halides to give vinylruthenium complex **116**, which can be trapped with various nucleophiles, providing new carbon−carbon bonds (Scheme 29). The $RuCl_2(PPh_3)_3$-

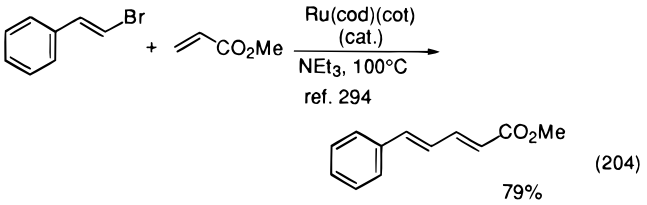
Scheme 29



catalyzed reaction of alkenyl halides with various nucleophiles such as organolithium compounds, Grignard reagents, and thiolates affords the corresponding alkenes and alkenyl sulfides with high stereospecificity (eq 203).[293] Heck-type reactions of vinyl halides

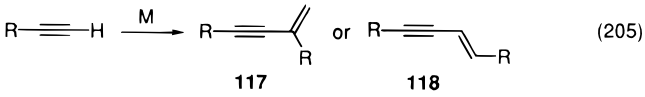


with electron-deficient olefins can be performed with Ru(cod)(cot) catalyst (eq 204).[294]

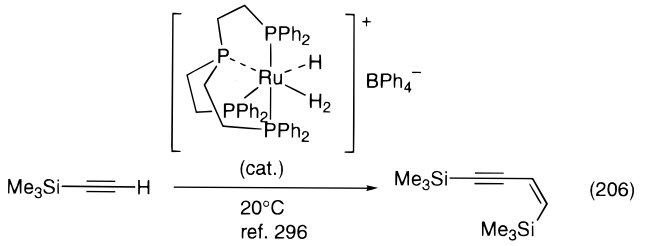


b. Reactions via sp-C–H Activation

The sp-C−H bond of terminal alkynes undergoes oxidative addition to transition metal complexes to afford reactive hydrido alkynyl complexes. Capture of the intermediate with carbon electrophiles provides catalytic carbon−carbon bond formations. Dimerization of terminal alkynes is one of the typical reactions in this field. Thus, the conjugated enyne synthesis has been studied with various transition metal catalysts such as Ti, Pd, and Rh,[295] where most of the reactions afford head-to-tail coupling products **117** preferentially (eq 205). Hydridoruthenium(II) complexes bearing tetradentate phosphine ligands, $[RuH(H_2)P(CH_2CH_2PPh_2)_3]BPh_4$ or $[RuH(N_2)P(CH_2$-

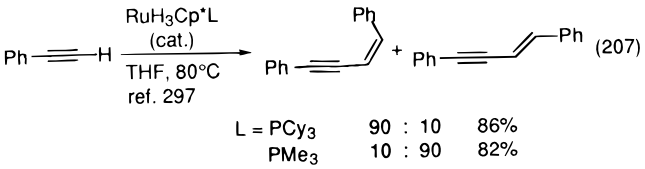


$CH_2PPh_2)_3]BPh_4$ catalyze selective tail-to-tail coupling reaction of terminal alkynes affording (*Z*)-1,4-disubstituted enynes **118** (eq 206).[296] RuH_3Cp^*L

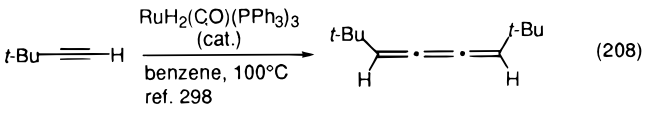


conv. 90%
selectivity 92%

complexes are also effective catalysts for the selective tail-to-tail dimerization of terminal alkynes,[297] where ligand environment of the metal catalysts plays an important role to the stereoselectivity of the product (eq 207). Similar treatment of *tert*-butylacetylene

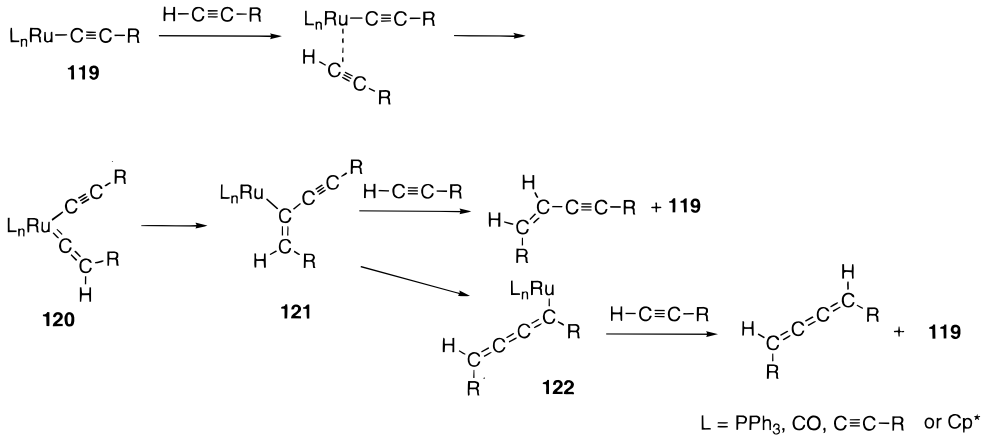


with $RuH_2(CO)(PPh_3)_3$ or Ru(cod)(cot) catalyst gives the corresponding cumulene compound, (*Z*)-1,4-di-*tert*-butylbutatriene (eq 208).[298]



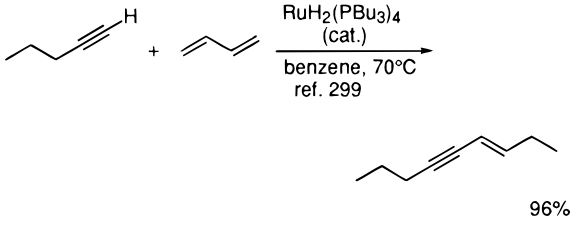
The mechanistic aspect of the dimerization of terminal alkynes has been studied extensively.[298b] The reactions can be rationalized by the formation of alkynyl ruthenium complex **119** which is derived from the reaction of dihydridoruthenium with terminal alkynes via sp-C−H activation (Scheme 30). Coordination of the second alkyne followed by 1,2-

Scheme 30



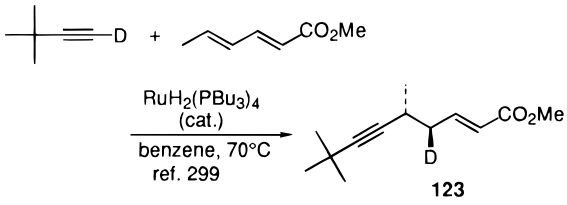
hydrogen shift affords alkynyl vinylidene complex **120**.[277] Migration of the alkynyl group to the α-position of the vinylidene group gives vinyl complex **121**. Protonation of **121** with alkynes would give the 1,3-enyne and complex **119** to complete the catalytic cycle.[298] Selective tail-to-tail dimerization observed specifically with ruthenium catalysts would be ascribed to the formation of **121** and **122**. In the particular case of *tert*-butylacetylene, the 1,3-shift of ruthenium metal of **121** would occur fast to give allenylidenyl complex **122**, which can be converted into cumulene and **119**.[298]

When activated alkynes are trapped with other electrophiles such as 1,3-dienes or allenes, a selective cross-coupling reaction can be performed with ruthenium catalysts. The reaction of terminal alkynes with 1,3-dienes in the presence of $RuH_2(CO)(PBu_3)_3$ or $RuH_2(PBu_3)_4$ catalyst affords the corresponding linear conjugated enyne with high regioselectivity (eq 209).[299] The reaction of deuterium-labeled phenylacetylene with methyl (*E*,*E*)-2,4-hexadienoate gives *erythro*-4-deuterated isomer **123** as a sole product (eq 210). By using hydroxy allenes as an electrophile, *exo*-enynes can be prepared upon treatment with a catalytic amount of $RuH_2(PPh_3)_4$ and ferrocenylphosphine.[300] The reaction of deuterium-labeled phenylacetylene with hydroxy allene **124** also gives the corresponding α-deuterated enyne **125** exclusively (eq 211). The deuterium incorporation as depicted in eqs 210 and 211 strongly suggests that the reactions are initiated by sp-C−H activation of terminal alkynes.



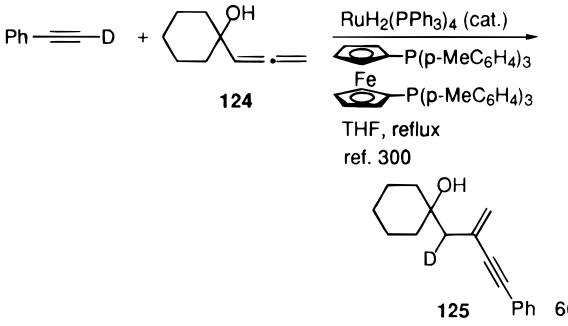
(209)

96%



(210)

123

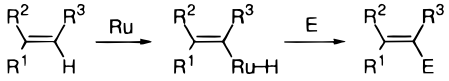


(211)

c. Reactions via sp²-C–H Activation

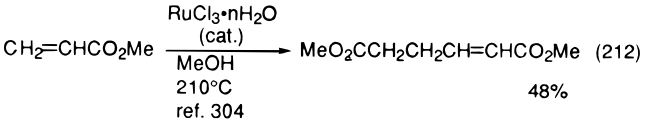
The sp²-C−H bond of alkenes also undergoes oxidative addition to low-valent ruthenium complexes

Scheme 31

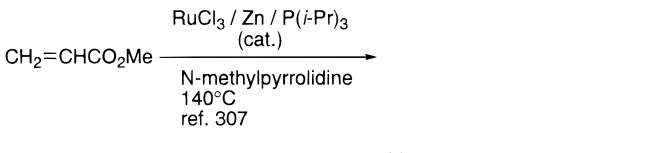


12 6

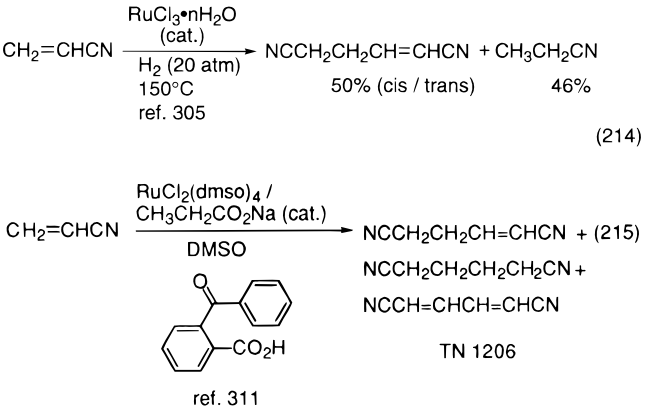
to afford reactive hydridoalkenyl complex **126**.[301] Capture of these intermediates with carbon electrophiles provides a variety of catalytic carbon−carbon bond formations (Scheme 31). Attack of **126** to the second olefins provides catalytic dimerization of olefins. The selective tail-to-tail dimerization of acrylates and acrylonitrile is attractive as an alternative to the currently practiced cyclohexane oxidation in the synthesis of adipic acid, an important nylon intermediate, and as an intermediate in fine chemical synthesis.[302,303] Ruthenium complexes such as $RuCl_3$ are effective catalysts for the selective tail-to-tail dimerization of methyl acrylate to give dimethyl hexenedioate (eq 212).[304] The reactions can be performed efficiently under milder reaction conditions in the presence of molecular hydrogen pressure (eq 214).[305] After these reports, several efficient catalytic systems such as (η^6-C_6H_6)(maleic anhydride)$_2$Ru/sodium naphthalenide,[306] $RuCl_3$/Zn/MeOH (eq 213),[307] $Ru_3(CO)_{12}$,[308] $RuH_2(CO)(PPh_3)_3/CF_3SO_3H$,[309] and Ru($\eta^6$-naphthalene)($\eta^4$-cod),[310] and $RuCl_2(dmso)_4/CH_3CH_2CO_2Na$/DMSO/carboxylic acid (eq 215)[311] have been reported. Selective tail-to-tail dimerization of reactive acrolein can be also performed with Ru(cod)(arene) catalyst, although the turnover number is rather low (eq 216).[312]



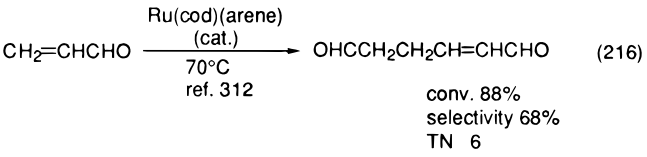
(212)



(213)



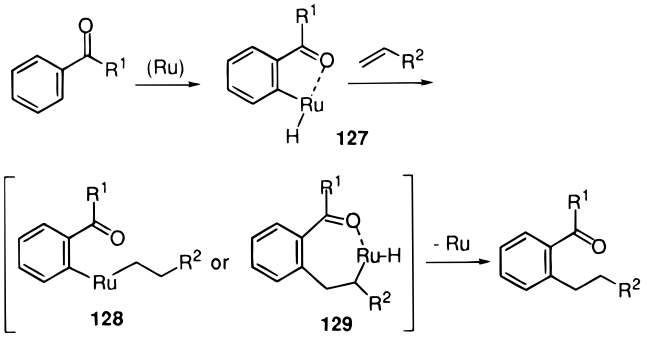
(214)



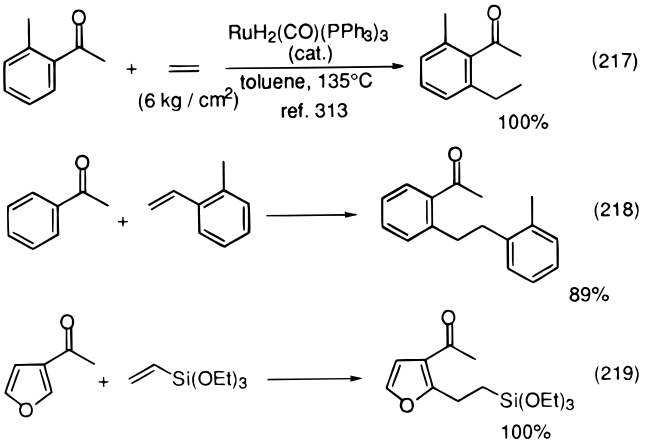
(216)

Chemoselective carbon−carbon bond formation at the ortho positions of aromatic carbonyl compounds can be performed by sp^2-C−H bond activation with ruthenium dihydride complexes. As shown in Scheme 32, oxidative addition to coordinatively unsaturated

Scheme 32



low-valent ruthenium complex of ortho C−H bonds proceeds regioselectively by assistance of chelation with carbonyl groups to afford hydridophenyl ruthenium complex **127**. Hydrometalation of **127** with olefin gives alkylphenylruthenium **128** which undergo reductive elimination of ruthenium to afford the *o*-alkylated aromatic carbonyl compound. The alternative pathway is the carbometalation of **127** to afford hydridoalkyl complex **129** which undergoes reductive elimination to give the coupling product. The latter mechanism seems unlikely since intermediate **129**, if formed, should give the corresponding olefins by fast β-hydrogen elimination. The reaction of aromatic and heteroaromatic ketones with various olefins such as ethylenes, styrenes, norbornenes, vinylsilanes, and allylsilanes in the presence of $RuH_2(CO)(PPh_3)_3$ gives the corresponding ortho-alkylated aromatic ketones with high regioselectivity (eqs 217−219).[313] Acetophenones bearing meta substituents

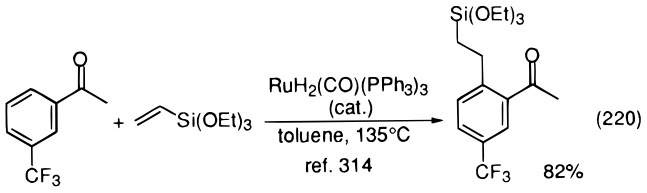


(217)

(218)

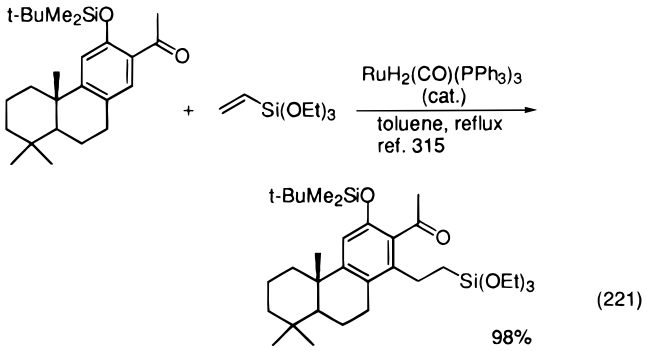
(219)

such as methyl, trifluoromethyl, and *N*,*N*-dimethylamino groups undergo regioselective alkylation at the 6-position (eq 220).[314] The method has been applied



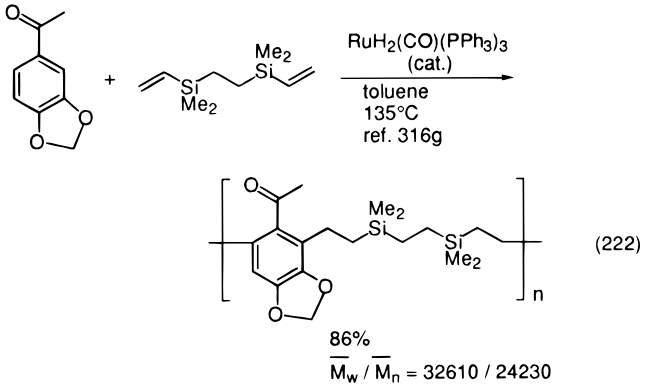
(220)

to the regioselective introduction of side chain to tricyclic terpenoid (eq 221).[315] The reaction also can



(221)

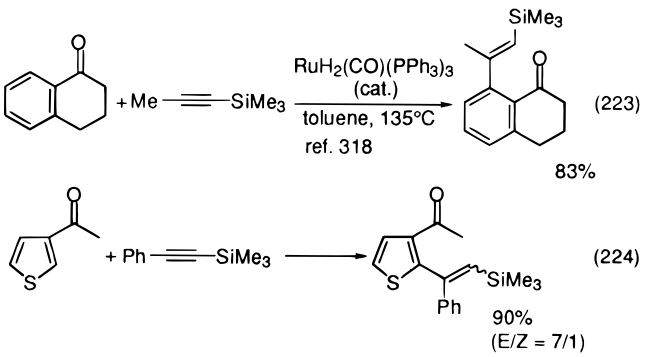
be applied to the copolymerization of various terminal dienes with acetophenone (eq 222).[316] Intermolec-



(222)

ular version of the reaction provides a method for the preparation of hyperbranched poly(4-acetylstyrene).[317]

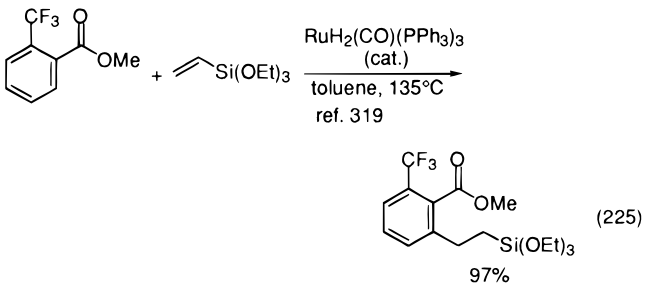
The coupling reaction of aromatic ketones with alkynes can be performed by trapping the intermediate **127** in Scheme 32. Only in the case of reactive substrates such as α-tetralone and heteroaromatic ketones, does the coupling reaction occur to give the corresponding α-divinyl compounds (eqs 223 and 224).[318]



(223)

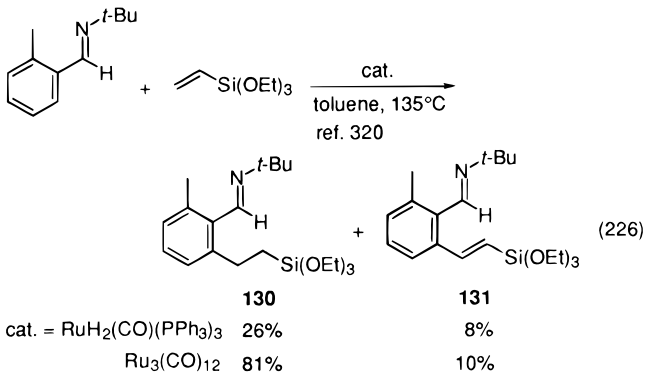
(224)

Similar treatment of aromatic esters also gives alkylated products at the ortho position,[319] although these substrates generally require CF_3 or F groups at the aromatic rings for completion of the reaction (eq 225). In the case of aromatic imines, the reaction



(225)

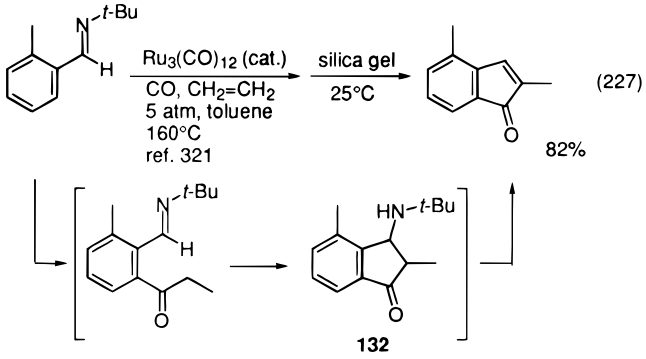
is contaminated by the dehydrogenated coupling product **131**, while use of $Ru_3(CO)_{12}$ catalyst greatly increases the yield of coupling product **130** (eq 226).[320]



(226)

	130	131
cat. = $RuH_2(CO)(PPh_3)_3$	26%	8%
$Ru_3(CO)_{12}$	81%	10%

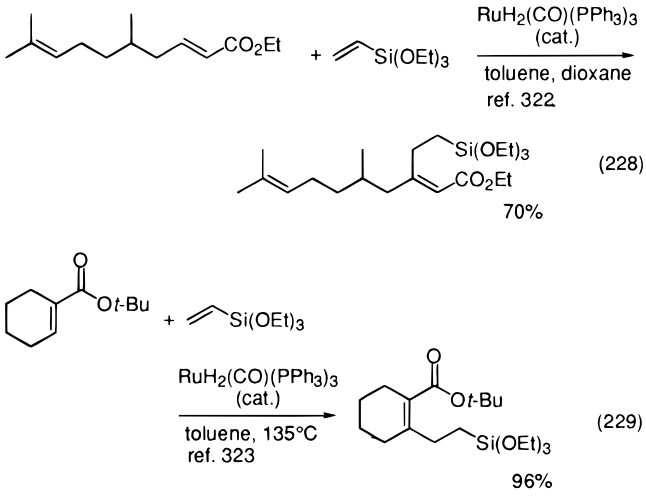
When a similar reaction was carried out under CO pressure in the presence of ethylene, propionylation at the ortho position, and the subsequent cyclization to give the corresponding aminoindanone **132**. Compound **132** can be converted into the corresponding indenones upon treatment with silica gel under mild conditions (eq 227).[321]



(227)

Catalytic carbon−carbon bond formation of α,β-unsaturated carbonyl compounds can be performed. Thus, treatment of α,β-unsaturated ketones and esters with olefins[322,323] and acetylenes[322] gives rise to similar regioselective coupling reactions at β-position (eqs 228 and 229).

Chemoselective activation of sp^2-C−H bonds of aromatic ketones and α,β-unsaturated esters has been confirmed by the stoichiometric reaction of low-valent dihydridoruthenium complex with these substrates. The reaction of benzophenone with $RuH_2(PPh_3)_4$[45c] or $RuH_4(PPh_3)_3$[324] gives the corresponding ortho-metalated ruthenium hydride complex (eq 230).



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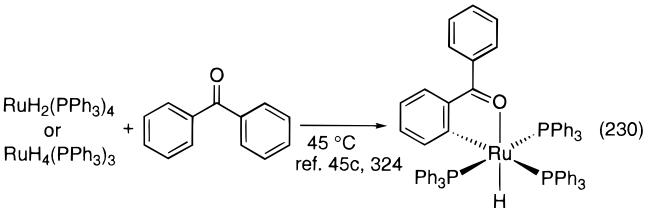
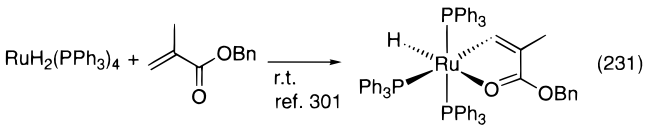
(229)



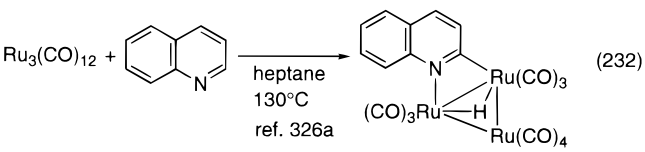
(230)

Similar chemoselective C−H bond cleavage was also observed in the reactions of acetophenone with $RuCl(OAc)(CO)(PPh_3)_2$[325] and alkyl methacrylates with $RuH_2(PPh_3)_4$ (eq 231)[301] to afford the corresponding arenyl and alkenyl ruthenium(II) hydride complexes.



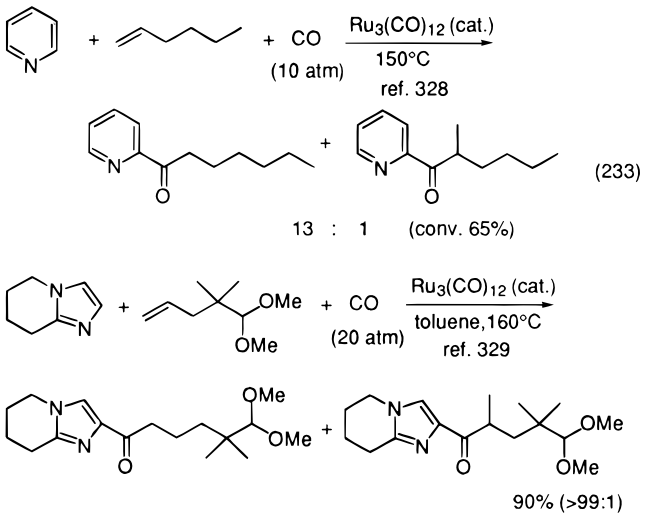
(231)

Heteroaromatic compounds such as pyridine, imidazole, furan, and thiophene undergo oxidative addition of metals at adjacent position of heteroatom. $Ru_3(CO)_{12}$ is reported to selectively activate the ortho position of nitrogen-containing aromatic heterocycles to form ortho-metalated species (eq 232).[326,327] In a

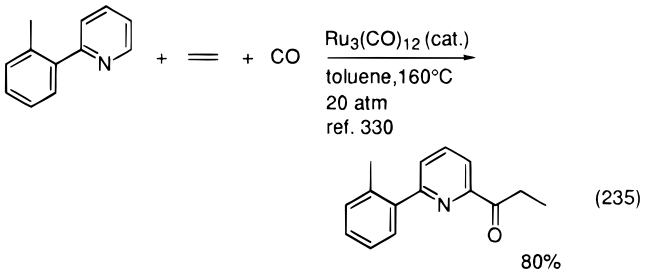


(232)

similar way, trapping the intermediate with electrophile provides chemoselective coupling reactions at the adjacent position of heteroaromatic compounds. Thus, catalytic carbonylative alkylation of pyridine[328] and 1,2-dimethylimidazole[329] can be performed upon treatment with terminal olefins in the presence of $Ru_3(CO)_{12}$ catalyst under CO pressure affording the corresponding 2-acylpyridines and 4-acylimidazole, respectively (eqs 233 and 234). Similar treatment of pyridylbenzenes with ethylene results in propio-

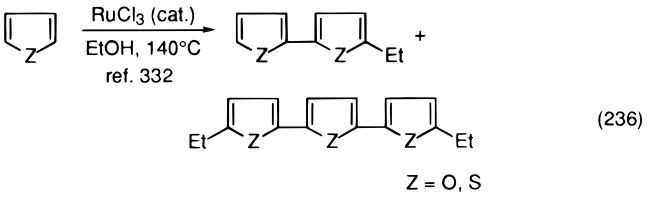


nylation at *o*-C−H bonds in the benzene ring (eq 235).[330] It is noteworthy that the assistance of

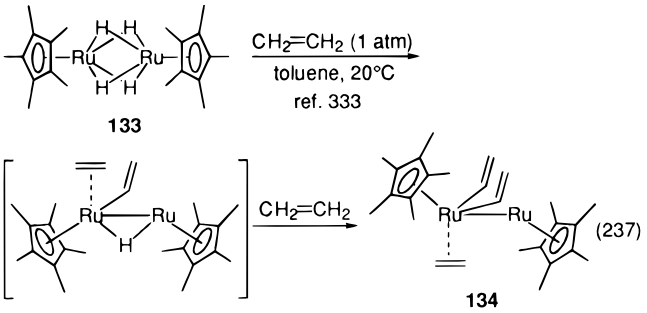


o-acetyl group toward the sp^2-C−H activation acts more effectively than that of nitrogen of pyridine. Thus, the reaction of 4-acetylpyridine with alkenes in the presence of $RuH_2(CO)(PPh_3)_3$ catalyst affords a mixture of the corresponding 3-alkylated and 3,5-dialkylpyridines without contamination of 2-alkylpyridines.[331]

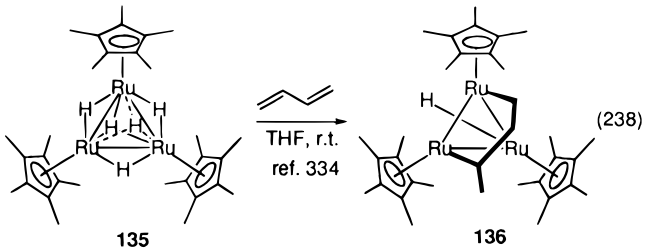
The reaction of furan or thiophene with alcohols in the pressure of $RuCl_3$ catalyst gives the corresponding α-alkylated dimers and trimers of furan and thiophene via similar C−H activation (eq 236).[332]



Recently, it was found that the cooperative action of the multinuclear center of ruthenium clusters plays an important role to selective activation of a sp^2-C−H bond of olefins. Treatment of tetrahydride-bridged ruthenium complex $[(\eta^5\text{-}C_5Me_5)Ru]_2(\mu\text{-}H)_4$ (**133**) in toluene with an atmospheric pressure of ethylene gives the corresponding divinyl complex **134** via bimetallic cooperative interaction (eq 237).[333] Similar selective C−H activation arising from multimetal cooperative interaction has been observed in the reaction of trinuclear pentahydride-bridged



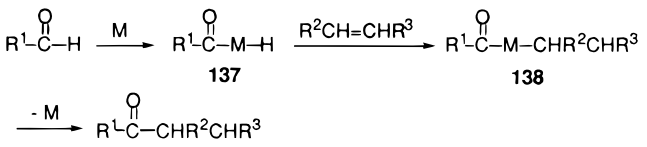
ruthenium complex $[(\eta_5\text{-}C_5Me_5)Ru]_3(\mu\text{-}H)_3(\mu_3\text{−}H)_2$ (**135**) with butadiene to afford **136** (eq 238).[334] These new



principles will open a new chemistry for selective catalytic carbon−carbon bond formations initiated by C−H activation.

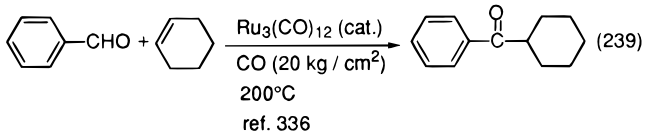
The sp^2-C−H bond of aldehydes or formate esters[335] undergoes oxidative addition to various transition metals to afford hydrido acyl complex **137**. Upon treatment with olefins, insertion reaction occurs to give the corresponding alkyl acyl complex **138** which undergoes subsequent reductive elimination to afford the corresponding carbonyl compound (Scheme 33).

Scheme 33



This type of catalytic hydroacylation reaction and hydroesterification reaction has been performed specifically using ruthenium complexes, while with other transition metals such as rhodium decarbonylation of **137** predominates.

Low-valent ruthenium complexes such as $Ru_3(CO)_{12}$, Ru(cod)(cot), and $Ru(cod)_2$ show high catalytic activity for the hydroacylation of olefins with various aromatic and heteroaromatic aldehydes at 180−200 °C under CO pressure to give unsymmetrical ketones (eq 239).[336] The pressure of CO is essen-



tial for efficient formation of ketones in order to avoid consumption of the starting aldehyde by decarbonylation reaction. Similarly, methyl formate can be converted into methyl propanoate with high selectivity upon treatment with ethylene and ruthenium

catalysts such as $RuCl_2(PPh_3)_3$,[337] $RuH_2(PPh_3)_4$,[338] $[Ru_3(CO)_{10}Cl][PPN]$ (PPN = bis(triphenylphosphoranylidene)ammonium),[339] $RuCl_3/2Et_4NI$,[340] and $Ru_3(CO)_{12}$/[PPN]Cl (eq 240).[341]

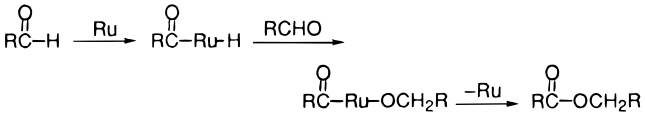
$$HCO_2CH_3 + CH_2{=}CH_2 \xrightarrow[\text{(20 atm)}]{\substack{Ru_3(CO)_{12}\ (cat.)\\ [PPN]Cl\\ DMF,\ 160°C\\ ref.\ 341}} CH_3CH_2CO_2CH_3 \quad 99\% \qquad (240)$$

Tischenko-type reactions, where two molecules of aldehydes are converted into the corresponding esters without water, can be performed with $RuH_2(PPh_3)_4$ catalyst under reduced pressure (eq 241).[342] The

$$2\ RCHO \xrightarrow[\substack{in\ vacuo\\ ref.\ 342}]{RuH_2(PPh_3)_4\ (cat.)} RCO_2CH_2R \qquad (241)$$

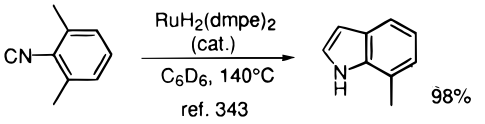
reaction can be rationalized by the oxidative addition of ruthenium into C−H bond of aldehyde, hydrometalation of the second aldehyde, and reductive elimination of ruthenium (Scheme 34).

Scheme 34



d. Reactions via sp³-C–H Activation

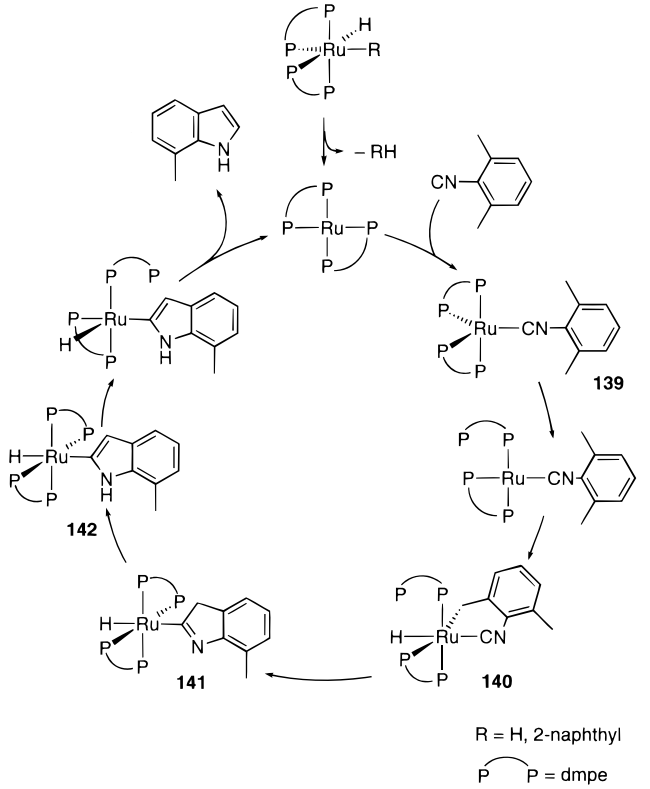
Although sp^3-C−H activation is a challenging problem and lies even at the level of stoichiometric reactions, several catalytic transformations initiated by sp^3-C−H activation have been reported by using ruthenium catalysts. Catalytic reactions via sp^3-C−H activation of benzylic positions can be performed with low-valent ruthenium complexes. Upon treatment with $RuH_2(dmpe)_2$ or RuH(2-naphthyl)-$(dmpe)_2$ catalyst at elevated temperature, 2,6-xylyl isocyanides undergo C−H activation at benzylic positions and the subsequent cyclization to afford 7-methylindoles selectively (eq 242).[343] The reaction



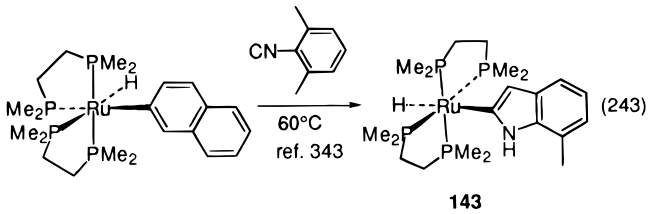
(242)

can be rationalized by the mechanism as shown in Scheme 35. Formation of coordinatively unsaturated $Ru(dmpe)_2$ species by reductive elimination followed by coordination of isocyanide affords complex **139**. Dissociation of one phosphine atom and intramolecular C−H insertion to the methyl group gives hydridobenzyl complex **140**. Migration of the methylene group to the isocyanide gives complex **141**, which undergoes isomerization to afford hydrido 2-indolyl complex **142**. Reductive elimination and dissociation of indole gives $Ru(dmpe)_2$ to complete catalytic cycles. This mechanism has been confirmed by the kinetic and the isotope labeling experiments and isolation of *trans*-RuH(dmpe)$_2$[2-(7-methylindole)] (**143**), which is formed from stoichiometric reaction of 2,6-xylyl

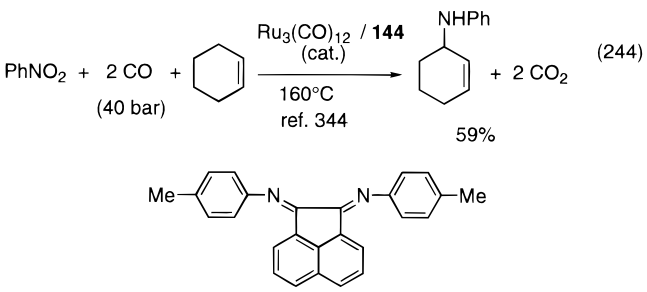
Scheme 35



isocyanide with $RuH_2(dmpe)_2$ or RuH(2-naphthyl)-$(dmpe)_2$ at 60 °C (eq 243).[343]



Allylic position of simple olefins has been functionalized by the low-valent ruthenium complex catalysts. In the presence of a catalytic amount of $Ru_3(CO)_{12}$ and diimino compound **144**, allylic amination of cyclohexene can be performed with aromatic nitro compounds under CO pressure to afford the corresponding industrially important allylamine derivatives (eq 244).[344] The reaction can be explained

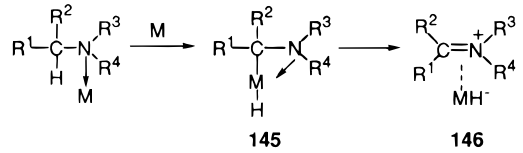


(244)

by the reduction of nitro compounds with CO, which we will discuss in section VII, and the subsequent amination reaction via selective C−H activation of allylic position.

The sp^3-C−H activation of α-position of heteroatom compounds occurs selectively by the assitance of coordination of heteroatoms with metal complexes. The activation of α-C−H bond of tertiary amines with low-valent metal proceeds efficiently by α-heteroatom effect (Scheme 36). Coordination of the nitrogen of

Scheme 36

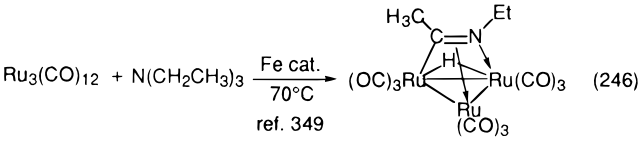


145 **146**

amines to metal, followed by oxidative addition of the α-C−H bond gives hydrido alkylmetal complex **145**, which is converted into hydrido iminium ion metal complex **146**. Trapping with nucleophiles such as amines and water provides novel catalytic reactions of tertiary amines. Transalkylation reaction[345] and hydrolysis reaction[346] of tertiary amines can be performed with zerovalent palladium catalysts. Similar reactions have been reported to proceed with ruthenium carbonyl cluster or $RuCl_3$ catalyst (eq 245).[347,348] Oxidative addition of the α-C−H bond of

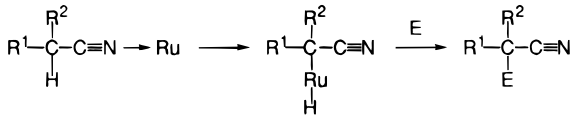
$$Et_3N + Pr_3N \xrightarrow[125°C,\ \text{ref. 347}]{Ru_3(CO)_{12}\ (cat.)} Et_2NPr + Pr_2NEt \qquad (245)$$

tertiary amines to ruthenium carbonyl cluster has been confirmed by the isolation and X-ray analysis of $(\mu\text{-H})(\mu^3\text{-}\eta^2\text{-}CH_3C{=}NCH_2CH_3)Ru_3(CO)_9$ and the related complexes (eq 246).[349]



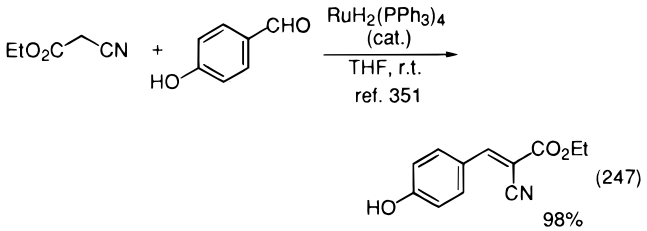
The concept leads to the new methodology for the activation of nitriles under neutral conditions. Oxidative insertion of coordinatively unsaturated ruthenium into α-C−H bond of nitriles occurred selectively to afford hydrido α-cyanoalkyl complex **147** (Scheme 37).[350] Trapping the intermediate with electrophiles

Scheme 37

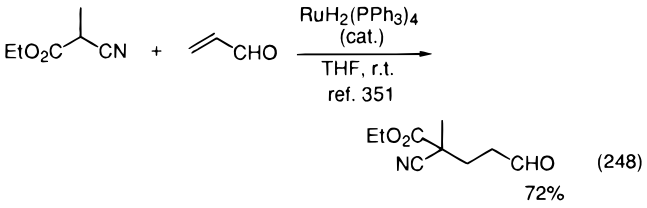


147

provide catalytic carbon−carbon bond formation at the α-position of nitriles under neutral conditions. Thus, aldol reaction of nitriles with carbonyl compounds proceeds with $RuH_2(PPh_3)_4$ catalyst under mild and neutral conditions to give α,β-unsaturated nitriles (eq 247).[351] Under similar reaction conditions, nitriles react with olefins bearing electron-withdrawing groups to give the corresponding Michael adducts (eq 248).[351] Acetylenic compounds bearing electron-withdrawing groups undergo conjugate addition with nitriles to give the corresponding olefinic compounds (eq 249).[351] An important feature of the



(247)



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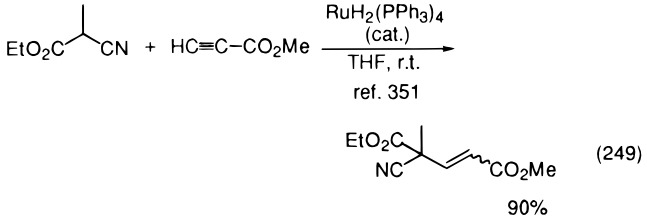
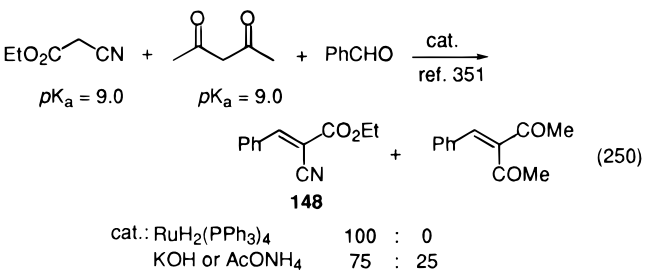


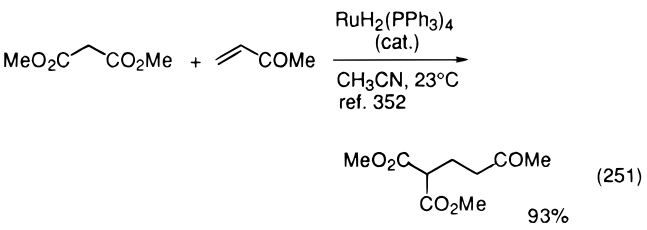
(249)

reaction is the chemoselective aldol and Michael reactions of nitriles in the presence of other active methylene compounds. Typically, the $RuH_2(PPh_3)_4$-catalyzed reaction of benzaldehyde with an equimolar mixture of ethyl cyanoacetate and 2,4-pentanedione, both pronucleophiles have similar pK_a values (pK_a = 9.0), gave (*E*)-ethyl 2-cyano-3-phenyl-2-propenoate (**148**) exclusively (eq 250). In contrast, the same



(250)

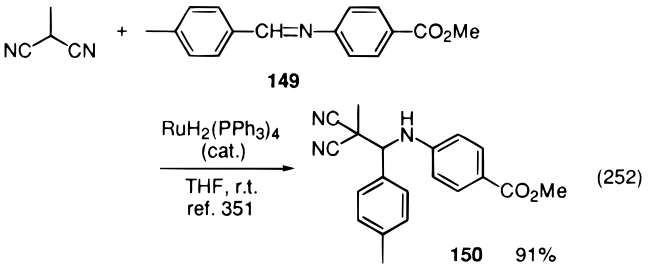
reaction in the presence of a catalytic amount of a conventional base such as $AcONH_4$ or KOH gave a mixture of **148** and 3-benzylidene-2,4-pentanedione (75:25). When the reactions are carried out in acetonitrile, various active methylene compounds such as 1,3-diketones, β-keto esters, dialkyl malonates, and nitroalkanes react with carbonyl compounds and Michael acceptors under the similar reaction conditions (eq 251).[352] The present methods



(251)

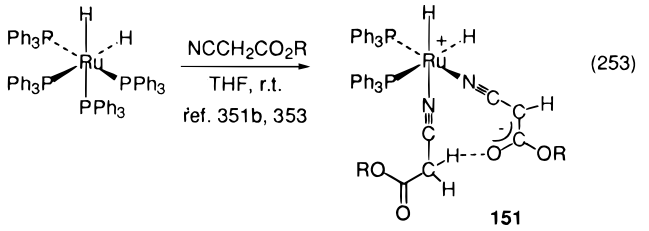
can be applied to the reactions of nitriles with other

electrophiles. Reactive imines such as 4-(methoxycarbonyl)-*N*-(4-methylbenzylidene)aniline (**149**) react with nitriles under similar reaction conditions to afford the corresponding cyano amine **150** (eq 252).[351]



(252)

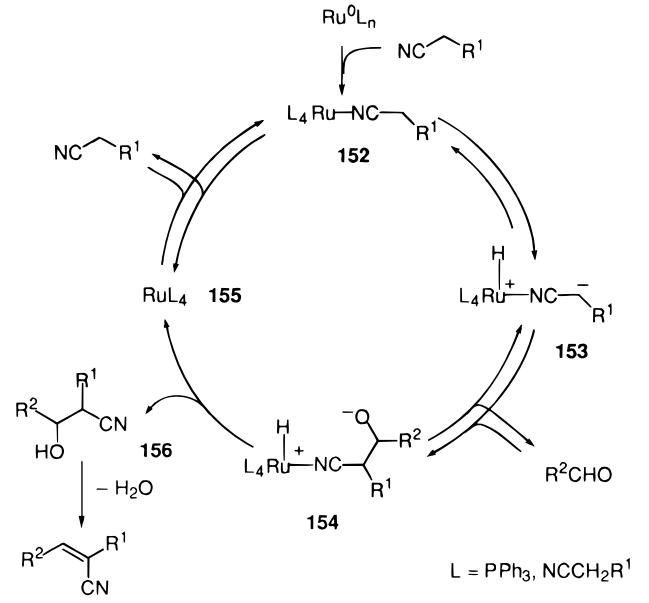
As key intermediates and active catalysts of these reactions, the oxidative addition products of alkyl cyanoacetate have been isolated. Thus, stoichiometric reaction of $RuH_2(PPh_3)_4$ or $RuH(C_2H_4)(PPh_3)_2(PPh_2C_6H_4)$ with alkyl cyanoacetates gave hydrido(*N*-bonded enolato)ruthenium(II) complexes, *mer*-$RuH(NCCHCO_2R)(PPh_3)_3$ (**151**), which are active catalysts for the aldol and Michael reactions of nitriles (eq 253).[351b,353]



(253)

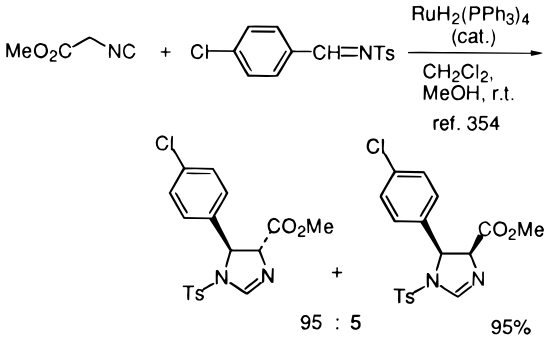
From various kinetic experiments, the catalytically active species seems to be zerovalent complex **152**, which is formed by coordination of nitrile to dihydridorutheium complex and subsequent reductive elimination of molecular hydrogen (Scheme 38).[351b]

Scheme 38



Oxidative addition of the α-C−H bond of the nitrile to the ruthenium affords a hydrido α-cyanoalkylruthenium complex, which is converted into hydrido(enolato)ruthenium complex **153**. Direct interaction of the enolato ligand with an aldehyde takes place to give hydrido(aldolato)ruthenium intermediate **154**, which undergoes elimination of aldol product **156** to give a coordinatively unsaturated ruthenium complex **155**. Coordination of the nitrile to **155** regenerates **152** to complete the catalytic cycle. Dehydration of **156** may proceed under the reaction conditions.

When isocyanoacetate was allowed to react with *N*-sulfonylimines in the presence of $RuH_2(PPh_3)_4$ catalyst, the carbon−carbon bond formation at the α-position of isocyanide and the subsequent cyclization occurred under mild conditions to afford the corresponding *trans*-2-imidazolines stereoselectively (eq 254).[354] The reaction can be rationalized by



(254)

assuming the similar redox mechanism which involves α-C−H activation of isocyanides and the subsequent reaction with imines.

The principle of the reactions has been applied to various transition metal-catalyzed carbon−carbon bond-forming reactions[31] including aldol reactions of nitriles with aldehydes[355−357] and imines,[358] Michael reactions of nitriles,[359,360] and the reactions of active methylene compounds with allenes.[361]

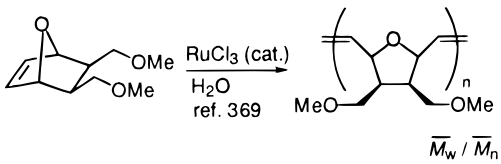
The intermediate $(Ru(bpy)_3^{2+})^*$ generated by irradiation of $Ru(bpy)_3^{2+}$ complex has proven to activate α-C−H bond of heteroatom compounds such as tertiary amines and acetals by electron-transfer reactions. Photoinduced reactions such as dealkylation[362] and hydrolysis[363] of tertiary amines and transacetalization reaction[364] have been performed using $Ru(bpy)_3^{2+}$ catalyst.

B. Carbon–Carbon Bond Formation Initiated by Ruthenium Carbene Complexes

a. Olefin Metathesis and Related Reactions

The olefin metathesis, the metal-catalyzed exchange of the alkylidene groups of two olefins are representative catalytic reactions initiated by metal carbene intermediates. It has been used in the polymer chemistry mainly using early transition metal complex catalysts.[34,365] Although certain metal carbene-based metathesis catalysts can polymerize strained cyclic olefins, their sensitivity to air and protic media severely limits their application as living ring opening metathesis polymerization (ROMP)

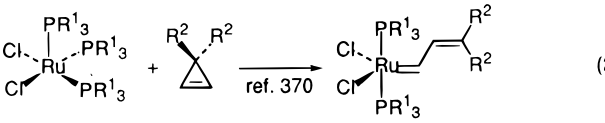
catalysts (eq 255). It has been known that $RuCl_3 \cdot nH_2O$ catalyzes the polymerization of cycloolefins such as cyclobutene,[366] norbornene,[367] and 7-oxanorbornene.[368] $RuCl_3 \cdot nH_2O$ has proven to be effective ROMP catalyst in protic media such as water.[369] Polymerization of 7-oxanorbornene derivatives proceeds rapidly in water alone to produce the ROMP polymer in nearly quantitative yields with narrow polydispersity (eq 256).



(256)

$\overline{M}_w / \overline{M}_n = 1.2$

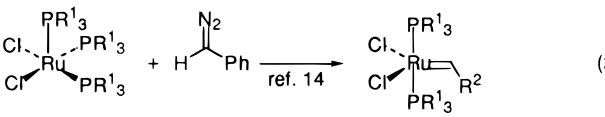
Although it was reasonably assumed that the active species are ruthenium−carbene complexes, the intermediate had remained unclear for a long time. Stable ruthenium alkenylidene phosphine complexes **157**[370] were found to be readily obtained by the reaction of $RuCl_2(PPh_3)_3$ with diphenylcyclopropene (eq 257), and complexes **157** have proven to be



(257)

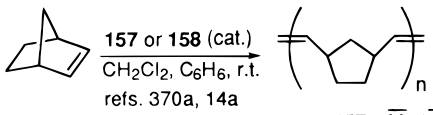
157 **a**: R^1, R^2 = Ph
b: R^1 = *c*-C_6H_{11}, R^2 = Ph
c: R^1 = *c*-C_6H_{11}, R^2 = Me

effective catalysts for ring-opening polymerization of olefinic substrates. Norbornene and 7-oxanorbornenes undergo the polymerization even in protic media such as alcohols and water to afford the corresponding polymers with narrow polydispersity (eq 259) (M_w/M_n = 1.25).[370] The linear relationship between molecular weight and monomer/catalyst ratios and the absence of chain-transfer and termination processes indicated that these systems are living.[370b] Air-stable alkylidene phosphine complexes **158**, which can be obtained by the reaction of $RuCl_2(PPh_3)_3$ with aryl diazomethane (eq 258),[14] or the reaction of $RuH_2(H_2)_2(PCy_3)_2$ with $PhCHCl_2$ and cyclohexene,[371] have proven to be more effective ROMP catalyst. With **158a** catalyst ROMP polymerization of norbornene proceeded 1000 times faster and with higher polydispersity (M_w/M_n = 1.04) than those with **157a** catalyst (eq 259).[14] Other ruthenium complex catalysts



(258)

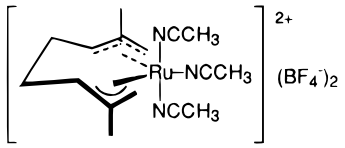
158 **a**: R^1, R^2 = Ph
b: R^1 = *c*-C_6H_{11}, R^2 = Ph
c: R^1 = *c*-C_6H_{11}, R^2 = H



(259)

cat: **157a** $\overline{M}_w / \overline{M}_n = 1.25$[370a]
158a $\overline{M}_w / \overline{M}_n = 1.04$[14a]

such as $RuCl_2(p\text{-cymene})PCy_3$[372] and a combination of allyl ruthenium complex **159** with ethyl diazoacetate[373] have also proven to be highly efficient ROMP catalysts. These are quite rare examples of living polymerization which can be performed in water media. This method has been applied to the preparation of ferroelectric liquid crystal **161** by **157b**-catalyzed oligomerization of mesogenic diene **160** (eq 260).[374]



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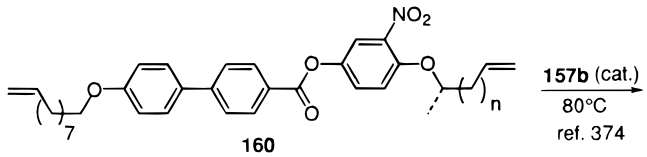

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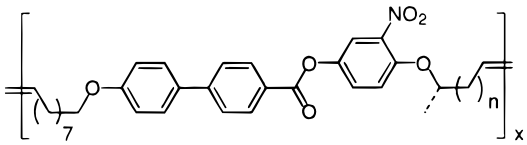
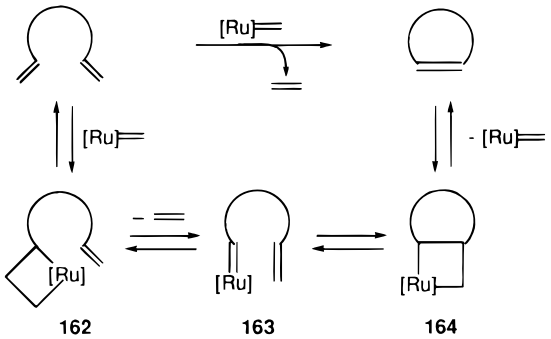


(260)

161

The intramolecular version of the principle of olefin metathesis provides a selective and versatile method for ring closure of olefinic compounds as shown in Scheme 39.[34e,f,375] The reaction of α,ω-dienes with

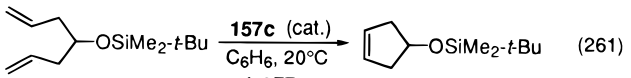
Scheme 39



ruthenium carbene complex gives ruthenacyclobutane **162**, which undergoes dissociation of ethylene to afford the second carbene complex **163**. Subsequent formation of the other ruthenacyclobutane **164** followed by elimination of the carbene complex affords the cyclic olefin catalytically. The catalytic activity of several ruthenium catalysts of the formula $(PR_3)_2X_2Ru{=}CHCHCPh_2$ have been examined for the conversion of diethyl diallylmalonate to the corresponding cyclopentene, and the following order of

increasing activity was determined: X = I < Br < Cl and $PR_3 = PPh_3 \ll$ P-*i*-Pr_2Ph < PCy_2Ph < P(*i*-Pr)$_3$ < PCy_3.[376]

Ruthenium−carbene complex-catalyzed reactions of various functionalized 1,6-, 1,7-, and 1,8-dienes give the corresponding five-, six-, and seven-membered cyclic olefins (eqs 261 and 262).[377] Various



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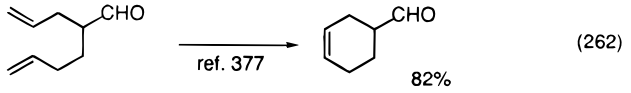
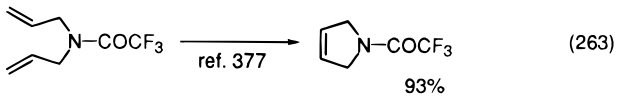


(262)

amines, amides (eqs 263 and 264),[377−379] ureas,[380]



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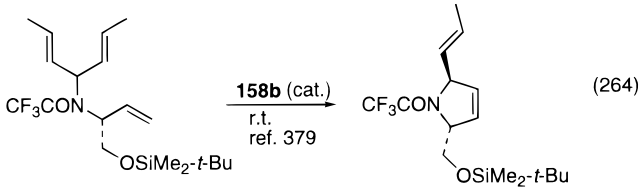
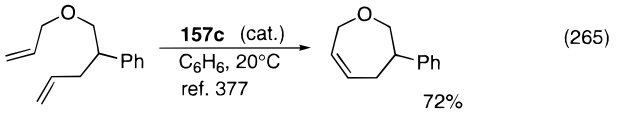


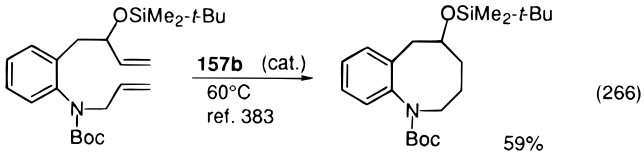
(264)

ethers (eq 265),[377,381] and siloxanes[382] can be cyclized



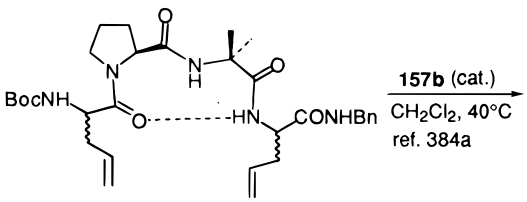
(265)

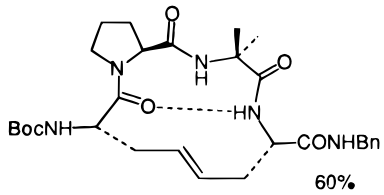
efficiently to afford the corresponding heterocyclic compounds. Diastereocontrolled cyclization can be performed from optically active α,α′-disubstituted diallylamine derivatives to afford the corresponding pyrrolidines (eq 264).[379] It is noteworthy that various modes of macrocyclizations can be performed with these catalysts. Macrocyclic compounds such as eight-membered cyclic amino compounds (eq 266),[383]



(266)

14-[384] and even 38-membered[385] macrocyclic peptides (eqs 267 and 268), 21-membered macrolides (eqs 269),[386] crown ethers,[387] and bridged calixarenes[388] can be prepared directly from the corresponding dienes without a high-dilution technique. This method has been utilized for the key step of the syntheses of various biologically active ring compounds such as epothilone A (eq 270),[389] manzamine A,[390] coronafacic acid,[391] lasiodiplodin,[392] bicyclic β-lactams,[393] castanospermine,[394] scalemic azocines,[395] and (+)-ricinelaidic acid lactone.[396] Atactic 1,2-polybutadienes also undergo similar ring-closing cyclization of neighboring vinyl substituents upon treatment with **158c** catalyst





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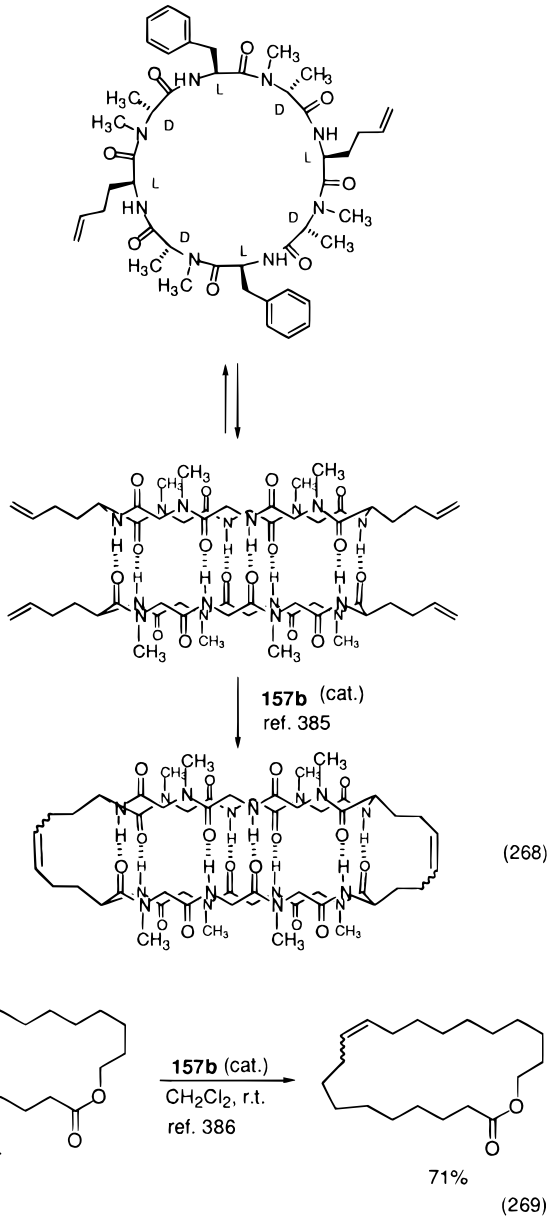
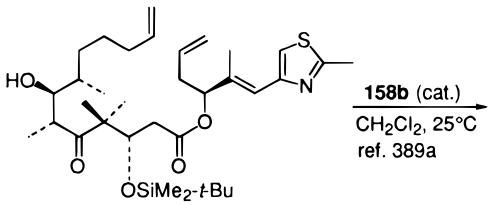
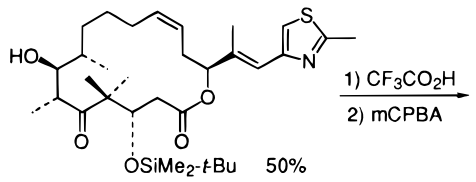


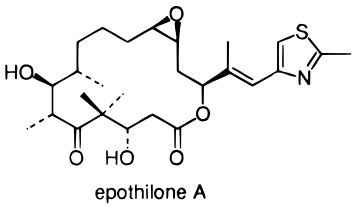
(268)

(269)

to give the polymer bearing methylene−cyclopentene unit (eq 271).[397] The method can be applied to the preparation of crown ethers,[398] [2]catenanes (eq 272),[399] and copper(I)-complexed 82-membered knotted ring[400] by utilizing template effect of alkali and transition metals.







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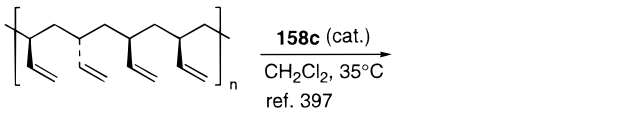

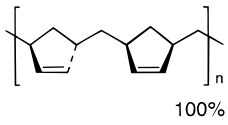

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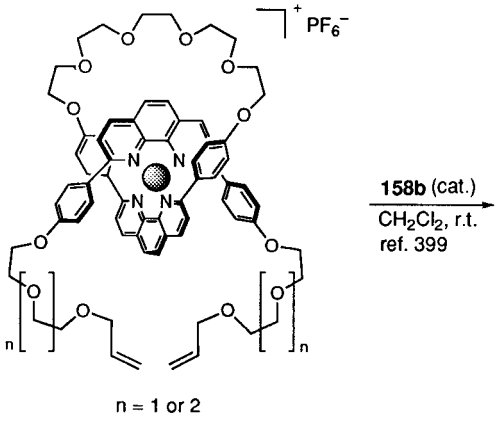
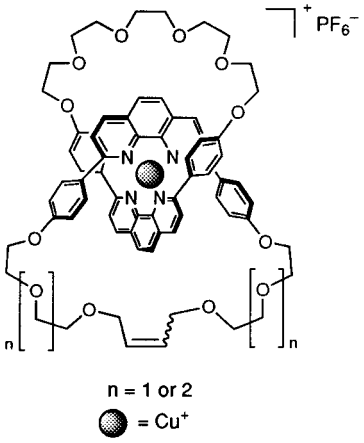
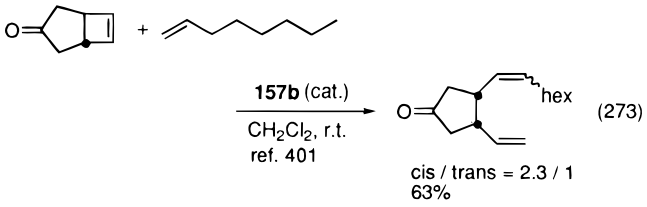




(272)

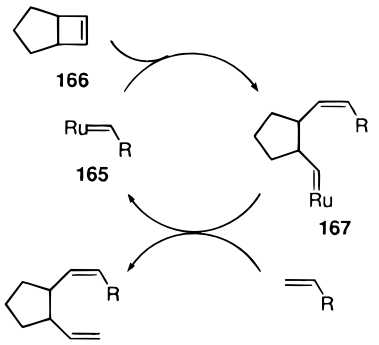
When strained olefins such as fused cyclobutenes are allowed to react with olefins in the presence of **157b** catalyst, ring-opening cross metathesis takes place selectively rather than ring-opening metathesis polymerization of the cyclobutene to give vicinal divinyl compounds (eq 273).[401] This ring-opening



(273)

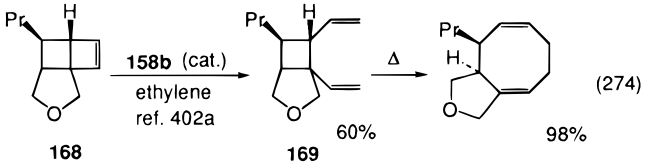
cross metathesis can be rationalized by assuming the mechanism as shown in Scheme 40. Alkylidene ru-

Scheme 40



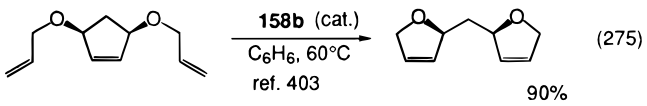
thenium complex **165** reacts selectively with more reactive strained olefin **166** to afford the corresponding alkylidene ruthenium complex **167**. Reaction of **165** with terminal olefins gives the product chemoselectively instead of ROMP product, since complex **165** bearing bulky substituted alkylidene moiety does not react with bulky olefin **167**.

Similar treatment of cyclobutene substrate **168** with ethylene gives divinyl compound **169** with high regio- and stereoselectivities.[402] This method provides a facile and convenient route to functionalized bicyclo[6.3.0] ring systems by pyrrolysis of the products (eq 274).



(274)

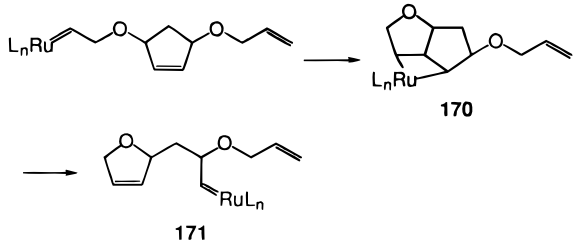
Bis(allyl) ethers of cycloolefin diols undergo tandem ring-opening−ring-closing metathesis under the similar reaction conditions to afford the corresponding cyclic ethers (eq 275).[403] The conversion would



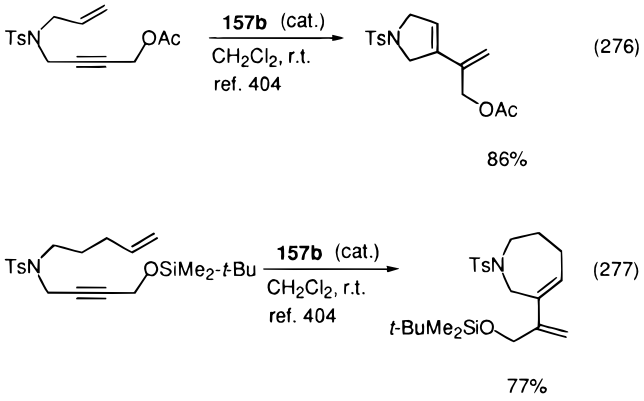
(275)

involve acyclic metathesis of the olefin followed by the formation and ring-opening of an intermediate metallacyclobutene **170**. A second ring-closing metathesis via carbene complex **171** gives the product and regenerates catalyst (Scheme 41).

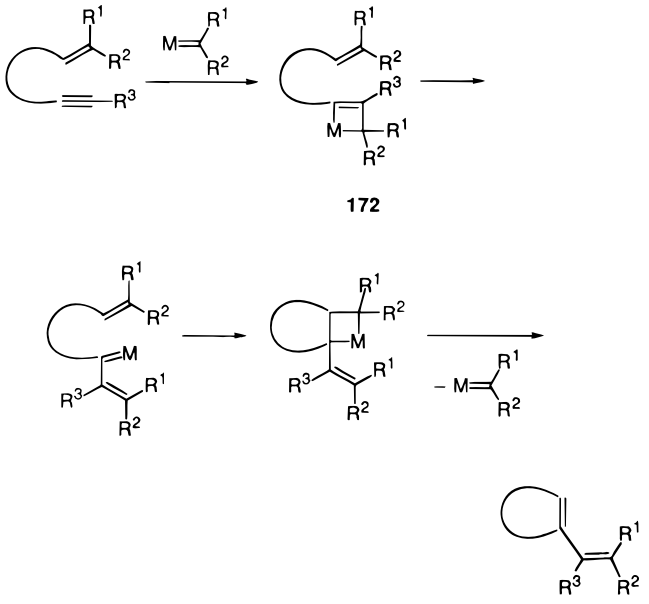
Scheme 41



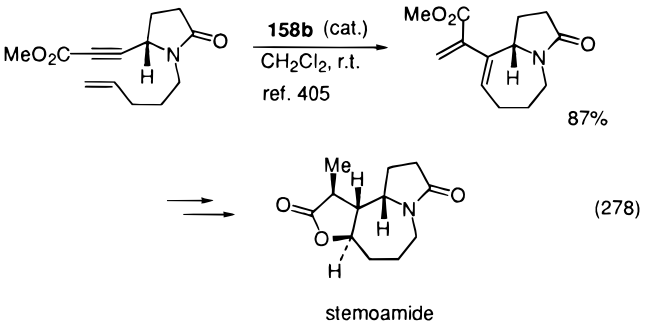
Enynes also undergo similar ring-closing metathesis reactions with these ruthenium carbene complex catalysts to afford the corresponding cycloalkenes bearing conjugate olefin moiety. Five-, six-, and seven-membered cyclic amine derivatives have been synthesized from the corresponding *N*-tosyl-*N*-alkenylpropargylamines highly efficiently (eqs 276 and 277).[404] The reaction can be explained by the chemoselective formation of ruthenacyclobutene intermediate **172**, which undergoes similar sequence of ring cleavage and formation of ruthenacycles to afford the product (Scheme 42). The method has been applied



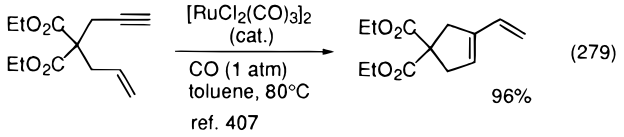
Scheme 42



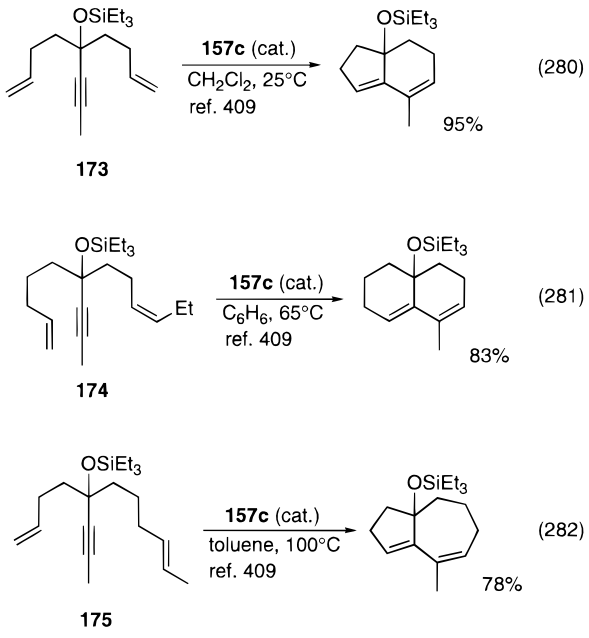
to total synthesis of (−)-stemoamide (eq 278)[405] and the preparation of bicyclic β-lactams.[406] Treatment of the 1,6- and 1,7-enynes with $[RuCl_2(CO)_3]_2$ catalyst



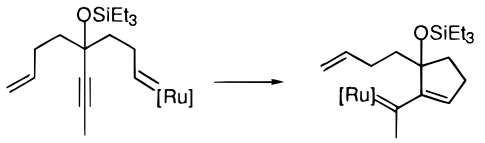
under CO atmosphere gives the conjugated vinylcycloalkenes (eq 279).[407] They are in contrast to the well-documented cycloisomerization of enynes with palladium catalysts producing 1,2-bis(ethylene)cycloalkanes.[408]



Dienynes, in which the alkyne moiety is located on the intervening position between two olefins, undergo the ring-closing sequential metathesis giving the corresponding fused bicyclic ring systems.[409] Symmetrical dienyne **173** can be converted into the fused bicyclo[4.3.0] ring (eq 280). Similar treatment of dienes such as **174** and **175** bearing sterically differentiated olefins produce only the bicyclo[4.4.0] and bicyclo[5.3.0] compounds, respectively (eqs 281 and 282). In these reactions, enyne metathesis starting from ruthenium carbene such as **176** would generate the first ring to regenerate carbene **177**. Ring-closing metathesis with a second diene produces the fused ring (Scheme 43). The high regiochemical control in eqs 281 and 282 is ascribed to the facility of initial acyclic metathesis reaction of sterically less bulky olefinic moiety.

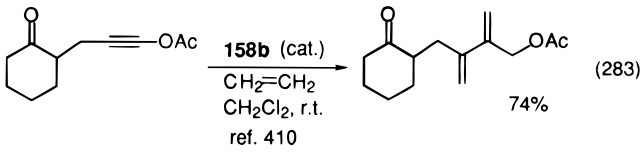


Scheme 43



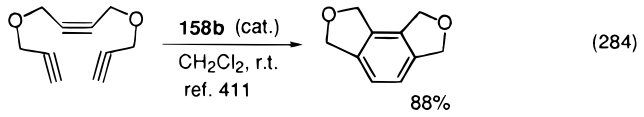
176 177

Intramolecular enyne metathesis of disubstituted alkynes with ethylene gas gives the corresponding 1,3-dienes (eq 283).[410] Triynes undergo a cascade of



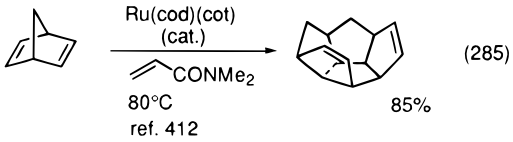
(283)

four metathesis reactions to give the corresponding benzene derivatives (eq 284).[411]



(284)

Specific cleavage and recombination of carbon skeletons have been observed in the Ru(cod)(cot)-catalyzed dimerization of norbornadiene, giving pentacyclo[5.4.2.^{1,7}.1^{3,6}.0^{10,13}.0^{12,14}]tetradeca-4,8-diene (eq 285),[412] where the structure of norbornadiene could

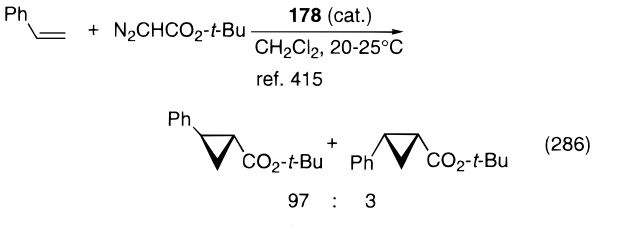


(285)

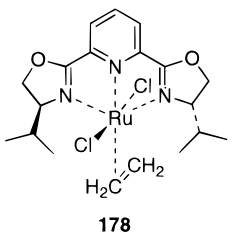
have initially decomposed to smaller molecules such as C_5 and C_2 moieties. The reaction seems likely to proceed via ruthenium carbene intermediate, although the precise mechanism remains unclear.

b. Cyclopropanation

One of the remarkable progresses in the catalytic reactions via carbene complex is the development of efficient asymmetric cyclopropanation of olefins. Practical asymmetric cyclopropanation reactions of olefins with diazo compounds can be performed with transition metal complex catalysts such as $RuCl_2(PPh_3)_3$,[413] Rh,[414a] and Cu complexes.[414b] By using chiral 2,6-bis(2-oxazolin-2-yl)pyridine (pybox) ruthenium complex catalyst **178**, the reaction of diazoacetates with styrenes can be carried out with high enantioselectivity to afford the corresponding *cis*- and *trans*-2-phenylcyclopropanecarboxylates (eq 286).[415] The high enantioselection of the reaction can be explained by exclusive *re* face attack of styrene to the resulting ruthenium carbene intermediate **179** as shown in Scheme 44. Similar asymmetric cyclopropanation

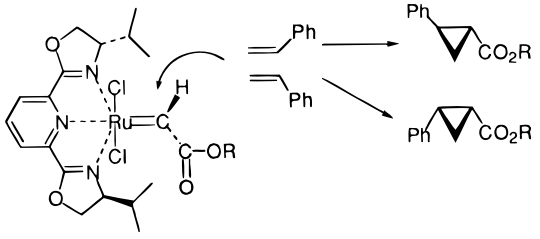


(286)



178

Scheme 44



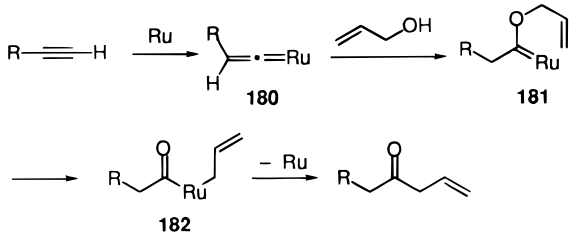
179

reactions can be performed by using optically active ruthenium porphyrin complexes with moderate to high enantioselectivity.[416]

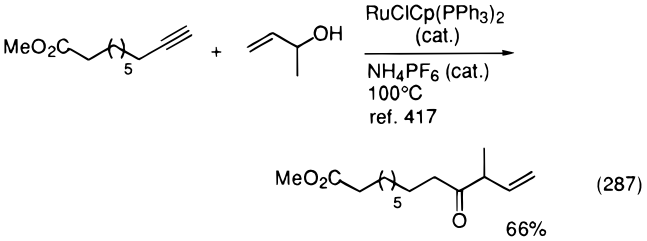
c. Reactions via Ruthenium Vinylidene Complexes

Vinylidene ruthenium complexes derived by the 1,2-hydrogen shift of cationic ruthenium alkyne complexes[277] are intermediates for various ruthenium-catalyzed coupling reactions of acetylenes with olefins. When vinylidene intermediate **180** is allowed to react with allyl alcohol, reconstitutive condensation takes place via the formation of allyloxy carbene complex **181**, subsequent metalla-Claisen rearrangement affording acylallyl complex **182**, and reductive elimination of ruthenium (Scheme 45).[33] A combina-

Scheme 45

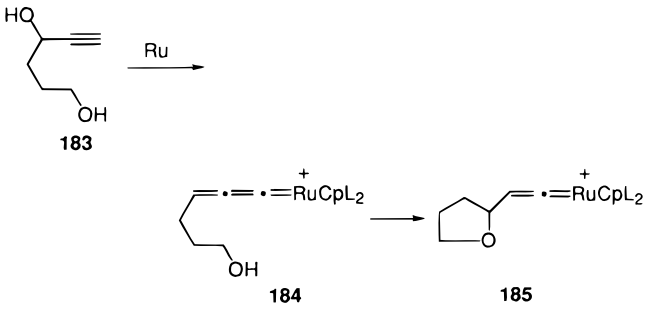


tion of $RuClCp(PPh_3)_2$ and NH_4PF_6 catalyzes the reaction of terminal alkynes with allyl alcohols to afford the corresponding β,γ-unsaturated ketones (eq 287).[417] When propargylic alcohol **183** is employed

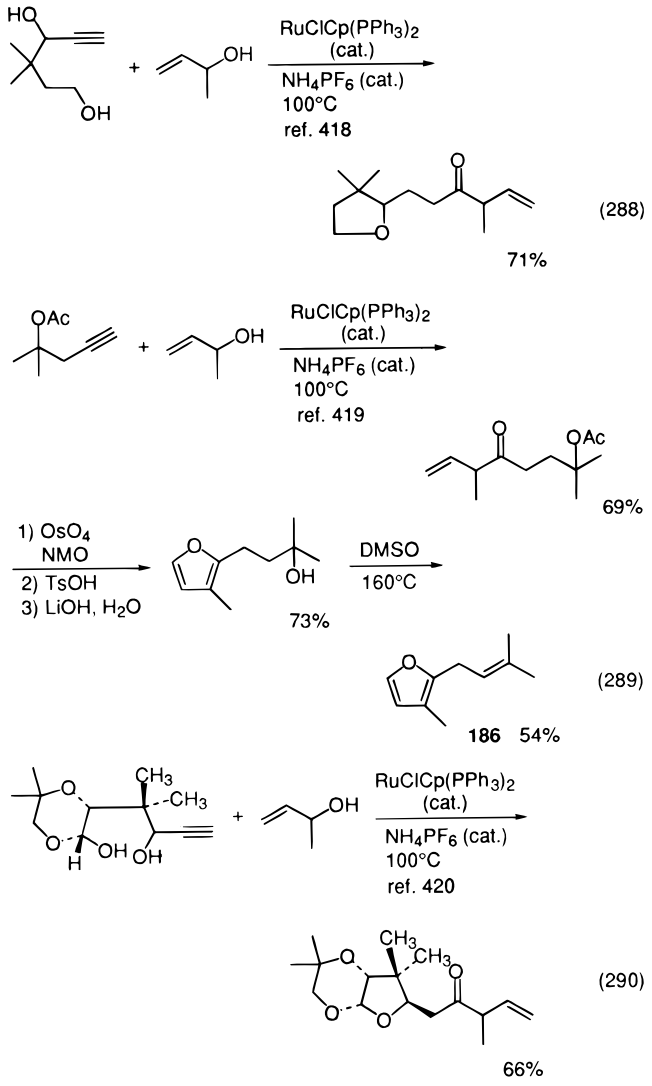


(287)

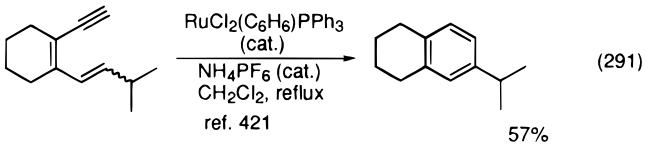
Scheme 46



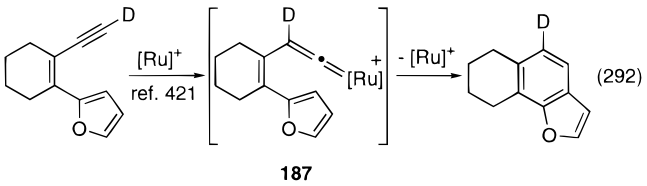
as an alkyne, the corresponding allenylidene ruthenium intermediate **184** is formed via 1,2-hydrogen shift and the subsequent dehydration (Scheme 46). Intramolecular nucleophilic attack of hydroxy group to the allenylidene moiety to afford the vinylidene complex **185**, which undergoes similar reconstitutive addition as shown in Scheme 45. β,γ-Unsaturated ketones bearing cyclic ether skeletons can be prepared directly by the reaction of hydroxy propargyl alcohols with allyl alcohol under the similar reaction conditions (eq 288).[418] Efficiencies of these reactions are illustrated by practical synthesis of rosefuran (**186**, eq 289)[419] and spiroketal subunit of (−)-calyculin A (eq 290).[420]



Under the similar reaction conditons, conjugated dienyl terminal alkynes undergo 6π-electrocyclization to give the corresponding aromatic rings (eq 291).[421]

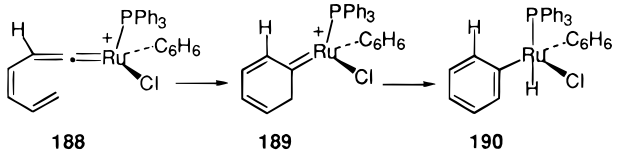


In this reaction, the deuterium atom at terminal alkynes migrates exclusively to the C_5 position of the product (eq 292), suggesting strongly of the formation



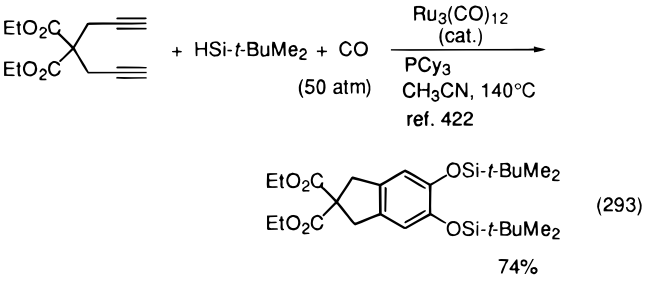
of vinylidene complex **187** via 1,2-hydrogen shift of the terminal alkynes. Thus, the reaction can be rationalized by cyclization of complex **188** to afford hexadienylidene complex **189**. Aromatization by hydrogen shift affording hydridophenyl complex **190** and reductive elimination of ruthenium would form substituted arenes (Scheme 47).

Scheme 47



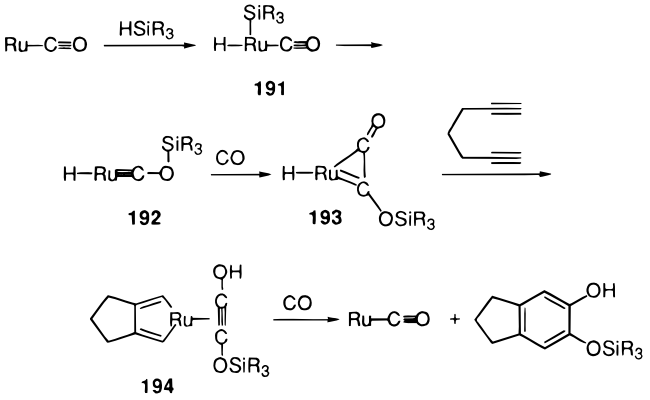
Selective dimerization of terminal alkynes (eqs 206−208)[296−298] and the reaction of terminal alkynes with secondary amines and CO_2 (eqs 186−189)[271−275] are also thought to proceed via ruthenium vinylidene complexes (Schemes 26 and 30).

The oxycarbyne metal intermediate M≡C−OY (Y = H, SiR_3) has been postulated for the novel cyclization reaction of diynes incorporating CO. $Ru_3(CO)_{12}$-catalyzed reaction of 1,6-diynes with hydrosilane under CO pressure gives the corresponding O-silylated catechol derivatives (eq 293).[422] This unusual



construction of carbon skeletons has been explained by the mechanism shown in Scheme 48. The oxidative addition of hydrosilane into ruthenium carbonyl complex gives hydrido silyl complex **191**. Migration of the silyl group to the oxygen atom would afford oxycarbyne complex **192**, which is converted into complex **193**. The reaction of complex **193** with

Scheme 48

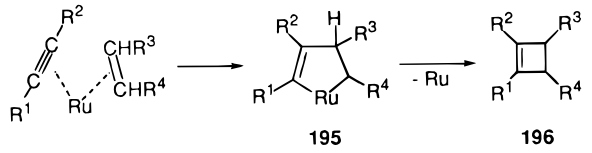


diynes gives the ruthenacyclopentadiene complex coordinated with hydroxy siloxyacetylene **194**. Insertion and reductive elimination of ruthenium gives the product to complete the catalytic cycle.

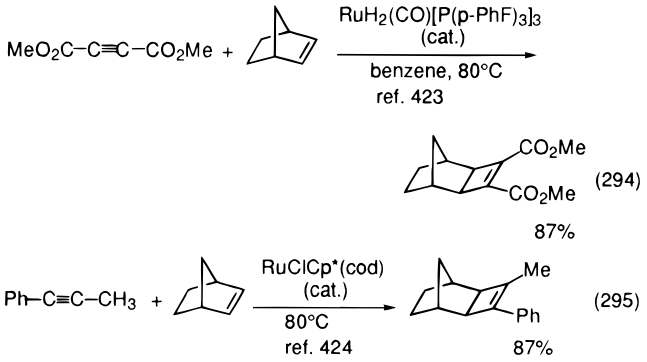
C. Carbon–Carbon Bond Formations via Ruthenacycle Intermediates

Ruthenacycles are versatile intermediates for coupling reactions of acetylenes with olefins. Because of easy generation of highly coordinatively unsaturated ruthenium complexes, precoordination of two reactant partners such as alkynes and alkenes could lead to various modes of carbon−carbon bond formation via ruthenacycle intermediates. As shown in Scheme 49, coordination of both alkynes and alkenes

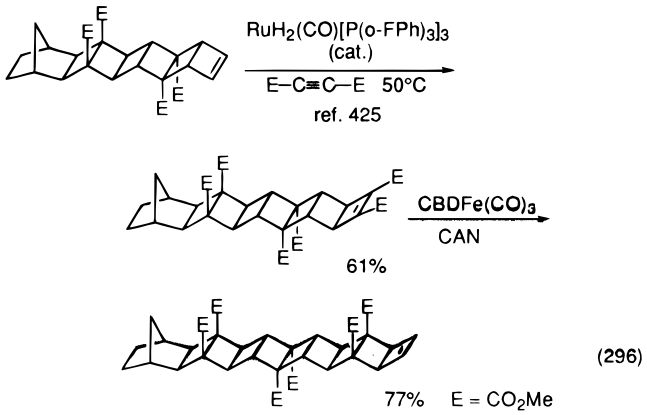
Scheme 49



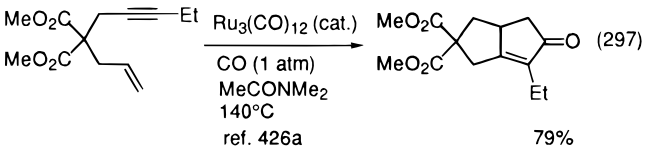
with ruthenium complex gives rise to the formation of ruthenacyclopentene **195**. When bulky olefins such as norbornene are used as an alkenes, reductive elimination of low-valent ruthenium occurs to give the corresponding cyclobutene **196**. Thus, [2+2] cycloaddition of norbornene with internal alkynes can be performed with ruthenium catalyst such as $RuH_2(CO)[P(p\text{-}PhF)_3]_3$[32,122,423] and RuClCp*(cod)[424] to afford the corresponding *exo*-tricyclo[4.2.1.$0^{2,5}$]non-3-enes stereoselectively (eqs 294 and 295). This method is



applied to the synthesis of new series of rigid linear rod compounds, *exo,exo*-fused [*n*]-ladderanes. For example, archetype [*n*]ladderane can be extended sequentially by one cyclobutane ring in the above [2+2] cycloaddition step and by [4+2] cycloaddition of cyclobutadiene using (cyclobutadiene)$Fe(CO)_3$ (eq 296).[425]

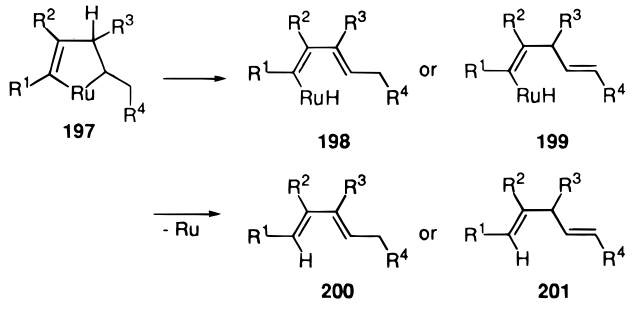


Trapping the intermediate **195** in Scheme 49 with CO provides the catalytic Pauson−Khand reaction. The reaction of 1,6-enynes with $Ru_3(CO)_{12}$ catalyst under CO pressure afforded the corresponding bicyclic cyclopentenones highly efficiently (eq 297).[426]

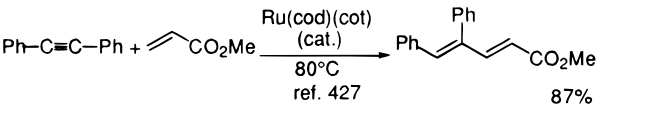


When simple linear alkenes are used as an olefinic substrate in Scheme 49, β-hydride elimination occurs from ruthenacyclopentene **197** to give hydrido vinyl complexes **198** or **199**, which undergo subsequent reductive elimination of ruthenium to afford the corresponding 1,3- or 1,4-dienes, **200** or **201**, respectively (Scheme 50). Ru(cod)(cot)-catalyzed reaction of in-

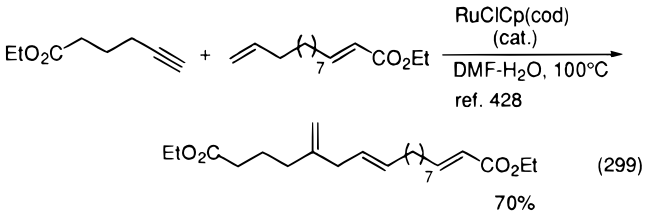
Scheme 50



ternal alkynes with electron-deficient olefins gives the corresponding *trans*-1,3-dienes (eq 298).[32,122,427]

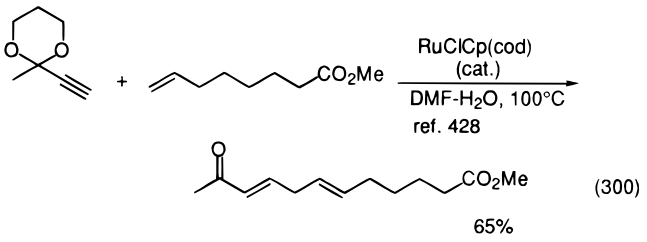


Heating an internal or terminal alkynes with monosubstituted alkenes in the presence of RuClCp(cod) catalyst gives rise to the equivalent of a highly selective Alder ene type reaction (eq 299).[428] The



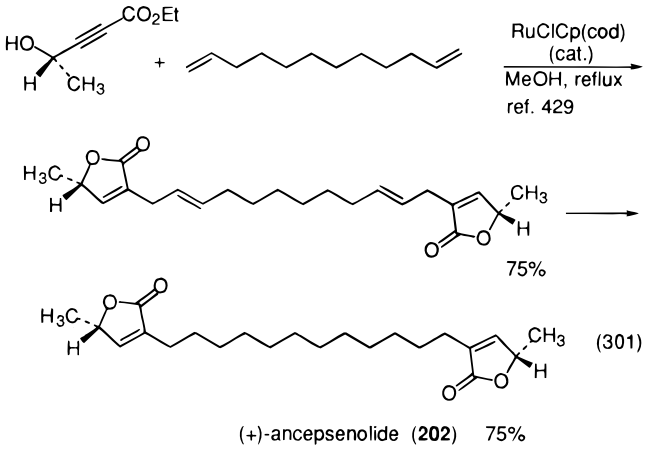
(299)

regioselective preference for formation of the branched product changes upon introduction of steric hindrance at the propargylic position (eq 300). Simi-



(300)

larly, preferential formation of linear product is also observed when employing γ-hydroxybutynoate as alkynes affording the corresponding butenolides via lactonization of the intermediate hydroxy esters.[429] The method can be applied to the short step synthesis of the acetogenin (+)-ancepsenolide (**202**) (eq 301).

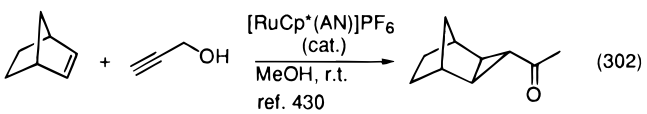


(301)

(+)-ancepsenolide (**202**) 75%

The regioselectivity is consistent with the metallacycle intermediate **197** proposed in Scheme 50, in which (1) steric hindrance is minimized and (2) substituents that may coordinate to ruthenium are preferentially located close to the metal.

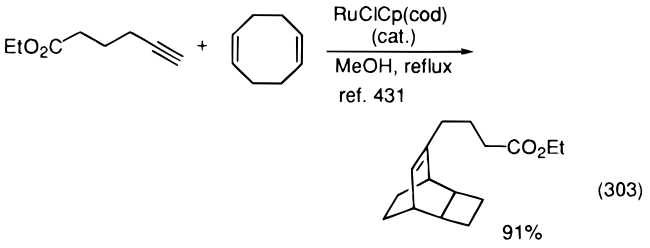
Treatment of propargyl alcohol with norbornene gives the corresponding cyclopropanation product, acetyltricyclooctane in a quantative yield (eq 302).[430]



(302)

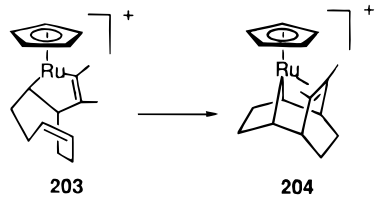
The formation of the ruthenacycle intermediate has been postulated as the key intermediate of the reaction.

Employment of cyclooctadiene as an olefinic substrate gives rise to unusual [4+2] cycloaddition reaction via intramolecular sequential annulation reaction (eq 303).[431] The reaction can be rationalized by assuming the formation of ruthenacyclopentene



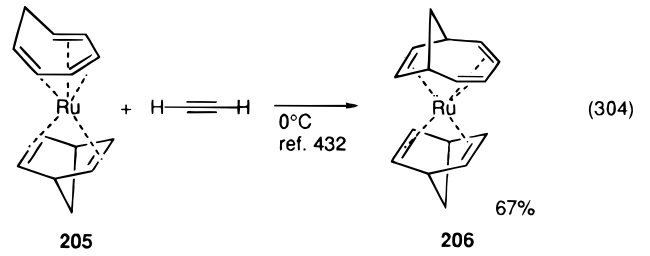
(303)

203. The intramolecular insertion reaction of ruthenium into the coordinated olefin affords intermediate **204**, which undergoes reductive elimination of ruthenium complex to give the tricyclic product.



203 **204**

The stoichiometric reaction of η^6-cycloheptatriene ruthenium complex **205** with terminal alkynes affords [6+2] cycloaddition product **206** under mild conditions (eq 304).[432] The reaction can be explained

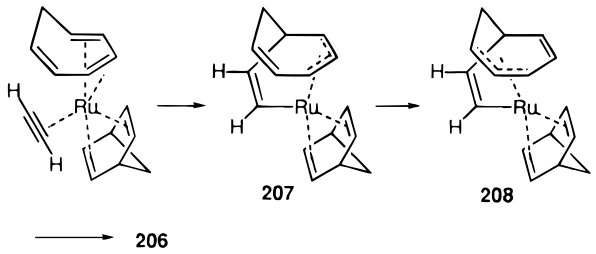


205 **206**

(304)

by the formation of ruthenacycle **207**, isomerization to the second ruthenacycle **208** and reductive elimination of ruthenium (Scheme 51).

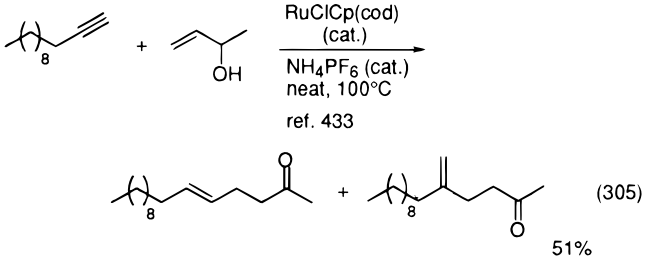
Scheme 51



207 **208**

206

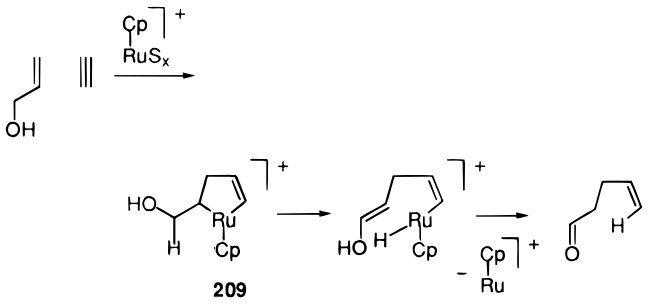
The reaction of terminal alkynes with allyl alcohols with RuClCp(COD) and NH_4PF_6 catalyst gives a mixture of linear and branched γ,δ-unsaturated ketones (eq 305).[433] The reaction gives linear enones



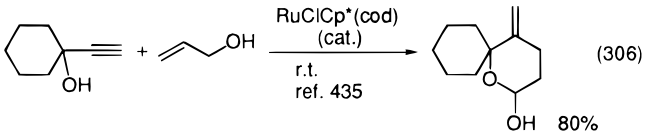
(305)

with RuClCp(cod) catalyst,[433] while the same compounds selectively leads to the branched isomer with RuClCp*(cod) catalyst.[434] Formation of ruthenacyclopentene **209** followed by β-hydrogen elimination is one of most reasonable pathways (Scheme 52). This

Scheme 52

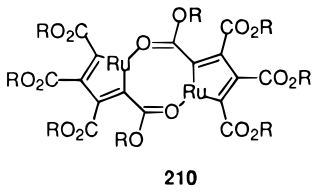


is in contrast to the fact that the reaction with the same substrates in the presence of $RuClCp(PPh_3)_2$ catalyst affords the corresponding β,γ-unsaturated ketones which are mentioned in section VI.Bc (eq 287).[417] Treatment of propargyl alcohols with allyl alcohol in the presence of RuClCp*(cod) catalyst gives 2-hydroxy-5-methylenetetrahydropyrans via the similar coupling reaction and the subsequent cyclization (eq 306).[435]



(306)

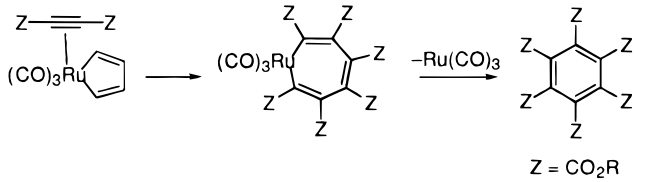
The reaction of $(\eta^2\text{-}C_2H_4)Ru(CO)_4$ with two alkyne molecules gives the tricyclic complex **210** containing two ruthenacyclopentadiene rings. In addition to Co and Ni catalysts, cyclotrimerization of alkynes can be performed catalytically using **210**.[436] The reaction



210

proceeds via a similar sequence of insertion of alkyne and reductive elimination of ruthenium (Scheme 53).

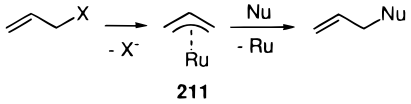
Scheme 53



D. Carbon–Carbon Bond Formation via π-Allylruthenium Intermediates

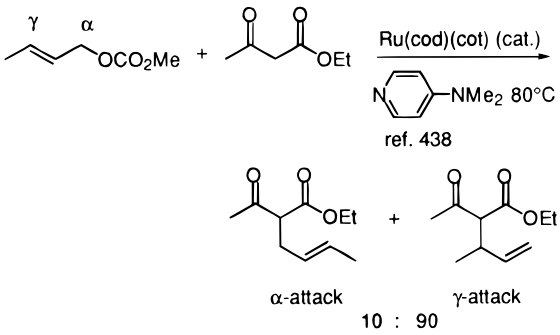
π-Allylpalladium complexes are versatile intermediates for a variety of catalytic transformations of allylic compounds.[2] Catalytic carbon−carbon bond-forming reactions via π-allylruthenium intermediates have been investigated. The reactions of allylic esters and carbonates with low-valent ruthenium complexes give π-allyl intermediate **211**, which undergoes reaction with a variety of nucleophiles to afford the corresponding allylated products (Scheme 54). $RuH_2(PPh_3)_4$-[437] and Ru(cod)(cot)-[438] catalyzed

Scheme 54



211

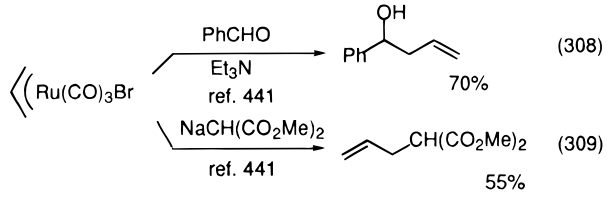
reactions of allyl carbonates with 1,3-dicarbonyl compounds gives allylated products. Selective attack of nucleophiles at the γ-positions of allyl carbonates is observed in these reactions, while similar treatment with π-allylpalladium predominates the α-attack (eq 307).[438] The γ-selectivity has been observed



(307)

in the carbonylation of allyl carbonates to afford β,γ-unsaturated esters.[439] The $Ru_3(CO)_{12}$-catalyzed carbonylation of allyl phenyl sulfides giving thioesters also proceeds via π-allyl ruthenium intermediates.[440]

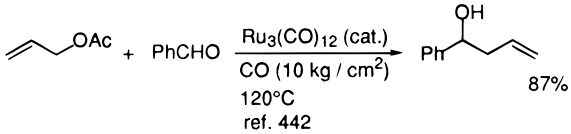
Another remarkable contrast to palladium chemistry is the ambiphilic character of π-allylruthenium complexes. η^3-Allylruthenium(II) complexes prefer attack of electrophiles such as aldehydes as well as attack of nucleophiles such as $NaCH(CO_2Me)_2$, while π-allylpalladium complexes react with nucleophiles exclusively.[2] Thus, the stoichiometric reactions of π-allylruthenium complex with benzaldehyde and sodium salt of diethyl malonate afford homoallyl alcohol and allylmalonate, respectively (eqs 308 and 309).[441] The reaction can be carried out catalytically



(308)

(309)

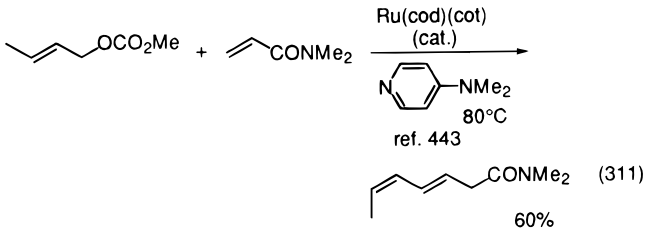
using $Ru_3(CO)_{12}$ catalyst under CO pressure (eq 310).[441,442]



(310)

When electron-deficient olefins are employed as an electrophile, a selective linear coupling reaction occurs under the similar reaction conditions. Typically,

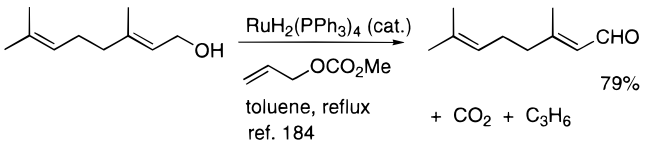
the Ru(cod)(cot)-catalyzed reaction of allylic carbonates with α,β-unsaturated amides affords the corresponding 3,5-dienoic derivatives (eq 311).[443] Treat-



(311)

ment of allyl acetate with primary alcohols in the presence of $RuCl_2(PPh_3)_3$ catalyst and inorganic base gives α,β-unsaturated ketone via dehydrogenation of alcohols followed by the similar coupling reactions.[444] Synthesis of α-hydroxycarboxylic acids from α-ketocarboxylates can be performed by ruthenium catalysts via π-allylruthenium intermediates.[445]

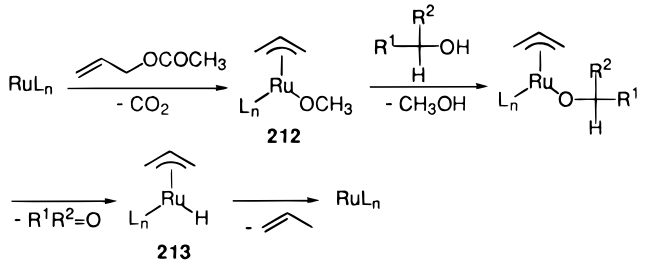
π-Allylruthenium complexes also act as intermediates for catalytic oxidation of alcohols under mild reaction conditions. The $RuH_2(PPh_3)_4$-catalyzed oxidation of primary and secondary alcohols in the presence of allyl methyl carbonate affords the corresponding aldehydes and ketones with evolution of CO_2 and propene (eq 312).[184]



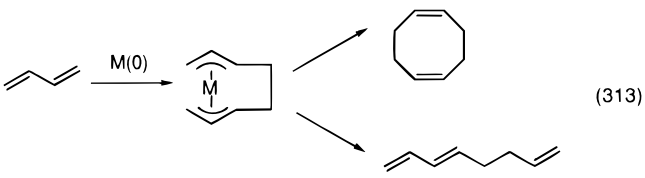
(312)

The reaction can be rationalized by assuming the formation of π-allylruthenium methoxide **212** by the oxidative addition of ruthenium species to allyl methyl carbonate followed by decarboxylation. Ligand exchange with alcohol substrate and subsequent β-elimination give carbonyl compound and π-allylruthenium hydride **213**. Reductive elimination of propene affords low-valent ruthenium to complete the catalytic cycle (Scheme 55).

Scheme 55

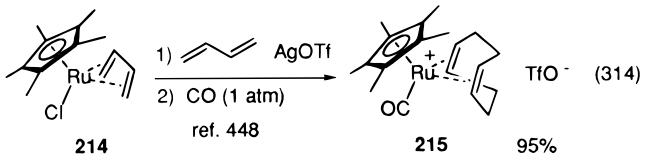


Oligomerization and cooligomerization of conjugated dienes are one of the representative reactions proceeding via transition metal π-allyl intermediates. Typically, nickel(0)-catalyzed reaction of butadiene gives cyclooctadiene,[446] while palladium-catalyzed reaction affords linear dimerization products.[2] These reactions can be explained by the formation of bis(π-allyl)metal complexes, where reductive elimination and β-elimination of metals are controlling factors for the product selectivity (eq 313). Similar dimerization

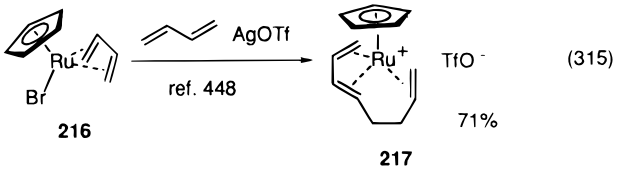


(313)

reactions mediated by ruthenium complexes have been investigated by stoichiometric reactions of conjugated diene complexes of ruthenium.[447] When Cp*Ru(η⁴-butadiene)X (**214**) in dichloromethane was treated with an acetone solution of equimolar silver trifluoromethanesulfonate in the presence of excess butadiene at ambient temperature, followed by allowing the mixture to react with carbon monoxide (1 atm), a cationic 1,5-cyclooctadiene carbonyl complex **215** was isolated in 95% yield (eq 314), whereas selective linear dimerization took place upon similar treatment with cyclopentadienyl complex **216** affording complex **217** (eq 315).[448] The intermediacy of bis-

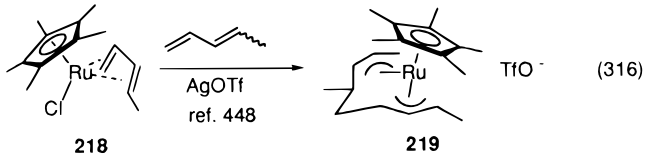


(314)



(315)

(π-allyl) complexes for the present dimerization reaction has been strongly suggested by the fact that similar treatment of Cp*Ru(η⁴-1,3-pentadiene)Cl (**218**) with 1,3-pentadiene afforded bis(π-allyl)ruthenium(IV) complex **219** via regioselective tail−head dimerization (eq 316).



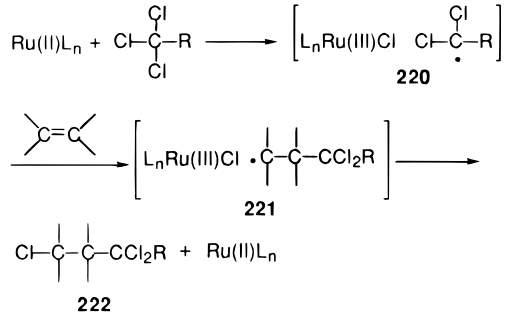
(316)

Catalytic cyclodimerization of dienes can be also performed selectively. 1,5-Cyclooctadiene, dimethylcyclooctadienes, and 6-methyl-2,4,7-nonatriene can be obtained from butadiene, isoprene, and 1,3-pentadiene, respectively, upon treatment with a catalytic amount of Cp*RuCl(diene) and AgOTf.[448] The reaction of $[Ru(\eta^3:\eta^3\text{-}C_{10}H_{16})(solv)_3](BF_4)_2$ undergoes similar dimerization of 1,3-butadiene to afford $[Ru(\eta^6\text{-}C_8H_{10})(1,3:5,6\text{-}\eta\text{-}C_8H_{11})](BF_4)$.[449] Treatment of $RuCl_3 \cdot nH_2O$ with 1,3-butadiene in refluxing 2-ethoxyethanol results in trimerization of butadiene to give bis(allyl)ruthenium(IV) compound $Ru(\eta^3:\eta^2:\eta^3\text{-}C_{12}H_{18})Cl_2]$.[450]

E. Radical Reactions

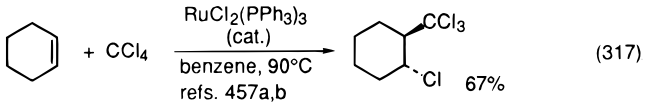
Metal-catalyzed radical coupling reactions with olefins have been performed by using metal complex catalysts[451] such as $CuCl_2$,[452] Cu_2Cl_2,[453] $[Co(CO)_4]_2$,[454]

Scheme 56

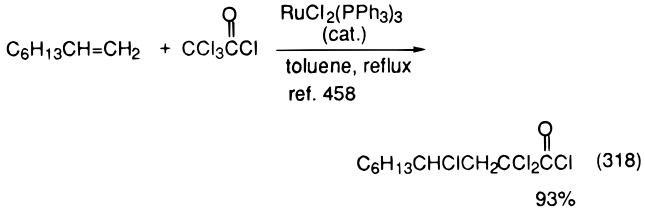


$Fe_2(CO)_9$,[455] and (naphthalene)$Cr(CO)_3$.[456] Owing to their ability to promote fast electron transfer, low-valent ruthenium complexes have proven to be one of the effective catalysts for generating radicals from various organic halides. As shown in Scheme 56, the reaction of divalent ruthenium complexes with polyhalomethyl compounds gives ruthenium(III)-caged radical intermediate **220**. Trapping the intermediate with radicophiles such as olefins affords intermediate **221** which undergoes recombination of halogen group to give the corresponding radical coupling product **222** and ruthenium(II) complex to complete the catalytic cycle. Representative results of ruthenium-catalyzed radical coupling reactions of polyhalomethane compounds with olefins are shown below.

On heating with $RuCl_2(PPh_3)_3$ catalyst, various substrates bearing polychloromethyl groups such as CCl_4,[457] trichloroacetyl chloride,[458] and CF_3CCl_3[459] react with olefins to afford the corresponding 1-chloro-2-polychloromethylalkanes with high efficiency (eqs 317 and 318). Under similar reaction conditions CF_2-

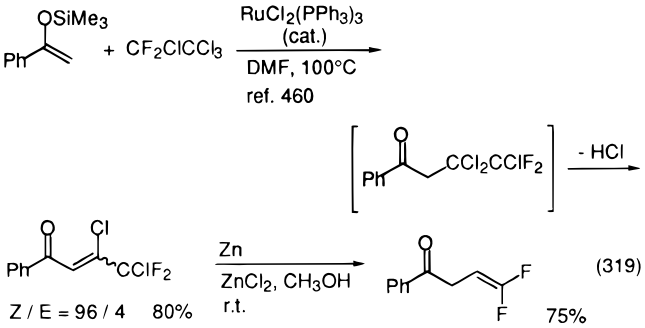


(317)



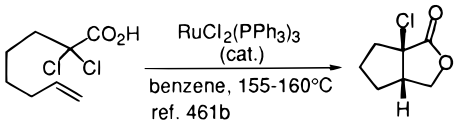
(318)

$ClCCl_3$ reacts with silyl enol ethers to give the corresponding β-chloro-α,β-unsaturated ketones via hydration and dehydrochlorination.[460] Reductive dechlorination with zinc powder gives γ,γ-difluoroallyl ketones (eq 319).



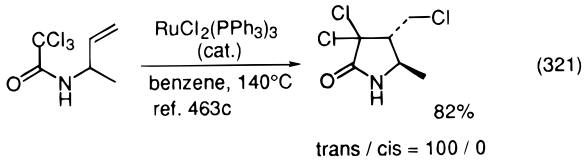
(319)

An intramolecular version of the reaction provides a useful method for cyclization of olefins bearing a variety of polychloromethyl moieties. Olefinic α,α'-dichloro esters[461] (eq 320), acids,[461] nitriles,[461] and



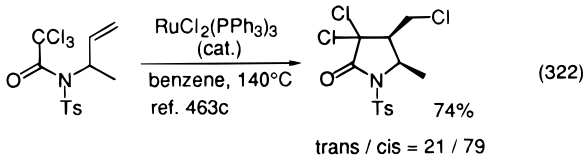
(320)

trichloromethylalkenes[462] afford radical cyclization products upon heating with $RuCl_2(PPh_3)_3$ catalyst. Pyrrolidine skeletons can be constructed from *N*-trichloroacetylallylamines,[463] which are readily prepared by the reaction of allylic alcohols with CH_3CN.[463d] Application of this process to the cyclization of 1-buten-3-yl trichloroacetamides gives rise to selective preparation of *trans*-β,γ-dialkyl γ-lactam as a single product (eq 321).[463b-d] In sharp contrast,



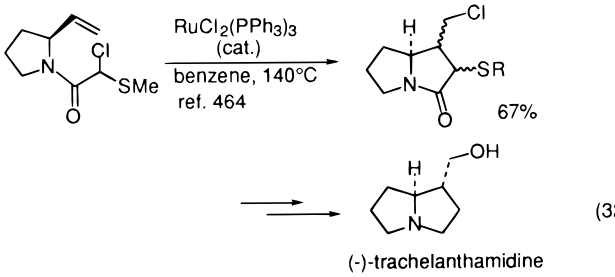
(321)

trichloroacetamides bearing electron-withdrawing substituents on the nitrogen such as Ts, Ms, Cbz, and Boc groups afford the cis isomer as a major product (eq 322). *N*-Allylic α-chloro-α-thioacetamides un-



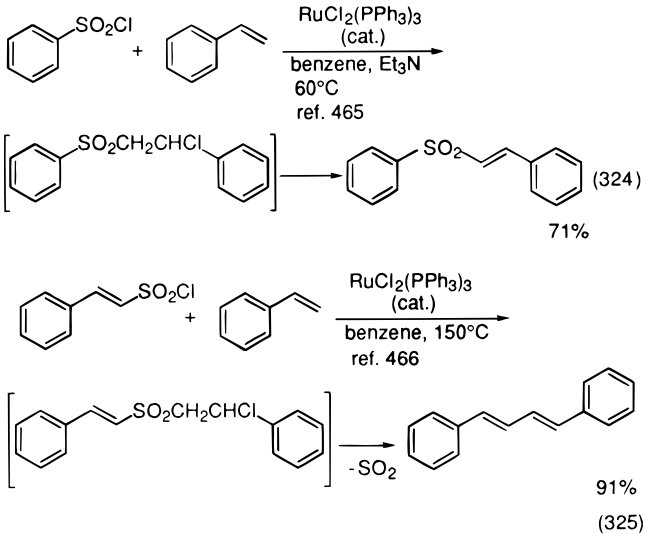
(322)

dergo similar radical cyclization upon treatment with $RuCl_2(PPh_3)_3$ catalyst.[464] These methods can be applied to the stereoselective synthesis of indole[463b] and indolizidine alkaloids (eq 323).[464]

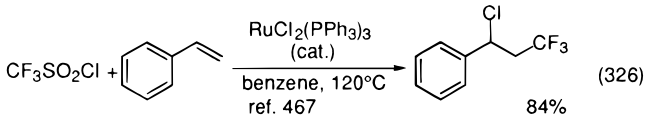


(323)

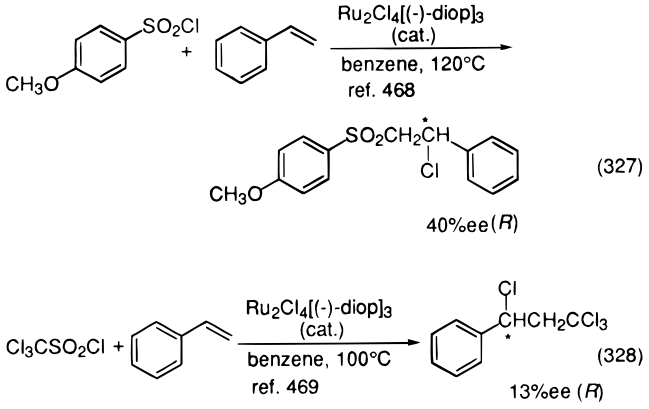
The addition of arenyl,[465,468] vinyl,[466] and trihalomethyl sulfonyl chloride[467,469] to olefins with $RuCl_2(PPh_3)_3$ catalyst also proceeds in a radical manner.[470] When the reaction was carried out in the presence of Et_3N, the radical coupling reaction and the subsequent elimination of HCl occurred to afford the corresponding (*E*)-α,β-unsaturated sulfones selectively (eq 324).[465] Similar treatment with vinylsulfonyl chloride at elevated temperature gives *E*,*E*-dienes stereoselectively via subsequent elimination of HCl and SO_2 (eq 325).[466]



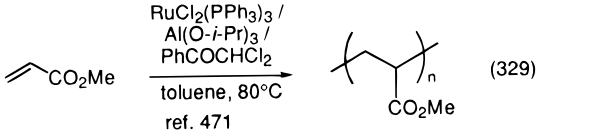
Desulfonylative radical couplings are also observed in the reactions of trifluoromethanesulfonyl chloride with styrene (eq 326).[467] Asymmetric radical cou-



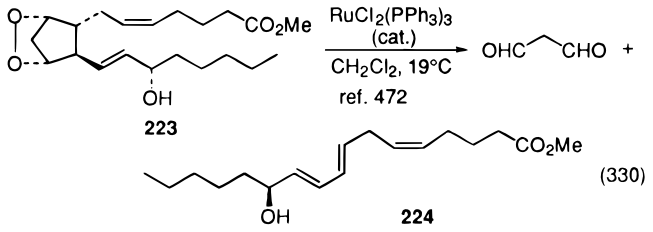
pling reactions of styrene with phenylsulfonyl chloride (eq 327)[468] and trichloromethylsulfonyl chloride (eq 328)[469] have been investigated using $Ru_2Cl_4[(-)\text{-diop}]_3$ catalyst.



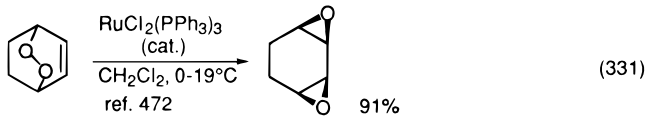
The present radical provides a new method for radical polymerization of olefins. In the presence of a catalytic amount of $RuCl(PPh_3)_3/Al(O\text{-}i\text{-}Pr)_3/PhCOCHCl_2$ methyl methacrylate undergoes living radical polymerization in toluene at 80 °C (eq 329).[471]



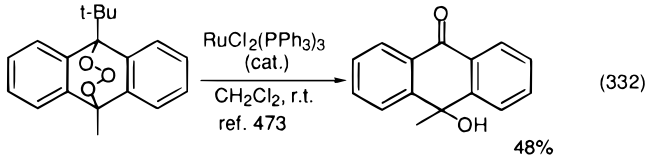
1,4-Bicyclic epiperoxides undergo specific cleavage reactions initiated by homogeneous O−O bond scission with $RuCl_2(PPh_3)_3$ catalyst.[472] When the reaction is applied to PGH_2 methyl ester **223**, smooth fragmentation give rise to afford methyl (5*Z*,8*E*,10*E*,-12*S*)-12-hydroxy-5,8,10-heptadecatrienoate (**224**, HHT methyl ester) selectively (eq 330). 1,4-Epiperoxides



bearing internal olefins are converted into the corresponding 1,2,3,4-diepoxides by trapping the resulting oxy radicals with internal olefins (eq 331).[472] The



transannular ozonide of 9-*tert*-butyl-10-methylanthracene undergoes similar homogeneous scission of the O−O bond to afford the corresponding hydroxy ketone (eq 332).[473]

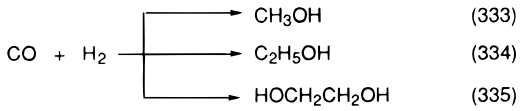


The intermediates $(RuL_3^{2+})^*$ generated by irradiation of RuL_3^{2+} complexes have a strong ability to promote electron transfer to heteroatom compounds such as tertiary amines, generating radicals at α-positions.[474] Thus, some photoinduced reactions including homolytic α-carbon−carbon bond scission of tertiary amines[475] and transacetalization reaction[476] can be performed by using $Ru(bpy)_3^{2+}$ catalyst.

VII. Reaction of CO and CO_2

Efficient utilization of CO and CO_2 is very important as C_1 chemistry in view of industrial, economical, and environmental aspects. Much effort has been devoted to developing the efficient and selective catalytic reactions.[477] Ruthenium complexes play an important role in this field of chemistry.

Synthesis gas (CO + H_2), obtained readily by gasification of coals, can be converted into hydrocarbons (Fischer−Tropsch Synthesis)[478] and oxygen-containing C_1 and C_2 molecules by using homogeneous ruthenium catalysts.[479] Ethanol and ethylene glycol can be obtained by heating synthesis gas in the presence of catalytic systems such as $Ru_3(CO)_{12}$-AcOOH,[480] RuO_2-Bu_4PBr,[481] $Ru_3(CO)_{12}$-KI,[482] and $Ru_3(CO)_{12}$−1-alkylbenzimidazole (eqs 334 and 335).[483]



Bimetallic catalysts have been used for controlling the distribution of small molecule products. Ru/Rh[484,485] and Ru/Re[486] bimetallic systems exhibit good selectivity for the formation of ethylene glycol. When

the Ru/Co catalyst is used, ethanol is formed preferentially,[487] while methanol is obtained with Ru/Mn and Ru/Ti catalysts (eq 333).[488] In the presence of ammonia, the synthesis gas can be converted into the corresponding formamides with the $Ru_3(CO)_{12}$-Bu_4-PBr catalyst.[489] The homologation reaction, a one-carbon extension reaction, is one of the important reactions using synthesis gas. Homologation of methanol and methyl esters to ethanol and its derivatives can be carried out with Ru/CH_3I[490] and Ru/Co catalysts (eq 336).[491] Hydroformylation of

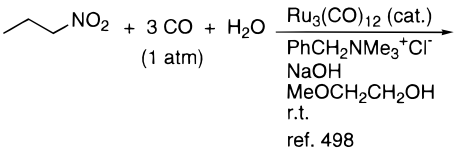
$$CH_3OH + CO + 2H_2 \longrightarrow CH_3CH_2OH \qquad (336)$$

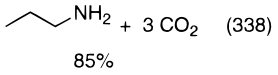
olefins to the corresponding aldehydes can be performed under synthesis gas in the presence of ruthenium catalysts,[492] although catalytic activities are lower than those of cobalt and rhodium complexes.

Water gas shift reactions that afford CO_2 and H_2 from CO and H_2O are performing worldwide as an important industrial process (eq 337).[493] Catalysis

$$CO + H_2O \longrightarrow CO_2 + H_2 \qquad (337)$$

with various homogeneous catalysts including $Ru_3(CO)_{12}$,[494] $H_2FeRu_3(CO)_{13}$,[495] and K[Ru(Hedta)(CO)][496] has been extensively studied for efficient production of molecular hydrogen. The reactions provide a convenient method for reduction of organic substrates without operating hydrogen gas.[497] Reduction of nitroalkanes (eq 338)[498] and nitroarenes[499] to primary

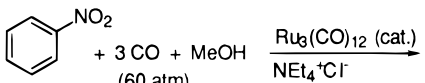


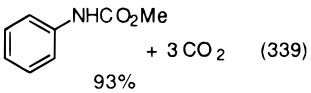


(338)

amines has been performed efficiently using $Ru_3(CO)_{12}$ catalyst under water gas shift conditions.

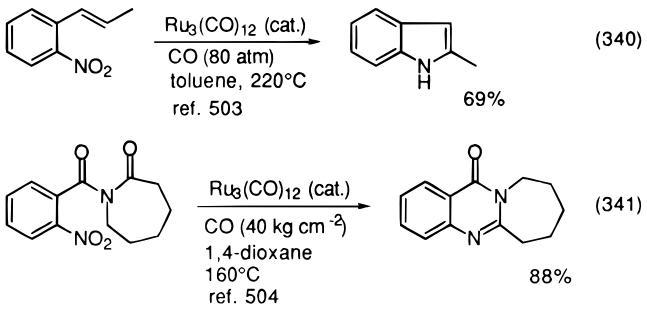
The catalytic reaction utilizing reducing ability of CO itself has been performed with ruthenium cluster catalysts. Various reductive transformations of nitro compounds have been performed with low-valent ruthenium catalysts under CO pressure.[500] Reductive carbonylation of nitroarenes with alcohols in the presence of $Ru_3(CO)_{12}$ catalysts affords the corresponding *N*-(alkoxycarbonyl)anilines which are important synthetic intermediates for the isocyanates (eq 339).[501,502] Reductive cyclization of 2-nitrosty-





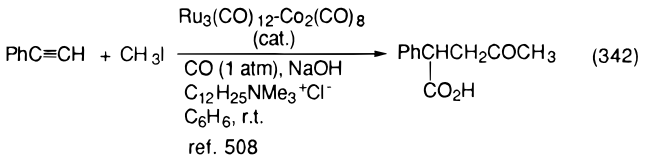
(339)

renes (eq 340)[503] and *N*-(2-nitrobenzoyl)amides (eq 341)[504] can be carried out under CO pressure to give



the corresponding indoles and 4(3*H*)-quinazolinones, respectively. γ-Nitroketones undergo similar reduction with CO and the subsequent cyclization to give the corresponding cyclic imines.[505] Reduction of oximes can be also performed with the $Ru_3(CO)_{12}$ catalyst under CO pressure to afford the corresponding imines.[506]

Although metal-catalyzed carbonylation reactions are useful tools for the construction of a variety of carbonyl compounds,[507] the reactions using ruthenium catalysts are limited to a few cases. Alkynes undergo specific carbonylation reactions with methyl iodide in the presence of $Ru_3(CO)_{12}$-$Co_2(CO)_8$ bimetallic catalyst under phase-transfer conditions to afford the corresponding γ-ketocarboxylic acids (eq 342).[508]



(342)

Oxidative cyclocarbonylation of allyl alcohols can be performed with $RuCl_2(PPh_3)_3$ and K_2CO_3 catalyst to give 2(5*H*)-furanones.[509] The unusual construction of catechol skeletons has been performed by $Ru_3(CO)_{12}$-catalyzed reaction of 1,6-diynes with hydrosilanes and CO (eq 293).[423] The formation of siloxycarbyne ruthenium intermediate ($Ru{\equiv}C{-}OSiR_3$) has been postulated as the reactive intermediates (Scheme 48).

Catalytic transformation of CO_2 to basic chemicals is one of particular interest because the use of CO_2 for chemical syntheses are an economically valuable extension to the carbon sources.[510] The photochemical reduction of CO_2 is important in view of artificial photosynthesis and many methods for photoinduced conversion of CO_2 to formic acid and its derivatives,[511] CO,[512] and methane[513] have been performed with the aid of ruthenium complex catalysts. An alternative useful method is electrochemical reductions,[510e] where various low-valent ruthenium complexes bearing bipyridyl ligands catalyze two electron reduction of CO_2 to afford formic acid and CO (eqs 343 and 344).[514]

$$CO_2 + 2H^+ + 2e^- \xrightarrow[\text{refs. 510, 514}]{\text{Ru cat.}} HCO_2H \qquad (343)$$

$$CO_2 + 2H^+ + 2e^- \xrightarrow[\text{refs. 510, 514}]{\text{Ru cat.}} CO + H_2O \qquad (344)$$

Hydrogenation of CO_2 to formic acid and its derivatives is the most straightforward chemical method for transformation of CO_2 to organic small molecules (eq 345); hence, many methods have been reported

$$CO_2 + H_2 \xrightarrow{\text{Ru cat.}} HCO_2H \qquad (345)$$

using transition metal complex catalysts.[510e,f] Hydridoruthenium phosphine complexes such as $RuH_2(PPh_3)_4$ are one of the effective catalysts for hydrogenation of CO_2. The $RuH_2(PPh_3)_4$-catalyzed reaction of CO_2 (25 bar) and H_2 (25 bar) in benzene in the presence of triethylamine and water gives formic acid with a turnover number of 87.[515] When the reactions are carried out in the presence of alcohols and dimethylamine under similar reaction conditions, alkyl formates[516] and *N*,*N*-dimethylformamide[517] can be obtained, respectively. Methanol is obtained preferentially when the hydrogenation of CO_2 is carried out with $Ru_3(CO)_{12}$-KI catalyst.[518] Recently, extremely high efficiency for the conversion of CO_2 to formic acid has been achieved using ruthenium catalyst in a supercritical mixture of H_2, CO_2, and NEt_3 without solvent.[519] A turnover number of 7200 is obtained using $RuH_2(PMe_3)_4$ and $RuCl_2(PMe_3)_4$ catalysts. The reaction rate in the supercritical phase is 18 times faster than that in THF under comparable conditions. Under the similar supercritical phase conditions, methyl formate[519c,520] and DMF[519c,521] can be prepared with extremely high turnover numbers (3500 and 370 000) in the presence of methanol and dimethylamine, respectively. A turnover number of 740 000 has been achieved in the reaction of dimethylamine with CO_2 and H_2 when using $RuCl_2(dppe)_2$ as a catalyst.[522] The representative results are shown in eqs 346−348.

$$\underset{\text{(125 bar)}}{scCO_2} + \underset{\text{(80 bar)}}{H_2} \xrightarrow[\text{ref. 519}]{\overset{RuCl_2(PMe_3)_4\ (cat.)}{Et_3N,\ 50°C}} HCO_2H \quad \text{TON} = 7200 \qquad (346)$$

$$\underset{\text{(125 bar)}}{scCO_2} + \underset{\text{(80 bar)}}{H_2} + CH_3OH \xrightarrow[\text{ref. 520}]{\overset{RuCl_2(PMe_3)_4\ (cat.)}{Et_3N,\ 80°C}} HCO_2CH_3 + H_2O \quad \text{TON} = 3500 \qquad (347)$$

$$\underset{\text{(130 bar)}}{scCO_2} + \underset{\text{(80 bar)}}{H_2} + Me_2NH \xrightarrow[\text{ref. 521}]{\overset{RuCl_2(PMe_3)_4\ (cat.)}{100°C}} HCONMe_2 + H_2O \quad \text{TON} = 370000 \qquad (348)$$

One of the successful catalytic organic reactions, employing CO_2 as a substrate, is ruthenium-catalyzed synthesis of vinyl carbamates from alkynes, CO_2, and secondary amines, which is described in section V.[271−276] Other catalytic transformations such as photoinduced CO_2 fixation into pyruvic acid (eq 349),[523] hydrosilylation (eq 350),[524] and aminosilylation[525] of CO_2 have been performed using ruthenium catalysts.

$$CH_3\overset{O}{\overset{\|}{C}}\text{-}CO_2^- + CO_2 + 2\,RSH \xrightarrow[\text{ref. 523}]{\overset{Ru(bpy)_3^{2+}\ (cat.)}{h\upsilon}} {}^-O_2CCH_2\overset{OH}{\overset{|}{C}}HCO_2^- + RSSR + H^+ \qquad (349)$$

$$\underset{\text{(30 kg cm}^{-2}\text{)}}{CO_2} + HSiMeEt_2 \xrightarrow[\text{ref. 524a}]{\overset{RuCl_2(PPh_3)_3\ (cat.)}{C_6H_6,\ 100°C}} HCO_2SiMeEt_2 \quad 14\% \qquad (350)$$

VIII. Concluding Remarks

This review compiled recent advances in ruthenium-catalyzed reactions mainly in view of organic synthesis. Because of limitation of space of the manuscript, many details of each reaction, i.e., reaction mechanism, limitation of the applicable substrates, and synthetic applications, have not been described precisely. For further details, refer to the review articles and original papers cited in the references. Startling progress on ruthenium chemistry has been made in the past decade, and a large number of fundamental principles characteristic of the ruthenium complexes has been presented. Presently, many organic chemists see intense possibilities of ruthenium chemistry toward new world of catalytic reactions and organic synthesis. Novel transformations based on new principles and useful reactions bearing higher efficiency and selectivities will be continuously developed in the future. Furthermore, the importance of ruthenium chemistry will be increasing from industrial points of view because of their efficiencies, selectivities, and the exceptional cheapness of ruthenium metal compared to other precious metals such as palladium and rhodium being widely used in industrial processes. It will surely become a powerful tool for organic synthesis and related industrial processes and their utilities will be increased in the future.

IX. Abbreviations

aca	acetylacetonato
acac-F_6	perfluoroacetylacetonato
Ala	alanine
BINAP	2,2′-bis(diphenylphosphino)-1,1′-binaphthyl
H_8-BINAP	2,2′-bis(diphenylphosphino)-5,5′,6,6′,7,7′,8,8′-octahydro-1,1′-binaphthyl
BIPHEMP	2,2′-dimethyl-6,6′-bis(diphenylphosphino)biphenyl
Boc	*tert*-butoxycarbonyl
BOM	(benzyloxy)methyl
bpy	2,2′-bipyridine
Bz	benzyl
TEMPO	2,2,6,6-tetramethylpiperidine-1-oxyl
CAN	cerium ammonium nitrate
CBD	cyclobutadiene
Cbz	carbobenzyloxy
chiraphos	(2*R*,3*R*)- or (2*S*,3*R*)-bis(diphenylphosphino)-butane
cod	1,5-cyclooctadiene
cot	1,3,5-cyclooctatriene
Cp	cyclopentadienyl
Cp*	1,2,3,4,5-pentamethylcyclopentadienyl
p-cymene	4-isopropyltoluene
DDAB	didecyldimethylammonium bromide
diglyme	bis(2-methoxyethyl) ether
diop	2,3-*O*-isopropylidene-2,3-dihydroxy-1,4-bis-(diphenylphosphino)butane
DME	1,2-dimethoxyethane
DMF	*N*,*N*-dimethylformamide
DMSO	dimethyl sulfoxide
dmp	2,9-dimethyl-1,10-phenanthroline
dmpe	1,2-bis(dimethylphosphino)ethane
dppb	1,4-bis(diphenylphosphino)butane
dppe	1,2-bis(diphenylphosphino)ethane
edta	ethylenediaminetetraacetic acid
HHT	(5*Z*,8*E*,10*E*,12*S*)-12-hydroxy-5,8,10-heptadecatrienoic acid

mCPBA	*m*-chloroperbenzoic acid
MEM	2-methoxyethoxymethyl
mesitylene	1,3,5-trimethylbenzene
Me_3tacn	1,4,7-trimethyl-1,4,7-triazacyclononane
MOM	methoxymethyl
Ms	methylsulfonyl
MS4A	molecular sieves 4A
NMO	*N*-methylmorpholine *N*-oxide
OEP	2,3,7,8,12,13,17,18-octaethylporphyrinato
PCy_3	tricyclohexylphosphine
i-Pr-BPE	1,2-bis(*trans*-2,5-diisopropylphospholano)-ethane
PTA	1,3,5-triaza-7-phosphaadamantane
ppy	1-diphenylphosphino-2-(2′-pyridyl)ethane
PPN	bis(triphenylphosphoranylidene)ammonium
py	pyridine
pybox	2,6-bis(oxazolin-2-yl)pyridine
ROMP	ring-opening metathesis polymerization
salophen	*N*,*N*′-bis(salicylidene)-*o*-phenylenediamine
SEM	2-(trimethylsilyl)ethoxymethyl
Ser	serine
skewphos	(*R*,*R*)- or (*S*,*S*)-1,3-dimethyl-1,3-bis(diphenylphosphino)propane
TDCPP	5,10,15,20-tetrakis(2,6-dichlorophenyl)porphyrinato
$T_{2,6}$diFPP	5,10,15,20-tetrakis(2,6-difluorophenyl)porphyrinato
TEOC	2-(trimethylsilyl)ethoxycarbonyl
Tet-Me_6	*N*,*N*,*N*′,*N*′-tetramethyl-3,6-diazaoctane-1,8-diamine
tetracyclone	2,3,4,5-tetraphenyl-2,4-cyclopentadienone
THAHS	tetrahexylammonium hydrogen sulfate
THF	tetrahydrofuran
THP	2-tetrahydropyranyl
TMC	1,4,8,11-tetramethyl-1,4,8,11-tetraazacyclotetradecane
TMP	5,10,15,20-tetramesitylporphyrinato
TOF	turnover frequency
TON	turnover number
Ts	*p*-toluenesulfonyl
trityl	triphenylmethyl
trpy	2,2′,2″-terpyridine
TPFPP	5,10,15,20-tetrakis(pentafluorophenyl)porphyrinato
TPP	5,10,15,20-tetraphenylporphyrinato

X. References

(1) (a) Bateson, J. H.; Mitchell, M. B. *Organometallic Reagents in Organic Synthesis*; Academic Press: London, 1994. (b) *Organometallics in Synthesis*; Schlosser, M., Ed.; John Wiley & Sons: Chichester, 1994. (c) McQuillin, F. J.; Parker, D. G.; Stephenson, G. R. *Transition Metal Organometallics for Organic Synthesis*; Cambridge University Press: Cambridge, 1991. (d) Yamamoto, A. *Organotransition Metal Chemistry. Fundamental Concepts and Applications*; Wiley: New York, 1986. (e) Colquhoun, H. M.; Holton, J.; Thompson, D. J.; Twigg, M. V. *New Pathways for Organic Synthesis*; Plenum Press: New York, 1984. (f) Davies, S. G. *Organotransition Metal Chemistry: Applications to Organic Synthesis*; Pergamon Press: Oxford, 1982. (g) Negishi, E. *Organometallics in Organic Synthesis*; John Wiley & Sons: New York, 1980.

(2) (a) Hegedus, L. S. Transition Metal Organometallics in Organic Synthesis. In *Comprehensive Organometallic Chemistry*; Pergamon Press: Oxford, 1995; Vol 12. (b) Tsuji, J. *Palladium Reagents and Catalysts*; John Wiley & Sons: Chichester, 1995. (c) Crabtree, R. H. *The Organometallic Chemistry of the Transition Metals*; John Wiley & Sons: New York, 1994. (d) Collman, J. P.; Hegedus, L. S.; Norton, J. R.; Finke, R. G. *Principles and Applications of Organotransition Metal Chemistry*; University Science Books: Mill Valley, CA, 1987. (e) Heck, R. F. *Palladium Reagents in Organic Syntheses*; Academic Press: New York, 1985. (f) Trost, B. M.; Verhoeven, T. R. Organopalladium Compounds in Organic Synthesis and in Catalysis. In *Comprehensive Organometallic Chemistry*; Pergamon Press: Oxford, 1982; Vol 8. p 799. (g) Henry, P. M. *Palladium Catalyzed Oxidation of Hydrocarbons*; D. Reidel Pub. Co.: Dordrecht, 1980. (h) Tsuji, J. *Organic Synthesis with Palladium Compounds*; Springer: Berlin, 1980. (i) Maitlis, P. M. *The Organic Chemistry of Palladium*; Academic Press: New York, 1971; Vols. 1 and 2.

(3) (a) Seddon, E. A.; Seddon K. R. *The Chemistry of Ruthenium*; Elsevier: Amsterdam, 1984. (b) Griffith, W. P. *The Chemistry of the Rarer Platinum Metals; Os, Ru, Ir and Rh*; Wiley-Interscience: New York, 1967. (c) Cotton, F. A.; Wilkinson, G. *Advanced Inorganic Chemistry*, 4th ed.; John Wiley & Sons: New York, 1980.

(4) (a) Lee, D. G.; van den Engh, M. *Oxidation in Organic Chemistry*; Trahanovsky, W. S., Ed.; Academic Press: New York, 1973; part B, Chapter 4. (b) Courtney, J. L. *Organic Synthesis by Oxidation with Metal Compounds*; Mijs, W. J., de Jonge, C. R. H. I., Eds.; Plenum Press: New York, 1986; Chapter 8, p 445. (c) Martín, V. S.; Palazón, J. M.; Rodríguez, C. M. *Encyclopedia of Reagents for Organic Synthesis*; Paquette, L. A., Ed.; John Wiley & Sons: Chichester, 1996; Vol. 6, p 4415.

(5) Siegel, S. *Encyclopedia of Reagents for Organic Synthesis*; Paquette, L. A., Ed.; John Wiley & Sons: Chichester, 1996; Vol. 6, p 4410.

(6) (a) Bennett, M. A.; Matheson, T. W. In *Comprehensive Organometallic Chemistry*; Wilkinson, G., Stone, F. G. A., Abel, E. W., Eds.; Pergamon Press: Oxford, 1982; Vol. 4, p 931. (b) James, B. R. *Homogeneous Hydrogenation*; Wiley: New York, 1973. (c) Freifelder, M. *Practical Catalytic Hydrogenation*; Wiley-Interscience: New York, 1971.

(7) Komiya, S.; Hirano, M. In *Synthesis of Organometallic Compounds*; Komiya, S., Ed.; John Wiley & Sons: Chichester, 1997; p 159.

(8) (a) Ley, S. V.; Norman, J.; Griffith, W. P.; Marsden, S. P. *Synthesis* **1994**, 639. (b) Griffith, W. P.; Ley, S. V. *Aldrichimica Acta* **1990**, *23*, 13.

(9) (a) Mantovani, A.; Cenini, S. *Inorg. Synth.* **1976**, *16*, 51. (b) Teulon, P.; Roziere, J. *J. Organomet. Chem.* **1981**, *214*, 391.

(10) Humphries, A. P.; Knox, S. A. R. *J. Chem. Soc., Dalton Trans.* **1975**, 1710.

(11) Cobbledick, R. E.; Einstein, F. W. B.; Pomeroy, R. K.; Spetch, E. R. *J. Organomet. Chem.* **1980**, *195*, 77.

(12) Hallman, P. S.; Stephenson, T. A.; Wilkinson. G. *Inorg. Synth.* **1970**, *12*, 237.

(13) (a) Yamamoto, A.; Kitazume, S.; Ikeda, S. *J. Am. Chem. Soc.* **1968**, *90*, 1089. (b) Young, R.; Wilkinson, G.; Komiya, S.; Yamamoto, A. *Inorg. Synth.* **1977**, *17*, 75.

(14) (a) Schwab, P.; France, M. B.; Ziller, J. W.; Grubbs, R. H. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 2039. (b) Schwab, P.; Grubbs, R. H.; Ziller, J. W. *J. Am. Chem. Soc.* **1996**, *118*, 100.

(15) Ahmad, N.; Levison, J. J.; Robinson, S. D.; Uttley, M. F. *Inorg. Synth.* **1974**, *15*, 45.

(16) Pertici, P.; Vitulli, G.; Paci, M.; Porri, L. *J. Chem. Soc., Dalton Trans.* **1980**, 1961.

(17) Chaudret, B.; Commenges, G.; Poilblanc, R. *J. Chem. Soc., Chem. Commun.* **1982**, 1388.

(18) Bennett, M. A.; Smith, A. K. *J. Chem. Soc., Dalton Trans.* **1974**, 233.

(19) Oshima, N.; Suzuki, H.; Moro-oka, Y. *Chem. Lett.* **1984**, 1161.

(20) Suzuki, H.; Omori, H.; Lee, D. H.; Yoshida, Y.; Moro-oka, Y. *Organometallics* **1988**, *7*, 2243.

(21) Oshima, N.; Suzuki, H.; Moro-oka, Y.; Nagashima, H.; Ito, K. *J. Organomet. Chem.* **1986**, *314*, C46.

(22) (a) Noyori, R. *Asymmetric Catalysis in Organic Synthesis*; John Wiley & Sons: New York, 1994; Chapter 2. (b) Takaya, H.; Ohta, T.; Noyori, R. In *Catalytic Asymmetric Synthesis*; Ojima, I., Ed.; VCH: Weinheim, 1993; Chapter 1. (c) Brunner, H.; Zettlmeier, W. *Handbook of Enantioselective Catalysis*; VCH: Weinheim, 1993. (d) Noyori, R.; Takaya, H. *Acc. Chem. Res.* **1990**, *23*, 345. (e) Noyori, R. *Chem. Soc. Rev.* **1989**, *18*, 187. (f) Noyori, R.; Kitamura, M. In *Modern Synthetic Methods*; Scheffold, R., Ed.; Springer-Verlag: Berlin, 1989; Vol. 5, pp 115−198. (g) Kitamura, M. *Kikan Kagaku Sosetsu* **1993**, *19*, 77.

(23) Noyori, R.; Hashiguchi, S. *Acc. Chem. Res.* **1997**, *30*, 97.

(24) Bäckvall, J.-E.; Chowdhury, R. L.; Karlsson, U.; Wang, G.-Z. In *Perspectives in Coordination Chemistry*; Williams, A. F., Floriani, C., Merbach, A. E., Eds.; Verlag Helvetica Chimica Acta: Basel, 1992; pp 463−486.

(25) Murahashi, S.-I. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 2443.

(26) Murahashi, S.-I.; Komiya, N. *Catalysts Catalysis* **1997**, *39*, 16.

(27) Higuchi, T. *J. Synth. Org. Chem. Jpn.* **1995**, *53*, 633.

(28) (a) Murahashi, S.-I.; Naota, T. *Adv. Met.-Org. Chem.* **1994**, *3*, 225. (b) Watanabe, Y.; Mitsudo, T.; Tsuji, Y. *J. Synth. Org. Chem. Jpn.* **1988**, *46*, 789.

(29) (a) Bruneau, C.; Dixneuf, P. H. *J. Chem. Soc., Chem. Commun.* **1997**, 507. (b) Bruneau, C.; Neveux, M.; Kabouche, Z.; Ruppin, C.; Dixneuf, P. H. *Synlett* **1991**, 755.

(30) Murahashi, S.-I.; Naota, T. *Chemtracts Org. Chem.* **1994**, *7*, 281.

(31) Murahashi, S.-I.; Naota, T. *Bull. Chem. Soc. Jpn.* **1996**, *69*, 1805.

(32) (a) Mitsudo, T.; Watanabe, Y. *J. Synth. Org. Chem. Jpn.* **1990**, *48*, 968. (b) Watanabe, Y.; Mitsudo, T.; Kondo, T. *Catalysts Catalysis* **1992**, *34*, 173.
(33) Trost, B. M. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 259.
(34) (a) Grubbs, R. H. In *Comprehensive Organometallic Chemistry*: Wilkinson, G., Stone, F. G. A., Abel, E. W., Eds.; Pergamon: New York, 1982; Vol. 8, p 499. (b) Ivin, K. J. *Olefin Metathesis*; Academic Press: London, 1983. (c) Dragutan, V.; Balaban, A. T.; Dimonie, M. *Olefin Metathesis and Ring Opening Polymerization of Cyclo-Olefins*, 2nd ed.; Wiley-Interscience: New York, 1985. (d) Grubbs, R. H.; Pine, S. H. In *Comprehensive Organic Synthesis*; Trost, B. M., Ed.; Pergamon: New York, 1991; Vol. 5, Chapter 9.3. (e) Schmalz, H.-G. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 1833. (f) Grubbs, R. H.; Miller, S. J.; Fu, G. C. *Acc. Chem. Res.* **1995**, *28*, 446.
(35) Murahashi, S.-I.; Naota, T. *J. Synth. Org. Chem. Jpn.* **1988**, *46*, 930.
(36) (a) Review: Chaloner, P. A.; Esteruelas, M. A.; Joó, F.; Oro, L. A. *Homogeneous Hydrogenation*; Kluwer Academic Publishers: Dordrecht, 1994; Chapter 4, p 119. (b) Halpern, J.; Harrod, J. F.; James, B. R. *J. Am. Chem. Soc.* **1966**, *88*, 5150.
(37) Hallman, P. S.; Evance, D.; Osborn, J. A.; Wilkinson, G. *J. Chem. Soc., Chem. Commun.* **1967**, 305.
(38) (a) Nishimura, S.; Ichino, T.; Akimoto, A.; Tsuneda, K. *Bull. Chem. Soc. Jpn.* **1973**, *46*, 279. (b) Nishimura, S.; Ichino, T.; Akimoto, A.; Tsuneda, K.; Mori, H. *Bull. Chem. Soc. Jpn.* **1975**, *48*, 2852.
(39) (a) Fahey, D. R. *J. Org. Chem.* **1973**, *38*, 80. (b) Fahey, D. R. *J. Org. Chem.* **1973**, *38*, 3343.
(40) Tsuji, J.; Suzuki, H. *Chem. Lett.* **1977**, 1083.
(41) Airoldi, M.; Deganello, G.; Dia, G.; Gennaro, G. *J. Organomet. Chem.* **1980**, 187, 391.
(42) (a) Nagahara, H. *Rev. J. Surf. Sci. Technol. Avant-Garde* **1992**, *30*, 951. (b) Fukuoka, Y.; Nagahara, H. *Prepr. of 202th ACS Meeting, Division of Petr. Chem.* **1991**, *36*, 548. (c) Asahi Chemical Co. Jpn. Kokai Tokkyo Koho 62−45541, 62−45544. (d) Asahi Chemical Co. Jpn. Kokai Tokkyo Koho 62−205037, 63−15233. (e) Asahi Chemical Co. Jpn. Kokai Tokkyo Koho 62−81332, 62−201830, 63−17834, 63−63627.
(43) Nagashima, H.; Suzuki, A.; Nobata, M.; Itoh, K. *J. Am. Chem. Soc.* **1996**, *118*, 687.
(44) (a) $RuCl_2(PPh_3)_3$: Tsuji, J.; Suzuki, H. *Chem. Lett.* **1977**, 1085. $RuHCl(CO)(PPh_3)_3$: (b) Sánchez-Delgado, R. A.; de Ochoa, O. L. *J. Mol. Catal.* **1979**, *6*, 303. (c) Sánchez-Delgado, R. A.; Andriollo, A.; de Ochoa, O. L.; Suárez, T.; Valencia, N. *J. Organomet. Chem.* **1981**, *209*, 77. (d) $RuCl_3$-$P(m\text{-}C_6H_4SO_3Na)_3$: Grosselin, J. M.; Mercier, C.; Allmang, G.; Grass, F. *Organometallics* **1991**, *10*, 2126.
(45) $RuCl_2(PPh_3)_3$: (a) Kruse, W. M. U. S. Patent **1977**, 4,024,193. (b) Osakada, K.; Ikariya, T.; Yoshikawa, S. *J. Organomet. Chem.* **1982**, *231*, 79. (c) $RuCl_2(PPh_3)_4$, $RuH_2(CO)(PPh_3)_3$, $Ru(CF_3CO_2)_2$-$(CO)(PPh_3)_2$: Cole-Hamilton, D. J.; Wilkinson, G. *Nouv. J. Chem.* **1977**, *1*, 141. (d) $RuHCl(PPh_3)_3$: Sánchez-Delgado, R. A.; de Ochoa, O. L. *J. Organomet. Chem.* **1980**, *202*, 427. (e) RuH_2-$(PPh_3)_4$: Cole-Hamilton, D. J.; Wilkinson, G. *Nouv. J. Chem.* **1977**, 144. (f) $H_4Ru_4(CO)_{12}$: Frediani, P.; Matteroli, M.; Bianchi, M.; Piacenti, F.; Menchi, G. *J. Organomet. Chem.* **1978**, *150*, 273. Ru/SiO_2: (g) Sungbom, C.; Tanaka, K. *Bull. Chem. Soc. Jpn.* **1982**, *55*, 2275. (h) Bonnet, M.; Geneste, P.; Rodriguez, M. *J. Org. Chem.* **1980**, *45*, 40. (i) $K^+[(PPh_3)_2Ph_2P(C_6H_4)RuH_2]^-\cdot C_{10}H_8\cdot(C_2H_5)_2O$: Grey, R. A.; Pez, G. P.; Wallo, A. *J. Am. Chem. Soc.* **1981**, *103*, 7536. (j) $H_4Ru_4(CO)_8(PBu_3)_4$: Bianchi, M.; Menchi, G.; Francalanci, F.; Piacenti, F.; Matteoli, U.; Frediani, P.; Botteghi, C. *J. Organomet. Chem.* **1980**, *188*, 109.
(46) $Ru(acac)_3$-$CH_3C(CH_2PPh_2)_3$: Teunissen, H. T.; Elsevier, C. J. *J. Chem. Soc., Chem. Commun.* **1997**, 667.
(47) $RuCl_2(PPh_3)_3$: (a) Lyons, J. E. *J. Chem. Soc., Chem. Commun.* **1975**, 412. (b) Morand, P.; Kayser, M. *J. Chem. Soc., Chem. Commun.* **1976**, 314. (c) $Ru_2Cl_4(dppb)_3$: Ikariya, T.; Osakada, K.; Ishii, Y.; Osawa, S.; Saburi, M.; Yoshikawa, S. *Bull. Chem. Soc. Jpn.* **1984**, *57*, 897. (d) Ru(acac)-$P(C_8H_{17})_3$-*p*-TsOH: Hara, Y.; Wada, K. *Chem. Lett.* **1991**, 553.
(48) Ishii, Y.; Ikariya, T.; Saburi, M.; Yoshikawa, S. *Tetrahedron Lett.* **1986**, *27*, 365.
(49) Knifton, J. F. *J. Org. Chem.* **1975**, *40*, 519.
(50) (a) Knifton, J. F. *J. Org. Chem.* **1976**, *41*, 1200. (b) Knifton, J. F. *Chem. Abstr.*, *81*, P 135689z, US Pat. 3832401.
(51) Onopchenko, A.; Sabourin, E. T.; Selwitz, C. M. *J. Org. Chem.* **1979**, *44*, 1233.
(52) (a) Ikariya, T.; Ishii, Y.; Kawano, H.; Arai, T.; Saburi, M.; Yoshikawa, S.; Akutagawa, S. *J. Chem. Soc., Chem. Commun.* **1985**, 922. (b) Kawano, H.; Ishii, Y.; Ikariya, T.; Saburi, M.; Yoshikawa, S.; Uchida, Y.; Kumobayashi, H. *Tetrahedron Lett.* **1987**, *28*, 1905. (c) Ohta, T.; Takaya, H.; Kitamura, M.; Nagai, K.; Noyori, R. *J. Org. Chem.* **1987**, *52*, 3174. (d) Manimaran, T.; Wu, T.-C.; Klobucar, W. D.; Kolich, C. H.; Stahly, G. P.; Fronczek, F. R.; Watkins, S. E. *Organometallics* **1993**, *12*, 1467. (e) Zhang, X.; Uemura, T.; Matsumura, K.; Sayo, N.; Kumobayashi, H.; Takaya, H. *Synlett* **1994**, 501.
(53) Ohta, T.; Miyake, T.; Takaya, H. *J. Chem. Soc., Chem. Commun.* **1992**, 1725.
(54) Le Gendre, P.; Braun, T.; Bruneau, C.; Dixneuf, P. H. *J. Org. Chem.* **1996**, *61*, 8453.
(55) (a) Noyori, R.; Ohta, M.; Hsiao, Y.; Kitamura, M.; Ohta, T.; Takaya, H. *J. Am. Chem. Soc.* **1986**, *108*, 7117. (b) Tschaen, D. M.; Abramson, L.; Cai, D.; Desmond, R.; Dolling, U.-H.; Frey, L.; Karady, S.; Shi, Y.-J.; Verhoeven, T. R. *J. Org. Chem.* **1995**, *60*, 4324.
(56) (a) Ohta, T.; Takaya, H.; Sayo, N.; Kumobayashi, H.; Akutagawa, S.; Inoue, S.; Kasahara, I.; Noyori, R. *J. Am. Chem. Soc.* **1987**, *109*, 1596. (b) Heiser, B.; Broger, E. A.; Crameri, Y. *Tetrahedron: Asymmetry* **1991**, *2*, 51.
(57) Takaya, H.; Ohta, T.; Noyori, R. *Tetrahedron Lett.* **1990**, *31*, 7189.
(58) Xiao, J.; Nefkens, S. C. A.; Jessop, P. G.; Ikariya, T.; Noyori, R. *Tetrahedron Lett.* **1996**, *37*, 2813.
(59) (a) Kitamura, M.; Ohkuma, T.; Inoue, S.; Sayo, N.; Kumobayashi, H.; Akutagawa, S.; Ohta, T.; Takaya, H.; Noyori, R. *J. Am. Chem. Soc.* **1988**, *110*, 629. (b) Buser, H.-P.; Spindler, F. *Tetrahedron: Asymmetry* **1993**, *4*, 2451. (c) Kawano, H.; Ishii, Y.; Saburi, M.; Uchida, Y. *J. Chem. Soc., Chem. Commun.* **1988**, 87.
(60) Cesarotti, E.; Antognazza, P.; Mauri, A.; Pallavicini, M.; Villa, L. *Helv. Chim. Acta* **1992**, *75*, 2563.
(61) (a) Noyori, R.; Ohkuma, T.; Kitamura, M.; Takaya, H.; Sayo, N.; Kumobayashi, H.; Akutagawa, S. *J. Am. Chem. Soc.* **1987**, *109*, 5856. (b) Kitamura, M.; Ohkuma, T.; Takaya, H.; Noyori, R. *Tetrahedron Lett.* **1988**, *29*, 1555. (c) Kitamura, M.; Tokunaga, M.; Ohkuma, T.; Noyori, R. *Tetrahedron Lett.* **1991**, *32*, 4163. (d) Taber, D. F.; Silverberg, L. J. *Tetrahedron Lett.* **1991**, *32*, 4227. (e) King, S. A.; Thompson, A. S.; King, A. O.; Verhoeven, T. R. *J. Org. Chem.* **1992**, *57*, 6689. (f) Hoke, J. B.; Hollis, L. S.; Stern, E. W. *J. Organomet. Chem.* **1993**, 455, 193. (g) Ohta, T.; Miyake, T.; Seido, N.; Kumobayashi, H.; Takaya, H. *J. Org. Chem.* **1995**, *60*, 357. (h) Genêt, J. P.; Cano de Andrade, M. C.; Ratovelomanana-Vidal, V. *Tetrahedron Lett.* **1995**, *36*, 2063. (i) Genêt, J. P.; Ratovelomanana-Vidal, V.; Cano de Andrade, M. C.; Pfister, X.; Guerreiro, P.; Lenoir, J. Y. *Tetrahedron Lett.* **1995**, *36*, 4801. (j) Tas, D.; Thoelen, C.; Vankelecom, I. F. J.; Jacobs, P. A. *J. Chem. Soc., Chem. Commun.* **1997**, 2323.
(62) (a) Kitamura, M.; Tokunaga, M.; Noyori, R. *J. Am. Chem. Soc.* **1995**, *117*, 2931. (b) Gautier, I.; Ratovelomanana-Vidal, V.; Savignac, P.; Genêt, J.-P. *Tetrahedron Lett.* **1996**, *37*, 7721.
(63) Tranchier, J.-P.; Ratovelomanana-Vidal, V.; Genêt, J.-P.; Tong, S.; Cohen, T. *Tetrahedron Lett.* **1997**, *38*, 2951.
(64) Charette, A. B.; Giroux, A. *Tetrahedron Lett.* **1996**, *37*, 6669.
(65) (a) Noyori, R.; Ikeda, T.; Ohkuma, T.; Widhalm, M.; Kitamura, M.; Takaya, H.; Akutagawa, S.; Sayo, N.; Saito, T.; Taketomi, T.; Kumobayashi, H. *J. Am. Chem. Soc.* **1989**, *111*, 9134. (b) Genêt, J. P.; Pinel, C.; Mallart, S.; Juge, S.; Thorimbert, S.; Laffitte, J. A. *Tetrahedron: Asymmetry* **1991**, *2*, 555.
(66) Nishi, T.; Kitamura, M.; Ohkuma, T.; Noyori, R. *Tetrahedron Lett.* **1988**, *29*, 6327.
(67) Kitamura, M.; Tokunaga, M.; Noyori, R. *J. Am. Chem. Soc.* **1993**, *115*, 144.
(68) Kitamura, M.; Kasahara, I.; Manabe, K.; Noyori, R.; Takaya, H. *J. Org. Chem.* **1988**, *53*, 708.
(69) Balavoine, G.; Moradpour, A.; Kagan, H. B. *J. Am. Chem. Soc.* **1974**, *96*, 5152.
(70) (a) Faller, J. W.; Tokunaga, M. *Tetrahedron Lett.* **1993**, *34*, 7359. (b) Faller, J. W.; Parr, J. *J. Am. Chem. Soc.* **1993**, *115*, 804.
(71) Uemura, T.; Zhang, X.; Matsumura, K.; Sayo, N.; Kumobayashi, H.; Ohta, T.; Nozaki, K.; Takaya, H. *J. Org. Chem.* **1996**, *61*, 5510.
(72) Schmid, R.; Cereghetti, M.; Heiser, B.; Schönholzer, P.; Hansen, H.-J. *Helv. Chim. Acta* **1988**, *71*, 897.
(73) (a) Mezzetti, A.; Consiglio, G. *J. Chem. Soc., Chem. Commun.* **1991**, 1675. (b) Genêt, J. P.; Pinel, C.; Ratovelomanana-Vidal, V.; Mallart, S.; Pfister, X.; Bischoff, L.; Cano de Andrade, M. C.; Darses, S.; Galopin, C.; Laffitte, J. A. *Tetrahedron: Asymmetry* **1994**, *5*, 675.
(74) Enev, V.; Ewers, C. L. J.; Harre, M.; Nickisch, K.; Mohr, J. T. *J. Org. Chem.* **1997**, *62*, 7092.
(75) Burk, M. J.; Harper, T. G. P.; Kalberg, C. S. *J. Am. Chem. Soc.* **1995**, *117*, 4423.
(76) Blanc, D.; Henry, J.-C.; Ratovelomanana-Vidal, V.; Genêt, J. P. *Tetrahedron Lett.* **1997**, *38*, 6603.
(77) (a) Rane, V. H.; Tas, D.; Parton, R. F.; Jacobs, P. A. *Catal. Lett.* **1996**, *41*, 111. (b) Doucet, H.; Le Gendre, P.; Bruneau, C.; Dixneuf, P. H. *Tetrahedron: Asymmetry* **1996**, *7*, 525.
(78) Ohkuma, T.; Ooka, H.; Hashiguchi, S.; Ikariya, T.; Noyori, R. *J. Am. Chem. Soc.* **1995**, *117*, 2675.
(79) Ohkuma, T.; Ooka, H.; Yamakawa, M.; Ikariya, T.; Noyori, R. *J. Org. Chem.* **1996**, *61*, 4872.
(80) Ohkuma, T.; Ooka, H.; Ikariya, T.; Noyori, R. *J. Am. Chem. Soc.* **1995**, *117*, 10417.
(81) (a) Chaloner, P. A.; Esteruelas, M. A.; Joó, F.; Oro, L. A. *Homogeneous Hydrogenation*; Kluwer Academic Publishers: Dordrecht, 1994; Chapter 3, p 87. (b) Zassinovich, G.; Mestroni,

G.; Gladiali, S. *Chem. Rev.* **1992**, *92*, 1051. (c) Brieger, G.; Nestrick, T. J. *Chem. Rev.* **1974**, *74*, 567.
(82) Imai, H.; Nishiguchi, T.; Kobayashi, M.; Fukuzumi, K. *Bull. Chem. Soc. Jpn.* **1975**, *48*, 1585.
(83) (a) Sasson, Y.; Blum, J. *Tetrahedron Lett.* **1971**, 2167. (b) Blum, J.; Sasson, Y.; Iflah, S. *Tetrahedron Lett.* **1972**, 1015. (c) Sasson, Y.; Blum, J. *J. Org. Chem.* **1975**, *40*, 1887. (d) Bar, R.; Sasson, Y. *Tetrahedron Lett.* **1981**, *22*, 1709.
(84) (a) Darensbourg, D. J.; Joo, F.; Kannisto, M.; Katho, A.; Reibenspies, J. M. *Organometallics* **1992**, *11*, 1990. (b) Gordon, E. M.; Gaba, D. C.; Jebber, K. A.; Zacharias, D. M. *Organometallics* **1993**, *12*, 5020.
(85) (a) Imai, H.; Nishiguchi, T.; Fukuzumi, K. *J. Org. Chem.* **1976**, *41*, 665. (b) Watanabe, Y.; Ohta, T.; Tsuji, Y. *Bull. Chem. Soc. Jpn.* **1982**, *55*, 2441. (c) Smith, T. A.; Maitlis, P. M. *J. Organomet. Chem.* **1984**, *269*, C7. (d) Smith, T. A.; Maitlis, P. M. *J. Organomet. Chem.* **1985**, *289*, 385. (e) Chowdhury, R. L.; Bäckvall, J.-E. *J. Chem. Soc., Chem. Commun.* **1991**, 1063.
(86) (a) Basu, A.; Bhaduri, S.; Sharma, K.; Jones, P. G. *J. Chem. Soc., Chem. Commun.* **1987**, 1126. (b) Wang, G.-Z.; Bäckvall, J.-E. *J. Chem. Soc., Chem. Commun.* **1992**, 980. (c) Mizushima, E.; Yamaguchi, M.; Yamagishi, T. *Chem. Lett.* **1997**, 237.
(87) Watanabe, Y.; Ohta, T.; Tsuji, Y.; Hiyoshi, T.; Tsuji, Y. *Bull. Chem. Soc. Jpn.* **1984**, *57*, 2440.
(88) (a) Sasson, Y.; Rempel, G. L. *Tetrahedron Lett.* **1974**, 3221. (b) Sasson, Y. Wiener, H.; Bashir, S. *J. Chem. Soc., Chem. Commun.* **1987**, 1574.
(89) (a) Sasson, Y.; Rempel, G. L. *Tetrahedron Lett.* **1974**, 4133. (b) Smadja, W.; Ville, G.; Georgoulis, C. *J. Chem. Soc., Chem. Commun.* **1980**, 594. (c) Trost, B. M.; Kulawiec, R. *J. Am. Chem. Soc.* **1993**, *115*, 2027. (d) Bäckvall, J.-E.; Andreasson, U. *Tetrahedron Lett.* **1993**, *34*, 5459. (e) McGrath, D. V.; Grubbs, R. H. *Organometallics* **1994**, *13*, 224.
(90) (a) Ma, D.; Lu, X. *J. Chem. Soc., Chem. Commun.* **1989**, 890. (b) Trost, B. M.; Livingston, R. C. *J. Am. Chem. Soc.* **1995**, *117*, 9586.
(91) (a) Bianchi, M.; Matteoli, U.; Menchi, G.; Frediani, P.; Pratesi, S.; Piacenti, F.; Botteghi, G. *J. Organomet. Chem.* **1980**, *198*, 73. (b) Chauvin, R. *J. Mol. Catal.* **1990**, *62*, 147. (c) Genêt, J.-P.; Ratovelomanana-Vidal, V.; Pinel, C. *Synlett* **1993**, 478. (d) Krasik, P.; Alper, H. *Tetrahedron* **1994**, *50*, 4347. (e) Jiang, Q.; Van Plew, D.; Murtuza, S.; Zhang, X. *Tetrahedron Lett.* **1996**, *37*, 797.
(92) Brown, J. M.; Brunner, H.; Leitner, W.; Rose, M. *Tetrahedron: Asymmetry* **1991**, *2*, 331.
(93) (a) Hashiguchi, S.; Fujii, A.; Takehara, J.; Ikariya, T.; Noyori, R. *J. Am. Chem. Soc.* **1995**, *117*, 7562. (b) Fujii, A.; Hashiguchi, S.; Uematsu, N.; Ikariya, T.; Noyori, R. *J. Am. Chem. Soc.* **1996**, *118*, 2521.
(94) Püntener, K.; Schwink, L.; Knochel, P. *Tetrahedron Lett.* **1996**, *37*, 8165.
(95) Touchard, F.; Gamez, P.; Fache, F.; Lemaire, M. *Tetrahedron Lett.* **1997**, *38*, 2275.
(96) Takehara, J.; Hashiguchi, S.; Fujii, A.; Inoue, S.; Ikariya, T.; Noyori, R. *J. Chem. Soc., Chem. Commun.* **1996**, 233.
(97) Palmer, M.; Walsgrove, T.; Wills, M. *J. Org. Chem.* **1997**, *62*, 5226.
(98) Langer, T.; Helmchen, G. *Tetrahedron Lett.* **1996**, *37*, 1381.
(99) Sammakia, T.; Stangeland, E. L. *J. Org. Chem.* **1997**, *62*, 6104.
(100) Jiang, Y.; Jiang, Q.; Zhu, G.; Zhang, X. *Tetrahedron Lett.* **1997**, *38*, 215.
(101) Gao, J.-X.; Ikariya, T.; Noyori, R. *Organometallics* **1996**, *15*, 1087.
(102) Matsumura, K.; Hashiguchi, S.; Ikariya, T.; Noyori, R. *J. Am. Chem. Soc.* **1997**, *119*, 8738.
(103) Ohkuma, T.; Ikehira, H.; Ikariya, T.; Noyori, R. *Synlett* **1997**, 467.
(104) Haack, K.-J.; Hashiguchi, S.; Fujii, A.; Ikariya, T.; Noyori, R. *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 285.
(105) Hashiguchi, S.; Fujii, A.; Haack, K.-J.; Matsumura, K.; Ikariya, T.; Noyori, R. *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 288.
(106) Uematsu, N.; Fujii, A.; Hashiguchi, S.; Ikariya, T.; Noyori, R. *J. Am. Chem. Soc.* **1996**, *118*, 4916.
(107) Murahashi, S.-I.; Watanabe, S.; Shiota, T. *J. Chem. Soc., Chem. Commun.* **1994**, 725.
(108) (a) Murahashi, S.-I.; Ito, K.; Naota, T.; Maeda, Y. *Tetrahedron Lett.* **1981**, *22*, 5327. (b) Murahashi, S.-I.; Naota, T.; Ito, K.; Maeda, Y.; Taki, H. *J. Org. Chem.* **1987**, *52*, 4319.
(109) Blum, Y.; Shvo, Y. *J. Organomet. Chem.* **1985**, *282*, C7.
(110) (a) Blum, Y.; Reshef, D.; Shvo, Y. *Tetrahedron Lett.* **1981**, *22*, 1541. (b) Shvo, Y.; Blum, Y.; Reshef, D.; Menzin, M. *J. Organomet. Chem.* **1982**, *226*, C21.
(111) Tomioka, H.; Takai, K.; Oshima, K.; Nozaki, H. *Tetrahedron Lett.* **1981**, *22*, 1605.
(112) Ishii, Y.; Osakada, K.; Ikariya, T.; Saburi, M.; Yoshikawa, S. *J. Org. Chem.* **1986**, *51*, 2034.
(113) Ishii, Y.; Ikariya, T.; Saburi, M.; Yoshikawa, S. *Tetrahedron Lett.* **1986**, *27*, 365.
(114) Saburi, M.; Ishii, Y.; Kaji, N.; Aoi, T.; Sasaki, I.; Yoshikawa, S.; Uchida, Y. *Chem. Lett.* **1989**, 563.
(115) (a) Ishii, Y.; Osakada, K.; Ikariya, T.; Saburi, M.; Yoshikawa, S. *Chem. Lett.* **1982**, 1179. (b) Nozaki, K.; Yoshida, M.; Takaya, H. *J. Organomet. Chem.* **1994**, *473*, 253.
(116) Regen, S. L.; Whitesides, G. M. *J. Org. Chem.* **1972**, *37*, 1832.
(117) (a) Wang, G.-Z.; Bäckvall, J.-E. *J. Chem. Soc., Chem. Commun.* **1992**, 337. (b) Almeida, M. L. S.; Kocovsky, P.; Bäckvall, J.-E. *J. Org. Chem.* **1996**, *61*, 6587.
(118) (a) Bäckvall, J.-E.; Chowdhury, R. L.; Karlsson, U. *J. Chem. Soc., Chem. Commun.* **1991**, 473. (b) Wang, G.-Z.; Andreasson, U.; Bäckvall, J.-E. *J. Chem. Soc., Chem. Commun.* **1994**, 1037.
(119) Karlsson, U.; Wang, G.-Z.; Bäckvall, J.-E. *J. Org. Chem.* **1994**, *59*, 1196.
(120) Murahashi, S.-I.; Kondo, K.; Hakata, T. *Tetrahedron Lett.* **1982**, *23*, 229.
(121) (a) Watanabe, Y.; Tsuji, Y.; Ohsugi, Y. *Tetrahedron Lett.* **1981**, *22*, 2667. (b) Watanabe, Y.; Tsuji, Y.; Ige, H.; Ohsugi, Y.; Ohta, T. *J. Org. Chem.* **1984**, *49*, 3359. (c) Arcelli, A.; Khai, B.-T.; Porzi, G. *J. Organomet. Chem.* **1982**, *235*, 93.
(122) Watanabe, Y.; Mitsudo, T.; Tsuji, Y. *Synth. Org. Chem. Jpn.* **1988**, *46*, 789.
(123) (a) Huh, K.-T.; Tsuji, Y.; Kobayashi, M.; Okuda, F.; Watanabe, Y. *Chem. Lett.* **1988**, 449. (b) Tanaka, N.; Hatanaka, M.; Watanabe, Y. *Chem. Lett.* **1992**, 575. (c) Marsella, J. A. *J. Org. Chem.* **1987**, *52*, 467.
(124) Watanabe, Y.; Morisaki, Y.; Kondo, T.; Mitsudo, T. *J. Org. Chem.* **1996**, *61*, 4214.
(125) (a) Tsuji, Y.; Huh, K.-T.; Ohsugi, Y.; Watanabe, Y. *J. Org. Chem.* **1985**, *50*, 1365. (b) Tsuji, Y.; Yokoyama, Y.; Huh, K.-T.; Watanabe, Y. *Bull. Chem. Soc. Jpn.* **1987**, *60*, 3456.
(126) Kondo, T.; Yang, S.; Huh, K.-T.; Kobayashi, M.; Kotachi, S.; Watanabe, Y. *Chem. Lett.* **1991**, 1275.
(127) Kondo, T.; Kotachi, S.; Ogino, S.; Watanabe, Y. *Chem. Lett.* **1993**, 1317.
(128) Tsuji, Y.; Kotachi, S.; Huh, K.-T.; Watanabe, Y. *J. Org. Chem.* **1990**, *55*, 580.
(129) Watanabe, Y.; Tsuji, Y.; Ohsugi, Y.; Shida, J. *Bull. Chem. Soc. Jpn.* **1983**, *56*, 2452.
(130) Tsuji, Y.; Huh, K.-T.; Watanabe, Y. *Tetrahedron Lett.* **1986**, *27*, 377.
(131) Tsuji, Y.; Huh, K.-T.; Watanabe, Y. *J. Org. Chem.* **1987**, *52*, 1673.
(132) Naota, T.; Murahashi, S.-I. *Synlett* **1991**, 693.
(133) Watanabe, Y.; Ohta, T.; Tsuji, Y. *Bull. Chem. Soc. Jpn.* **1983**, *56*, 2647.
(134) Kondo, T.; Kotachi, S.; Watanabe, Y. *J. Chem. Soc., Chem. Commun.* **1992**, 1318.
(135) Grigg, R.; Mitchell, T. R. B.; Sutthivaiyakit, S. *Tetrahedron Lett.* **1981**, *22*, 4107.
(136) (a) Cook, J.; Hamlin, J. E.; Nutton, A.; Maitlis, P. M. *J. Chem. Soc., Chem. Commun.* **1980**, 144. (b) Cook, J.; Hamlin, J. E.; Nutton, A.; Maitlis, P. M. *J. Chem. Soc., Dalton Trans.* **1981**, 2342.
(137) Kondo, T.; Kotachi, S.; Tsuji, Y.; Watanabe, Y.; Mitsudo, T. *Organometallics* **1997**, *16*, 2562.
(138) Jung, C. W.; Garrou, P. E. *Organometallics* **1982**, *1*, 658.
(139) Shinoda, S.; Itagaki, H.; Saito, Y. *J. Chem. Soc., Chem. Commun.* **1985**, 860.
(140) Morton, D.; Cole-Hamilton, D. J. *J. Chem. Soc., Chem. Commun.* **1988**, 1154.
(141) (a) Carlsen, P. H. J.; Katsuki, T.; Martin, V. S.; Sharpless, K. B. *J. Org. Chem.* **1981**, *46*, 3936. (b) Morris, P. E., Jr.; Kiely, D. E. *J. Org. Chem.* **1987**, *52*, 1149. (c) Yamamoto, Y.; Suzuki, H.; Moro-oka, Y. *Tetrahedron Lett.* **1985**, *26*, 2107. (d) Kanemoto, S.; Tomioka, H.; Oshima, K.; Nozaki, H. *Bull. Chem. Soc. Jpn.* **1986**, *59*, 105. (e) Giddings, S.; Mills, A. *J. Org. Chem.* **1988**, *53*, 1103. (f) Torii, S.; Inokuchi, T.; Sugiura, T. *J. Org. Chem.* **1986**, *51*, 155.
(142) (a) Lee, D. G.; Chen, T. *Comprehensive Organic Synthesis*; Trost, B. M., Fleming, I., Ed.; Pergamon Press: Oxford, 1991; Vol. 7, Chapter 3.8, pp 541−591. (b) Torii, S.; Inokuchi, T.; Kondo, K. *J. Org. Chem.* **1985**, *50*, 4980. (c) Webster, F. X.; Rivas-Enterrios, J.; Silverstein, R. M. *J. Org. Chem.* **1987**, *52*, 689. (d) Albarella, L.; Giordano, F.; Lasalvia, M.; Piccialli, V.; Sica, D. *Tetrahedron Lett.* **1995**, *36*, 5267. (e) Denisenko, M. V.; Pokhilo, N. D.; Odinokova, L. E.; Denisenko, V. A.; Uvarova, N. I. *Tetrahedron Lett.* **1996**, *37*, 5187. (f) Shing, T. K. M.; Tai, V. W.-F.; Tam, E. K. W. *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 2312. (g) Orita, H.; Hayakawa, T.; Takehira, K. *Bull. Chem. Soc. Jpn.* **1986**, *59*, 2637. (h) Wolfe, S.; Hasan, S. K.; Campbell, J. R. *J. Chem. Soc., Chem. Commun.* **1970**, 1420.
(143) (a) Caputo, J. A.; Fuchs, R. *Tetrahedron Lett.* **1967**, 4729. (b) Piatak, D. M.; Herbst, G.; Wicha, J.; Caspi, E. *J. Org. Chem.* **1969**, *34*, 116. (c) Chakraborti, A. K.; Ghatak, U. R. *Synthesis* **1983**, 746. (d) Kasai, M.; Ziffer, H. *J. Org. Chem.* **1983**, *48*, 2346. (e) Spitzer, U. A.; Lee, D. G. *J. Org. Chem.* **1974**, *39*, 2468. (f) Nuñez, M. T.; Martîn, V. S. *J. Org. Chem.* **1990**, *55*, 1928.
(144) (a) Torii, S.; Inokuchi, T.; Hirata, Y. *Synthesis* **1987**, 377. (b) Zibuck, R.; Seebach, D. *Helv. Chim. Acta* **1988**, *71*, 237.
(145) Laux, M.; Krause, N. *Synlett* **1997**, 765.

(146) Schuda, P. F.; Cichowicz, M. B.; Heimann, M. R. *Tetrahedron Lett.* **1983**, *24*, 3829.
(147) (a) Perrone, R.; Bettoni, G.; Tortorella, V. *Synthesis* **1976**, 598. (b) Bettoni, G.; Carbonara, G.; Franchini, C.; Tortorella, V. *Tetrahedron* **1981**, *37*, 4159.
(148) (a) Sheehan, J. C.; Tulis, R. W. *J. Org. Chem.* **1974**, *39*, 2264. (b) Yoshifuji, S.; Tanaka, K.; Nitta, Y. *Chem. Pharm. Bull.* **1985**, *33*, 1749. (c) Yoshifuji, S.; Tanaka, K.; Kawai, T.; Nitta, Y. *Chem. Pharm. Bull.* **1985**, *33*, 5515. (d) Yoshifuji, S.; Tanaka, K.; Kawai, T.; Nitta, Y. *Chem. Pharm. Bull.* **1986**, *34*, 3873. (e) Tanaka, K.; Yoshifuji, S.; Nitta, Y. *Chem. Pharm. Bull.* **1986**, *34*, 3879. (f) Tanaka, K.; Yoshifuji, S.; Nitta, Y. *Chem. Pharm. Bull.* **1987**, *35*, 364.
(149) Ranganathan, D.; Vaish, N. K.; Shah, K. *J. Am. Chem. Soc.* **1994**, *116*, 6545.
(150) (a) Tenaglia, A.; Terranova, E.; Waegell, B. *Tetrahedron Lett.* **1989**, *30*, 5271. (b) Tenaglia, A.; Terranova, E.; Waegell, B. *J. Org. Chem.* **1992**, *57*, 5523.
(151) Bakke, J. M.; Lundquist, M. *Acta Chem. Scand. B* **1986**, *40*, 430.
(152) Coudret, J. L.; Waegell, B. *Inorg. Chim. Acta* **1994**, *222*, 115.
(153) Tenaglia, A.; Terranova, E.; Waegell, B. *J. Chem. Soc., Chem. Commun.* **1990**, 1344.
(154) Spitzer, U. A.; Lee, D. G. *J. Org. Chem.* **1975**, *40*, 2539.
(155) (a) Hasegawa, T.; Niwa, H.; Yamada, K. *Chem. Lett.* **1985**, 1385. (b) Coudret, J. L.; Zöllner, S.; Ravoo, B. J.; Malara, L.; Hanisch, C.; Dörre, K.; de Meijere, A.; Waegell, B. *Tetrahedron Lett.* **1996**, *37*, 2425.
(156) Sasson, Y.; Zappi, G. D.; Neumann, R. *J. Org. Chem.* **1986**, *51*, 2880.
(157) (a) Balavoine, G.; Eskénazi, C.; Meunier, F.; Rivière, H. *Tetrahedron Lett.* **1984**, *25*, 3187. (b) Eskénazi, C.; Balavoine, G.; Meunier, F.; Rivière, H. *J. Chem. Soc., Chem. Commun.* **1985**, 1111.
(158) Bailey, A. J.; Griffith, W. P.; White, A. J. P.; Williams, D. J. *J. Chem. Soc., Chem. Commun.* **1994**, 1833.
(159) Gao, Y.; Sharpless, K. B. *J. Am. Chem. Soc.* **1988**, *110*, 7538.
(160) Murahashi, S.-I.; Naota, T. In *Comprehensive Organometallic Chemistry II*; Abel, E. W., Stone, F. G. A., Wilkinson, G., Ed.; Pergamon Press: Oxford, 1995; Vol. 12, pp 1177−1192.
(161) (a) Murahashi, S.-I.; Naota, T.; Nakajima, N. *Tetrahedron Lett.* **1985**, *26*, 925. (b) Murahashi, S.-I.; Naota, T. *Synthesis*, **1993**, 433. (c) Tanaka, M.; Kobayashi, T.; Sakakura, T. *Angew. Chem., Int. Ed. Engl.* **1984**, *23*, 518.
(162) Murahashi, S.-I.; Naota, T.; Oda, Y.; Hirai, N. *Synlett* **1995**, 733.
(163) Barak, G.; Dakka, J.; Sasson, Y. *J. Org. Chem.* **1988**, *53*, 3553.
(164) Kanemoto, S.; Oshima, K.; Matsubara, S.; Takai, K.; Nozaki, H. *Tetrahedron Lett.* **1983**, *24*, 2185.
(165) Müller, P.; Godoy, J. *Tetrahedron Lett.* **1981**, *22*, 2361.
(166) Sharpless, K. B.; Akashi, K.; Oshima, K. *Tetrahedron Lett.* **1976**, *29*, 2503.
(167) Higuchi, T.; Ohtake, H.; Hirobe, M. *Tetrahedron Lett.* **1991**, *32*, 7435.
(168) Inokuchi, T.; Nakagawa, K.; Torii, S. *Tetrahedron Lett.* **1995**, *36*, 3223.
(169) Thompson, M. S.; Meyer, T. J. *J. Am. Chem. Soc.* **1982**, *104*, 4106.
(170) Roecker, L.; Meyer, T. J. *J. Am. Chem. Soc.* **1987**, *109*, 746.
(171) (a) Cheng, S. Y. C.; Rajapakse, N.; Rettig, S. J.; James, B. R. *J. Chem. Soc., Chem. Commun.* **1994**, 2669. (b) Cheng, W.-C.; Yu, W.-Y.; Li, C.-K.; Che, C.-M. *J. Org. Chem.* **1995**, *60*, 6840. (c) Au, S.-M.; Fung, W.-H.; Cheng, M.-C.; Che, C.-M.; Peng, S.-M. *J. Chem. Soc., Chem. Commun.* **1997**, 1655.
(172) Ley, S. V.; Anthony, N. J.; Armstrong, A.; Brasca, M. G.; Clarke, T.; Culshaw, D.; Greck, C.; Grice, P.; Jones, A. B.; Lygo, B.; Madin, A.; Sheppard, R. N.; Slawin, A. M. Z.; Williams, D. J. *Tetrahedron* **1989**, *45*, 7161.
(173) Kerdesky, F. A. J.; Schmidt, S. P.; Brooks, D. W. *J. Org. Chem.* **1993**, *58*, 3516.
(174) Piers, E.; Roberge, J. Y. *Tetrahedron Lett.* **1991**, *32*, 5219.
(175) Mehta, G.; Karra, S. R. *Tetrahedron Lett.* **1991**, *32*, 3215.
(176) (a) Matsumoto, M.; Ito, S. *J. Chem. Soc., Chem. Commun.* **1981**, 907. (b) Matsumoto, M.; Watanabe, N. *J. Org. Chem.* **1984**, *49*, 3435.
(177) Matsumoto, M.; Ito, S. *Synth. Commun.* **1984**, *14*, 697.
(178) Tang, R.; Diamond, S. E.; Neary, N.; Mares, F. *J. Chem. Soc., Chem. Commun.* **1978**, 562.
(179) Bilgrien, C.; Davis, S.; Drago, R. S. *J. Am. Chem. Soc.* **1987**, *109*, 3786.
(180) Markó, I. E.; Giles, P. R.; Tsukazaki, M.; Chellé-Regnaut, I.; Urch, C. J.; Brown, S. M. *J. Am. Chem. Soc.* **1997**, *119*, 12661.
(181) Felthouse, T. R. *J. Am. Chem. Soc.* **1987**, *109*, 7566.
(182) (a) Bawn, C. E. H.; Williamson, J. B. *Trans. Faraday Soc.* **1951**, *47*, 721, 735. (b) Bawn, C. E. H.; Jolley, J. E. *Proc. R. Soc. London, Ser. A* **1956**, *237*, 297.
(183) Murahashi, S.-I.; Naota, T.; Hirai, N. *J. Org. Chem.* **1993**, *58*, 7318.
(184) (a) Minami, I.; Yamada, M.; Tsuji, J. *Tetrahedron Lett.* **1986**, *27*, 1805. (b) Minami, I.; Tsuji, J. *Tetrahedron* **1987**, *43*, 3903.
(185) Moyer, B. A.; Thompson, M. S.; Meyer, T. J. *J. Am. Chem. Soc.* **1980**, *102*, 2310.
(186) Cosgrove, S. L.; Waters, W. A. *J. Chem. Soc.* **1951**, 1726.
(187) Horswill, E. C.; Ingold, K. U. *Can. J. Chem.* **1966**, *44*, 269.
(188) Murahashi, S.-I.; Naota, T.; Miyaguchi, N.; Noda, S. *J. Am. Chem. Soc.* **1996**, *118*, 2509.
(189) Tsuji, Y.; Ohta, T.; Ido, T.; Minbu, H.; Watanabe, Y. *J. Organomet. Chem.* **1984**, *270*, 333.
(190) Ito, S.; Aihara, K.; Matsumoto, M. *Tetrahedron Lett.* **1983**, *24*, 5249.
(191) (a) Taylor, W. I.; Battersby, A. R. *Oxidative Coupling of Phenols*; Marcel Dekker: New York, 1967. (b) Kovacic, P.; Jones, M. B. *Chem. Rev.* **1987**, *87*, 357.
(192) Robin, J.-P.; Landais, Y. *J. Org. Chem.* **1988**, *53*, 224.
(193) (a) Landais, Y.; Robin, J.-P. *Tetrahedron Lett.* **1986**, *27*, 1785. (b) Landais, Y.; Lebrun, A.; Robin, J.-P. *Tetrahedron Lett.* **1986**, *27*, 5377.
(194) Landais, Y.; Rambault, D.; Robin, J.-P. *Tetrahedron Lett.* **1987**, *28*, 543.
(195) Matsumoto, M.; Kuroda, K. *J. Am. Chem. Soc.* **1982**, *104*, 1433.
(196) Murahashi, S.-I.; Imada, Y. *Transition Metals for Fine Chemicals in Organic Synthesis*; Bolm, C., Beller, M., Eds.; VCH: Weinheim, in press.
(197) Murahashi, S.-I.; Naota, T.; Yonemura, K. *J. Am. Chem. Soc.* **1988**, *110*, 8256.
(198) Murahashi, S.-I.; Naota, T.; Miyaguchi, N.; Nakato, T. *Tetrahedron Lett.* **1992**, *33*, 6991.
(199) Murahashi, S.-I.; Naota, T.; Nakato, T. *Synlett* **1992**, 835.
(200) Murahashi, S.-I.; Naota, T.; Taki, H. *J. Chem. Soc., Chem. Commun.* **1985**, 613.
(201) Goti, A.; Romani, M. *Tetrahedron Lett.* **1994**, *35*, 6567.
(202) Goti, A.; De Sarlo, F.; Romani, M. *Tetrahedron Lett.* **1994**, *35*, 6571.
(203) Murahashi, S.-I.; Naota, T.; Kuwabara, T.; Saito, T.; Kumobayashi, H.; Akutagawa, S. *J. Am. Chem. Soc.* **1990**, *112*, 7820.
(204) Naota, T.; Nakato, T.; Murahashi, S.-I. *Tetrahedron Lett.* **1990**, *31*, 7475.
(205) Cainelli, G.; DaCol, M.; Galletti, P.; Giacomini, D. *Synlett* **1997**, 923.
(206) Murahashi, S.-I.; Saito, T.; Naota, T.; Kumobayashi, H.; Akutagawa, S. *Tetrahedron Lett.* **1991**, *32*, 5991.
(207) Bailey, A. J.; James, B. R. *J. Chem. Soc., Chem. Commun.* **1996**, 2343.
(208) Meunier, B. In *Metalloporphyrins Catalyzed Oxidations*; Montanari, F., Casella, L., Eds.; Kluwer Academic: Dordrecht, 1994; p 1.
(209) (a) Leung, T. W.; James, B. R.; Dolphin, D. *Inorg. Chim. Acta* **1983**, *79*, 25. (b) Leung, T.; James, B. R.; Dolphin, D. *Inorg. Chim. Acta* **1983**, *79*, 180.
(210) (a) Higuchi, T.; Ohtake, H.; Hirobe, M. *Tetrahedron Lett.* **1989**, *30*, 6545. (b) Ohtake, H.; Higuchi, T.; Hirobe, M. *Tetrahedron Lett.* **1992**, *33*, 2521.
(211) Groves, J. T.; Bonchio, M.; Carofiglio, T.; Shalyaev, K. *J. Am. Chem. Soc.* **1996**, *118*, 8961.
(212) Liu, C.-J.; Li, S.-G.; Pang, W.-Q.; Che, C.-M. *J. Chem. Soc., Chem. Commun.* **1997**, 65.
(213) Fung, W.-H.; Cheng, W.-C.; Yu, W.-Y.; Che, C.-M.; Mak, T. C. W. *J. Chem. Soc., Chem. Commun.* **1995**, 2007.
(214) Gross, Z.; Ini, S.; Kapon, M.; Cohen, S. *Tetrahedron Lett.* **1996**, *37*, 7325.
(215) Cheng, W.-C.; Yu, W.-Y.; Cheung, K.-K.; Che, C.-M. *J. Chem. Soc., Chem. Commun.* **1994**, 1063.
(216) Bressan, M.; Morvillo, A. *J. Chem. Soc., Chem. Commun.* **1988**, 650.
(217) Nishiyama, H.; Shimada, T.; Itoh, H.; Sugiyama, H.; Motoyama, Y. *J. Chem. Soc., Chem. Commun.* **1997**, 1863.
(218) Ni: (a) Mukaiyama, T.; Yamada, T. *Bull. Chem. Soc. Jpn.* **1995**, *68*, 17. (b) Yamada, T.; Takai, T.; Rhode, O.; Mukaiyama, T. *Chem. Lett.* **1991**, 1. (c) Yamada, T.; Takai, T.; Rhode, O.; Mukaiyama, T. *Bull. Chem. Soc. Jpn.* **1991**, *64*, 2109. (d) Bouhlel, E.; Laszlo, P.; Levart, M.; Montaufier, M.-T.; Singh, G. P. *Tetrahedron Lett.* **1993**, *34*, 1123. (e) Laszlo, P.; Levart, M. *Tetrahedron Lett.* **1993**, *34*, 1127. (f) Irie, R.; Ito, Y.; Katsuki, T. *Tetrahedron Lett.* **1991**, *32*, 6891. Fe: (g) Takai, T.; Hata, E.; Yamada, T.; Mukaiyama, T. *Bull. Chem. Soc. Jpn.* **1991**, *64*, 2513. Mn: (h) Haber, J.; Mlodnicka, T. *J. Mol. Catal.* **1989**, *54*, 451. Co: (i) Bhatia, B.; Punniyamurthy, T.; Iqbal, J. *J. Org. Chem.* **1993**, *58*, 5518. (j) Punniyamurthy, T.; Bhatia, B.; Iqbal, J. *J. Org. Chem.* **1994**, *59*, 850. Heteropolyoxometalate: (k) Hamamoto, M.; Nakayama, K.; Nishiyama, Y.; Ishii, Y. *J. Org. Chem.* **1993**, *58*, 6421.
(219) Cu: (a) Murahashi, S.-I.; Oda, Y.; Naota, T.; Komiya, N. *J. Chem. Soc., Chem. Commun.* **1993**, 139. (b) Komiya, N.; Naota, T.; Oda, Y.; Murahashi, S.-I. *J. Mol. Catal.* **1997**, *117*, 21.
(220) Klement, I.; Lütjens, H.; Knochel, P. *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 1454.
(221) Groves, J. T.; Quinn, R. *J. Am. Chem. Soc.* **1985**, *107*, 5790.
(222) Leung, W.-H.; Che, C.-M.; Yeung, C.-H.; Poon, C.-K. *Polyhedron* **1993**, *12*, 2331.

(223) Neumann, R.; Dahan, M. *Nature* **1997**, *388*, 353.
(224) Goldstein, A. S.; Beer, R. H.; Drago, R. S. *J. Am. Chem. Soc.* **1994**, *116*, 2424.
(225) Bailey, C. L.; Drago, R. S. *J. Chem. Soc., Chem. Commun.* **1987**, 179.
(226) Murahashi, S.-I.; Saito, T.; Hanaoka, H.; Murakami, Y.; Naota, T.; Kumobayashi, H.; Akutagawa, S. *J. Org. Chem.* **1993**, *58*, 2929.
(227) Higuchi, T.; Satake, C.; Hirobe, M. *J. Am. Chem. Soc.* **1995**, *117*, 8879.
(228) Ohtake, H.; Higuchi, T.; Hirobe, M. *J. Am. Chem. Soc.* **1992**, *114*, 10660.
(229) Shingaki, T.; Miura, K.; Higuchi, T.; Hirobe, M.; Nagano, T. *J. Chem. Soc., Chem. Commun.* **1997**, 861.
(230) (a) Hill, C. L. *Activation and Functionalization of Alkanes*; Wiley: New York, 1989. (b) Haines, A. H. *Methods for the Oxidation of Organic Compounds, Alkanes, Alkenes Alkynes and Arenes*; Academic Press: London, 1985, Chapter 2.
(231) Barton, D. H. R.; Doller, D. *Acc. Chem. Res.* **1992**, *25*, 504.
(232) Lau, T.-C.; Mak, C.-K. *J. Chem. Soc., Chem. Commun.* **1995**, 943.
(233) Goldstein, A. S.; Drago, R. S. *J. Chem. Soc., Chem. Commun.* **1991**, 21.
(234) Murahashi, S.-I.; Oda, Y.; Naota, T.; Kuwabara, T. *Tetrahedron Lett.* **1993**, *34*, 1299.
(235) Lau, T.-C.; Che, C.-M.; Lee, W.-O.; Poon, C.-K. *J. Chem. Soc., Chem. Commun.* **1988**, 1406.
(236) Murahashi, S.-I.; Oda, Y.; Komiya, N.; Naota, T. *Tetrahedron Lett.* **1994**, *35*, 7953.
(237) Neumann, R.; Abu-Gnim, C. *J. Chem. Soc., Chem. Commun.* **1989**, 1324.
(238) (a) Thompson, M. S.; Meyer, T. J. *J. Am. Chem. Soc.* **1982**, *104*, 5070. (b) Che, C.-M.; Tang, W.-T.; Wong, W.-T.; Lai, T. F. *J. Am. Chem. Soc.* **1989**, *111*, 9048. (c) Lau, T.-C.; Mak, C.-K. *J. Chem. Soc., Chem. Commun.* **1993**, 766.
(239) Murahashi, S.-I.; Oda, Y.; Naota, T. *J. Am. Chem. Soc.* **1992**, *114*, 7913.
(240) Murahashi, S.-I.; Naota, T.; Komiya, N. *Tetrahedron Lett.* **1995**, *36*, 8059.
(241) Davis, S.; Drago, R. S. *J. Chem. Soc., Chem. Commun.* **1990**, 250.
(242) Neumann, R.; Khenkin, A. M.; Dahan, M. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 1587.
(243) (a) Reuter, J. M.; Salomon, R. G. *J. Org. Chem.* **1977**, *42*, 3360. (b) Mitchell, T. N.; Giesselmann, F. *Synlett* **1996**, 475.
(244) Zoran, A.; Sasson, Y.; Blum, J. *J. Org. Chem.* **1981**, *46*, 255.
(245) Stille, J. K.; Becker, Y. *J. Org. Chem.* **1980**, *45*, 2139.
(246) Suzuki, H.; Koyama, Y.; Moro-oka, Y.; Ikawa, T. *Tetrahedron Lett.* **1979**, 1415.
(247) (a) Suzuki, H.; Yashima, H.; Hirose, T.; Takahashi, M.; Moro-oka, Y.; Ikawa, T. *Tetrahedron Lett.* **1980**, *21*, 4927. (b) Takahashi, M.; Suzuki, H.; Moro-oka, Y.; Ikawa, T. *Chem. Lett.* **1981**, 1435. (c) Pertici, P.; Malanga, C.; Giuntoli, A.; Vitulli, G.; Martra, G. *Gazz. Chim. Ital.* **1996**, *126*, 587.
(248) Hirai, K.; Suzuki, H.; Kashiwagi, H.; Moro-oka, Y.; Ikawa, T. *Chem. Lett.* **1982**, 23.
(249) (a) Brunner, H.; Kürzinger, A. *J. Organomet. Chem.* **1988**, *346*, 413. (b) Frauenrath, H.; Philipps, T. *Angew. Chem., Int. Ed. Engl.* **1986**, *25*, 274. (c) Frauenrath, H.; Kaulard, M. *Synlett* **1994**, 517.
(250) Hirai, K.; Suzuki, H.; Moro-oka, Y.; Ikawa, T. *Tetrahedron Lett.* **1980**, *21*, 3413.
(251) Ma, D.; Yu, Y.; Lu, X. *J. Org. Chem.* **1989**, *54*, 1105.
(252) Ma, D.; Lu, X. *Tetrahedron Lett.* **1989**, *30*, 843.
(253) Li, C.-J.; Wang, D.; Chen, D.-L. *J. Am. Chem. Soc.* **1995**, *117*, 12867.
(254) Mitsudo, T.; Zhang, S.-W.; Satake, N.; Kondo, T.; Watanabe, Y. *Tetrahedron Lett.* **1992**, *33*, 5533.
(255) Garcia-Granados, A.; Martinez, A.; Onorato, M. E. *J. Org. Chem.* **1987**, *52*, 606.
(256) Ruppin, C.; Dixneuf, P. H. *Tetrahedron Lett.* **1986**, *27*, 6323.
(257) Mitsudo, T.; Hori, Y.; Watanabe, Y. *J. Org. Chem.* **1985**, *50*, 1566.
(258) (a) Mitsudo, T.; Hori, Y.; Yamakawa, Y.; Watanabe, Y. *Tetrahedron Lett.* **1986**, *27*, 2125. (b) Mitsudo, T.; Hori, Y.; Yamakawa, Y.; Watanabe, Y. *J. Org. Chem.* **1987**, *52*, 2230.
(259) Hori, Y.; Mitsudo, T.; Watanabe, Y. *Tetrahedron Lett.* **1986**, *27*, 5389.
(260) Kita, Y.; Maeda, H.; Omori, K.; Okuno, T.; Tamura, Y. *Synlett* **1993**, 273.
(261) Ruppin, C.; Dixneuf, P. H.; Lécolier, S. *Tetrahedron Lett.* **1988**, *29*, 5365.
(262) Kabouche, Z.; Bruneau, C.; Dixneuf, P. H. *Tetrahedron Lett.* **1991**, *32*, 5359.
(263) Philippot, K.; Devanne, D.; Dixneuf, P. H. *J. Chem. Soc., Chem. Commun.* **1990**, 1199.
(264) Neveux, M.; Bruneau, C.; Dixneuf, P. H. *J. Chem. Soc., Perkin Trans. 1* **1991**, 1197.
(265) Rotem, M.; Shvo, Y. *Organometallics* **1983**, *2*, 1689.
(266) Menashe, N.; Shvo, Y. *J. Org. Chem.* **1993**, *58*, 7434.
(267) (a) Devanne, D.; Ruppin, C.; Dixneuf, P. H. *J. Org. Chem.* **1988**, *53*, 925. (b) Darcel, C.; Bruneau, C.; Dixneuf, P. H.; Neef, G. *J. Chem. Soc., Chem. Commun.* **1994**, 333.
(268) (a) Doucet, H.; Höfer, J.; Bruneau, C.; Dixneuf, P. H. *J. Chem. Soc., Chem. Commun.* **1993**, 850. (b) Doucet, H.; Martin-Vaca, B.; Bruneau, C.; Dixneuf, P. H. *J. Org. Chem.* **1995**, *60*, 7247.
(269) Picquet, M.; Bruneau, C.; Dixneuf, P. H. *J. Chem. Soc., Chem. Commun.* **1997**, 1201.
(270) Kondo, T.; Tanaka, A.; Kotachi, S.; Watanabe, Y. *J. Chem. Soc., Chem. Commun.* **1995**, 413.
(271) (a) Mahé, R.; Dixneuf, P. H. *Tetrahedron Lett.* **1986**, *27*, 6333. (b) Sasaki, Y.; Dixneuf, P. H. *J. Org. Chem.* **1987**, *52*, 314. (c) Mahé, R.; Sasaki, Y.; Bruneau, C.; Dixneuf, P. H. *J. Org. Chem.* **1989**, *54*, 1518.
(272) Höfer, J.; Doucet, H.; Bruneau, C.; Dixneuf, P. H. *Tetrahedron Lett.* **1991**, *32*, 7409.
(273) Sasaki, Y.; Dixneuf, P. H. *J. Chem. Soc., Chem. Commun.* **1986**, 790.
(274) Mitsudo, T.; Hori, Y.; Yamakawa, Y.; Watanabe, Y. *Tetrahedron Lett.* **1987**, *28*, 4417.
(275) (a) Sasaki, Y.; Dixneuf, P. H. *J. Org. Chem.* **1987**, *52*, 4389. (b) Bruneau, C.; Dixneuf, P. H. *Tetrahedron Lett.* **1987**, *28*, 2005.
(276) Fournier, J.; Bruneau, C.; Dixneuf, P. H.; Lécolier, S. *J. Org. Chem.* **1991**, *56*, 4456.
(277) (a) Bullock, R. M. *J. Chem. Soc., Chem. Commun.* **1989**, 165. (b) Haquette, P.; Pirio, N.; Touchard, D.; Toupet, L.; Dixneuf, P. H. *J. Chem. Soc., Chem. Commun.* **1993**, 163. (c) de los Ríos, I.; Tenorio, M. J.; Puerta, M. C.; Valerga, P. *J. Am. Chem. Soc.* **1997**, *119*, 6529.
(278) Seiller, B.; Bruneau, C.; Dixneuf, P. H. *J. Chem. Soc., Chem. Commun.* **1994**, 493.
(279) Trost, B. M.; Portnoy, M.; Kurihara, H. *J. Am. Chem. Soc.* **1997**, *119*, 836.
(280) Trost, B. M.; Krause, L.; Portnoy, M. *J. Am. Chem. Soc.* **1997**, *119*, 11319.
(281) (a) Watanabe, H.; Asami, M.; Nagai, Y. *J. Organomet. Chem.* **1980**, *195*, 363. (b) Esteruelas, M. A.; Herrero, J.; Oro, L. A. *Organometallics* **1993**, *12*, 2377.
(282) Seki, Y.; Takeshita, K.; Kawamoto, K.; Murai, S.; Sonoda, N. *J. Org. Chem.* **1986**, *51*, 3890.
(283) (a) Murahashi, S.-I.; Sasao, S.; Saito, E.; Naota, T. *J. Org. Chem.* **1992**, *57*, 2521. (b) Murahashi, S.-I.; Sasao, S.; Saito, E.; Naota, T. *Tetrahedron* **1993**, *49*, 8805.
(284) Naota, T.; Shichijo, Y.; Murahashi, S.-I. *J. Chem. Soc., Chem. Commun.* **1994**, 1359.
(285) Murahashi, S.-I.; Naota, T.; Saito, E. *J. Am. Chem. Soc.* **1986**, *108*, 7846.
(286) Watanabe, K.; Yamada, Y.; Goto, K. *Bull. Chem. Soc. Jpn.* **1985**, *58*, 1401.
(287) Odenkirk, W.; Rheingold, A. L.; Bosnich, B. *J. Am. Chem. Soc.* **1992**, *114*, 6392.
(288) Ma, S.; Venanzi, L. M. *Tetrahedron Lett.* **1993**, *34*, 5269.
(289) Ma, S.; Venanzi, L. M. *Synlett* **1993**, 751.
(290) Faller, J. W.; Smart, C. J. *Tetrahedron Lett.* **1989**, *30*, 1189.
(291) Davies, D. L.; Fawcett, J.; Garratt, S. A.; Russell, D. R. *J. Chem. Soc., Chem. Commun.* **1997**, 1351.
(292) Carmona, D.; Cativiela, C.; Elipe, S.; Lahoz, F. J.; Lamata, M. P.; López-Ram de Viu, M. P.; Oro, L. A.; Vega, C.; Viguri, F. *J. Chem. Soc., Chem. Commun.* **1997**, 2351.
(293) Murahashi, S.-I.; Yamamura, M.; Yanagisawa, K.; Mita, N.; Kondo, K. *J. Org. Chem.* **1979**, *44*, 2408.
(294) Mitsudo, T.; Takagi, M.; Zhang, S.-W.; Watanabe, Y. *J. Organomet. Chem.* **1992**, *423*, 405.
(295) (a) Keim, W.; Behr, A.; Röper, M. In *Comprehensive Organometallic Chemistry*; Wilkinson, G., Stone, F. G. A., Abel, E. W., Eds.; Pergamon: Oxford, 1982; Vol. 8, p 371. Ti: (b) Akita, M.; Yasuda, H.; Nakamura, A. *Bull. Chem. Soc. Jpn.* **1984**, *57*, 480. Pd: (c) Trost, B. M.; Chan, C.; Ruhter, G. *J. Am. Chem. Soc.* **1987**, *109*, 3486. (d) Ishikawa, M.; Ohshita, J.; Ito, Y.; Minato, A. *J. Organomet. Chem.* **1988**, *346*, C58. Rh: (e) Kovalev, I. P.; Yevdakov, K. V.; Strelenko, Y. A.; Vinogradov, M. G.; Nikishin, G. I. *J. Organomet. Chem.* **1990**, *386*, 139.
(296) Bianchini, C.; Peruzzini, M.; Zanobini, F.; Frediani, P.; Albinati, A. *J. Am. Chem. Soc.* **1991**, *113*, 5453.
(297) Yi, C. S.; Liu, N. *Organometallics* **1996**, *15*, 3968.
(298) (a) Yamazaki, H. *J. Chem. Soc., Chem. Commun.* **1976**, 841. (b) Wakatsuki, Y.; Yamazaki, H.; Kumegawa, N.; Satoh, T.; Satoh, J. Y. *J. Am. Chem. Soc.* **1991**, *113*, 9604.
(299) (a) Mitsudo, T.; Nakagawa, Y.; Watanabe, K.; Hori, Y.; Misawa, H.; Watanabe, H.; Watanabe, Y. *J. Org. Chem.* **1985**, *50*, 565. (b) Mitsudo, T.; Hori, Y.; Watanabe, Y. *J. Organomet. Chem.* **1987**, *334*, 157.
(300) Yamaguchi, M.; Kido, Y.; Omata, K.; Hirama, M. *Synlett* **1995**, 1181.
(301) (a) Komiya, S.; Ito, T.; Cowie, M.; Yamamoto, A.; Ibers, J. A. *J. Am. Chem. Soc.* **1976**, *98*, 3874. (b) Tolman, C. A.; Ittel, S. D.; English, A. D.; Jesson, J. P. *J. Am. Chem. Soc.* **1979**, *101*, 1742.
(302) Nugent, W. A.; Hobbs, F. W., Jr. *J. Org. Chem.* **1983**, *48*, 5364.

(303) Review: Hidai, M. In *Aspects of Homogeneous Catalysis*; Ugo, R., Ed.; Reidel: Dordrecht, 1974; p 159.
(304) Alderson, T.; Jenner, E. L.; Lindsey, R. V., Jr. *J. Am. Chem. Soc.* **1965**, *87*, 5638.
(305) Misono, A.; Uchida, Y.; Hidai, M.; Kanai, H. *J. Chem. Soc., Chem. Commun.* **1967**, 357.
(306) McKinney, R. J. *Organometallics* **1986**, *5*, 1752.
(307) McKinney, R. J.; Calton, M. C. *Organometallics* **1986**, *5*, 1080.
(308) Ren, C. Y.; Cheng, W. C.; Chan, W. C.; Yeung, C. H.; Lau, C. P. *J. Mol. Catal.* **1990**, *50*, L1.
(309) Patzke, B.; Sustmann, R. *J. Organomet. Chem.* **1994**, *480*, 65.
(310) Pertici, P.; Ballantini, V.; Salvadori, P.; Bennett, M. A. *Organometallics* **1995**, *14*, 2565.
(311) Kashiwagi, K.; Sugise, R.; Shimakawa, T.; Matuura, T.; Shirai, M.; Kakiuchi, F.; Murai, S. *Organometallics* **1997**, *16*, 2233.
(312) Ohgomori, Y.; Ichikawa, S.; Sumitani, N. *Organometallics* **1994**, *13*, 3758.
(313) (a) Murai, S.; Kakiuchi, F.; Sekine, S.; Tanaka, Y.; Kamatani, A.; Sonoda, M.; Chatani, N. *Nature* **1993**, *366*, 529. (b) Murai, S.; Kakiuchi, F.; Sekine, S.; Tanaka, Y.; Kamatani, A.; Sonoda, M.; Chatani, N. *Pure Appl. Chem.* **1994**, *66*, 1527. (c) Kakiuchi, F.; Sekine, S.; Tanaka, Y.; Kamatani, A.; Sonoda, M.; Chatani, N.; Murai, S. *Bull. Chem. Soc. Jpn.* **1995**, *68*, 62.
(314) Sonoda, M.; Kakiuchi, F.; Chatani, N.; Murai, S. *J. Organomet. Chem.* **1995**, *504*, 151.
(315) (a) Harris, P. W. R.; Woodgate, P. D. *J. Organomet. Chem.* **1996**, *506*, 339. (b) Harris, P. W. R.; Woodgate, P. D. *J. Organomet. Chem.* **1997**, *530*, 211.
(316) (a) Guo, H.; Weber, W. P. *Polym. Bull.* **1994**, *32*, 525. (b) Tapsak, M. A.; Weber, W. P. *Polym. Bull.* **1994**, *33*, 417. (c) Guo, H.; Tapsak, M. A.; Weber, W. P. *Polym. Bull.* **1995**, *34*, 49. (d) Guo, H.; Weber, W. P. *Polym. Bull.* **1995**, *35*, 259. (e) Guo, H.; Tapsak, M. A.; Weber, W. P. *Macromolecules* **1995**, *28*, 4714. (f) Guo, H.; Wang, G.; Tapsak, M. A.; Weber, W. P. *Macromolecules* **1995**, *28*, 5686. (g) Wang, G.; Guo, H.; Weber, W. P. *J. Organomet. Chem.* **1996**, *521*, 351. (h) Londergan, T. M.; Weber, W. P. *Macromol. Rapid Commun.* **1997**, *18*, 207.
(317) Lu, P.; Paulasaari, J. K.; Weber, W. P. *Macromolecules* **1996**, *29*, 8583.
(318) Kakiuchi, F.; Yamamoto, Y.; Chatani, N.; Murai, S. *Chem. Lett.* **1995**, 681.
(319) Sonoda, M.; Kakiuchi, F.; Kamatani, A.; Chatani, N.; Murai, S. *Chem. Lett.* **1996**, 109.
(320) Kakiuchi, F.; Yamauchi, M.; Chatani, N.; Murai, S. *Chem. Lett.* **1996**, 111.
(321) Fukuyama, T.; Chatani, N.; Kakiuchi, F.; Murai, S. *J. Org. Chem.* **1997**, *62*, 5647.
(322) Trost, B. M.; Imi, K.; Davies, I. W. *J. Am. Chem. Soc.* **1995**, *117*, 5371.
(323) Kakiuchi, F.; Tanaka, Y.; Sato, T.; Chatani, N.; Murai, S. *Chem. Lett.* **1995**, 679.
(324) (a) Linn, D. E., Jr.; Halpern, J. *J. Organomet. Chem.* **1987**, *330*, 155. (b) Halpern, J. *Pure Appl. Chem.* **1987**, *59*, 173.
(325) McGuiggan, M. F.; Pignolet, L. H. *Inorg. Chem.* **1982**, *21*, 2523.
(326) (a) Fish, R. H.; Kim, T.-J.; Steward, J. L.,; Bushweller, J. H.; Rosen, R. K.; Dupon, J. W. *Organometallics* **1986**, *5*, 2193. (b) Eisenstadt, A.; Giandomenico, C. M.; Frederick, M. F.; Laine, R. M. *Organometallics* **1985**, *4*, 2033.
(327) Bruce, M. I.; Humphrey, M. G.; Snow, M. R.; Tiekink, E. R. T.; Wallis, R. C. *J. Organomet. Chem.* **1986**, *314*, 311.
(328) Moore, E. J.; Pretzer, W. R.; O'Connell, T. J.; Harris, J.; LaBounty, L.; Chou, L.; Grimmer, S. S. *J. Am. Chem. Soc.* **1992**, *114*, 5888.
(329) Chatani, N.; Fukuyama, T.; Kakiuchi, F.; Murai, S. *J. Am. Chem. Soc.* **1996**, *118*, 493.
(330) Chatani, N.; Ie, Y.; Kakiuchi, F.; Murai, S. *J. Org. Chem.* **1997**, *62*, 2604.
(331) Grigg, R.; Savic, V. *Tetrahedron Lett.* **1997**, *38*, 5737.
(332) Jaouhari, R.; Guénot, P.; Dixneuf, P. H. *J. Chem. Soc., Chem. Commun.* **1986**, 1255.
(333) (a) Suzuki, H.; Omori, H.; Moro-oka, Y. *Organometallics* **1988**, *7*, 2579. (b) Suzuki, H.; Omori, H.; Lee, D. H.; Yoshida, Y.; Fukushima, M.; Tanaka, M.; Moro-oka, Y. *Organometallics* **1994**, *13*, 1129.
(334) Takemori, T.; Suzuki, H.; Tanaka, M. *Organometallics* **1996**, *15*, 4346.
(335) Jemer, G. *Appl. Catal. A: General* **1995**, *121*, 25.
(336) Kondo, T.; Akazome, M.; Tsuji, Y.; Watanabe, Y. *J. Org. Chem.* **1990**, *55*, 1286.
(337) Isnard, P.; Denise, B.; Sneeden, R. P. A.; Cognion, J. M.; Durual, P. *J. Organomet. Chem.* **1983**, *256*, 135.
(338) Ueda, W.; Yokoyama, T.; Morikawa, Y.; Moro-oka, Y.; Ikawa, T. *J. Mol. Catal.* **1988**, *44*, 197.
(339) Keim, W.; Becker, J. *J. Mol. Catal.* **1989**, *54*, 95.
(340) Legrand, C.; Castanet, Y.; Mortreux, A.; Petit, F. *J. Chem. Soc., Chem. Commun.* **1994**, 1173.
(341) (a) Lavigne, G.; Lugan, N.; Kalck, P.; Soulié, J. M.; Lerouge, O.; Saillard, J. Y.; Halet, J. F. *J. Am. Chem. Soc.* **1992**, *114*, 10669. (b) Lugan, N.; Lavigne, G.; Soulié, J. M.; Fabre, S.; Kalck, P.; Saillard, J. Y.; Halet, J. F. *Organometallics* **1995**, *14*, 1712.
(342) Ito, T.; Horino, H.; Koshiro, Y.; Yamamoto, A. *Bull. Chem. Soc. Jpn.* **1982**, *55*, 504.
(343) (a) Jones, W. D.; Kosar, W. P. *J. Am. Chem. Soc.* **1986**, *108*, 5640. (b) Hsu, G. C.; Kosar, W. P.; Jones, W. D. *Organometallics* **1994**, *13*, 385.
(344) Cenini, S.; Ragaini, F.; Tollari, S.; Paone, D. *J. Am. Chem. Soc.* **1996**, *118*, 11964.
(345) Murahashi, S.-I.; Hirano, T.; Yano, T. *J. Am. Chem. Soc.* **1978**, *100*, 348.
(346) Murahashi, S.-I.; Watanabe, T. *J. Am. Chem. Soc.* **1979**, *101*, 7429.
(347) (a) Shvo, Y.; Laine, R. M. *J. Chem. Soc., Chem. Commun.* **1980**, 753. (b) Wilson, R. B., Jr.; Laine, R. M. *J. Am. Chem. Soc.* **1985**, *107*, 361. (c) Arcelli, A.; Khai, B.-T.; Porzi, G. *J. Organomet. Chem.* **1982**, *231*, C31.
(348) Laine, R. M.; Thomas, D. W.; Cary, L. W. *J. Am. Chem. Soc.* **1982**, *104*, 1763.
(349) (a) Aime, S.; Gobetto, R.; Padovan, F.; Botta, M.; Rosenberg, E.; Gellert, R. W. *Organometallics* **1987**, *6*, 2074. (b) Day, M.; Hajela, S.; Hardcastle, K. I.; McPhillips, T.; Rosenberg, E.; Botta, M.; Gobetto, R.; Milone, L.; Osella, D.; Gellert, R. W. *Organometallics* **1990**, *9*, 913.
(350) Ittel, S. D.; Tolman, C. A.; English, A. D.; Jesson, J. P. *J. Am. Chem. Soc.* **1978**, *100*, 7577.
(351) (a) Naota, T.; Taki, H.; Mizuno, M.; Murahashi, S.-I. *J. Am. Chem. Soc.* **1989**, *111*, 5954. (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.
(352) Gómez-Bengoa, E.; Cuerva, J. M.; Mateo, C.; Echavarren, A. M. *J. Am. Chem. Soc.* **1996**, *118*, 8553.
(353) Mizuho, Y.; Kasuga, N.; Komiya, S. *Chem. Lett.* **1991**, 2127.
(354) Lin, Y.-R.; Zhou, X.-T.; Dai, L.-X.; Sun, J. *J. Org. Chem.* **1997**, *62*, 1799.
(355) $IrH_5(i\text{-}PPr_3)_2$: Lin, Y.; Zhu, X.; Xiang, M. *J. Organomet. Chem.* **1993**, *448*, 215.
(356) $ReH(N_2)(PMe_2Ph)_4$: Hirano, M.; Ito, Y.; Hirai, M.; Fukuoka, A.; Komiya, S. *Chem. Lett.* **1993**, 2057.
(357) $Pd_2(dba)_3{\cdot}CHCl_3$-dppe: Nemoto, H.; Kubota, Y.; Yamamoto, Y. *J. Chem. Soc., Chem. Commun.* **1994**, 1665.
(358) $RhH(CO)(PPh_3)_3$: Yamamoto, Y.; Kubota, Y.; Honda, Y.; Fukui, H.; Asao, N.; Nemoto, H. *J. Am. Chem. Soc.* **1994**, *116*, 3161.
(359) $RhH(CO)(PPh_3)_3$: (a) Murahashi, S.-I.; Naota, T.; Maezaki, M. 61th Annual Meetings of the Chemical Society of the Chemical Society of Japan, Yokohama, March 29−April 1, 1991, Abstracts 1C940. (b) Paganelli, S.; Schionato, A.; Botteghi, C. *Tetrahedron Lett.* **1991**, *32*, 2807.
(360) Asymmetric Michael reactions with Rh-TRAP: (a) Sawamura, M.; Hamashima, H.; Ito, Y. *J. Am. Chem. Soc.* **1992**, *114*, 8295. (b) Sawamura, M.; Hamashima, H.; Ito, Y. *Tetrahedron* **1994**, *50*, 4439.
(361) $Pd_2(dba)_3{\cdot}CHCl_3$-dppb: (a) Yamamoto, Y.; Al-Masum, M.; Asao, N. *J. Am. Chem. Soc.* **1994**, *116*, 6019. (b) Yamamoto, Y.; Al-Masum, M. *Synlett* **1995**, 969. $(\eta^3\text{-}C_3H_5PdCl)_2$: (c) Trost, B. M.; Gerusz, V. J. *J. Am. Chem. Soc.* **1995**, *117*, 5156.
(362) Lee, L. Y. C.; Ci, X.; Giannotti, C.; Whitten, D. G. *J. Am. Chem. Soc.* **1986**, *108*, 175.
(363) DeLaive, P. J.; Sullivan, B. P.; Meyer, T. J.; Whitten, D. G. *J. Am. Chem. Soc.* **1979**, *101*, 4007.
(364) Noyori, R.; Kurimoto, I. *J. Chem. Soc., Chem. Commun.* **1986**, 1425.
(365) Ivin, K. J.; Mol, J. C. *Olefin Metathesis and Metathesis Polymerization*; Academic Press: New York, 1997.
(366) Natta, G.; Dall'Asta, G.; Porri, L. *Makromol. Chem.* **1965**, *81*, 253.
(367) (a) Michelotti, F. W.; Keaveney, W. P. *J. Polym. Sci. A* **1965**, *3*, 895. (b) Rinehart, R. E.; Smith, H. P. *J. Polym. Sci. B* **1965**, *3*, 1049. (c) Tanielian, C.; Kiennemann, A.; Ösparpucu, T. *Can. J. Chem.* **1980**, *58*, 2813. (d) Perez, E.; Alandis, N.; Laval, J. P.; Rico, I.; Lattes, A. *Tetrahedron Lett.* **1987**, *28*, 2343.
(368) Novak, B. M.; Grubbs, R. H. *J. Am. Chem. Soc.* **1988**, *110*, 960.
(369) Novak, B. M.; Grubbs, R. H. *J. Am. Chem. Soc.* **1988**, *110*, 7542.
(370) (a) Nguyen, S. T.; Johnson, L. K.; Grubbs, R. H.; Ziller, J. W. *J. Am. Chem. Soc.* **1992**, *114*, 3974. (b) Lynn, D. M.; Kanaoka, S.; Grubbs, R. H. *J. Am. Chem. Soc.* **1996**, *118*, 784.
(371) Belderrain, T. R.; Grubbs, R. H. *Organometallics* **1997**, *16*, 4001.
(372) (a) Stumpf, A. W.; Saive, E.; Demonceau, A.; Noels, A. F. *J. Chem. Soc., Chem. Commun.* **1995**, 1127. (b) Demonceau, A.; Stumpf, A. W.; Saive, E.; Noels, A. F. *Macromolecules* **1997**, *30*, 3127. (c) Hafner, A.; Mühlebach, A.; van der Schaaf, P. A. *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 2121.
(373) Herrmann, W. A.; Schattenmann, W. C.; Nuyken, O.; Glander, S. C. *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 1087.
(374) Walba, D. M.; Keller, P.; Shao, R.; Clark, N. A.; Hillmyer, M.; Grubbs, R. H. *J. Am. Chem. Soc.* **1996**, *118*, 2740.
(375) Schuster, M.; Blechert, S. *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 2037.

(376) Dias, E. L.; Nguyen, S. T.; Grubbs, R. H. *J. Am. Chem. Soc.* **1997**, *119*, 3887.
(377) (a) Fu, G. C.; Nguyen, S. T.; Grubbs, R. H. *J. Am. Chem. Soc.* **1993**, *115*, 9856. (b) Kirkland, T. A.; Grubbs, R. H. *J. Org. Chem.* **1997**, *62*, 7310.
(378) (a) Huwe, C. M.; Blechert, S. *Tetrahedron Lett.* **1995**, *36*, 1621. (b) Schuster, M.; Pernerstorfer, J.; Blechert, S. *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 1979. (c) Rutjes, F. P. J. T.; Schoemaker, H. E. *Tetrahedron Lett.* **1997**, *38*, 677. (d) Arisawa, M.; Takezawa, E.; Nishida, A.; Mori, M.; Nakagawa, M. *Synlett* **1997**, 1179.
(379) Huwe, C. M.; Velder, J.; Blechert, S. *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 2376.
(380) Dyatkin, A. B. *Tetrahedron Lett.* **1997**, *38*, 2065.
(381) (a) Shon, Y.-S.; Lee, T. R. *Tetrahedron Lett.* **1997**, *38*, 1283. (b) Crimmins, M. T.; Choy, A. L. *J. Org. Chem.* **1997**, *62*, 7548. (c) Delgado, M.; Martín, J. D. *Tetrahedron Lett.* **1997**, *38*, 6299. (d) Linderman, R. J.; Siedlecki, J.; O'Neill, S. A.; Sun, H. *J. Am. Chem. Soc.* **1997**, *119*, 6919.
(382) Meyer, C.; Cossy, J. *Tetrahedron Lett.* **1997**, *38*, 7861.
(383) Miller, S. J.; Kim, S.-H.; Chen, Z.-R.; Grubbs, R. H. *J. Am. Chem. Soc.* **1995**, *117*, 2108.
(384) (a) Miller, S. J.; Grubbs, R. H. *J. Am. Chem. Soc.* **1995**, *117*, 5855. (b) Miller, S. J.; Blackwell, H. E.; Grubbs, R. H. *J. Am. Chem. Soc.* **1996**, *118*, 9606. (c) Pernerstorfer, J.; Schuster, M.; Blechert, S. *J. Chem. Soc., Chem. Commun.* **1997**, 1949.
(385) Clark, T. D.; Ghadiri, M. R. *J. Am. Chem. Soc.* **1995**, *117*, 12364.
(386) (a) Fürstner, A.; Langemann, K. *Synthesis* **1997**, 792. (b) Fürstner, A.; Langemann, K. *J. Org. Chem.* **1996**, *61*, 3942.
(387) König, B.; Horn, C. *Synlett* **1996**, 1013.
(388) McKervey, M. A.; Pitarch, M. *J. Chem. Soc., Chem. Commun.* **1996**, 1689.
(389) (a) Nicolaou, K. C.; He, Y.; Vourloumis, D.; Vallberg, H.; Roschangar, F.; Sarabia, F.; Ninkovic, S.; Yang, Z.; Trujillo, J. I. *J. Am. Chem. Soc.* **1997**, *119*, 7960. (b) Nicolaou, K. C.; Ninkovic, S.; Sarabia, F.; Vourloumis, D.; He, Y.; Vallberg, H.; Finlay, M. R. V.; Yang, Z. *J. Am. Chem. Soc.* **1997**, *119*, 7974. (c) Yang, Z.; He, Y.; Vourloumis, D.; Vallberg, H.; Nicolaou, K. C. *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 166. (d) Nicolaou, K. C.; He, Y.; Vourloumis, D.; Vallberg, H.; Yang, Z. *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 2399. (e) Meng, D.; Bertinato, P.; Balog, A.; Su, D.-S.; Kamenecka, T.; Sorensen, E. J.; Danishefsky, S. J. *J. Am. Chem. Soc.* **1997**, *119*, 10073. (f) Meng, D.; Su, D.-S. Balog, A.; Bertinato, P.; Sorensen, E. J.; Danishefsky, S. J.; Zheng, Y.-H.; Chou, T.-C.; He, L.; Horwitz, S. B. *J. Am. Chem. Soc.* **1997**, *119*, 2733. (g) Bertinato, P.; Sorensen, E. J.; Meng, D.; Danishefsky, S. J. *J. Org. Chem.* **1996**, *61*, 8000. (h) Schinzer, D.; Limberg, A.; Bauer, A.; Böhm, O. M.; Cordes, M. *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 523.
(390) Borer, B. C.; Deerenberg, S.; Bieräugel, H.; Pandit, U. K. *Tetrahedron Lett.* **1994**, *35*, 3191.
(391) Hölder, S.; Blechert, S. *Synlett* **1996**, 505.
(392) Fürstner, A.; Kindler, N. *Tetrahedron Lett.* **1996**, *37*, 7005.
(393) Barrett, A. G. M.; Baugh, S. P. D.; Gibson, V. C.; Giles, M. R.; Marshall, E. L.; Procopiou, P. A. *J. Chem. Soc., Chem. Commun.* **1996**, 2231.
(394) Overkleeft, H. S.; Pandit, U. K. *Tetrahedron Lett.* **1996**, *37*, 547.
(395) Winkler, J. D.; Stelmach, J. E.; Axten, J. *Tetrahedron Lett.* **1996**, *37*, 4317.
(396) Fürstner, A.; Langemann, K. *J. Am. Chem. Soc.* **1997**, *119*, 9130.
(397) Coates, G. W.; Grubbs, R. H. *J. Am. Chem. Soc.* **1996**, *118*, 229.
(398) Marsella, M. J.; Maynard, H. D.; Grubbs, R. H. *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 1101.
(399) Mohr, B.; Weck, M.; Sauvage, J.-P.; Grubbs, R. H. *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 1308.
(400) Dietrich-Buchecker, C.; Rapenne, G.; Sauvage, J.-P. *J. Chem. Soc., Chem. Commun.* **1997**, 2053.
(401) Randall, M. L.; Tallarico, J. A.; Snapper, M. L. *J. Am. Chem. Soc.* **1995**, *117*, 9610.
(402) (a) Snapper, M. L.; Tallarico, J. A.; Randall, M. L. *J. Am. Chem. Soc.* **1997**, *119*, 1478. (b) Tallarico, J. A.; Bonitatebus, P. J., Jr.; Snapper, M. L. *J. Am. Chem. Soc.* **1997**, *119*, 7157.
(403) Zuercher, W. J.; Hashimoto, M.; Grubbs, R. H. *J. Am. Chem. Soc.* **1996**, *118*, 6634.
(404) Kinoshita, A.; Mori, M. *Synlett* **1994**, 1020.
(405) Kinoshita, A.; Mori, M. *J. Org. Chem.* **1996**, *61*, 8356.
(406) Barrett, A. G. M.; Baugh, S. P. D.; Braddock, D. C.; Flack, K.; Gibson, V. C.; Procopiou, P. A. *J. Chem. Soc., Chem. Commun.* **1997**, 1375.
(407) Chatani, N.; Morimoto, T.; Muto, T.; Murai, S. *J. Am. Chem. Soc.* **1994**, *116*, 6049.
(408) (a) Trost, B. M.; Lautens, M. *J. Am. Chem. Soc.* **1985**, *107*, 1781. (b) Trost, B. M.; Chen, S.-F. *J. Am. Chem. Soc.* **1986**, *108*, 6053. (c) Trost, B. M.; Tour, J. M. *J. Am. Chem. Soc.* **1987**, *109*, 5268. (d) Trost, B. M.; Lautens, M.; Chan, C.; Jebaratnam, D. J.; Mueller, T. *J. Am. Chem. Soc.* **1991**, *113*, 636.
(409) (a) Kim, S.-H.; Bowden, N.; Grubbs, R. H. *J. Am. Chem. Soc.* **1994**, *116*, 10801. (b) Kim, S.-H.; Zuercher, W. J.; Bowden, N. B.; Grubbs, R. H. *J. Org. Chem.* **1996**, *61*, 1073.
(410) Kinoshita, A.; Sakakibara, N.; Mori, M. *J. Am. Chem. Soc.* **1997**, *119*, 12388.
(411) Peters, J.-U.; Blechert, S. *J. Chem. Soc., Chem. Commun.* **1997**, 1983.
(412) Mitsudo, T.; Zhang, S.-W.; Watanabe, Y. *J. Chem. Soc., Chem. Commun.* **1994**, 435.
(413) Demonceau, A.; Lemoine, C. A.; Noels, A. F.; Chizhevsky, I. T.; Sorokin, P. V. *Tetrahedron Lett.* **1995**, *36*, 8419.
(414) (a) Doyle, M. P.; Winchester, W. R.; Hoorn, J. A. A.; Lynch, V.; Simonsen, S. H.; Ghosh, R. *J. Am. Chem. Soc.* **1993**, *115*, 9968. (b) Evans, D. A.; Woerpel, K. A.; Scott, M. J. *Angew. Chem., Int. Ed. Engl.* **1992**, *31*, 430.
(415) (a) Nishiyama, H.; Itoh, Y.; Matsumoto, H.; Park, S.-B.; Itoh, K. *J. Am. Chem. Soc.* **1994**, *116*, 2223. (b) Nishiyama, H.; Itoh, Y.; Sugawara, Y.; Matsumoto, H.; Aoki, K.; Itoh, K. *Bull. Chem. Soc. Jpn.* **1995**, *68*, 1247. (c) Park, S.-B.; Sakata, N.; Nishiyama, H. *Chem. Eur. J.* **1996**, *2*, 303.
(416) (a) Galardon, E.; Le Maux, P.; Simonneaux, G. *J. Chem. Soc., Chem. Commun.* **1997**, 927. (b) Lo, W.-C.; Che, C.-M.; Cheng, K.-F.; Mak, T. C. W. *J. Chem. Soc., Chem. Commun.* **1997**, 1205. (c) Frauenkron, M.; Berkessel, A. *Tetrahedron Lett.* **1997**, *38*, 7175.
(417) (a) Trost, B. M.; Dyker, G.; Kulawiec, R. J. *J. Am. Chem. Soc.* **1990**, *112*, 7809. (b) Trost, B. M.; Kulawiec, R. J. *J. Am. Chem. Soc.* **1992**, *114*, 5579. (c) Trost, B. M.; Kulawiec, R. J.; Hammes, A. *Tetrahedron Lett.* **1993**, *34*, 587.
(418) Trost, B. M.; Flygare, J. A. *J. Am. Chem. Soc.* **1992**, *114*, 5476.
(419) Trost, B. M.; Flygare, J. A. *J. Org. Chem.* **1994**, *59*, 1078.
(420) Trost, B. M.; Flygare, J. A. *Tetrahedron Lett.* **1994**, *35*, 4059.
(421) Merlic, C. A.; Pauly, M. E. *J. Am. Chem. Soc.* **1996**, *118*, 11319.
(422) Chatani, N.; Fukumoto, Y.; Ida, T.; Murai, S. *J. Am. Chem. Soc.* **1993**, *115*, 11614.
(423) Mitsudo, T.; Kokuryo, K.; Shinsugi, T.; Nakagawa, Y.; Watanabe, Y.; Takegami, Y. *J. Org. Chem.* **1979**, *44*, 4492.
(424) Mitsudo, T.; Naruse, H.; Kondo, T.; Ozaki, Y.; Watanabe, Y. *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 580.
(425) Warrener, R. N.; Abbenante, G.; Kennard, C. H. L. *J. Am. Chem. Soc.* **1994**, *116*, 3645.
(426) (a) Kondo, T.; Suzuki, N.; Okada, T.; Mitsudo, T. *J. Am. Chem. Soc.* **1997**, *119*, 6187. (b) Morimoto, T.; Chatani, N.; Fukumoto, Y.; Murai, S. *J. Org. Chem.* **1997**, *62*, 3762.
(427) Mitsudo, T.; Zhang, S.-W.; Nagao, M.; Watanabe, Y. *J. Chem. Soc., Chem. Commun.* **1991**, 598.
(428) (a) Trost, B. M.; Indolese, A. *J. Am. Chem. Soc.* **1993**, *115*, 4361. (b) Trost, B. M.; Indolese, A. F.; Müller, T. J. J.; Treptow, B. *J. Am. Chem. Soc.* **1995**, *117*, 615.
(429) (a) Trost, B. M.; Müller, T. J. J. *J. Am. Chem. Soc.* **1994**, *116*, 4985. (b) Trost, B. M.; Müller, T. J. J.; Martinez, J. *J. Am. Chem. Soc.* **1995**, *117*, 1888.
(430) Kikuchi, H.; Uno, M.; Takahashi, S. *Chem. Lett.* **1997**, 1273.
(431) Trost, B. M.; Imi, K.; Indolese, A. F. *J. Am. Chem. Soc.* **1993**, *115*, 8831.
(432) Itoh, K.; Mukai, K.; Nagashima, H.; Nishiyama, H. *Chem. Lett.* **1983**, 499.
(433) Trost, B. M.; Martinez, J. A.; Kulawiec, R. J.; Indolese, A. F. *J. Am. Chem. Soc.* **1993**, *115*, 10402.
(434) Dérien, S.; Jan, D.; Dixneuf, P. H. *Tetrahedron* **1996**, *52*, 5511.
(435) Dérien, S.; Gomez Vicente, B.; Dixneuf, P. H. *J. Chem. Soc., Chem. Commun.* **1997**, 1405.
(436) Lindner, E.; Jansen, R.-M.; Mayer, H. A.; Hiller, W.; Fawzi, R. *Organometallics* **1989**, *8*, 2355.
(437) Minami, I.; Shimizu, I.; Tsuji, J. *J. Organomet. Chem.* **1985**, *296*, 269.
(438) Zhang, S.-W.; Mitsudo, T.; Kondo, T.; Watanabe, Y. *J. Organomet. Chem.* **1993**, *450*, 197.
(439) Mitsudo, T.; Suzuki, N.; Kondo, T.; Watanabe, Y. *J. Org. Chem.* **1994**, *59*, 7759.
(440) Crudden, C. M.; Alper, H. *J. Org. Chem.* **1995**, *60*, 5579.
(441) Kondo, T.; Ono, H.; Satake, N.; Mitsudo, T.; Watanabe, Y. *Organometallics* **1995**, *14*, 1945.
(442) Tsuji, Y.; Mukai, T.; Kondo, T.; Watanabe, Y. *J. Organomet. Chem.* **1989**, *369*, C51.
(443) Mitsudo, T.; Zhang, S.-W.; Kondo, T.; Watanabe, Y. *Tetrahedron Lett.* **1992**, *33*, 341.
(444) Kondo, T.; Mukai, T.; Watanabe, Y. *J. Org. Chem.* **1991**, *56*, 487.
(445) Maruyama, Y.; Sezaki, T.; Tekawa, M.; Sakamoto, T.; Shimizu, I.; Yamamoto, A. *J. Organomet. Chem.* **1994**, *473*, 257.
(446) Wilke, G. *Angew. Chem., Int. Ed. Engl.* **1988**, *27*, 185.
(447) Itoh, K. *Kagaku Zokan* **1986**, *108*, 157.
(448) Itoh, K.; Masuda, K.; Fukahori, T.; Nakano, K.; Aoki, K.; Nagashima, H. *Organometallics* **1994**, *13*, 1020.
(449) Steed, J. W.; Tocher, D. A.; Rogers, R. D. *J. Chem. Soc., Chem. Commun.* **1996**, 1589.
(450) (a) Lydon, J. E.; Nicholson, J. K.; Shaw, B. L.; Truter, M. R. *Proc. Chem. Soc.* **1964**, 421. (b) Nicholson, J. K.; Shaw, B. L. *J. Chem. Soc. A* **1966**, 807.

(451) Review: Freidlina, R. K.; Chukovskaya, E. C. *Synthesis* **1974**, 477.
(452) Mori, Y.; Tsuji, J. *Tetrahedron* **1973**, *29*, 827.
(453) (a) Asscher, M.; Vofsi, D. *J. Chem. Soc.* **1963**, 1887, 3921. (b) Martin, P.; Greuter, H.; Bellus, D. *J. Am. Chem. Soc.* **1979**, *101*, 5853.
(454) Susuki, T.; Tsuji, J. *J. Org. Chem.* **1970**, *35*, 2982.
(455) Elzinga, J.; Hogeveen, H. *J. Org. Chem.* **1980**, *45*, 3957.
(456) Gandolfi, O.; Cais, M. *J. Organomet. Chem.* **1977**, *125*, 141.
(457) (a) Matsumoto, H.; Nikaido, T.; Nagai, Y. *Tetrahedron Lett.* **1975**, 899. (b) Matsumoto, H.; Nakano, T.; Takasu, K.; Nagai, Y. *J. Org. Chem.* **1978**, *43*, 1734. (c) Bland, W. J.; Davis, R.; Durrant, J. L. A. *J. Organomet. Chem.* **1985**, *280*, 397.
(458) Nakano, T.; Shimada, Y.; Sako, R.; Kayama, M.; Matsumoto, H.; Nagai, Y. *Chem. Lett.* **1982**, 1255.
(459) Okano, T.; Uekawa, T.; Sawaki, H.; Eguchi, S. *Synlett* **1990**, 403.
(460) Okano, T.; Shimizu, T.; Sumida, K.; Eguchi, S. *J. Org. Chem.* **1993**, *58*, 5163.
(461) (a) Hayes, T.; Freyer, A. J.; Parvez, M.; Weinreb, S. M. *J. Org. Chem.* **1986**, *51*, 5501. (b) Haynes, T. K.; Villani, R.; Weinreb, S. M. *J. Am. Chem. Soc.* **1988**, *110*, 5533.
(462) (a) Phelps, J. C.; Bergbreiter, D. E.; Lee, G. M.; Villani, R.; Weinreb, S. M. *Tetrahedron Lett.* **1989**, *30*, 3915. (b) Lee, G. M.; Weinreb, S. M. *J. Org. Chem.* **1990**, *55*, 1281.
(463) (a) Nagashima, H.; Wakamatsu, H.; Itoh, K. *J. Chem. Soc., Chem. Commun.* **1984**, 652. (b) Nagashima, H.; Ara, K.; Wakamatsu, H.; Itoh, K. *J. Chem. Soc., Chem. Commun.* **1985**, 518. (c) Nagashima, H.; Ozaki, N.; Seki, K.; Ishii, M.; Itoh, K. *J. Org. Chem.* **1989**, *54*, 4497. (d) Nagashima, H.; Wakamatsu, H.; Ozaki, N.; Ishii, T.; Watanabe, M.; Tajima, T.; Itoh, K. *J. Org. Chem.* **1992**, *57*, 1682. (e) Rachita, M. A.; Slough, G. A. *Tetrahedron Lett.* **1993**, *34*, 6821.
(464) (a) Ishibashi, H.; Nakatani, H.; Iwami, S.; Sato, T.; Nakamura, N.; Ikeda, M. *J. Chem. Soc., Chem. Commun.* **1989**, 1767. (b) Ishibashi, H.; Uemura, N.; Nakatani, H.; Okazaki, M.; Sato, T.; Nakamura, N. Ikeda, M. *J. Org. Chem.* **1993**, *58*, 2360.
(465) Kamigata, N.; Sawada, H.; Kobayashi, M. *J. Org. Chem.* **1983**, *48*, 3793.
(466) Kamigata, N.; Ozaki, J.; Kobayashi, M. *J. Org. Chem.* **1985**, *50*, 5045.
(467) Kamigata, N.; Fukushima, T.; Yoshida, M. *J. Chem. Soc., Chem. Commun.* **1989**, 1559.
(468) Kameyama, M.; Kamigata, N.; Kobayashi, M. *J. Org. Chem.* **1987**, *52*, 3312.
(469) Kameyama, M.; Kamigata, N. *Bull. Chem. Soc. Jpn.* **1987**, *60*, 3687.
(470) Kamigata, N.; Kameyama, M. *J. Synth. Org. Chem. Jpn.* **1989**, *47*, 436.
(471) (a) Kato, M.; Kamigaito, M.; Sawamoto, M.; Higashimura, T. *Macromolecules* **1995**, *28*, 1721. (b) Ando, T.; Kato, M.; Kamigaito, M.; Sawamoto, M. *Macromolecules* **1996**, *29*, 1070. (c) Kotani, Y.; Kato, M.; Kamigaito, M.; Sawamoto, M. *Macromolecules* **1996**, *29*, 6979. (d) Matsuyama, M.; Kamigaito, M.; Sawamoto, M. *J. Polym. Sci., Part A: Polym. Chem.* **1996**, *34*, 3585. (e) Nishikawa, T.; Ando, T.; Kamigaito, M.; Sawamoto, M. *Macromolecules* **1997**, *30*, 2244.
(472) Suzuki, M.; Noyori, R.; Hamanaka, N. *J. Am. Chem. Soc.* **1982**, *104*, 2024.
(473) Ito, Y.; Matsuura, A.; Otani, R.; Matsuura, T.; Fukuyama, K.; Katsube, Y. *J. Am. Chem. Soc.* **1983**, *105*, 5699.
(474) (a) DeLaive, P. J.; Lee, J. T.; Sprintschnik, H. W.; Abruna, H.; Meyer, T. J.; Whitten, D. G. *J. Am. Chem. Soc.* **1977**, *99*, 7094. (b) DeLaive, P. J.; Sullivan, B. P.; Meyer, T. J.; Whitten D. G. *J. Am. Chem. Soc.* **1979**, *101*, 4007.
(475) Lee, L. Y. C.; Ci, X.; Giannotti, C.; Whitten, D. G. *J. Am. Chem. Soc.* **1986**, *108*, 175.
(476) Noyori, R.; Kurimoto, I. *J. Chem. Soc., Chem. Commun.* **1986**, 1425.
(477) *Catalysis in C_1 Chemistry*; Keim, W., Ed.; D. Reidel: Dordrecht, 1983.
(478) Rodriguez, E.; Leconte, M.; Basset, J. M.; Tanaka, K.; Tanaka, K. *J. Am. Chem. Soc.* **1988**, *110*, 275 and references therein.
(479) Henrici-Olive, G.; Olive, S. *The Chemistry of the Catalyzed Hydrogenation of Carbon Monoxide*; Springer-Verlag: Berlin, 1984.
(480) Dombek, B. D. *J. Am. Chem. Soc.* **1980**, *102*, 6855.
(481) Knifton, J. F. *J. Am. Chem. Soc.* **1981**, *103*, 3959.
(482) Dombek, B. D. *J. Am. Chem. Soc.* **1981**, *103*, 6508.
(483) Kiso, Y.; Saeki, K.; Hayashi, T.; Tanaka, M.; Matsunaga, Y.; Ishino, M.; Tamura, M. Deguchi, T.; Nakamura, S. *J. Organomet. Chem.* **1987**, *335*, C27.
(484) (a) Knifton, J. F. *J. Chem. Soc., Chem. Commun.* **1983**, 729. (b) Dombek, B. D. *Organometallics* **1985**, *4*, 1707.
(485) Whyman, R. *J. Chem. Soc., Chem. Commun.* **1983**, 1439.
(486) Tanaka, M.; Kiso, Y.; Saeki, K. *J. Organomet. Chem.* **1987**, *329*, 99.
(487) Knifton, J. F.; Grigsby, R. A., Jr.; Lin, J. J. *Organometallics* **1984**, *3*, 62.
(488) Izumi, Y.; Chihara, T.; Yamazaki, H.; Iwasawa, Y. *J. Chem. Soc., Chem. Commun.* **1992**, 1395.
(489) Knifton, J. F. *J. Chem. Soc., Chem. Commun.* **1985**, 1412.
(490) (a) Braca, G.; Sbrana, G.; Valentini, G.; Andrich, G.; Gregorio, G. *J. Am. Chem. Soc.* **1978**, *100*, 6238. (b) Moloy, K. G.; Wegman, R. W. *J. Chem. Soc., Chem. Commun.* **1988**, 820.
(491) (a) Hidai, M.; Orisaku, M.; Ue, M.; Koyasu, Y.; Kodama, T.; Uchida, Y. *Organometallics* **1983**, *2*, 292. (b) Doyle, G. J. *J. Mol. Catal.* **1983**, *18*, 251. (c) Fakley, M. E.; Head, R. A. *Appl. Catal.* **1983**, *5*, 3.
(492) (a) Sanchez-Delgado, R. A.; Bradley, J. S.; Wilkinson, G. *J. Chem. Soc., Dalton* **1976**, 399. (b) Süss-Fink, G.; Herrmann, G. *J. Chem. Soc., Chem. Commun.* **1985**, 735.
(493) Reviews: (a) Ford, P. C. *Acc. Chem. Res.* **1981**, *14*, 31. (b) Sneeden, R. P. A. In *Comprehensive Organometallic Chemistry*; Wilkinson, G., Stone, F. G. A., Abel, E. W., Eds.; Pergamon: Oxford, 1982; Vol. 8, p 9. (c) Laine, R. M.; Wilson, R. B., Jr. *Aspects Homogeneous Catal.* **1984**, *5*, 217.
(494) (a) Laine, R. M. *J. Am. Chem. Soc.* **1978**, *100*, 6451. (b) King, A. D.; King, R. B.; Yang, D. B. *J. Chem. Soc., Chem. Commun.* **1980**, 529. (c) Bricker, J. C.; Nagel, C. C.; Bhattacharyya, A. A.; Shore, S. G. *J. Am. Chem. Soc.* **1985**, *107*, 377.
(495) Ungermann, C.; Landis, V.; Moya, S. A.; Cohen, H.; Walker, H.; Pearson, R. G.; Rinker, R. G.; Ford, P. C. *J. Am. Chem. Soc.* **1979**, *101*, 5922.
(496) Taqui Khan, M. M.; Halligudi, S. B.; Shukla, S. *Angew. Chem., Int. Ed. Engl.* **1988**, *27*, 1735.
(497) Review: Escaffre, P.; Thorez, A.; Kalck, P. *J. Mol. Catal.* **1985**, *33*, 87.
(498) Alper, H.; Amaratunga, S. *Tetrahedron Lett.* **1980**, *21*, 2603.
(499) (a) Cann, K.; Cole, T.; Slegeir, W.; Pettit, R. *J. Am. Chem. Soc.* **1978**, *100*, 3969. (b) Nomura, K. *Chem. Lett.* **1991**, 1679.
(500) Review: Tafesh, A. M.; Weiguny, J. *Chem. Rev.* **1996**, *96*, 2035.
(501) Cenini, S.; Ragaini, F. *Catalytic Reductive Carbonylation of Organic Nitro Compounds*, Kluwer Academic Publishers: Dordrecht, 1997.
(502) $Ru_3(CO)_{12}$: (a) Cenini, S.; Crotti, C.; Pizzotti, M.; Porta, F. *J. Org. Chem.* **1988**, *53*, 1243. $Ru_3(CO)_{12}$/Pd clay: (b) Valli, V. L. K.; Alper, H. *J. Am. Chem. Soc.* **1993**, *115*, 3778. Ru(dppp)-$(CO)_3$: (c) Gargulak, J. D.; Berry, A. J.; Noirot, M. D.; Gladfelter, W. L. *J. Am. Chem. Soc.* **1992**, *114*, 8933. (d) Gargulak, J. D.; Gladfelter, W. L. *J. Am. Chem. Soc.* **1994**, *116*, 3792. (e) Skoog, S. J.; Campbell, J. P.; Gladfelter, W. L. *Organometallics* **1994**, *13*, 4137. Ru black/KI: (f) Fukuoka, S.; Chono, M.; Kohno, M. *J. Org. Chem.* **1984**, *49*, 1458.
(503) Crotti, C.; Cenini, S.; Rindone, B.; Tollari, S.; Demartin, F. *J. Chem. Soc., Chem. Commun.* **1986**, 784.
(504) Akazome, M.; Kondo, T.; Watanabe, Y. *J. Org. Chem.* **1993**, *58*, 310.
(505) Watanabe, Y.; Yamamoto, J.; Akazome, M.; Kondo, T.; Mitsudo, T. *J. Org. Chem.* **1995**, *60*, 8328.
(506) Akazome, M.; Tsuji, Y.; Watanabe, Y. *Chem. Lett.* **1990**, 635.
(507) Colquhoun, H. M.; Thompson, D. J.; Twigg, M. V. *Carbonylation: Direct Synthesis of Carbonyl Compounds*; Plenum Press: New York, 1991.
(508) Alper, H.; Petrignani, J.-F. *J. Chem. Soc., Chem. Commun.* **1983**, 1154.
(509) Kondo, T.; Kodoi, K.; Mitsudo, T.; Watanabe, Y. *J. Chem. Soc., Chem. Commun.* **1994**, 755.
(510) Reviews: (a) *Organic and Bio-organic Chemistry of Carbon Dioxide*; Inoue, S., Yamazaki, N., Eds.; Wiley: New York, 1982. (b) Behr, A. *Carbon Dioxide Activation by Metal Complexes*; VCH: Weinheim, 1988. (c) Halmann, M. M. *Chemical Fixation of Carbon Dioxide*; CRC: Boca Raton, 1993. (d) *Carbon Dioxide Chemistry: Environmental Issues*; Paul, J., Pradier, C.-M., Eds.; Royal Society of Chemistry: London, 1994. (e) Leitner, W. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 2207. (f) Jessop, P. G.; Ikariya, T.; Noyori, R. *Chem. Rev.* **1995**, *95*, 259.
(511) (a) Kitamura, N.; Tazuke, S. *Chem. Lett.* **1983**, 1109. (b) Hawecker, J.; Lehn, J.-M.; Ziessel, R. *J. Chem. Soc., Chem. Commun.* **1985**, 56. (c) Lehn, J.-M.; Ziessel, R. *J. Organomet. Chem.* **1990**, *382*, 157. (d) Ishida, H.; Tanaka, K.; Tanaka, T. *Chem. Lett.* **1987**, 1035. (e) Ishida, H.; Tanaka, K.; Tanaka, T. *Chem. Lett.* **1988**, 339. (f) Ishida, H.; Terada, T.; Tanaka, K.; Tanaka, T. *Inorg. Chem.* **1990**, *29*, 905.
(512) Hawecker, J.; Lehn, J.-M.; Ziessel, R. *J. Chem. Soc., Chem. Commun.* **1983**, 536.
(513) Willner, I.; Maidan, R.; Mandler, D.; Dürr, H.; Dörr, G.; Zengerle, K. *J. Am. Chem. Soc.* **1987**, *109*, 6080.
(514) (a) Review: Collin, J.-P.; Sauvage, J.-P. *Coord. Chem. Rev.* **1989**, *93*, 245. (b) $[Ru(bpy)_2(CO)_2]^{2+}$: Ishida, H.; Tanaka, K.; Tanaka, T. *Organometallics* **1987**, *6*, 181. (c) Ishida, H.; Tanaka, H.; Tanaka, K.; Tanaka, T. *J. Chem. Soc., Chem. Commun.* **1987**, 131. (d) Ishida, H.; Tanaka, H.; Tanaka, K.; Tanaka, T. *Chem. Lett.* **1987**, 597. (e) *trans*-$[Ru(bpy)_2(CO)_2Cl_2]Cl$: Ishida, H.; Fujiki, K.; Ohba, T.; Ohkubo, K.; Tanaka, K.; Terada, T.; Tanaka, T. *J. Chem. Soc., Dalton Trans.* **1990**, 2155. (f) [Ru(trpy)-(dppene)Cl]$^+$: Bolinger, C. M.; Sullivan, B. P.; Conrad, D.; Gilbert, J. A.; Story, N.; Meyer, T. J. *J. Chem. Soc., Chem.*

Commun. **1985**, 796. (g) $[Ru(bpy)(CO)_2]_n$ on carbon: Collomb-Dunand-Sauthier, M.-N.; Deronzier, A.; Ziessel, R. *J. Chem. Soc., Chem. Commun*. **1994**, 189. (h) $Ru(bpy)(CO)_2Cl_2$: Collomb-Dunand-Sauthier, M.-N.; Deronzier, A.; Ziessel, R. *Inorg. Chem*. **1994**, *33*, 2961. (i) $[Ru(bpy)(trpy)(CO)]^{2+}$: Nagao, H.; Mizukawa, T.; Tanaka, K. *Inorg. Chem*. **1994**, *33*, 3415. (j) $[Ru(bpy)_2(quinoline)(CO)]^{2+}$: Nakajima, H.; Kushi, Y.; Nagao, H.; Tanaka, K. *Organometallics* **1995**, *14*, 5093.

(515) Inoue, Y.; Izumida, H.; Sasaki, Y.; Hashimoto, H. *Chem. Lett*. **1976**, 863.

(516) (a) $RuH_2(PPh_3)_4$: Inoue, Y.; Sasaki, Y.; Hashimoto, H. *J. Chem. Soc., Chem. Commun*. **1975**, 718. (b) $HRu_3(CO)_{11}^-$: Darensbourg, D. J.; Ovalles, C.; Pala, M. *J. Am. Chem. Soc*. **1983**, *105*, 5937. (c) *cis*-$[Ru(6,6'\text{-}(Cl_2bpy)_2(H_2O)_2](CF_3SO_3)_2$: Lau, C. P.; Chen, Y. Z. *J. Mol. Catal. A. Chem*. **1995**, *101*, 33.

(517) Kiso, Y.; Saeki, K. JP 36617, 1977; *Chem. Abstr*. **1977**, *87*, 84562s.

(518) Tominaga, K.; Sasaki, Y.; Watanabe, T.; Saito, M. *Bull. Chem. Soc. Jpn*. **1995**, *68*, 2837.

(519) (a) Jessop, P. G.; Ikariya, T.; Noyori, R. *Nature* **1994**, *368*, 231. (b) Jessop, P. G.; Ikariya, T.; Noyori, R. *Science* **1995**, *269*, 1065. (c) Jessop, P. G.; Hsiao, Y.; Ikariya, T.; Noyori, R. *J. Am. Chem. Soc*. **1996**, *118*, 344.

(520) Jessop, P. G.; Hsiao, Y.; Ikariya, T.; Noyori, R. *J. Chem. Soc., Chem. Commun*. **1995**, 707.

(521) Jessop, P. G.; Hsiao, Y.; Ikariya, T.; Noyori, R. *J. Am. Chem. Soc*. **1994**, *116*, 8851.

(522) Kröcher, O.; Köppel, R. A.; Baiker, A. *J. Chem. Soc., Chem. Commun*. **1997**, 453.

(523) Willner, I.; Mandler, D.; Riklin, A. *J. Chem. Soc., Chem. Commun*. **1986**, 1022.

(524) (a) $RuCl_2(PPh_3)_3$: Koinuma, H.; Kawakami, F.; Kato, H.; Hirai, H. *J. Chem. Soc., Chem. Commun*. **1981**, 213. (b) $[N(PPh_3)_2][HRu_3(CO)_{11}]$: Süss-Fink, G.; Reiner, J. *J. Organomet. Chem*. **1981**, *221*, C36.

(525) Zoeckler, M. T.; Laine, R. M. *J. Org. Chem*. **1983**, *48*, 2539.

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