Selective Synthetic Transformations
Based on Vanadium–Mediated Redox Reactions

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Abstract: Low-valent vanadium–, or titanium-catalyzed reduction reactions including dehalogenation, pinacol coupling, and the related radical reaction have been developed by constructing a multi-component redox system in combination with a co-reductant and an additive, which serve for the recycling and liberation of the catalyst. High stereoselectivity is attained in these catalytic transformations. Oxovanadium(V) compounds, which are evaluated as Lewis acids with oxidation capability, induce one-electron oxidative desilylation of organosilicon compounds such as silyl enol ethers, allylic silanes, and benzylic silanes, allowing chemoselective–catalyzed with the less oxidizable organosilicon compounds. The oxovanadium(V)-induced or catalyzed oxidation of benzylsilane and benzyltin compounds is carried out under oxygen atmosphere to afford aromatic aldehydes (ketones) and/or carboxylic acids. Oxidative ligand coupling of dialkylarylaluminums is achieved by treatment with oxovanadium(V) compounds, leading to the formation of the alkylarenes. The ate complexes derived from arylaluminums or 1-alkenylaluminums and 1-alkynyllithiums undergo facile oxidative ligand coupling. Similar oxidation is observed with organoborons and organozincs or their ate complexes. This method is applied to vicinal dialkylation with the diorganosilanes or ate complexes at both the α and β positions of 2-cycloalkenones.

1. Introduction

One-electron reduction or oxidation of organic compounds provides a useful route to generate anion radicals or cation radicals, respectively, as exemplified by Scheme 1. These methods are of potential utility in synthetic radical reactions. A redox process of transition metals is able to be applied to efficient one-electron reduction or oxidation reactions. In particular, the redox of early transition metals including titanium, vanadium, and manganese, has been employed from this point of view.1,2 The redox of transition metals is controlled by a ligand, allowing a more efficient interaction between the orbitals of metals and substrates for facile electron transfer. The interaction with a Lewis acid as an additive towards a substrate also contributes to such electron transfer.

Scheme 1

![Scheme 1](image)

Synthetic limitation exists in the use of stoichiometric or excess amounts of metallic reductants or oxidants to complete the reaction. A catalytic system should be constructed to avoid the use of stoichiometric, expensive and/or toxic metallic reagents. It is important to select stoichiometric co-reductants or co-oxidants for the reversible cycle of a catalyst (Scheme 2). A metallic co-reductant is ultimately converted to the corresponding metal salt in a higher oxidation state, which may work as a Lewis acid or, on the contrary, impede the reduction reaction. Taking these interactions into account, the requisite catalytic system is envisioned to be formed by multi-component interaction. Steric control by means of coordination may permit the stereoselective and/or stereospecific transformations. An alternative method for recycling a catalyst is achieved by electrolysis. Electrochemical reactions catalyzed by various complexes including Vitamin B12, Ni(II)-cyclam, and Ni(II)-salen have been reported.3

Scheme 2

![Scheme 2](image)

Redox interaction between a metal and a metal or a ligand (or an organic group) through inner- or outer-sphere electron transfer is considered to change the oxidation state of these components. Precise regulation of the redox process based on the electronic interaction between HOMO and LUMO orbitals is required for this purpose, which allows development of novel and selective methods for oxidative or reductive transformations under redox potential control.

2. A Catalytic System for Reductive Transformations via One-Electron Transfer

2.1 Dehalogenative Reduction

Homolytic cleavage of organic halides is induced by one-electron reduction to afford the corresponding radical intermediates. A catalytic dehalogenation is achieved in the vanadium–induced reduction. The highly stereoselective monodebromination of gem-dibromocyclopropane 1 to monobromide 2 proceeds with a catalytic amount of a low-valent vanadium species generated from VCl₃ or
CpV(CO)₄ and Zn as a stoichiometric co-reductant, in cooperation with diethyl phosphonate or triethyl phosphite (Scheme 3).

The phosphonate or phosphate is likely to play an important role in the debromination step. The coordination to vanadium leads to a bulky and stronger reductant. The former effect is related to the stereoselectivity, since the bulky reductant is liable to approach the bromide from the less hindered side. Furthermore, a hydrogen source is assumed to be available from the phosphate or phosphate in the coordination sphere. In this manner, the ternary reductant system contributes to the stereoselective catalytic debromination.

Scheme 3

The combination of YbI₂ catalyst and Al is effective for the photo-induced catalytic hydrogenative debromination of alkyl bromide. In both vanadium- and ytterbium-catalyzed reactions, the multi-component redox system is formed in an appropriate combination of a catalyst, a co-reductant, and an additive.

2.2 Pinacol Coupling

The reductive dimerization of carbonyl compounds is a useful synthetic method for constructing vicinally functionalized carbon–carbon bonds. One-electron transfer from a metal to a carbonyl group generates the corresponding ketyl radical, which can dimerize to give either dl- or meso-1,2-diols. A complementary route to 1,2-diols has been developed by the osmium-catalyzed dihydroxylation of olefins.

For stoichiometric reductive dimerization, low-valent metals such as aluminum amalgam, zinc, titanium, vanadium, and samarium have been employed conveniently. For example, the pinacol coupling reaction using TiCl₃/Zn-Cu and [V₂Cl₃(THF)₆][Zn₂Cl₆] has been developed successfully for the synthesis of paclitaxel and C₂-symmetrical HIV protease inhibitors, respectively.

In the absence of a chlorosilane, a catalytic reaction is not observed. Silylation is considered to liberate the catalyst. The Lewis-acidic–like interaction of a chlorosilane with a carbonyl oxygen is suggested to facilitate the electron transfer to the carbonyl group, generating the stabilized silyloxyalkyl radical for dimerization. Another interaction with the vanadium catalyst is possible since the UV–vis spectrum of Cp₂VCl₂ changes on the addition of Me₂SiCl. The diastereoselectivity depends on the substituent of chlorosilanes, which implies its steric effect in the coupling step.

Fiirstner has independently developed a catalytic method for the McMurry coupling by using a similar ternary-component system. The oxamide undergoes reductive cyclization to indoles in the presence of a catalytic amount of TiCl₃, Zn, and a chlorosilane.

Based on these observations, a variety of modified catalytic systems have been investigated for the diastereoselective carbon–carbon bond formation. A trinuclear complex derived from Cp₂TiCl₂ and MgBr₂ is considered to be an active catalyst for the dl-diastereoselective pinacol coupling of aromatic aldehydes. The observed dl selectivity is explained by minimization of steric interference through anti-orientation in the intermediate. Using rac-ethylenbis(η⁵-tetrahydroindenyltitanium) dichloride, the diastereoselective pinacol coupling of aromatic aldehydes also proceeds via.

Scheme 4

Use of THF as a solvent leads to the highly diastereoselective formation of the dl-1,2-diols from secondary aliphatic aldehydes.

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Scheme 4
This method is applied to the enantioselective pinacol coupling by using a chiral catalyst 10 or 11.16

As shown in eqs 4–5, 1,5- and 1,6-dialdehydes undergo annulative pinacol coupling to give cyclic vic-diols.17 The vanadium-catalyzed intramolecular coupling reaction of 1,5-diketone also takes place with excellent selectivity (eq 6) although the intermolecular coupling of ketones such as acetophenone results in low diastereoselectivity under the conditions.11a

The ligand or additive effect is studied in the diastereoselective titanium-catalyzed coupling of aromatic aldehydes.17 Higher selectivity is attained especially with OC[N(Et)Ph]2 as a ligand. Sub-stoichiometric quantities of a protic (t-BuOH, catechol, 2,2'-biphenol) or Lewis basic (DMF, N,N-dimethylethylacetamide) additive afford five- to ten-fold acceleration of the reaction rate relative to the parent TiCl3(THF)3 catalyst.

A catalytic turnover is formed by protonation of the metal-oxygen bond instead of silylation. 2,6-Lutidine hydrochloride or 2,4,6-collidine hydrochloride serves as an appropriate proton source in the Cp2TiCl2-catalyzed pinacol coupling of aromatic aldehydes in the presence of Mn.18 Ac2O or AcCl can be utilized instead of a chlorosilane in the VOCl3- or TiCl4-catalyzed pinacol coupling reaction of aromatic aldehyde to give the diacetate 12 (eq 7).19

Low-valent lanthanides, represented by Sm(II) compounds, induce one-electron reduction. The recycling for the Sm(II) species is first performed by electrochemical reduction of the Sm(III) species.20 In one-component cell electrolysis, the samarium-catalyzed pinacol coupling proceeds with sacrificial anodes of Mg or Al. Furthermore, redox interaction between the Sm species and Mg allows the use of Mg as a reducing agent to form a ternary-component catalytic system for pinacol coupling in combination with Me3SiCl as mentioned above.21 A catalytic amount of Cr(II) salt or chromocene, Mn powder, and a chlorosilane are effective in the reductive coupling.22

The coupling reaction of imines has been less investigated despite the frequent occurrence of vic-diamine units in naturally occurring compounds. A cat. PbBr2/Al system is effective for the coupling of aromatic imines in the presence of trifluoroacetic acid or AlBr3.23 This recycling step is also performed using an undivided cell under constant current density.24 A cat. Cp2TiCl2/Sm system is effective to provide df-diamines with moderate selectivity.25 The Cp2VCl2/R3SiCl/Zn catalytic system can be also used for the reductive coupling of aldimines (eq 8).26 meso-Diastereoselectivity is observed in contrast to the coupling with cat. Cp2TiCl2/Sm system. The selectivity depends on the substituents on both the nitrogen and silane atoms. The allyl or benzyl group on the nitrogen atom is advantageous for meso selection.

2.3 Radical Cyclization

The above-mentioned reagent-controlled catalytic system is of synthetic potential in radical reactions. The generated ketyl radicals undergo the inter- and intra-molecular coupling with a variety of radical acceptors. A multi-component catalytic reductant system consisting of cat. SmI2, Zn/Hg, LiI, and Me3SiOTf induces the spirolactonization.27

The reaction of the δ,ε-unsaturated aldehyde 13 with cat. Cp2VCl2/Me3SiCl/Zn is conducted in THF to afford the cyclic alcohol 14 with excellent diastereoselectivity (eq 9).28 The result seems to be due to the 5-exo-cyclization of the radical anion intermediate, followed by chlorination.

Catalytic cyclodimerization of the arylidene malononitriles 15 proceeds diastereoselectively in the presence of Me3SiCl as shown in eq 10.29

This method is applied to the Cp2TiCl2-catalyzed reductive radical cyclization of the ketonitriles 16, giving the 2-amino-3-cyano-2-cyclopenten-1-ols in moderate to good yields with high trans selectivity (up to 94% trans, eq 11).29
Olefinic iodoethers 17 similarly undergo the Cp₂TiCl₂-catalyzed reductive cyclization in the presence of Mn and Me₃SiCl (eq 12).3° This protocol provides a versatile method for the selective formation of multi-substituted tetrahydrofurans 18.

Although a stoichiometric amount of a low-valent titanium reagent is required, acylsilanes 19 react with ketones to give the reductive acylated compounds 20 as shown in eq 13.31

A combination of Zn and Zn(II) species can activate the reductive transformation. Cross-coupling of alkyl acrylates and arylaldehydes occurs on treatment with metallic zinc and zinc(II) iodide in DMF, giving dialkyl α-aroyladipates 21 (eq 14).32

3. Oxovanadium(V)-induced oxidative transformations of main-group organometallics

Vanadium compounds in a high oxidation state are capable of inducing oxidative transformations. Pentavalent vanadium compounds are generally considered to be one-electron oxidants which utilize the V(V)–V(IV) couple. The redox potential of this couple increases with acidity, so the reactions are usually carried out in acidic aqueous media.

A variety of oxidative transformations with vanadium oxidants have been developed in an organic solvent,2a as exemplified by the oxidative coupling of phenols or naphthols.33 The scope of synthetic reactions can be broadened even further by exploiting the versatility of vanadium compounds as an oxidant.34 VO(OR)X₂ can act as a Lewis acid towards carbonyl compounds, which permits versatile oxidative transformations. Scheme 5 summarizes its synthetic utility: dehydrogenative aromatization, allylic oxidation, ring-opening oxygenation, oxidative decarboxylation, and ring-opening oxidation and so on.35,36

Oxidation of main-group organometallic compounds with a metallic oxidant is considered to proceed via redox interaction between them, affording the corresponding radical species (Scheme 6). Another reaction path lies in the interaction between different metallics to result in transmetalation. Such an oxidative transformation induced by oxovanadium(V) compounds is described here.

Scheme 6
3.1 Oxidative transformation of organosilicon compounds

Silyl enol ethers are susceptible to one-electron oxidation.\textsuperscript{37} VO(OR)Cl\textsubscript{2} is capable of inducing chemoselective homo- or cross-coupling of silyl enol ethers 22 to give the corresponding 1,4-diketones 28 via regioselective carbon–carbon bond formation (Scheme 7).\textsuperscript{39,40} The radical cation 23, obtained by one-electron oxidation, is desilylated to the radical 24. The radical 24 adds intermolecularly to another silyl enol ether 25 to form the adduct 26, which is further oxidized by the oxovanadium(V) species to form the cation 27. Finally, this cation undergoes desilylation to yield the 1,4-diketone 28. The one-electron oxidation process depends on the redox potentials of the substrates and oxovanadium(V) compounds. The more readily oxidizable silyl enol ethers work as radical precursors and the less oxidizable ones are radicophiles. The silyl ketene acetals 29 undergo more facile oxidation for the cross-coupling with the silyl enol ethers 25 to give the \( \gamma \)-keto esters 30 (eq (15)).

Scheme 7

\[
\begin{align*}
\text{R'OSiMe}_3 + \text{R}^2 & \rightarrow \text{R}^1\text{O}-\text{SiMe}_3 + \text{R}^2 \\
\text{R'OSiMe}_3 + \text{R}^3 & \rightarrow \text{R}^1\text{O}-\text{SiMe}_3 + \text{R}^3 \\
\text{R'O} + \text{R}^2 & \rightarrow \text{R}^1\text{O}-\text{SiMe}_3 + \text{R}^2
\end{align*}
\]

This method is applied to the chemoselective oxovanadium(V)-induced cross-coupling reaction of silyl enol ethers and allylic silanes (Scheme 8).\textsuperscript{41}

Similar chemoselective oxidative desilylation is also observed with benzylic silanes. The electron-donating group on the arene ring lowers the ionization potential of the benzylsilane 31, thus activating it for desilylation. The intermolecular regioselective coupling of the substituted benzyl silane occurs with an allylic silane or silyl enol ether (eq (16)).

\[
\begin{align*}
\text{MeO}-\text{CH}_2\text{SiMe}_3 + \text{VO(OR)Cl}_2 & \rightarrow \text{MeO}-\text{CH}_2\text{CHO} \\
\text{31a} & \rightarrow \text{33} \quad \text{R} = \text{H}
\end{align*}
\]

The reaction of 4-methoxybenzyltrimethylsilane (31a) with VO(OR)Cl\textsubscript{2} is carried out in \( t \)-BuOH under oxygen atmosphere to give the benzaldehyde (eq 17).\textsuperscript{43} VO(OCH\textsubscript{2}CF\textsubscript{3})-Cl\textsubscript{2} exhibits higher reactivity than VO(OEt)Cl\textsubscript{2}.

\[
\begin{align*}
\text{31a} & \rightarrow \text{33} \quad \text{R} = \text{H}
\end{align*}
\]

The redox potentials of organosilicon compounds, which are predicted from MOPAC calculated ionization potentials, determine whether they act as radical precursors or acceptors. The oxovanadium(V) reagent, which differentiates the oxidation process effectively, is a versatile oxidant to promote the chemoselective coupling via oxidative desilylation of organosilicon compounds under controlled conditions. The reactivity order is as follows: VO(OR)Cl\textsubscript{2}-AgOTf or Me\textsubscript{3}SiOTf > VO(OR)Cl\textsubscript{2} > VO(OR)Cl > VO(OR)\textsubscript{3}.\textsuperscript{35} Thus, the oxidation of organosilicon compounds provides a useful route to synthetic equivalents for cationic intermediates for the selective carbon–carbon bond formation.

3.2 Oxidative transformation of organotin compounds

Allylic and benzylic tins are known to undergo more facile oxidation than the corresponding silicon compounds,\textsuperscript{44} and are converted to the alcohols or their derivatives by a metallic oxidant such as Mn(IV), Ce(IV), Tl(III), or Fe(III).\textsuperscript{45} The oxidation of benzyltributyltins 32 with VO(OCH\textsubscript{2}CF\textsubscript{3})-Cl\textsubscript{2} in \( t \)-BuOH under oxygen atmosphere leads to the aldehydes (ketones) 33 and the corresponding carboxylic acids 34 (eq. (18)).\textsuperscript{43,46} The susceptibility to the oxidation depends on the substituent on the arene ring of 32. VO(OR)-Cl\textsubscript{2} and VO(OCH\textsubscript{2}CF\textsubscript{3})Cl\textsubscript{2} are superior to a weaker oxidant such as VO(acac\textsubscript{2}, VO(OPr-\text{t})\textsubscript{2}, or VO(OEt\textsubscript{2}). Furthermore, the catalytic reaction proceeds with VO(OCH\textsubscript{2}CF\textsubscript{3})Cl\textsubscript{2}.

\[
\begin{align*}
\text{32} & \rightarrow \text{33} \quad \text{R} = \text{H}
\end{align*}
\]
1-Cyclopropyl-1-phenylmethyltributyltin (32a) is oxidized to the cyclopropyl ketone 33a as a major product (eq 19). As for ring-opened compounds, neither the aldehyde nor the carboxylic acid is detected, although only a small amount of the chloride 35a is obtained.

Plausible reaction paths are illustrated in Scheme 9. In the case of benzylsilanes, electron-transfer mechanism is considered to operate as mentioned above. Although benzyltin compounds undergo more facile oxidation rather than benzylsilanes, an electron-transfer process may not be favorable judging from the reactivities of the cyclopropylmethyltin 32a. Either an electron-transfer process or homolytic scission of the carbon–vanadium bond of a benzylvanadium species is suggested to be a minor pathway, and the ketone 33a may be derived by transmetallation with a non-radical process. A low-valent vanadium species generated in situ is oxidized under oxygen atmosphere to regenerate a vanadium species in its high oxidation state for catalytic reaction.46

3.3 Oxidative transformation of organoaluminum compounds

The redox processes of organometallics are important in synthetic transformations, especially in transition-metal-induced reactions. The transition-metal-catalyzed cross-coupling reactions of main-group organometallic compounds with organic halides provide versatile synthetic tools in organic synthesis. As mentioned above, the transmetallation and/or electronic interaction can widen the reactivities of main-group organometallic compounds. One-electron oxidation of d°-transition metal complexes such as titanocene, zirconocene, and platinum complex with a metallic oxidant permits synthetically useful transformations via organometallic radical cation species as key intermediates.47 In these reactions, selective coupling is achieved between two ligands on the transition metal, providing a useful method for carbon–carbon bond formation.

The oxidation of the aryldiethylaluminums 36, obtained from aryllithiums and diethylaluminum chloride, with VO(OEt)Cl₂ results in novel ethylation (Scheme 10).49 This method can be applied to a wide variety of arylaluminums bearing an electron-donating group, which permits the selective ligand coupling of the organic groups on aluminum.

The addition of 1-alkynyllithium to the 1-alkenylaluminum 37, followed by treatment with VO(OEt)Cl₂, leads to the coupling of organic substituents on aluminum, giving the corresponding trans-ene 38 via chemoselective and stereoselective bond formation between sp and sp² carbons (Scheme 11).50

Although the reaction mechanism is ambiguous, coordination of the o xo atom of the oxovanadium(V) species to
organoa luminums is considered to promote electron transfer or transmetallation for the oxidative coupling. The transformation is evaluated to be the first formal reductive elimination on aluminum.\textsuperscript{51}

### 3.4 Oxidative transformation of organoboron compounds

The organoboron compound 41, derived from dicyclohexylborane and phenylacetylene or acetylenecarboxylic ester, is oxidized with VO(OEt)Cl\textsubscript{2} to give the (E)-ethenylcyclohexane 42 selectively without the formation of b(cyclohexyl) and 1,4-butadiene derivative (eq 20).\textsuperscript{52}

\[ R - B - C - H \xrightarrow{VO(OEt)Cl_2, CH_2Cl_2} \text{42} \]

When an equimolar mixture of bis(2-methylcyclohexyl)-[(E)-2-(4-methylphenylethenyl)]borane (41a) and dicyclohexyl[(E)-2-(4-methylphenylethenyl)]borane (41b) is treated with VO(OEt)Cl\textsubscript{2}, 1-methyl-2-(2-phenylethenyl)cyclohexane (42a) and [2-(4-methylphenylethenyl)cyclohexane (42b) are predominantly produced, with only trace amounts of the crossover products (eq 21). The finding suggests that the coupling reaction proceeds mostly in an intramolecular way.

\[ \text{41a} + \text{41b} \xrightarrow{VO(OEt)Cl_2, CH_2Cl_2} \text{42a} : \text{42b} = 32:63:3:2 \]

The ate complexes 43 of the organoborons undergo more facile oxidation with VO(OEt)Cl\textsubscript{2}, as observed in the oxidation of the aluminum ate complexes. The organic groups are effectively differentiated in the coupling reaction. Although the Z isomer is obtained in a small amount, use of the organoborate derived from CsF\textsuperscript{53} improves the stereoselectivity, giving the E isomer exclusively (Scheme 13).

Alkenyltrialkylborates have been reported to be oxidized to alkylated alkenes with 12 or BrCN.\textsuperscript{54} Biaryl formation also occurs by electrochemical, photochemical, and chemical oxidation, for example with Ir(IV), of tetraarylboration.\textsuperscript{55} The oxovanadium(V)-induced ligand coupling provides another effective method for the carbon-carbon bond formation on boron.

### 3.5 Oxidative transformation of organozinc compounds

Organozinc compounds can tolerate a broad range of functional groups. Cross-coupling reactions between organozinc reagents and electrophiles such as organic halides are catalyzed by transition metal complexes.\textsuperscript{56} However, examples for the selective cross-coupling of two ligands of organozinc compounds are limited to a few cases, which include 1,2-migration of zincate carbonyls and intramolecular coupling of organozinc compounds by organocopper reagents.\textsuperscript{57}

The organozinc compound 44a, which is prepared in situ by transmetallation of the methylzinc chloride with the aryllithium, is oxidized with Cp\textsubscript{2}FePF\textsubscript{6}, to give the homo-coupling compound 46a selectively (Scheme 14). AgBF\textsubscript{4} serves as a useful oxidant to give the desired cross-coupling compound 45a, probably via a one-electron oxidation process. Using VO(OEt)Cl\textsubscript{2} instead of AgBF\textsubscript{4}, the cross-coupling reaction proceeds in preference to the homo-coupling reaction.\textsuperscript{58}

Higher selectivity for the cross-coupling is observed with VO(OEt)Cl\textsubscript{2} than with VO(OPr-i)Cl\textsubscript{2} or VO(OPr-i)\textsubscript{2}Cl.

The coupling reaction of organozinc compounds 44 bearing an o-methoxy, o-phenyl, or o-methylthio group on the arene ring proceeds smoothly, but the o-cyano-substituted alkylarylzinc exhibits a lower reactivity, although organoaluminum compounds having an electron-withdrawing substituent do not undergo oxidative coupling under similar conditions. Alkyl and 1-alkynyl groups can couple with the aryl group successfully (Scheme 15).

Triorganozincates 47 are readily oxidized with VO(OEt)Cl\textsubscript{2} smoothly to give the cross-coupling compounds 45 (Scheme 16).\textsuperscript{58}

To avoid homo-coupling reactions of aryllithium compounds with oxovanadium(V) compounds,\textsuperscript{59} arylzincates from R\textsubscript{2}ZnLi\textsuperscript{60} and aryl iodides through iodine–zinc exchange are used. Oxidation of the thus-obtained zincate complexes...
47 results in the exclusive formation of the cross-coupling product 45 as shown in Scheme 17.

The organozincates 48, obtained from various bromoarenes and Me₄ZnLi₂, are similarly oxidized with VO(OEt)Cl₂ to give the methylarene 45a (Scheme 18). Thus, the coupling between sp²-carbon (aryl group) and sp³-carbon (methyl group) of arytrimethylzincates is achieved chemoselectively.

The oxovanadium(V)-induced oxidative transformation is applied to the selective carbon-carbon bond formation between sp³-carbons. A bromine-zinc exchange reaction of 49 selectively occurs at the position cis to the phenyl group by treatment with Me₄ZnLi₂. The oxidation of the thus-obtained zincate 50 with VO(OEt)Cl₂ leads to the stereoselective formation of 1-bromo-1-methyl-2-phenylcyclopropane (51). On the other hand, when the reaction mixture is warmed up to 0°C, followed by treatment of VO(OEt)Cl₂, dimethylation takes place to give the dimethylcyclopropane 53 via the organozinc 52 (Scheme 19).

Dialkylzinc reagent (R₂Zn) is recognized as a mild nucleophile in the presence of an additional promoter such as a Lewis acid. Characteristics of oxovanadium(V) compounds as a Lewis acid and one-electron oxidant permit vicinal dialkylation at both the α and β positions of α,β-unsaturat-
References by the members in our laboratory, whose names are cited in Acknowledgment. The work in this review was mostly done useful to generate radical intermediates (Scheme 1). Attain-
and main-group organometallics.

are effectively controlled by the substituent of oxovanadi-
various main-group organometallic compounds based on
with oxidation ability to induce the oxidation reactions of
catalyst from the reaction adduct. 

Additives, which are considered to contribute to the redox
cycle, possibly facilitate the electron transfer and liberate the
catalyst from the reaction adduct.

Oxovanadium(V) compounds are potential Lewis acids with oxidation ability to induce the oxidation reactions of various main–group organometallic compounds based on their characteristics. Oxidation capability and redox potential are effectively controlled by the substituent of oxovanadi-
(V) compounds. The oxidative ligand coupling proceeds via the intermetallic interaction between vanadium species and main–group organometallics.

Both synthetic methods are expected to be promising in synthetic chemistry. These methods are complementary and useful to generate radical intermediates (Scheme 1). Attainment of higher stereoselectivity is expected to be one of the coming goals in this field. Redox of vanadium compounds is also useful in the design of materials.

Acknowledgment The work in this review was mostly done by the members in our laboratory, whose names are cited in the references.

4. Conclusion and Outlook

The multi-component system consisting of a catalyst, a co–reductant, and an additive cooperates with each other to construct the catalytic systems for efficient one–electron reduction. In this system, the active catalyst is smoothly regenerated by redox interaction with the co–reductant. The selection of the co–reductant is, of course, important from this point of view. Furthermore, the oxidized form of the co–reductant should not interfere with, but assist the reduction reaction or at least, be tolerant under the conditions. Additives, which are considered to contribute to the redox

acked the catalytic systems for efficient one-electron
co-reductant, and an additive cooperates with each other to

Scheme 22

22) Svatos, A.; Boland, W. Synlett 1998, 549.


PROFILE

Toshikazu Hirao is a Professor of Osaka University. He graduated from Kyoto University in 1973, where he obtained his doctorate in 1978. He became Assistant Professor at Osaka University and was a postdoctoral fellow at the University of Wisconsin with Professor B. M. Trost (1981–1982). Dr. Hirao was promoted to Associate Professor in 1992 and Professor in 1994. He has been involved in development of synthetic methodology and received the Chemical Society of Japan Award for Young Chemists. His current research interests lie in the area of the construction of efficient systems for electron transfer, which allows the development of new methods in organic synthesis, and novel redox-active systems consisting of transition metals and/or π-conjugated compounds. These researches are correlated to the development of artificial bioconjugate systems.