CHEMICAL REVIEWS

Volume 97, Number 8 December 1997

Vanadium in Modern Organic Synthesis

Toshikazu Hirao

Department of Applied Chemistry, Faculty of Engineering, Osaka University, Yamada-oka, Suita, Osaka 565, Japan

Received February 28, 1997 (Revised Manuscript Received August 25, 1997)

Contents

Toshikazu Hirao was born in Osaka, Japan, and graduated from Kyoto University in 1973, where he also obtained his doctorate in 1978. He became an Assistant Professor at Osaka University and was a postdoctoral fellow at the University of Wisconsin with Professor Barry M. Trost (1981–1982). Dr. Hirao was promoted to Associate Professor in 1992 and to Professor in 1994. He has been involved in the development of synthetic methodologies and received the Chemical Society of Japan's Award for Young Chemists in 1984. Dr. Hirao's current research interests lie in the area of constructing efficient electron transfer systems, which will allow the development of novel, redox-active supramolecules based on organometallic and conjugated polymer complexes. He is also interested in developing new synthetic methods which involve radical reactions. These pursuits are intended to ultimately lead to the development of artificial biochemical systems.

I. Introduction

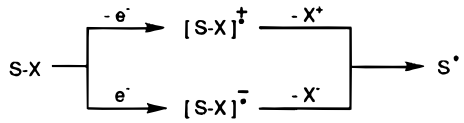
Transition metal complexes induce oxidative and reductive transformations, depending on their oxidation state. When these redox processes are efficient, they lead to a variety of novel and selective organic reactions. Since the electronic interaction between transition metals and their ligands contributes to controlling the redox process, ligand design is important in attaining their efficiency. A great deal of progress has been made in designing organometallic complexes to facilitate organic syntheses via redox processes.

High oxidation state transition metals and their oxides are able to induce oxidative transformations. Furthermore, metal peroxides, which are obtained from the reaction of metal oxides (Cr, Mo, Nb, Ta, Ti, W, Zr, etc.) with hydrogen peroxide or alkyl peroxides, serve as useful oxidants. High stereoselectivities and stereospecificities, comparable to those obtained with organic oxidants, have been achieved by using these reagents.

Transition metal complexes can generate radicals by a one-electron oxidation involving either inner- or outer-sphere electron transfer. This reaction proceeds through an intermediate radical cation as shown in Scheme 1. Likewise, radicals can be generated by a one-electron reduction, which involves the formation of a radical anion. The complementary nature of these processes could be profitably exploited

S0009-2665(96)00014-3 CCC: $28.00

Scheme 1



for organic synthesis, but little work has been done in this area. This is unfortunate, since careful regulation of the electron-transfer process should allow the selective generation of radicals under redox potential control. There is an increasing demand for reduction reactions involving low-valent transition metals, and this has led to investigations into the redox chemistry of species such as chromium(II), titanium(II), and samarium(II). Our focus in this review is on reactions involving the related metal, vanadium.

Vanadium is a biologically essential element. Its inclusion in enzymes such as bromoperoxidase[1] and nitrogenase[2] reveals the importance of its redox chemistry. A number of model complex systems have been investigated in order to elucidate vanadium's redox mechanisms.[3] Some tunicates, marine sea squirts, selectively accumulate vanadium ions from the ocean.[4] This vanadium is incorporated into tunichromes, a class of reducing blood pigments, which have been isolated and characterized. The metabolism, physiological role, and pharmacological effects of biologically active vanadium compounds have been reviewed.[5]

Vanadium complexes, including organovanadium compounds, exist in a variety of configurations depending on their oxidation state and coordination number.[6] Vanadium can exist in oxidation states ranging from −3 to +5 and generally converts between states via one-electron redox processes. This versatility permits the development of a wide range of organic reactions by controlling the vanadium compound's redox potential. While this control can be achieved by carefully selecting the substituents or ligands on the vanadium compound and solvent, the actual potential is usually measured in aqueous solution. In general, however, more positive potentials are obtained through electron-withdrawing interactions with the vanadium while electron-donating interactions lead to more negative potentials.

Vanadium compounds in high oxidation states can induce oxidative transformations. Pentavalent vanadium compounds, which exist in one of five possible configurations (e.g., $VOCl_3$, tetrahedral; VF_5, octahedral), 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. One-electron oxidation is also possible with the V(IV)−V(III) couple (E_0, 0.38 V), but the V(V)−V(III) couple (E_0, 0.68 V) is less useful for organic oxidation.

A variety of oxidative synthetic reactions which utilize vanadium oxidants have been developed as exemplified by the oxidative coupling of phenols. The scope of useful synthetic reactions can be broadened even further by exploiting the versatility of vanadium compound as an oxidant. For example, VOX_3 has been observed to act as a Lewis acid and interact with carbonyl or organosilicon compounds.

The oxo functionality of oxovanadium compounds participates in a number of unique oxo-transfer reactions. Vanadium peroxides can cause either oxygenation or epoxidation, both of which have been extensively studied. Vanadium compounds can also activate molecular oxygen for oxygenation reactions, which further increases vanadium's synthetic utility.

The redox process of V(II) to V(III) is known to induce one-electron reduction reactions, which has led to various synthetic methods. For example, vanadium(II) is a useful reductant which mediates carbon−carbon bond formation and reduction. Vanadium(I) species also can serve as similar reductants.

Organovanadium compounds also possess the abovementioned, oxidation state-dependent redox properties. Although the synthetic utility of these organometallic reactions has not been thoroughly investigated, they are expected to prove highly profitable.

To construct efficient redox systems for organic synthesis, the redox potential of the vanadium complexes must be controlled precisely in organic solvents. Furthermore, the redox cycles must be made to be reversible and catalytic. Thus far, only a few catalytic homogeneous processes have been reported, although many heterogeneous catalytic systems have been developed for industrial processes. This review primarily surveys redox reactions with synthetic potential which utilize homogeneous vanadium compounds either stoichiometrically or catalytically.

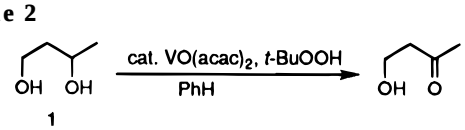
II. Oxidation

A. Dehydrogenation

The synthetic utility of vanadium(V)-induced dehydrogenation of alcohols has been limited because of competitive α-carbon−α-hydrogen and α-carbon−*β*-carbon bond cleavage in the vanadium(V) alkoxide intermediates. The preferred bond cleavage is dictated by the redox potential of the vanadium oxidant and the stability of the radicals formed by one-electron oxidation. For example, 2-phenylethanol and 2,2-dimethyl-1-phenylpropanol exclusively undergo oxidative carbon−carbon bond cleavage with ammonium metavanadate(V) to give benzaldehyde.[7]

Furthermore, a mixture of $VO(acac)_2$ and *tert*-butyl hydroperoxide (TBHP) is effective for the chemoselective, catalytic dehydrogenation of acyclic and cyclic secondary alcohols to the corresponding ketones, as exemplified by the selective oxidation of **1** (Scheme 2).[8]

Scheme 2



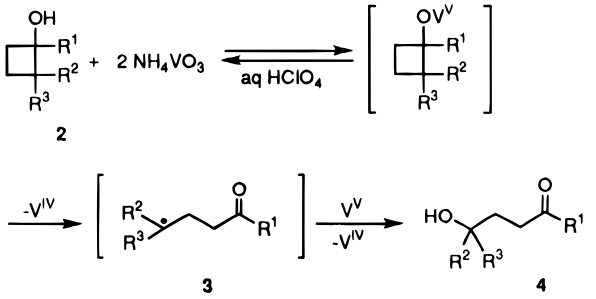
1

$VO(OPr\text{-}i)_3$ similarly catalyzes the oxidation of 2-propanol with hydrogen peroxide, leading to acetone.[9] A vanadium(V) peroxo complex has been shown to act as the key oxidant without any change in the charge on the metal.

A different vanadium(V) species in aqueous perchloric acid regioselectively oxidizes cyclobutanols (**2**) to the 4-hydroxy carbonyl compounds **4** via the acyclic radicals **3**.[10] This reaction proceeds by an α-carbon−

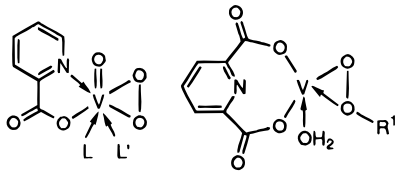
β-carbon bond cleavage, such that ring cleavage occurs between the more substituted carbon and the incipient carbonyl carbon. A similar ring-opening transformation is observed during the one-electron oxidation of cyclobutanols by Cr(IV)[11] or Ce(IV).[12] Conversely, two-electron oxidants leave the ring intact and form the corresponding cyclobutanones. Thus, whether α-carbon−α-hydrogen or α-carbon−β-carbon bond cleavage is obtained depends on the oxidants used (Scheme 3).

Scheme 3



B. Oxygenation

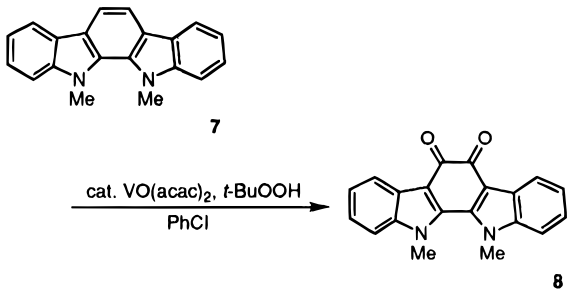
Oxovanadium peroxo complexes efficiently oxygenate organic compounds. One such oxovanadium(V) peroxo complex is **5**, $VO(O_2)(pic)LL'$ (pic = pyridine-2-carboxylate; L, L′ = H_2O or MeOH, either η^1 or η^2), which is generated from vanadium(V) oxide and hydrogen peroxide. Upon treatment with **5**, alkenes are nonstereoselectively oxidized to epoxides, allylic oxygenated products, and oxygenated cleavage products.[13] Likewise, benzene and toluene undergo hydroxylation at the ring carbons with a high NIH shift value. Alkanes are hydroxylated less readily and undergo a significant amount of epimerization and radical intermediate trapping with carbon tetrachloride. The oxovanadium(V) alkylperoxide **6**, (dipic)$VO(OOR^1)$ (dipic = 2,6-pyridinedicarboxylate, R^1 = *t*-Bu, CMe_2Ph), induces a similar oxidation in nonprotic solvents.[14] These oxidation reactions probably proceed through a vanadium-containing radical species.[15] A polymer-supported Schiff base oxovanadium(V) complex related to **5** is effective for the catalytic hydroxylation of benzene with hydrogen peroxide.[16]



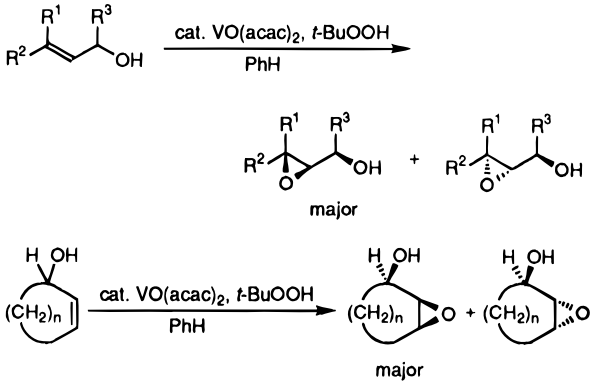
The indolocarbazole **7** is oxidized to the corresponding 9,10-dione **8** with *tert*-butyl hydroperoxide in the presence of a catalytic amount of $VO(acac)_2$ (Scheme 4).[17]

The $VO(acac)_2$-catalyzed epoxidation of allylic alcohols with alkyl hydroperoxide provides a useful route to epoxy alcohols.[18] Unfunctionalized alkenes react more slowly by this method, which allows the highly chemoselective monoepoxidation of olefinic alcohols like geraniol. Furthermore, $VO(acac)_2$, in combination with *tert*-butyl hydroperoxide, diastereoselectively epoxidizes allylic alcohols with a selectivity complementary to that obtained by using *m*-chloroperbenzoic acid (Scheme 5).[19] In this connection, catalytic, enantioselective epoxidation of allylic alcohols can be readily performed by a system consisting of titanium(IV) alkoxide and an optically active tartarate ester.[20]

Scheme 4

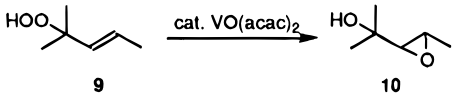


Scheme 5



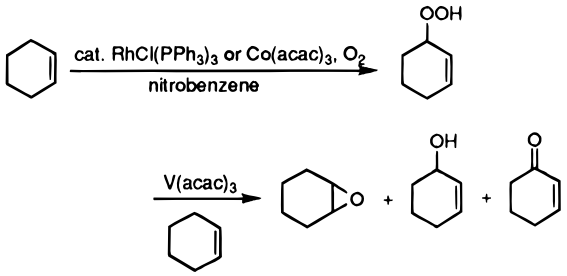
$VO(acac)_2$-catalyzed oxygenations also extend to the transformation of allylic hydroperoxide **9** into the epoxy alcohol **10** (Scheme 6).[21]

Scheme 6



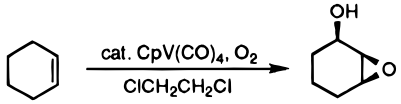
A bimetallic catalyst consisting of $V(acac)_3$ and $RhCl(PPh_3)_3$ or $Co(acac)_3$ induces the aerobic oxidation of cyclohexene to cyclohexene oxide, 2-cyclohexen-1-ol, and 2-cyclohexen-1-one, as shown in Scheme 7. An allylic hydroperoxide is formed initially, which then serves as an oxidant for intermolecular epoxidation.[22] A combination of $VO(acac)_2$ or $V(acac)_3$ and rhodium(II) carboxylates also catalyzes the oxidation of cyclohexene to 1,2-epoxycyclohexen-3-ol.[23]

Scheme 7



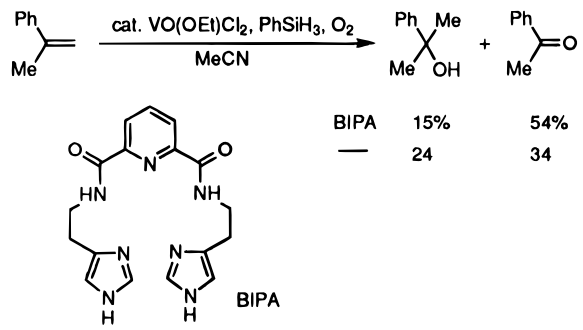
A $V(acac)_3$−AIBN system also aerobically oxidizes cyclic olefins to produce epoxy alcohols.[24] Likewise, low-valent vanadium catalyst, $CpV(CO)_4$, induces stereoselective, aerobic epoxidation of cyclohexene to form *cis*-1,2-epoxycyclohexan-3-ol (Scheme 8).[25]

Scheme 8



The $VO(OEt)Cl_2$-catalyzed reaction of styrenes with molecular oxygen in the presence of a coreductant such as $PhSiH_3$ results in both oxidation−reduction and oxidative bond cleavage of the styrene, as shown in Scheme 9.[26] Coordination of the *N*-heterocyclic

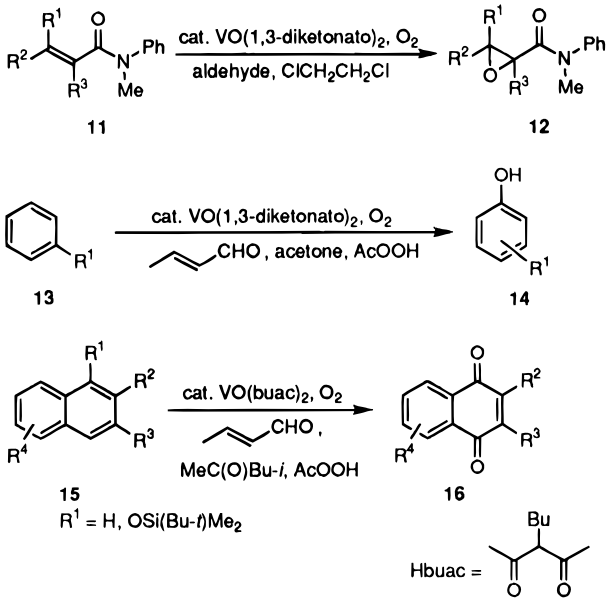
Scheme 9



multidentate ligand BIPA, which is the 2,6-pyridinedicarboxamide of histamine, increases the relative yield of the latter product.[26]

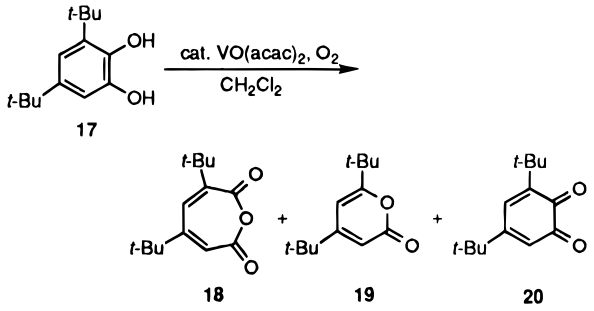
Oxovanadium(IV) complexes bearing 1,3-diketone ligands catalyze the aerobic oxygenation of α,β-unsaturated carboxamides **11** in the presence of a coreducing aldehyde to give 2,3-epoxycarboxamides **12**.[27] This catalytic system also directly oxygenates benzene derivatives **13** to phenols **14**.[28] Naphthalenes and naphthols **15** undergo further oxidation to 1,4-naphthoquinones **16** (Scheme 10).[29]

Scheme 10



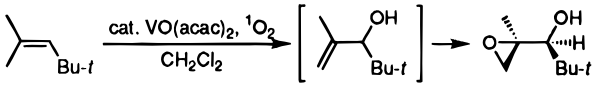
In the presence of a catalytic amount of $VO(acac)_2$, 3,5-di-*tert*-butylpyrocatechol (**17**) is aerobically oxidized to the muconic acid anhydride **18**, the 2-pyrone **19**, and the *o*-quinone **20** (Scheme 11).[30]

Scheme 11



Finally, $VO(acac)_2$ catalyzes the photooxygenation of olefins to yield a one-pot diastereoselective synthesis of epoxy alcohols, as shown in Scheme 12.[31]

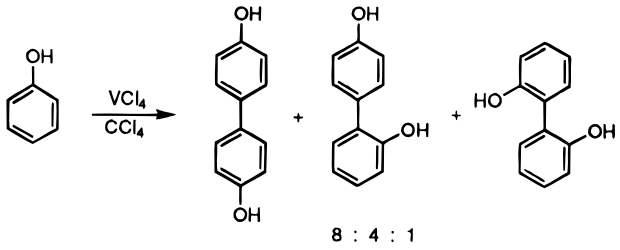
Scheme 12



C. Oxidative Coupling

The coupling of phenol derivatives via one-electron oxidation constitutes a useful synthetic method for regioselectively forming carbon−carbon bonds between aromatic compounds. High-valent vanadium complexes are known to be effective oxidants for this transformation. Thus, vanadium tetrachloride and vanadyl trichloride oxidatively couple phenols to afford the corresponding biphenols (Scheme 13),[32]

Scheme 13

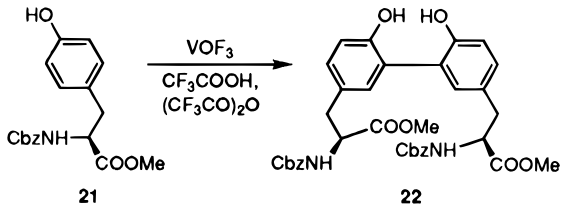


although vanadyl trichloride is less reactive than vanadium tetrachloride.[33] This method has potential for being synthetically useful in the coupling of naphthols and aniline derivatives. The phenolic oxidative coupling can also occur intramolecularly, as exemplified by the cyclization of benzyltetrahydroisoquinolines. For example, *cis*-3,*N*-bis(methoxycarbonyl)-*N*-norreticuline is converted to the corresponding isoboldine analogue by this method.[34]

Vanadyl trifluoride is an effective coupling agent for reactions which are carried out in trifluroacetic acid.[35] Thus, while vanadyl trichloride oxidizes Cbz-protected tyrosine **21** to the dityrosine derivative **22**, the use of vanadyl trifluoride doubles the yield of the desired *ortho*−*ortho* coupled product (Scheme 14).[36]

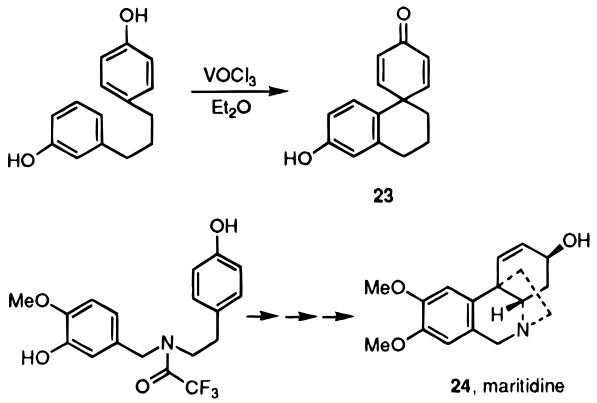
Vanadium-induced oxidative carbon−carbon bond formation can even occur at substituted aromatic sp^2 carbons, yielding, for example, the intramolecular *para*-*para* coupling product **23**. This cyclization

Scheme 14



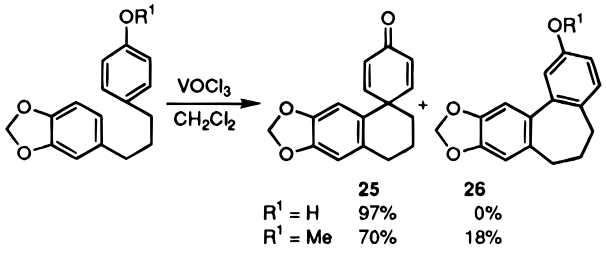
reaction is employed as a key step in the total synthesis of naturally occurring compounds[37] such as (±)-maritidine (**24**) (Scheme 15).[38]

Scheme 15



Application of the phenolic oxidative coupling reaction to an analogous methoxy substrate yields the dienone **25** and a rearranged product **26**.[39] The dienone is formed via cleavage of the alkyl-oxygen bond, while the alkoxy substituent remains intact in the rearranged product. Both products are believed to arise through successive one-electron oxidations (Scheme 16).

Scheme 16

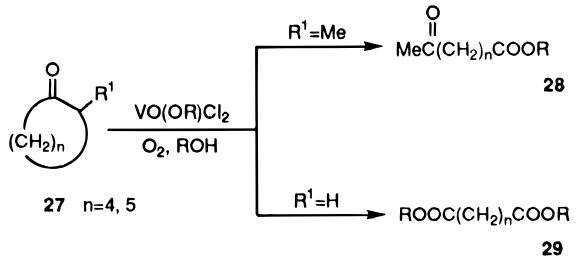


D. Oxidation of Carbonyl Compounds

Carbonyl compounds bearing α-hydrogens undergo facile oxidation with pentavalent vanadyl ions in acidic media. However, it is difficult to control the oxidation reaction, due to the susceptibility of the initial product to further oxidation. The ability of pentavalent vanadium compounds to oxidize a variety of carbonyl compounds has been surveyed.[40] The first step in these reactions involves the coordination of a Lewis acidic vanadium ion to the carbonyl. Therefore, this coordination must be taken into account in developing versatile oxidation methods. For example, oxovanadium(V) compounds of the type $VO(OR)X_2$ are Lewis acids which are capable of performing one-electron oxidations and thus are useful in oxidatively transforming carbonyl compounds.

Cyclic ketones **27** undergo ring-opening catalytic oxygenation in the presence of an alkanol and molecular oxygen to give a keto ester **28** or diester **29**, depending on the α-substituent (Scheme 17).[41] Oxy-

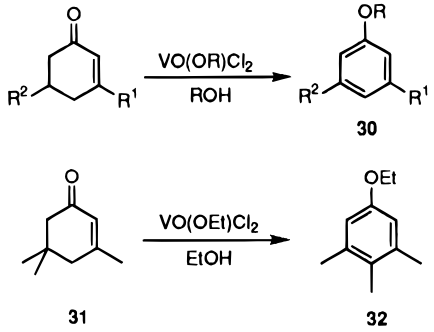
Scheme 17



genation accompanies the introduction of an alkoxy group, and the bond between the more substituted α-carbon and the carbonyl carbon is cleaved regioselectively. This controlled oxygenation reaction takes place under milder conditions than conventional methods.[42] Despite their lower reactivities, $VO(OR)_3$ and $VO(acac)_2$ also can be employed as oxidants, although a stoichiometric amount is required in each case.

α,β-Unsaturated ketones show different reactivities. 2-Cyclohexen-1-ones undergo dehydrogenative aromatization to yield the aryl alkyl ethers **30**.[43] More than 2 equiv of $VO(OR)Cl_2$ are needed to complete the reaction, since the oxovanadium compound is a one-electron oxidant. Surprisingly, isophorone (**31**) is also oxidatively aromatized to the aryl ether **32** (Scheme 18).

Scheme 18

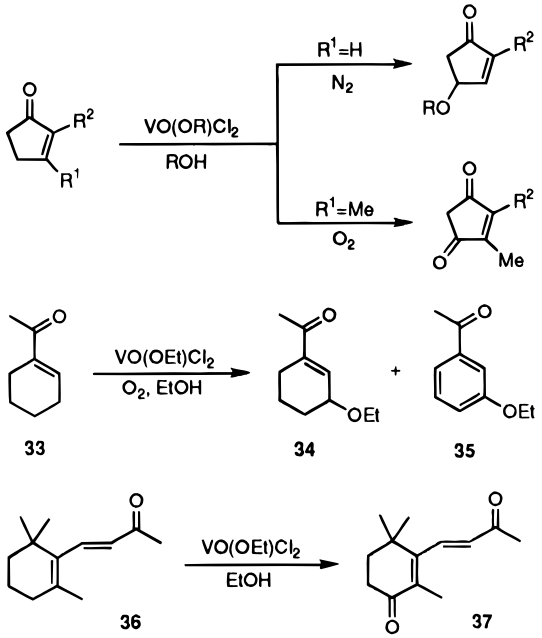


An oxovanadium species generated from $VO(OR)Cl_2$ and AgOTf or Me_3SiOTf induces the aromatization more effectively and under the milder conditions than $VO(OR)Cl_2$ alone.[44] This is probably due to the *in situ* generation of an oxovanadium triflate species. The following reactivity order, which is found for oxovanadium compounds, appears to be due to their different Lewis acidities:

$$VO(OR)Cl_2{-}AgOTf \text{ or } Me_3SiOTf > VO(OR)Cl_2 > VO(OR)_3 > VO(acac)_2$$

An oxo or alkoxy group is introduced at the allylic position of 2-cyclopentenones depending on their substitution pattern, as illustrated in Scheme 19.[45] Similarly, 1-acetyl-1-cyclohexene (**33**) undergoes allylic oxidation to yield 1-acetyl-3-ethoxy-1-cyclohexene (**34**) and 3-ethoxyacetophenone (**35**). The latter

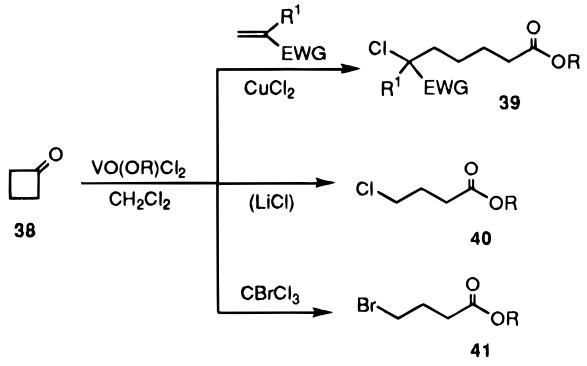
Scheme 19



transformation is accompanied by dehydrogenative aromatization. β-Ionone (**36**) also undergoes allylic oxygenation to form the dione **37**. A one-electron oxidation of the dienolate intermediate is assumed to be a key step in these reactions.

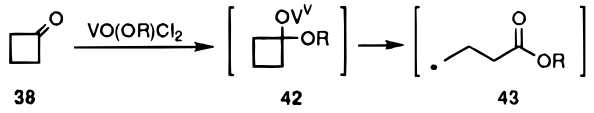
The oxidation of cyclobutanone (**38**) with more than 2 molar equiv of $VO(OEt)Cl_2$, in the presence of an olefin bearing an electron-withdrawing group, results in tandem oxidative ring opening and addition to the olefin to yield **39**.[46] This reaction is facilitated by the addition of $CuCl_2$ as a cocatalyst.[47] In the absence of an olefin, **38** undergoes chlorination to the alkyl 4-chlorobutyrate (**40**), while the addition of bromotrichloromethane leads to 4-bromobutyrate **41** (Scheme 20).

Scheme 20



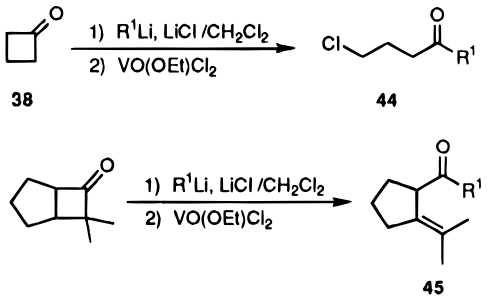
These reactions are believed to proceed through the radical intermediate **43**, which is generated by ring-opening and one-electron oxidation of the alkoxide adduct **42**. A similar mechanism has been reported to operate in the oxidative ring cleavage of cyclobutanols.[10] In accordance with frontier molecular orbital theory, carbon−carbon bond formation between **43** and an olefin is believed to result from the interaction of the half-filled orbital on the radical with the lowest unoccupied orbital on the olefin (Scheme 21).

Scheme 21



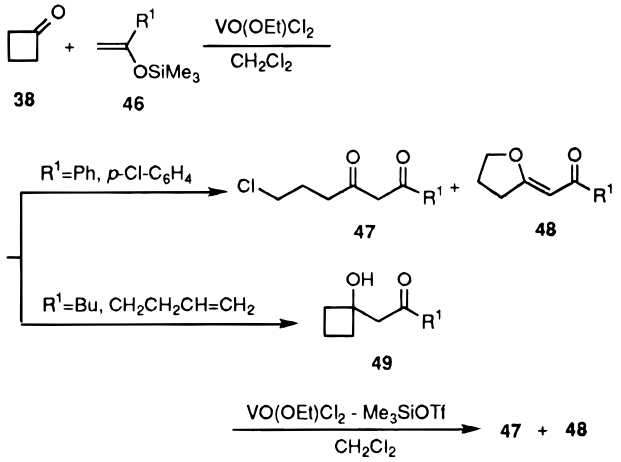
The treatment of cyclobutanones with an alkyllithium followed by $VO(OEt)Cl_2$ is thought to lead to alkoxide intermediates similar to **42**. In this case, the alkoxide intermediates undergo oxidative ring opening to the γ-chloro ketone **44** or the olefinic ketone **45**, depending on the cyclobutanone's substituents. An additional one-electron oxidation of the radical intermediate affords a cationic species, which is then deprotonated to form the olefin **45** (Scheme 22).

Scheme 22



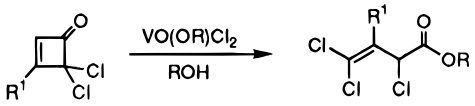
The silyl enol ether **46** is considered to be activated for nucleophilic addition to cyclobutanone by prior interaction with the Lewis acidic $VO(OR)Cl_2$. The addition is followed by ring-opening oxidation which leads to the 6-chloro-1,3-diketone **47** and 2-tetrahydrofurylidene ketone **48**.[48] Adding lithium chloride to the reaction facilitates the formation of **47**. Starting from an alkyl-substituted silyl enol ether, the addition alcohol **49** is formed. This product is not oxidized under the reaction conditions, but undergoes ring-opening oxidation when treated with $VO(OEt)Cl_2$ and Me_3SiOTf (Scheme 23).

Scheme 23



A similar oxidation of 2,2-dichloro-3-cyclobuten-1-ones (**50**) with $VO(OR)Cl_2$ results in the regioselective formation of alkyl 2,4,4-trichloro-3-butenoates (**51**) with chlorination at the α-position (Scheme 24).[49]

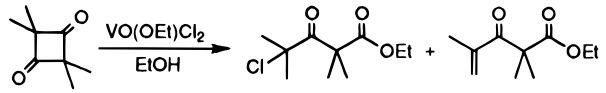
Scheme 24



50 51

1,1,3,3-Tetramethylcyclobutane-2,4-dione (**52**) undergoes $VO(OEt)Cl_2$-induced oxidative ring cleavage to 4-chloro-3-oxo-2,2,4-trimethylpentanoate (**53**) and 3-oxo-2,2,4-trimethyl-4-pentenoate (**54**) (Scheme 25).[50]

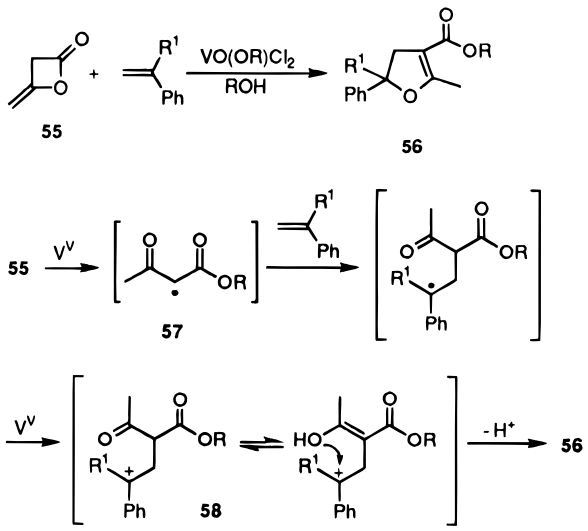
Scheme 25



52 53 54

The ring-opening cycloaddition of diketene (**55**) with styrenes, which produces the 4,5-dihydofurans **56**, is induced by $VO(OR)Cl_2$.[51] The interaction of **55** with the $VO(OR)Cl_2$ generates a radical intermediate **57**, which then adds to the olefin. This is followed by a one-electron oxidation to the cation **58**, which cyclizes to the dihydrofuran **56** (Scheme 26). A

Scheme 26

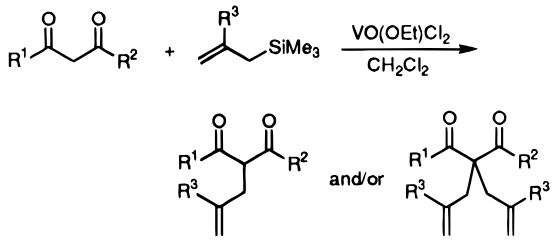


55 56 57 58

similar transformation has been reported in the metal-induced radical cyclization of ethyl acetoacetate.[52]

The oxidative mono- or di-allylation of 1,3-dicarbonyl compounds by allylic silanes proceeds upon treating them with $VO(OEt)Cl_2$ as shown in Scheme 27.[53] The 1,3-dicarbonyl compounds formally act as

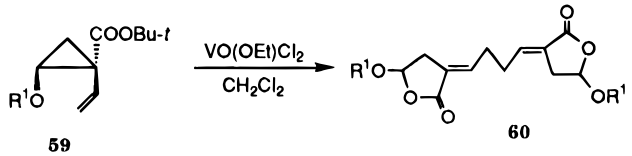
Scheme 27



electrophiles in this oxidative, carbon−carbon bond forming reaction.

When 2-alkoxycyclopropanecarboxylates **59** bearing donor and acceptor substituents are oxidized by using $VO(OEt)Cl_2$, they dimerize to form the α-ethylidenebutyrolactones **60** (Scheme 28).[54]

Scheme 28

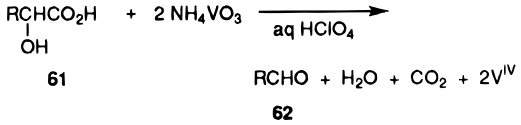


59 60

E. Oxidative Decarboxylation

Lactic, maleic, and mandelic acids **61** undergo oxidative decarboxylation with ammonium metavanadate(V) to give the corresponding aldehydes **62** (Scheme 29).[55] Likewise, D-galacturonic acid is oxi-

Scheme 29

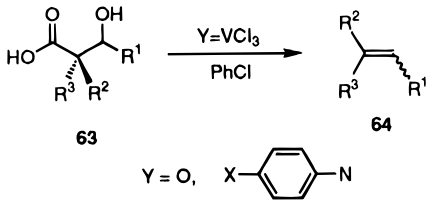


61 62

dized to formic acid by sodium metavanadate(V) in aqueous HCl solution.[56] The aerobic oxidation of *N*-(phosphonomethyl)iminodiacetic acid to *N*-(phosphonomethyl)glycine is catalyzed by vanadyl sulfate in a similar manner.[57]

Either vanadyl trichloride or trichloro(arylimino)vanadium(V) also can induce oxidative decarboxylation of the 3-hydroxy carboxylic acids **63** to give the olefins **64** (Scheme 30).[58] The stereospecificity of the

Scheme 30

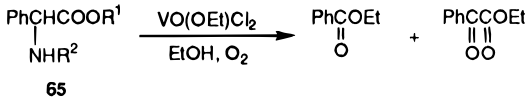


63 64

olefin formation depends on the electron-withdrawing ability of the groups attached to vanadium.

The oxidative decarboxylation of α-amino acids can be achieved by using $VO(OEt)Cl_2$, but not $VO(OEt)_3$.[59] Thus, the 2-phenylglycine **65** undergoes decarboxylation, dehydrogenation, and oxidative esterification to form ethyl benzoate as a major product in the presence of $VO(OEt)Cl_2$ (Scheme 31).

Scheme 31

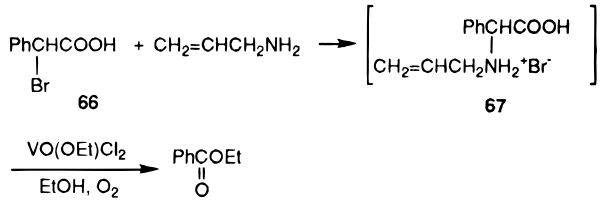


65

This method can also be applied to the oxidation of 2-bromo-2-phenylacetic acid (**66**), which proceeds

via the formation of the ammonium salt **67** of allylamine (Scheme 32).

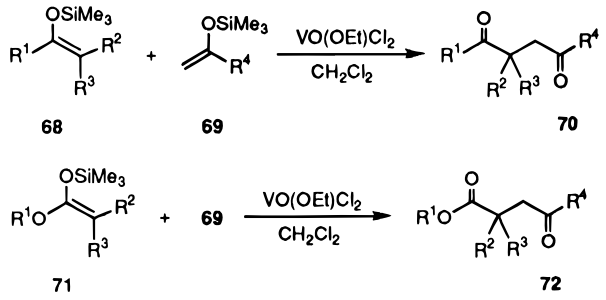
Scheme 32



F. Oxidative Desilylation

Silyl enol ethers are electron-rich olefins which are susceptible to oxidation, and one-electron oxidations have been performed on these species by metallic oxidants.[60] The chemoselectivity in the oxidative transformations can be controlled by the redox potentials of the reactants. $VO(OEt)Cl_2$ induces chemoselective homo- or cross-coupling of silyl enol ethers **68** with **69** to give the 1,4-diketones **70** via a regioselective carbon−carbon bond formation (Scheme 33).[61] The more highly substituted the silyl enol

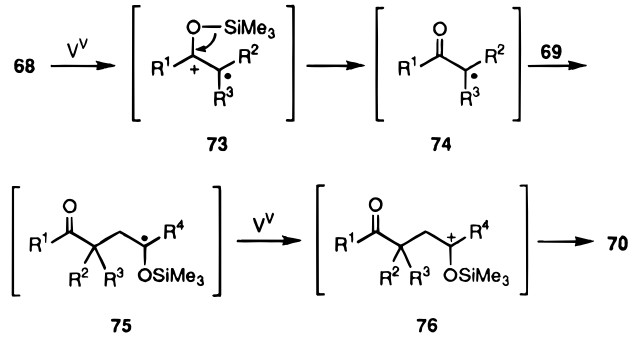
Scheme 33



ethers are, the more readily they are oxidized. The silyl ketene acetals **71** are also easily oxidized and exclusively undergo cross coupling with silyl enol ethers **69** to form the γ-keto esters **72**.

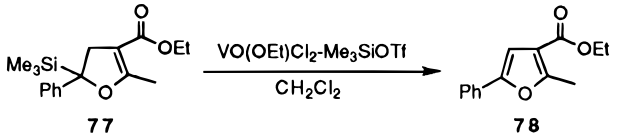
One-electron oxidation of the silyl enol ether **68** with an oxovanadium(V) species affords the radical cation **73**. This radical cation then is desilylated to the radical **74**. The radical **74** adds intermolecularly to another equivalent of the silyl enol ether **69** to form the adduct **75**, which is further oxidized by the oxovanadium(V) species to form the cation **76**. Finally, this cation undergoes desilylation to yield the 1,4-diketone **70** (Scheme 34).

Scheme 34



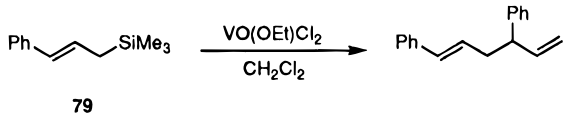
Oxidative carbon−silicon bond cleavage is similarly achieved through oxovanadium(V)-induced one-electron oxidation. As previously described (see Scheme 26), the dihydrofuran **77** is obtained from the $VO(OR)Cl_2$-induced cyclization of diketene with α-trimethylsilylstyrene. The carbon−silicon bond of this dihydrofuran can be oxidatively cleaved by using $VO(OEt)Cl_2-Me_3SiOTf$, to give the furan **78** in quantitative yield (Scheme 35).[62]

Scheme 35



Carbon−silicon bond cleavage has definite synthetic potential. For example, cinnamyltrimethylsilane (**79**) undergoes desilylative coupling either to itself (Scheme 36), or to less oxidizable allylic silanes.

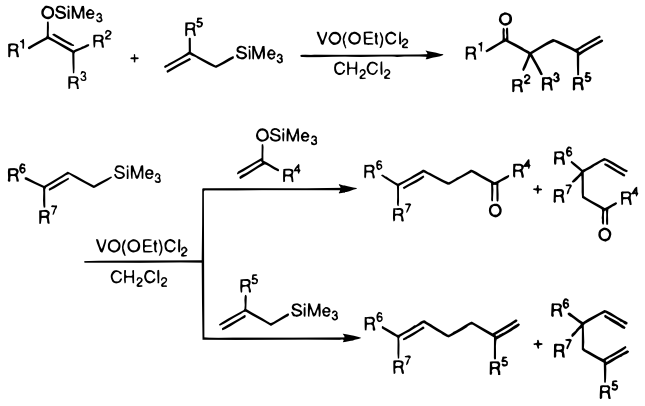
Scheme 36



The cross coupling reaction yields the corresponding 1,5-hexadienes as shown in Scheme 37.[62]

The cross coupling of silyl enol ethers and allylic silanes occurs chemoselectively to form γ,δ-unsaturated ketones. In these reactions, the oxovanadium(V) oxidatively desilylates the more readily oxidizable organosilicon compound.[63] The redox potentials of the silyl enol ethers and allylic silanes determine whether they will act as a radical generator or acceptor in this reaction. Fortunately, these redox potentials can be predicted from MOPAC calculated ionization potentials. $VO(OR)Cl_2$ is a versatile oxidant which can induce chemoselective coupling via the oxidative desilylation of a variety of organosilicon compounds under controlled conditions, as shown in Scheme 37.

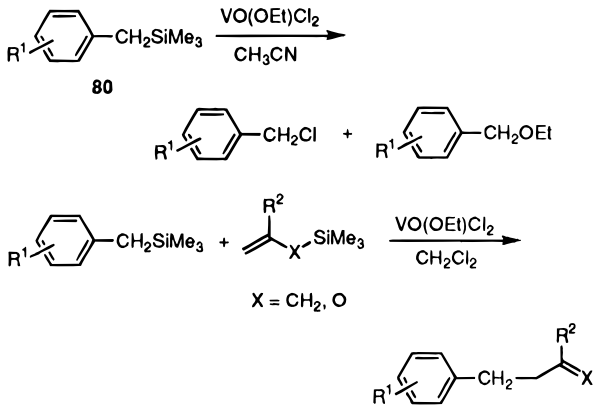
Scheme 37



Benzylic silanes **80** bearing an electron-donating group at the *ortho*- or *para*-position undergo a similar oxidative desilylation. The electron-donating group lowers the ionization potential of the unsubstituted

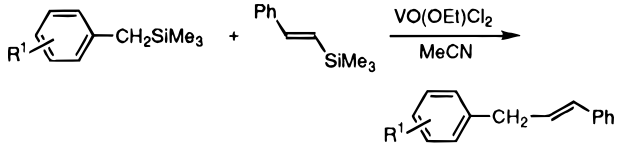
benzylsilane, thus activating it for desilylation. The desilylation reaction can be applied to intermolecular regioselective coupling between the substituted benzylic silane and an allylic silane or silyl enol ether (Scheme 38).[64]

Scheme 38



The β-stabilizing effect of the trimethylsilyl group is a key factor in controlling the regiochemistry of the carbon−carbon bond formation. Thus, benzyltrimethylsilanes react with β-trimethylsilylstyrene, but not with α-trimethylsilylstyrene (Scheme 39).

Scheme 39

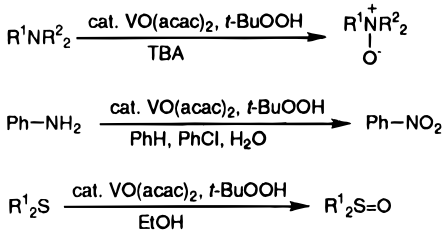


The oxidative desilylation reactions mentioned in this section provide a versatile method for intermolecular carbon−carbon bond formation, in which the organosilicon compounds formally act as electrophiles (umpolung).

G. Oxidation of Heteroatoms

Heteroatoms can be oxygenated by reacting them with *tert*-butyl hydroperoxide in the presence of VO(acac)$_2$ as a catalyst. In this manner, tertiary amines are oxidized to *N*-oxides, aniline to nitrobenzene, and sulfides to sulfoxides (Scheme 40).[65] Optically active

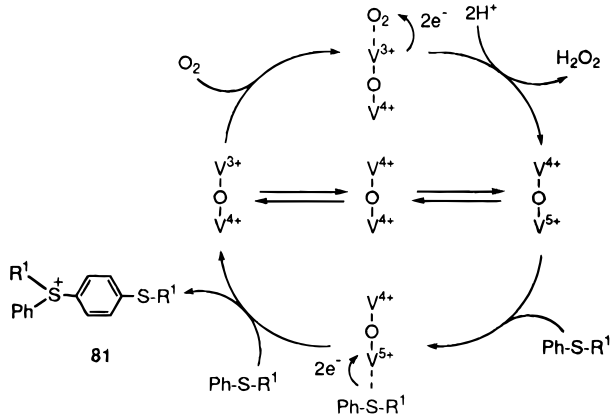
Scheme 40



oxovanadium(IV) and oxovanadium(V) Schiff base complexes catalyze the asymmetric oxidation of sulfides to the corresponding sulfoxides.[66] For example, a chiral methyl phenyl sulfoxide (ee 8−12%) is obtained when [VO(*N*-salicylidene-L-alaninate)(OMe)(MeOH)] is used as the catalyst.

A two-electron oxidation has been reported to occur in one step of the VO(acac)$_2$-catalyzed oxidative polymerization of diphenyl disulfide to polyphenylene sulfide. During this step, an aryl sulfide is oxidatively dimerized to the sulfonium **81**, and molecular oxygen acts as an electron acceptor.[67] A vanadium μ-oxo complex has been identified as a key oxidant in this coupling reaction (Scheme 41).[68]

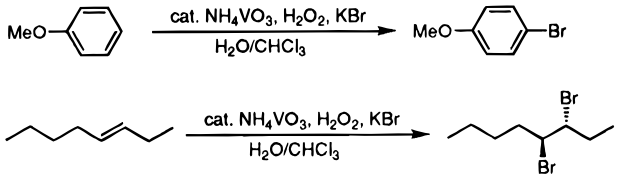
Scheme 41



H. Bromoperoxidase Mimic

Bromoperoxidases, which are vanadium-containing enzymes, can be mimicked by a two-phase system.[69] In this system, aromatic hydrocarbons and alkenes in chloroform undergo NH_4VO_3-catalyzed bromination in an aqueous acid solution of hydrogen peroxide and KBr, as shown in Scheme 42.

Scheme 42



I. Heterogeneous Oxidation

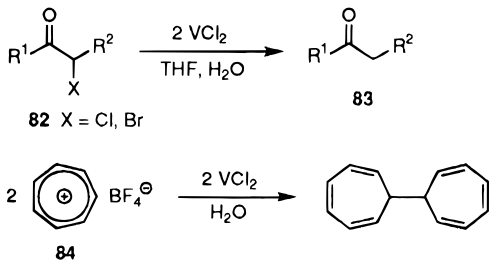
Although homogeneous reactions are surveyed in this review, a few heterogeneous systems are worth mentioning. Heterogeneous vanadium catalysts are important from an industrial viewpoint, in that they provide a variety of useful alternative methods for enabling oxidation reactions. For example, vapor-phase ammoxidation over an antimony-promoted vanadium phosphorus oxide catalyst supported on alumina is useful in the selective, one-step synthesis of adiponitrile[70] from cyclohexanol, cyclohexanone, cyclohexane, and *n*-hexane and in the synthesis of nicotinonitrile[71] from β-picoline. A vanadyl pyrophosphate catalyst also is highly active and selective in oxidizing butane to maleic anhydride.[72] Similarly, isobutyric acid can be oxidatively dehydrogenated and methacrolein oxidized to produce methacrylic acid.[73] The catalysis of oxidative transformations of alkanes, olefins, unsaturated alcohols, aldehydes, aromatics, amines, and thioethers with hydrogen peroxide and vanadium silicate molecular sieve catalyst has been reviewed.[74]

III. Reduction

A. Dehalogenation

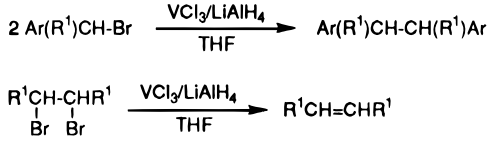
While high-valent vanadium species are one-electron acceptors, low-valent vanadium(II) ions are known to be one-electron donors in aqueous media. For example, vanadium(II) species hydrodehalogenate α-haloketones **82** to ketones **83** in aqueous THF.[75] Vanadium(II) species also reductively dimerize tropylium tetrafluoroborate (**84**) in nearly quantitative yield (Scheme 43).[76]

Scheme 43



Most of these reduction reactions have been carried out in aqueous media, which decreases their synthetic utility. However, a similar reduction can be carried out in organic solvents by using a vanadium(II) species generated from vanadium(III) chloride and $LiAlH_4$ in THF. This method has been utilized for the dehalogenative coupling of benzylic and allylic halides and the debromination of *vic*-dibromides (Scheme 44).[77]

Scheme 44

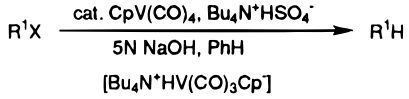


The vanadium(II) complex $VCl_2(py)_4$ effectively induces the reductive coupling of aralkyl halides.[78] The substrates' reactivities follow the order: $-CX_3 \gg -C(R)X_2 \gg -C(R)_2X$. The reaction is believed to proceed by the vanadium(II) complex initially attacking a halide via an outer-sphere mechanism to form a radical. This radical then rapidly reacts with another V(II) species to give an aralkyl vanadium(III) intermediate, which in turn reacts with the halide to give the coupling product. *vic*-Dihalides are also dehalogenated to olefins by this method, although dicyclopentadienylvanadium is more reactive than $VCl_2(py)_4$.

The anionic vanadium carbonyl hydride [$CpV(CO)_3H$] reduces various organic halides, such as alkyl bromides, *gem*-dibromoyclopropanes, acid chlorides, *vic*-bromides, alkenyl bromides, and bromobenzene.[79] The reaction proceeds by a free-radical chain process with an extremely rapid metal-to-carbon hydrogen transfer step, similar to Bu_3SnH reductions. This is probably because [$CpV(CO)_3H$] contains a hydrogen atom.

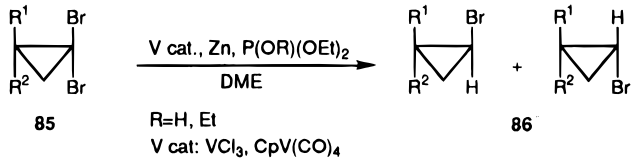
Phase transfer conditions can be employed for these catalytic reductive transformations. In this case, an (η^5-cyclopentadienyl)tricarbonylhydridovanadate anion is generated *in situ*, and catalyzes the dehalogenation as shown in Scheme 45.[80]

Scheme 45



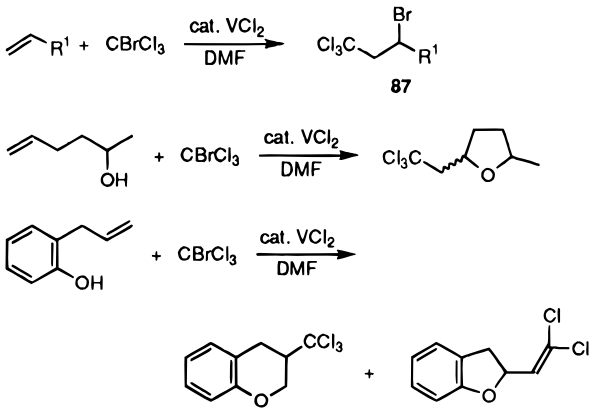
A low-valent vanadium species coordinated to diethyl phosphonate or triethyl phosphite is effective for the stereoselective reduction of *gem*-dibromocyclopropanes **85** to the corresponding monobromocyclopropanes **86**.[81] The less hindered bromine atom is reduced almost exclusively. The catalytic reaction proceeds with a higher stereoselectivity in the presence of zinc as a stoichiometric coreductant. The addition of diethyl phosphonate or triethyl phosphite as a hydrogen source is also essential to the reaction.[82] In the catalytic version of this system, the zinc and vanadium species form an efficient, reversible redox cycle (Scheme 46).

Scheme 46



Vanadium(II) chloride catalyzes the radical-chain addition of bromotrichloromethane to terminal olefins such as allyl acetate, allyl phenyl ether, and vinyl acetate, to regioselectively form the adduct **87**.[83] When hydroxy olefins are used as the substrate, the addition is followed by cyclization to form oxacycloalkanes (Scheme 47).

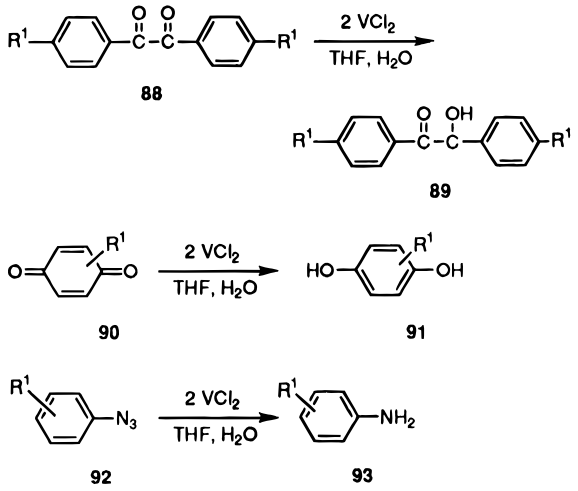
Scheme 47



B. Deoxygenation and Hydrogenation

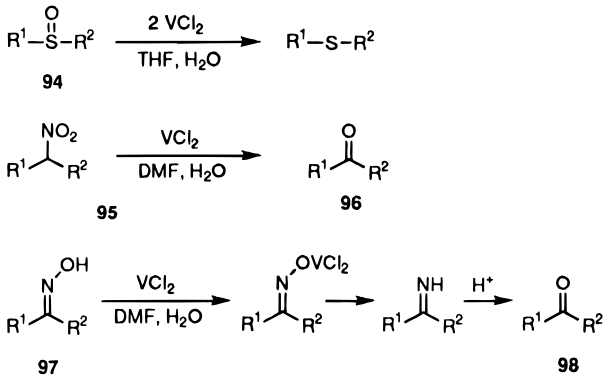
Upon treatment with vanadium(II) chloride, benzils **88** and *p*-quinones **90** are facilely reduced to give the benzoins **89** and hydroquinones **91**, respectively.[84] Similarly, aryl azides **92** are reduced to anilines **93** (Scheme 48).[85] Sterically encumbered nitro compounds can be reduced to the corresponding amines by the (η^5-cyclopentadienyl)tricarbonylhydridovanadate anion under phase transfer conditions.[80]

Scheme 48



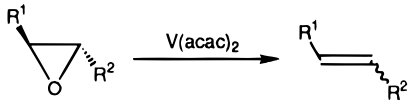
Vanadium(II) ions in aqueous media also are capable of reductively deoxygenating sulfoxides **94**.[86] In addition, primary or secondary aliphatic nitro compounds **95** in aqueous, acidic DMF are converted to the corresponding ketones **96** via intermediary carbonyl imines.[87] Oximes **97** are reductively cleaved to carbonyl compounds **98** (Scheme 49).[88]

Scheme 49



Epoxides are known to undergo deoxygenation to olefins by reducing metals such as $TiCl_3/LiAlH_4$.[89] The vanadium(II) complex $V(acac)_2$ is also effective in promoting this reduction (Scheme 50), which

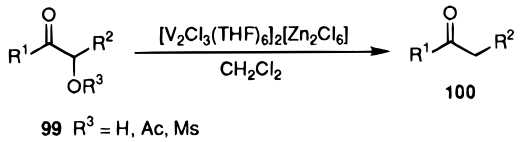
Scheme 50



proceeds via a metallooxetane intermediate.[90] The V(II) species generated from $V(OTf)_3$ and Zn/Hg shows even higher activity under the mild conditions of this reaction.[91] Tris(mesityl)vanadium(III) also deoxygenates styrene oxide to produce styrene and the corresponding oxovanadium(V) complex.[92] The cocondensation of vanadium metal enables a similar deoxygenation.[93]

The vanadium(II) compound, $[V_2Cl_3(THF)_6]_2[Zn_2Cl_6]$, which is prepared from vanadium(III) chloride and zinc,[94] reduces α-hydroxy, acetoxy, or mesyloxy ketones **99** to the simple ketones **100** in dichloromethane (Scheme 51).[95]

Scheme 51

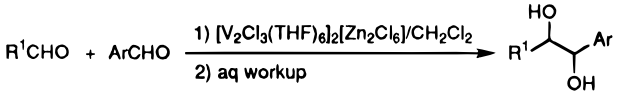


C. Reductive Coupling

A low-valent vanadium species, generated from vanadium pentoxide, Zn/Hg, and conc. hydrochloric acid, reduces aromatic aldehydes, α,β-unsaturated aldehydes, and benzylideneacetophenone to their corresponding coupled products.[96]

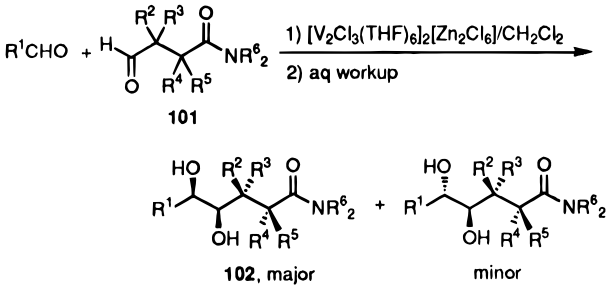
Aryl aldehydes, or their corresponding dimethyl acetals, intermolecularly couple with non-aryl aldehydes in the presence of $[V_2Cl_3(THF)_6]_2[Zn_2Cl_6]$ (Scheme 52).[97]

Scheme 52



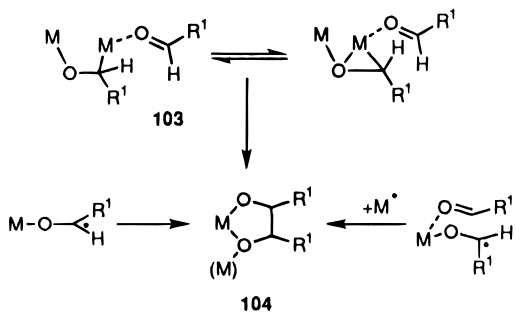
In general, non-aryl aldehydes do not undergo reductive coupling at an appreciable rate. However, if the aldehyde can chelate to the vanadium center, its susceptibility to reductive coupling is significantly increased. For example, this ability to chelate permits the intermolecular cross coupling of 3-formylpropanamides (**101**) with less reactive aldehydes, to give the *threo*-1,2-diols **102** diastereoselectively (Scheme 53).[98]

Scheme 53



The mechanism proposed for this reaction involves a vanadium(II) intermediate **103** and the coupled adduct **104**. This reaction pathway is shown in Scheme 54, along with other possible, but less preferred, pathways.

Scheme 54

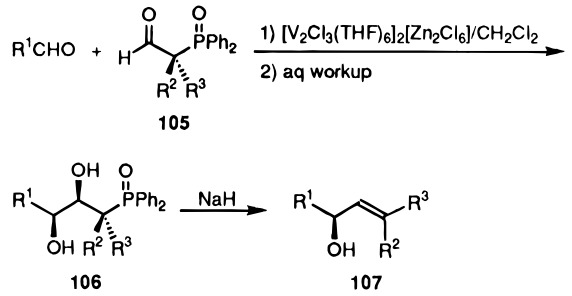


Sulfonyl aldehydes are also able to chelate to the vanadium center and thus couple with aliphatic aldehydes. The diastereoselectivity of this reaction depends on the size of the sulfonyl group.[99] Likewise,

2-[*N*-(alkoxycarbonyl)amino] aldehydes couple diastereoselectively to aliphatic aldehydes to produce 1,2-diols, where the yield of the reaction is influenced by the alkyl group on the *N*-alkoxycarbonyl.[100]

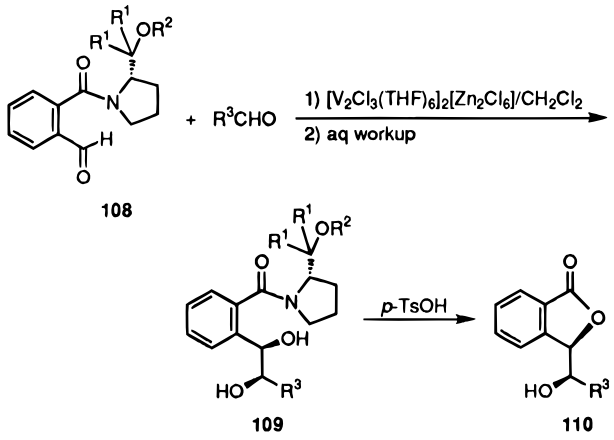
α,α-Disubstituted α-(diphenylphosphinoyl)acetaldehydes **105** undergo a similar reaction which results in the stereoselective synthesis of the diols **106**. These diols are then converted to (*E*)-allylic alcohols **107** via a Horner−Wittig elimination (Scheme 55).[101]

Scheme 55



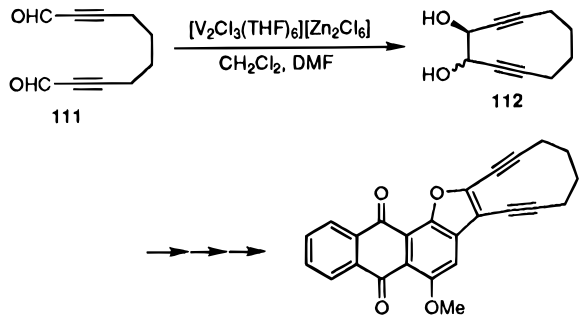
Enantioselectivity has been observed in appropriate V(II)-promoted pinacol cross coupling reactions. Thus, aromatic aldehydes **108** bearing a chiral amide auxiliary couple with aliphatic aldehydes to produce optically active 3-(1-hydroxyalkyl)phthalides **109**. Removing the auxiliary group ultimately affords the hydroxy lactone **110** (Scheme 56).[102]

Scheme 56



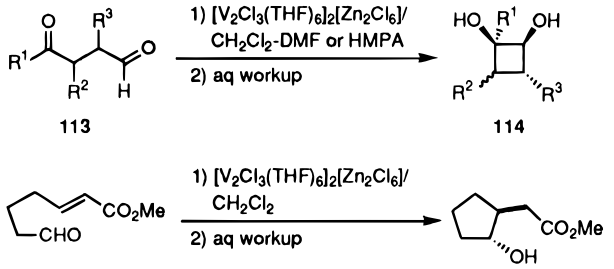
The $[V_2Cl_3(THF)_6]_2[Zn_2Cl_6]$-induced coupling method is conveniently applied to the synthesis of (*Z*)-enediyne derivatives. This intramolecular coupling of aldehyde **111** affords the diol **112** as a 4:1 mixture of *cis* and *trans* isomers. These diastereomers then are converted to the corresponding enediyne (Scheme 57).[103]

Scheme 57



The intramolecular coupling of the 4-oxoaldehydes **113** requires the presence of DMF or HMPA to give *cis*-1,2-cyclobutanediols **114** (Scheme 58).[104] A simi-

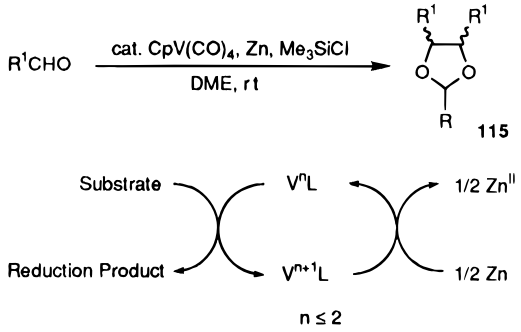
Scheme 58



lar reductive cyclization of alkenals or alkynals leads to the stereoselective formation of *trans*-2-alkyl- or *trans*-2-alkylidenecyclopentanols, respectively.[105]

As mentioned above, low-valent vanadium compounds can induce synthetically useful one-electron reductions. Lanthanides and other low-valent early transition metals also have been used for this purpose; however, the metallic reductants must be present in greater than stoichiometric amounts in order to complete the reduction reaction. Attempts have been made to construct a catalytic system, but these have been largely unsuccessful.[106] Fortunately, the debromination catalyzed by vanadium and zinc, which was described above, has led to the development of just such a catalytic system. The $CpV(CO)_4$-catalyzed reductive coupling of aliphatic aldehydes is achieved in the presence of zinc and chlorotrimethylsilane to give the corresponding 1,3-dioxolanes **115** or diols, depending on the reaction conditions.[107] This novel method involves carbon−carbon bond formation via one-electron reduction. The catalytic coupling proceeds with a high degree of diastereoselectivity.[108] The presence of chlorotrimethylsilane is essential to the reaction. Other Cp-substituted vanadium compounds such as Cp_2V and Cp_2VCl_2 can be used as the catalyst. The redox interaction between vanadium and zinc forms an efficient, reversible, one-electron reduction cycle (Scheme 59).

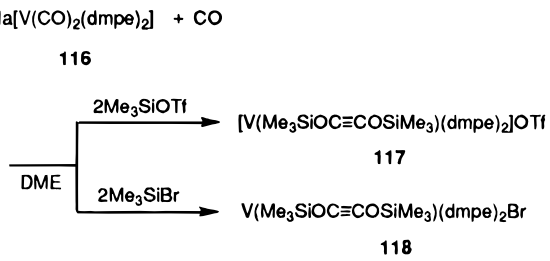
Scheme 59



An unusual carbon monoxide coupling reaction has been achieved by using a vanadium reagent. In this reaction, the interaction of $Na[V(CO)_2(dmpe)_2]$ (**116**) with trimethylsilyl reagents results in the reductive coupling of two CO ligands to form a coordinated bis(trimethylsiloxy)acetylene ligand. The use of Me_3SiOTf leads to a six-coordinate paramagnetic complex **117**, while a diamagnetic complex **118** is obtained with Me_3SiBr.[109] Hydrogenation of the vanadium

complexes affords *cis*-bis(trimethylsiloxy)ethylene as the final product (Scheme 60).

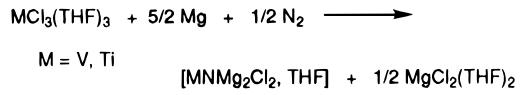
Scheme 60



D. Nitrogen Fixation

Dinitrogen fixation and activation processes have been investigated with low-valent vanadium compounds.[110] Nitrogen is reduced by the $V(OH)_2/Mg(OH)_2$ and $V(OH)_2/ZrO_2H$ systems to yield predominantly hydrazine or ammonia depending on the reaction conditions.[111] A related V(II) or Ti(II)/Mg system reductively coordinates nitrogen with a stoichiometry as shown in Scheme 61.[112]

Scheme 61



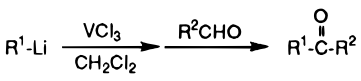
The reducing ability of the V(II) nitrogen activating species also allows it to reduce carbon monoxide to formaldehyde or methanol.[113] Likewise, the vanadium-containing nitrogenase from Azotobacter catalyzes the reduction of acetylene to ethylene.[114]

IV. Organometallics

A. Synthetic Transformations

Organovanadium compounds exhibit unique reactivities based on the redox characteristics of the vanadium. For example, treatment of VCl_3 in THF with a stoichiometric amount of *n*- or *s*-alkylmagnesium halides affords alkanes, alkenes, and a dimer.[115] The organovanadium compounds generated *in situ* couple chemoselectively with acid chlorides or allyl halides.[116] A related reaction with aldehydes yields coupled ketones by an oxidative nucleophilic addition mechanism (Scheme 62).[117] Allylic vanadium and oxovanadium compounds are characterized.[118]

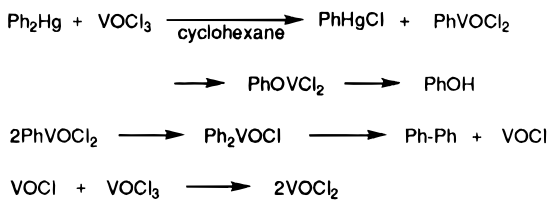
Scheme 62



The reaction of $VOCl_3$ with Ph_2Hg affords phenylmercuric chloride and biphenyl via an unstable phenylvanadyl dichloride complex. When the ratio of Ph_2Hg to $VOCl_3$ is <1, phenol is also produced. This reaction may proceed by a migration of the phenyl group from the vanadium to its oxygen ligand (Scheme 63).[119] The formation of phenol therefore represents an example of the functionalization of an organic species by an oxovanadium compound (see the oxometal reagents section).

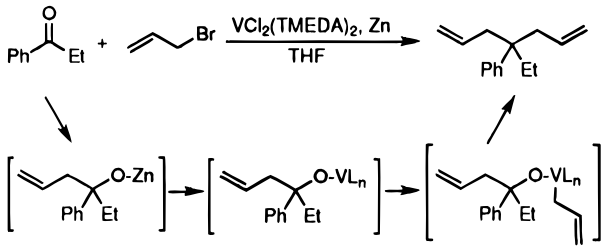
Direct geminal allylation of propiophenone with allyl bromide proceeds in the presence of $VCl_3(THF)_3$/

Scheme 63



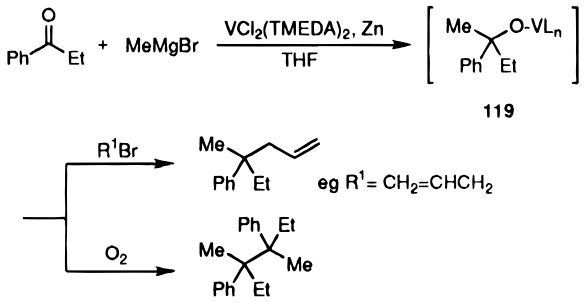
Zn or $VCl_2(TMEDA)_2/Zn$.[120] This deoxygenative transformation is made possible by the oxophilicity of low-valent vanadium (Scheme 64). Successive treatment

Scheme 64



of propiophenone with a Grignard reagent, $VCl_2(TMEDA)_2$, and allylic bromide results in geminal carbon−carbon bond formation at the carbonyl carbon (Scheme 65). Homocoupling, rather than ally-

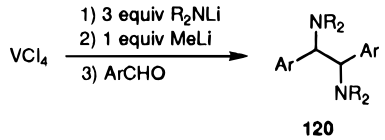
Scheme 65



lation, of the akoxyvanadium intermediate **119** occurs in the presence of a catalytic amount of molecular oxygen.[121]

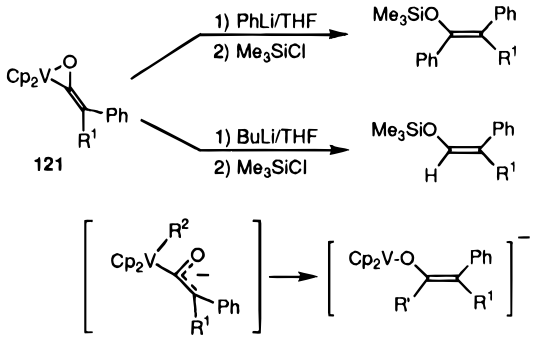
Aromatic aldehydes react with tris(dialkylamino)methylvanadium(IV), obtained by sequential treatment of vanadium tetrachloride with lithium dialkylamide and methyllithium, to produce *N*,*N*,*N*′,*N*′-tetraalkyl-1,2-diarylethylenediamines **120** (Scheme 66).[122]

Scheme 66



The addition of organolithiums or Grignard reagents to the vanadium ketene complex **121**, followed by treatment with trimethylsilyl chloride, leads to the stereoselective formation of silyl enol ethers as shown in Scheme 67. The reactive organic species initially coordinates to the vanadium center. From there it is transferred to the bound ketene via a vanadium-mediated internal nucleophilic attack, to form the (*Z*)-enolate. When the reaction is carried out using butyllithium, the resulting vanadium-bound butyl

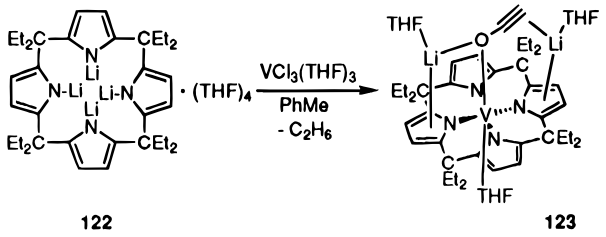
Scheme 67



ligand transfers a β-hydrogen to the ketene, rather than the entire butyl group as expected.[123]

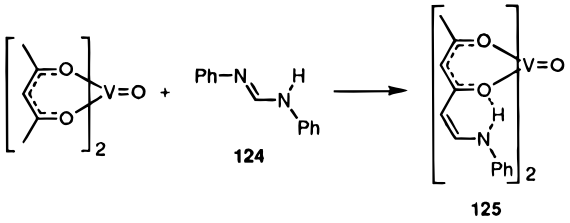
Ynolate anions are envisioned to be useful synthetic reagents, although they have received limited attention. One such vanadium-coordinated ynolate has been observed, which may indicate that further advances are possible in this area. The vanadium ynolate complex **123** is isolated from the reaction of $VCl_3(THF)_3$ with the tetralithium of octaethylporphyrin **122**. The ynolate moiety is believed to form via cleavage of a coordinated THF molecule (Scheme 68).[124]

Scheme 68



VO(acac)$_2$ is converted to oxobis[6-(phenylamino)-hexane-2,4-dionato-*O*,*O*′]vanadium(IV) (**125**) through *N*,*N*′-diphenylformamidine (**124**) substitution onto a methyl group of the acetyl acetonate ligand (Scheme 69).[125]

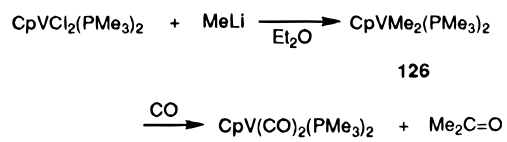
Scheme 69



B. Insertion

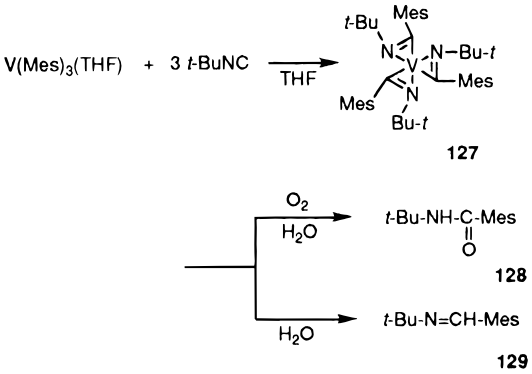
Insertion into a carbon−vanadium bond provides a variety of useful synthetic strategies. For example, the methylvanadium complex **126**, obtained from $CpVCl_2(PMe_3)_2$ and MeLi, rapidly inserts carbon monoxide to give acetone and $CpV(CO)_2(PMe_3)_2$ (Scheme 70).[126]

Scheme 70



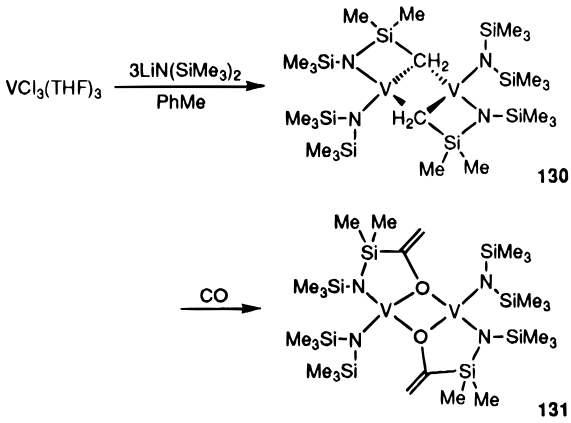
tert-Butyl isocyanide is likewise inserted into three carbon−vanadium bonds of [V(Mes)$_3$(THF)] to give the tris(η^2-iminoacyl) complex **127**. When exposed to air, the complex **127** is converted to the corresponding amide **128**, while its exposure to water produces the imine **129** by hydrolysis (Scheme 71).[127]

Scheme 71



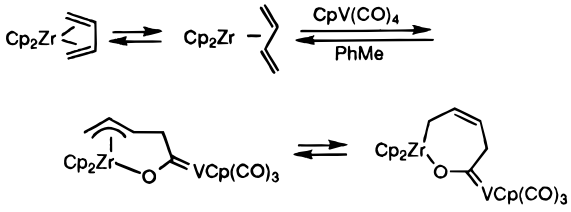
The reaction of $VCl_3(THF)_3$ with 3 equiv of $(Me_3Si)_2NLi$ leads to the dimeric complex **130** via C−H σ-bond metathesis of a trimethylsilyl group. The dinuclear enolate complex **131** then is formed by treatment of **130** with CO, which is inserted into the vanadium−carbon bonds (Scheme 72).[128]

Scheme 72



Carbene complexes are useful in reactions such as catalytic olefin metathesis and polymerization; however, only a few carbene vanadium complexes have been reported. An oxycarbene complex is obtained from the reaction of *s-cis*- and *s-trans*-(diene)zirconocene isomers with $CpV(CO)_4$. Carbon−carbon bond formation between the zirconium-bound diene ligand and the V−CO unit forms the carbene complex as shown in Scheme 73.[129]

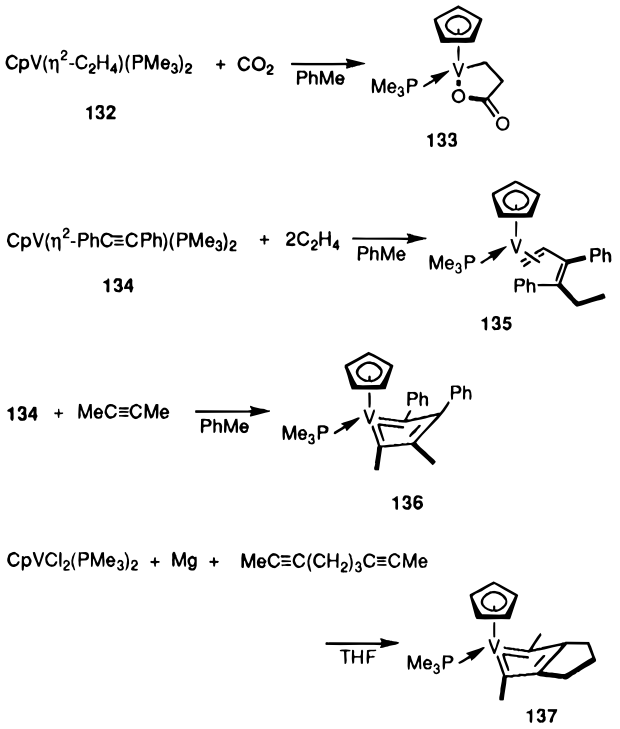
Scheme 73



In other insertion reactions, CO_2 adds to the vanadium(I) ethene compound **132** to afford the

vanadalactone **133**.[130] Complex **132** catalyzes the dimerization of 1-hexene via an insertion process. Likewise, the alkyne complex **134** reacts with 2 equiv of ethene to give the *s-cis*-3,4-(*E*)-diphenyl-1,3-hexadiene complex **135**. On the contrary, the reaction with 2-butyne leads to metallacycle **136** via a bis(alkyne) complex. The bicyclic vanadacyclopentatriene complex **137** can be formed from 2,7-nonadiyne (Scheme 74).

Scheme 74



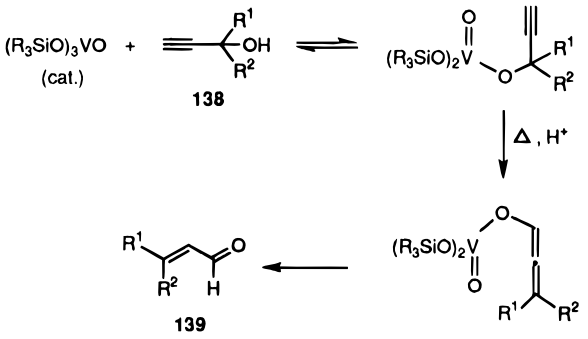
Complexation of the oxo group of $VO(CH_2SiMe_3)_n(OSiPh_3)_{3-n}$ ($n = 0-3$) with $Al(CH_2SiMe_3)_3$ facilitates the insertion of ethylene into the carbon−vanadium bond by reducing the degree of π-donation from the oxo ligand. This type of interaction is important in olefin polymerization.[131] In one final example of an insertion reaction involving vanadium, when $(\eta\text{-}C_5Me_5)_2V$ is incubated with O_2 at −78 °C, the oxygen is inserted into the carbon−vanadium bond to yield $[(\mu\text{-}\eta^3\text{-}C_5Me_5O_3)V(O)]_2$.[132]

V. Oxometal Reagents

The oxo group of oxometal compounds is expected to introduce an oxygen-containing functional group into organic compounds. Oxovanadium compounds are no exception. For example, α-acetylenic alcohols **138** are rearranged to α,β-unsaturated carbonyl compounds **139** in the presence of a silylvanadate catalytst,[133] where the oxo group of the silylvanadate mediates a sigmatropic-like rearrangement (Scheme 75).

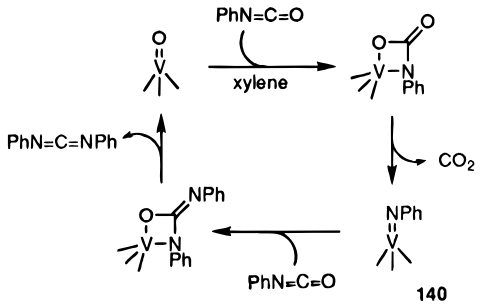
$VO(OR)_3$, $V(NC_6H_4Me)(OBu\text{-}t)_3$, and $VO(acac)_2$ each catalyze the condensation of phenyl isocyanates to form *N*,*N*′-diphenylcarbodiimide (Scheme 76). An imido transfer, similar to reported oxo transfers, from

Scheme 75



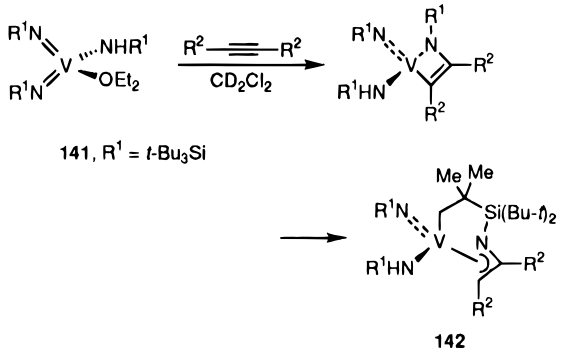
the imido complex **140** to phenyl isocyanate is presumed to complete the catalytic cycle.[134]

Scheme 76



Imidovanadium complexes are believed to form metallacycle intermediates. In this manner, complex **141** undergoes [2 + 2] cycloaddition with alkynes and ethene to give η^3-1-azaallyl (**142**) and ethenyl complexes, respectively (Scheme 77).[135]

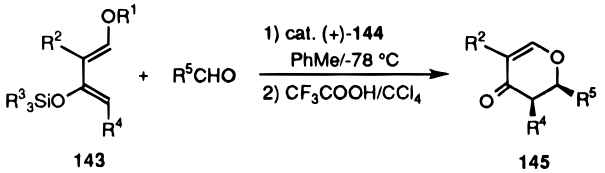
Scheme 77



VI. Lewis Acid Promoted Reaction

The Lewis acidic properties of oxovanadium compounds allow them to be utilized as catalysts in the hetero Diels−Alder reaction. Thus, oxovanadium(IV) bis((1*R*)-3-(heptafluorobutyryl)camphorate) (**144**) catalyzes the enantioselective condensation of an aldehyde with an activated diene, 1-alkoxy-3-(siloxy)butadiene (**143**), to give 5,6-γ-dihydropyrones **145** via protonolysis of the primary cycloadduct (Scheme 78).[136]

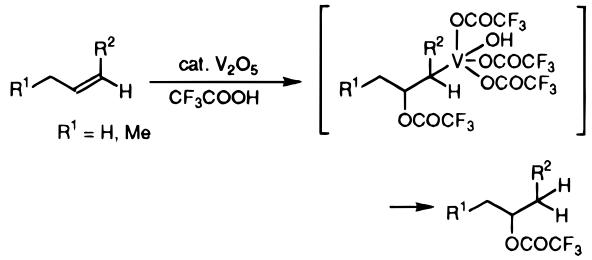
Scheme 78



144: oxovanadium(IV) bis((1*R*)-3-(heptafluorobutyryl)camphorate)

The trifluoroacetoxylation of alkenes is catalyzed by vanadium pentoxide in trifluoroacetic acid and yields the Markovnikov adduct regioselectively (Scheme 79). This reaction generates a vanadyl

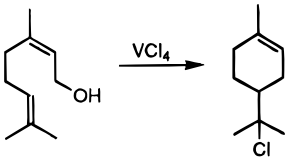
Scheme 79



trifluoroacetate species, which is assumed to electrophilically attack the double bond.[137]

Vanadium tetrachloride can act as a Lewis acid to mediate the cyclization of nerol (**146**) to the corresponding terpinyl chloride **147** (Scheme 80).[138]

Scheme 80



146 **147**

VII. Conclusions

This article surveys recent advances in synthetic methodologies using vanadium compounds. Additional information can be found in previous reviews.[50,139] Vanadium's unique one-electron transfer redox process provides a variety of novel oxidation and reduction methods for organic synthesis. These redox properties also have made vanadium as an essential element in biosystems and paramagnetic materials and have led to the development of synthetic, bioactive compounds based on vanadium. The Lewis acidic nature of vanadium and oxovanadium compounds is another key factor in their reactivities.

In addition, the ability of oxovanadium compounds to uniquely functionalize substrates through oxygen transfer has opened the door to functionalization methods which were previously difficult to access.

It is expected that controlling the vanadium-based redox systems more precisely will lead to even greater selectivities in their electron transfer reactions. Likewise, fine-tuning the ligands coordinated to vanadium is expected to result in more efficient systems. These and other approaches promise to yield many more fruitful, vanadium-induced reactions for organic synthesis.

VIII. References

(1) Vilter, H. *Phytochemistry* **1984**, *23*, 1387. Arber, J. M.; de Boer, E.; Garner, C. D.; Hasnain, S. S.; Wever, R. *Biochemistry* **1989**, *28*, 7968.
(2) McKenna, C. E.; Benemann, J. R.; Traylor, T. G. *Biochem. Biophys. Res. Commun.* **1970**, *41*, 1501. Hales, B. J.; Case, E. E.; Moringstar, J. E.; Dzeda, M. F.; Mautner, A. *Biochemistry* **1986**, *25*, 7251. Robson, R. L.; Eady, R. R.; Richardson, T. H.; Miller, R. W.; Hawkins, M.; Postgate, J. R. *Nature* **1986**, *322*, 388. George, G. N.; Coyle, C. L.; Hales, B. J.; Cramer, S. P. *J. Am. Chem. Soc.* **1988**, *110*, 4057. Hales, B. J.; True, A. E.; Hoffman, B. M. *J. Am. Chem. Soc.* **1989**, *111*, 8519.
(3) Floriani, C.; Mazzanti, M.; Chiesi-Villa, A.; Guastini, C. *Angew. Chem., Int. Ed. Engl.* **1988**, *27*, 576. Rehder, D.; Priebsch, W.; von Oeynhausen, M. *Angew. Chem., Int. Ed. Engl.* **1989**, *28*, 1221. Sakurai, H.; Tsuchia, K. *FEBS Lett.* **1990**, *260*, 109. Holmes, S.; Carrano, C. J. *Inorg. Chem.* **1991**, *30*, 1231. Clague, M. J.; Keder, N. L.; Butler, A. *Inorg. Chem.* **1993**, *32*, 4754. Clague, M. J.; Butler, A. *J. Am. Chem. Soc.* **1995**, *117*, 3475. Andersson, M.; Conte, V.; Di Furia, F.; Moro, S. *Tetrahedron Lett.* **1995**, *36*, 2675.
(4) Macara, I. G.; McLeod, G. C.; Kustin, K. *Comp. Biochem. Physiol., B: Comp. Biochem.* **1979**, *63B*, 299. Oltz, E. M.; Bruening, R. C.; Smith, M. J.; Kustin, K.; Nakanishi, K. *J. Am. Chem. Soc.* **1988**, *110*, 6162. Kustin, K. *Acc. Chem. Res.* **1991**, *24*, 117. Taylor, S. W.; Kammerer, B. Bayer, E. *Chem Rev.* **1997**, *97*, 333.
(5) Kustin, K.; Macara, I. G. *Comments Inorg. Chem.* **1982**, *2*, 1. Nechay, B. R. *Annu. Rev. Pharmacol. Toxicol.* **1984**, *24*, 501. Stoecker, B. J.; Hopkins, L. L. *Biochemistry of the Essential Ultratrace Elements*; Plenum Press: New York, 1984; p 239. Nielsen, F. H. *Trace Minerals in Foods*; Marcel Dekker: New York, 1988; p 398. McLaughlin, M. L.; Cronan, J. M., Jr.; Schaller, T. R.; Snelling, R. D. *J. Am. Chem. Soc.* **1990**, *112*, 8949. Rehder, D. *Angew. Chem., Int. Ed. Engl.* **1991**, *30*, 148.
(6) Cotton, F. A.; Wilkinson, G. *Advanced Inorganic Chemistry*, 4th ed.; John Wiley & Sons: New York, 1980.
(7) Jones, J. R.; Waters, W. A. *J. Chem. Soc.* **1960**, 2772. Jones, J. R.; Waters, W. A.; Littler, J. S. *J. Chem. Soc.* **1961**, 630.
(8) Kaneda, K.; Kawanishi, Y.; Jitsukawa, K.; Teranishi, S. *Tetrahedron Lett.* **1983**, *24*, 5009.
(9) Conte, V.; Di Furia, F.; Modena, G. *J. Org. Chem.* **1988**, *53*, 1655.
(10) Roček, J.; Radkowsky, A. E. *J. Org. Chem.* **1973**, *38*, 89. Roček, J.; Aylward, D. E. *J. Am. Chem. Soc.* **1975**, *97*, 5452.
(11) Liu, H.-J. *Can. J. Chem.* **1976**, *54*, 3113.
(12) Meyer, K.; Roček, J. *J. Am. Chem. Soc.* **1972**, *94*, 1209. Hunter, N. R.; MacAlpine, G. A.; Liu, H.-J. Valenta, Z. *Can. J. Chem.* **1970**, *48*, 1436.
(13) Mimoun, H.; Saussine, L.; Daire, E.; Postel, M.; Fischer, J.; Weiss, R. *J. Am. Chem. Soc.* **1983**, *105*, 3101.
(14) Mimoun, H.; Chaumette, P.; Mignard, M.; Saussine, L. *Nouv. J. Chim.* **1983**, *7*, 467. Mimoun, H. *Isr. J. Chem.* **1983**, *23*, 451.
(15) Bonchio, M.; Conte, V.; Di Furia, F.; Modena, G.; Moro, S. *J. Org. Chem.* **1994**, *59*, 6262.
(16) Das, S. K.; Kumar, A., Jr.; Nandrajog, S.; Kumar, A. *Tetrahedron Lett.* **1995**, *36*, 7909.
(17) McCombie, S. W.; Vice, S. F. *J. Org. Chem.* **1996**, *61*, 413.
(18) Gould, E. S.; Hiatt, R. R.; Irwin, K. C. *J. Am. Chem. Soc.* **1968**, *90*, 4573. Sharpless, K. B.; Michaelson, R. C. *J. Am. Chem. Soc.* **1973**, *95*, 6136. Sharpless, K. B.; Verhoeven, T. R. *Aldrichim. Acta* **1979**, *12*, 63.
(19) Itoh, T.; Jitsukawa, K.; Kaneda, K.; Teranishi, S. *J. Am. Chem. Soc.* **1979**, *101*, 159. Mihelich, E. D. *Tetrahedron Lett.* **1979**, 4729. Rossiter, B. E.; Verhoven, T. R.; Sharpless, K. B. *Tetrahedron Lett.* **1979**, 4733. Luteijn, J. M.; de Groot, A. *J. Org. Chem.* **1981**, *46*, 3448. Stevens, R. V.; Chang, J. H.; Lapalme, R.; Schow, S.; Schlageter, M. G.; Shapiro, R.; Weller, H. N. *J. Am. Chem. Soc.* **1983**, *105*, 7719. Corey, E. J.; De, B. *J. Am. Chem. Soc.* **1984**, *106*, 2735. Nakayama, K.; Yamada, S.; Takayama, H.; Nawata, Y.; Iitaka, Y. *J. Org. Chem.* **1984**, *49*, 1537. Ziegler, F. E.; Jaynes, B. H.; Saindane, M. T. *Tetrahedron Lett.* **1985**, *26*, 3307. Prat, D.; Left, R. *Tetrahedron Lett.* **1986**, *27*, 707. Marino, J. P.; de la Pradilla, R. F.; Laborde, E. *J. Org. Chem.* **1987**, *52*, 4898. Singh, A. K.; Bakshi, R. K.; Corey, E. J. *J. Am. Chem. Soc.* **1987**, *109*, 6187. Rowley, M.; Kishi, Y. *Tetrahedron Lett.* **1988**, *29*, 4909. Pirrung, M. C.; Thomson, S. A. *J. Org. Chem.* **1988**, *53*, 227. Marshall, J. A.; Robinson, E. D. *Tetrahedron Lett.* **1989**, *30*, 1055.
(20) Katsuki, T.; Sharpless, K. B. *J. Am. Chem. Soc.* **1980**, *102*, 5974.
(21) Allison, K.; Johnson, P.; Foster, G.; Sparke, M. B. *Ind. Eng. Chem., Prod. Res. Dev.* **1966**, *5*, 166.
(22) Arzoumanian, H.; Blanc, A.; Hartig, U.; Metzger, J. *Tetrahedron Lett.* **1974**, 1011.
(23) Noels, A. F.; Hubert, A. J.; Teyssie, Ph. *J. Organomet. Chem.* **1979**, *166*, 79.
(24) Kaneda, K.; Jitsukawa, K.; Itoh, T.; Teranishi, S. *J. Org. Chem.* **1980**, *45*, 3004.
(25) Lyons, J. E. *Tetrahedron Lett.* **1974**, 2737.
(26) Hirao, T.; Mikami, S.; Ohshiro, Y. *Synlett* **1990**, 541.
(27) Inoki, S.; Takai, T.; Yamada, T.; Mukaiyama, T. *Chem. Lett.* **1991**, 941.
(28) Hata, E.; Takai, T.; Yamada, T.; Mukaiyama, T. *Chem. Lett.* **1994**, 1849.
(29) Takai, T.; Hata, E.; Mukaiyama, T. *Chem. Lett.* **1994**, 885.
(30) Tatsuno, Y.; Tatsuda, M.; Otsuka, S. *J. Chem. Soc., Chem. Commun.* **1982**, 1100.
(31) Adam, W.; Braun, M.; Giesbeck, A.; Lucchini, V.; Staab, E.; Will, B. *J. Am. Chem. Soc.* **1989**, *111*, 203.
(32) Carrick, W. L.; Karapinka, G. L.; Kwiatkowski, G. T. *J. Org. Chem.* **1969**, *34*, 2388.

(33) Carrick, W. L.; Karapinka, G. L.; Kwiatkowski, G. T. *J. Org. Chem.* **1969**, *34*, 2388. Tashiro, M.; Fukata, G.; Yamato, T.; Watanabe, H.; Oe, K.; Tsuge, O. *Org. Prep. Proced. Int.* **1976**, *8*, 249.
(34) Burnett, D. A.; Hart, D. J. *J. Org. Chem.* **1987**, *52*, 5662. Schwartz, M. A. *Synth. Commun.* **1973**, *3*, 33. Franck, B.; Teetz, V. *Angew. Chem., Int. Ed. Engl.* **1971**, *10*, 411. Schwartz, M. A.; Pham, P. T. K. *J. Org. Chem.* **1988**, *53*, 2318.
(35) Kuchan, S. M.; Liepa, A. *J. Am. Chem. Soc.* **1973**, *95*, 4062.
(36) Brown, A. G.; Edwards, P. D. *Tetrahedron Lett.* **1990**, *31*, 6581.
(37) Damon, R. E.; Schlessinger, R. H.; Blount, J. F.; *J. Org. Chem.* **1976**, *41*, 3772. Kuchan, S. M.; Kameswaran, V.; Lynn, J. T.; Williams, D. K.; Liepa, A. J. *J. Am. Chem. Soc.* **1975**, *97*, 5622. Kende, A. S.; Liebeskind, L. S. *J. Am. Chem. Soc.* **1976**, *98*, 267. Biftu, T.; Hazra, B. G.; Stevenson, R. *J. Chem. Soc., Chem. Commun.* **1978**, 492. Gottlieb, L.; Meyers, A. I. *J. Org. Chem.* **1990**, *55*, 5659. White, J. D.; Butlin, R. J.; Hahn, H.-G.; Johnson, A. T. *J. Am. Chem. Soc.* **1990**, *112*, 8595. Brown, A. G.; Edwards, P. D. *Tetrahedron Lett.* **1990**, *31*, 6581. Comins, D. L.; Morgan, L. A. *Tetrahedron Lett.* **1991**, *32*, 5919. Evans, D. A.; Dinsmore, C. J.; Evrard, D. A.; DeVries, K. M. *J. Am. Chem. Soc.* **1993**, *115*, 6426.
(38) Schwartz, M. A.; Holton, R. A.; Scott, S. W. *J. Am. Chem. Soc.* **1969**, *91*, 2800. Schwartz, M. A.; Holton, R. A. *J. Am. Chem. Soc.* **1970**, *92*, 1090.
(39) Schwartz, M. A.; Hudec, T. T. *Synth. Commun.* **1986**, *16*, 1599.
(40) Littler, J. S.; Waters, W. A. *J. Chem. Soc.* **1959**, 1299 and 3014.
(41) Hirao, T.; Mori, M.; Ohshiro, Y. *Bull. Chem. Soc. Jpn.* **1989**, *62*, 2399.
(42) Waters, W. A.; Littler, J. S. In *Oxidation in Organic Chemistry*; Wilberg, K. B., Ed.; Academic: New York, 1965; part A, p 185.
(43) Hirao, T.; Mori, M.; Ohshiro, Y. *J. Org. Chem.* **1990**, *55*, 358.
(44) Hirao, T.; Mori, M.; Ohshiro, Y. *Chem. Lett.* **1991**, 783.
(45) Hirao, T.; Mikami, S.; Mori, M.; Ohshiro, Y. *Tetrahedron Lett.* **1991**, *32*, 1741.
(46) Hirao, T.; Fujii, T.; Miyata, S.-i.; Ohshiro, Y. *J. Org. Chem.* **1991**, *56*, 2264.
(47) Nikishin, G. I.; Vinogradov, M. G.; Fedorova, T. M. *J. Chem. Soc., Chem. Commun.* **1973**, 693. Snider, B. B.; Mohan, R.; Kates, S. A. *J. Org. Chem.* **1985**, *50*, 3659.
(48) Hirao, T.; Fujii, T.; Tanaka, T.; Ohshiro, Y. *Synlett* **1994**, 845.
(49) Hirao, T.; Fujii, T.; Tanaka, T.; Ohshiro, Y. *J. Chem. Soc., Perkin Trans. 1* **1994**, 3.
(50) Hirao, T.; Fujii, T.; Tanaka, T.; Ohshiro, Y.; Ikeda, I. *J. Synth. Org. Chem., Jpn.* **1994**, *52*, 197.
(51) Hirao, T.; Fujii, T.; Tanaka, T.; Ohshiro, Y. *J. Organometal. Chem.* **1991**, *407*, C1.
(52) Ichikawa, K.; Uemura, S.; Sugita, T. *Tetrahedron* **1966**, *22*, 407. Ichikawa, K. Uemura, S. *J. Org. Chem.* **1967**, *32*, 493. Heiba, E. I.; Dessau, R. M. *J. Org. Chem.* **1974**, *39*, 3456. Snider, B. B.; Patricia, J. J.; Kates, S. A. *J. Org. Chem.* **1988**, *53*, 541.
(53) Hirao, T.; Sakaguchi, M.; Ishikawa, T.; Ikeda, I. *Synth. Commun.* **1995**, *25*, 845.
(54) Davies, H. M. L.; Hu, B. *J. Org. Chem.* **1992**, *57*, 4309.
(55) Jones, J. R.; Waters, W. A.; Litter, J. S. *J. Chem. Soc.* **1961**, 630.
(56) Micera, G.; Deiana, S.; Dessi, A.; Pusino, A.; Gessa, G. *Inorg. Chim. Acta* **1986**, *120*, 49.
(57) Riley, D. P.; Fields, D. L.; Rivers, W. *Inorg. Chem.* **1991**, *30*, 4191.
(58) Meier, I. K.; Schwartz, J. *J. Am. Chem. Soc.* **1989**, *111*, 3069. Meier, I. K.; Schwartz, J. *J. Org. Chem.* **1990**, *55*, 5619.
(59) Hirao, T.; Ohshiro, Y. *Tetrahedron Lett.* **1990**, *31*, 3917.
(60) Ito, Y.; Konoike, T.; Saegusa, T. *J. Am. Chem. Soc.* **1975**, *97*, 649. Kobayashi, Y.; Taguchi, T.; Morikawa, T.; Tokuno, E.; Sekiguchi, S. *Chem. Pharm. Bull.* **1980**, *28*, 262. Baciocchi, E.; Casu, A.; Ruzziconi, R. *Synlett* **1990**, 679.
(61) Fujii, T.; Hirao, T.; Ohshiro, Y. *Tetrahedron Lett.* **1992**, *33*, 5823.
(62) Fujii, T.; Hirao, T.; Ohshiro, Y. *Tetrahedron Lett.* **1993**, *34*, 5601.
(63) Hirao, T.; Fujii, T.; Ohshiro, Y. *Tetrahedron* **1994**, *50*, 10207.
(64) Hirao, T.; Fujii, T.; Ohshiro, Y. *Tetrahedron Lett.* **1994**, *35*, 8005.
(65) Sheng, M. N.; Zajacek, J. G. *J. Org. Chem.* **1968**, *33*, 588. Kuhnen, L. *Chem. Ber.* **1966**, *99*, 3384. Howe, G. R.; Hiatt, R. R. *J. Org. Chem.* **1970**, *35*, 4007. Curci, R.; Di Furia, F.; Testi, R.; Modena, G. *J. Chem. Soc., Perkin Trans. 2* **1974**, 752. Takano, S.; Sugihara, Y.; Ogasawara, K. *Heterocycles* **1992**, *34*, 1519.
(66) Nakajima, K.; Kojima, M.; Toriumi, K.; Saito, K.; Fujita, J. *Bull. Chem. Soc. Jpn.* **1989**, *62*, 760. Nakajima, K.; Kojima, K.; Kojima, M.; Fujita, J. *Bull. Chem. Soc. Jpn.* **1990**, *63*, 2620.
(67) Yamamoto, K.; Tsuchida, E.; Nishide, H.; Jikei, M.; Oyaizu, K. *Macromolecules* **1993**, *26*, 3432.
(68) Yamamoto, K.; Oyaizu, K.; Iwasaki, N.; Tsuchida, E. *Chem. Lett.* **1993**, 1223.
(69) Conte, V.; Di Furia, F.; Moro, S. *Tetrahedron Lett.* **1994**, *35*, 7429.
(70) Reddy, B. M.; Manohar, B. *J. Chem. Soc., Chem. Commun.* **1993**, 330.
(71) Reddy, B. N.; Reddy, B. M.; Subrahmanyam, M. *J. Chem. Soc., Chem. Commun.* **1988**, 33.
(72) Busca, G.; Centi, G. *J. Am. Chem. Soc.* **1989**, *111*, 46.
(73) Hamano, S.; Matuura, I. *Chem. Express* **1991**, *6*, 895.
(74) Kumar, P.; Kumar, R.; Pandey, B. *Synlett* **1995**, 289.
(75) Ho, T.-L.; Olah, G. A. *Synthesis* **1976**, 807.
(76) Olah, G. A.; Ho, T.-L. *Synthesis* **1976**, 798.
(77) Ho, T.-L.; Olah, G. A. *Synthesis* **1977**, 170.
(78) Cooper, T. A. *J. Am. Chem. Soc.* **1973**, *95*, 4158. Cooper, T. A.; Sonnenberg, F. M. *J. Org. Chem.* **1975**, *40*, 55.
(79) Kinney, R. J.; Jones, W. D.; Bergman, R. G. *J. Am. Chem. Soc.* **1978**, *100*, 635.
(80) Falicki, S.; Alper, H. *Organometallics* **1988**, *7*, 2548.
(81) Hirao, T.; Hirano, K.; Hasegawa, T.; Ohshiro, Y.; Ikeda, I. *J. Org. Chem.* **1993**, *58*, 6529.
(82) Barton, D. H. R.; Jang, D. O.; Jaszberenyi, J. C. *Tetrahedron Lett.* **1992**, *33*, 2311.
(83) Hirao, T.; Ohshiro, Y. *Synlett* **1990**, 217.
(84) Ho, T.-L.; Olah, G. A. *Synthesis* **1976**, 815.
(85) Ho, T.-L.; Henninger, M; Olah, G. A. *Synthesis* **1976**, 815.
(86) Olah, G. A.; Prakash, G. K. S.; Ho, T.-L. *Synthesis* **1976**, 810.
(87) Kirchoff, R. *Tertahedron Lett.* **1976**, 2533.
(88) Olah, G. A.; Arvanaghi, M.; Surya, G. K. *Synthesis* **1980**, 220.
(89) For example, McMurry, J. E.; Silvestri, M. G.; Fleming, M. P.; Hoz, T.; Grayston, M. W. *J. Org. Chem.* **1978**, *43*, 3249.
(90) Hayasi, Y.; Schwartz, J. *Inorg. Chem.* **1981**, *20*, 3473.
(91) Dobson, J. C.; Sano, M.; Taube, H. *Inorg. Chem.* **1991**, *30*, 456.
(92) Ruiz, J.; Vivanco, M.; Floriani, C.; Chiesi-Villa, A.; Guastini, C. *J. Chem. Soc., Chem. Commun.* **1991**, 762. Vivanco, M.; Ruiz, J.; Floriani, C.; Chiesi-Villa, A.; Rizzoli, C. *Organometallics* **1993**, *12*, 1802.
(93) Gladysz, J. A.; Fulcher, J. G.; Togashi, S. *J. Org. Chem.* **1976**, *41*, 3647.
(94) Cotton, F. A.; Duraj, S. A.; Extine, M. W.; Lewis, G. E.; Roth, W. J.; Schmulbach, C. D.; Schwotzer, W. J. *J. Chem. Soc., Chem. Commun.* **1983**, 1377. Bouma, R. J.; Teuben, J. H.; Beukema, W. R.; Bansemer, R. L.; Huffman, J. C.; Caulton, K. G. *Inorg. Chem.* **1984**, *23*, 2715. Canich, J. A. M.; Cotton, F. A.; Duraj, S. A.; Roth, W. J. *Polyhedron* **1987**, *6*, 1433.
(95) Inokuchi, T.; Kawafuchi, H.; Torii, S. *Chem. Lett.* **1992**, 1895.
(96) Conant, J. B.; Cutter, H. B. *J. Chem. Soc.* **1926**, *48*, 1016.
(97) Takahara, P. M.; Freudenberger, J. H.; Konradi, A. W.; Pedersen, S. F. *Tetrahedron Lett.* **1989**, *30*, 7177.
(98) Freudenberger, J. H.; Konradi, A. W.; Pedersen, S. F. *J. Am. Chem. Soc.* **1989**, *111*, 8014.
(99) Kraynack, E. A.; Pedersen, S. F. *J. Org. Chem.* **1993**, *58*, 6114.
(100) Konradi, A. W.; Kemp, S. J.; Pedersen, S. F. *J. Am. Chem. Soc.* **1994**, *116*, 1316.
(101) Park, J.; Pedersen, S. F. *J. Org. Chem.* **1990**, *55*, 5924.
(102) Annunziata, R.; Cinquini, M.; Cozzi, F.; Giaroni, P. *Tetrahedron: Asymmetry* **1990**, *1*, 355. Annunziata, R.; Benaglia, M.; Cinquini, M.; Cozzi, F.; Giaroni, P. *J. Org. Chem.* **1992**, *57*, 782.
(103) Myers, A. G.; Dragovich, P. S. *J. Am. Chem. Soc.* **1992**, *114*, 5859.
(104) Raw, A. S.; Pedersen, S. F. *J. Org. Chem.* **1991**, *56*, 830.
(105) Inokuchi, T.; Kawafuchi, H.; Torii, S. *J. Org. Chem.* **1991**, *56*, 4983.
(106) Lénard, E.; Duñach, E.; Péichon, J. *J. Chem. Soc., Chem. Commun.* **1989**, 276.
(107) Hirao, T. Hasegawa, T.; Muguruma, Y.; Ikeda, I. *J. Org. Chem.* **1996**, *61*, 366.
(108) Hirao, M. Asahara, T.; Muguruma, Y., unpublished results.
(109) Protasiewicz, J. D.; Lippard, S. J. *J. Am. Chem. Soc.* **1991**, *113*, 6564.
(110) Gambarotta, S. *J. Organomet. Chem.* **1995**, *500*, 117.
(111) Zones, S. I.; Vickrey, T. M.; Palmer, J. G.; Schrauzer, G. N. *J. Am. Chem. Soc.* **1976**, *98*, 7289. Schrauzer, G. N.; Strampach, N.; Hughes, L. A. *Inorg. Chem.* **1982**, *21*, 2184.
(112) Yamamoto, A.; Go, S.; Ookawa, M.; Takahashi, M.; Ikeda, S.; Keii, T. *Bull. Chem. Soc. Jpn.* **1972**, *45*, 3110.
(113) Zones, S. I.; Palmer, M. R.; Palmer, J. G.; Doemeny, J. M.; Schrauzer, G. N. *J. Am. Chem. Soc.* **1978**, *100*, 2113. Schrauzer, G. N.; Palmer, M. R. *J. Am. Chem. Soc.* **1981**, *103*, 2659.
(114) Dilworth, M. J.; Eady, R. R.; Robson, R. L.; Miller, R. W. *Nature* **1987**, *327*, 167. Dilworth, M. J.; Eady, R. R.; Eldridge, M. E. *Biochem. J.* **1988**, *249*, 745.
(115) Sneeden, R. P. A.; Zeiss, H. H. *J. Organomet. Chem.* **1970**, *22*, 713.
(116) Hirao, T.; Misu, D.; Yao, K.; Agawa, T. *Tetrahedron Lett.* **1986**, *27*, 929.
(117) Hirao, T.; Misu, D.; Agawa, T. *J. Am. Chem. Soc.* **1985**, *107*, 7179. Hirao, T.; Misu, D.; Agawa, T. *Tetrahedron Lett.* **1986**, *27*, 933.
(118) Kauffmann, T.; Bonrath, W.; Beirich, C.; Li, W.; Pahde, C.; Raedeker, S.; Wichmann, B.; Wingbermühle, D. *Chem. Ber.* **1993**, *126*, 2093.
(119) Reichle, W.; Carrick, W. L. *J. Organomet. Chem.* **1970**, *24*, 419.
(120) Kataoka, Y.; Makihira, I.; Akiyama, H.; Tani, K. *Tetrahedron Lett.* **1995**, *36*, 6495.
(121) Kataoka, Y.; Akiyama, H.; Makihira, I.; Tani, K. *J. Org. Chem.* **1996**, *61*, 6094.
(122) Imwinkelried, V. R.; Seebach, D. *Helv. Chim. Acta* **1984**, *67*, 1496.
(123) Galante, J. M.; Bruno, J. W.; Hazin, P. N.; Folting, K.; Huffman, J. C. *Organometallics* **1988**, *7*, 1066.
(124) Jubb, J.; Gambarotta, S. *J. Am. Chem. Soc.* **1993**, *115*, 10410.

(125) Arnold, D. I.; Cotton, F. A.; Matonic, J. H.; Murillo, C. A. *J. Chem. Soc., Chem. Commun.* **1996**, 2113.
(126) Hessen, B.; Teuben, J. H.; Lemmen, T. H.; Huffman, J. C.; Caulton, K. G. *Organometallics* **1985**, *4*, 946.
(127) Vivanco, M.; Ruiz, J.; Floriani, C.; Chiesi-Villa, A.; Guastini, C. *Organometallics* **1990**, *9*, 2185.
(128) Berno, P.; Minhas, M.; Hao, S.; Gambarotta, S. *Organometallics* **1994**, *13*, 1052.
(129) Erker, G.; Lecht, R.; Schlund, R.; Angermund, K.; Krüger, C. *Angew. Chem., Int. Ed. Engl.* **1987**, *26*, 666.
(130) Hessen, B.; Meetsma, A.; van Bolhuis, F.; Teuben, J. H. *Organometallics* **1990**, *9*, 1925.
(131) Feher, F. J.; Blanski, R. L. *Organometallics* **1993**, *12*, 958.
(132) Bottomley, F.; Magill, C. P.; White, P. S. *J. Am. Chem. Soc.* **1989**, *111*, 3070.
(133) Pauling, H.; Andrews, D. A.; Hindley, N. C. *Helv. Chim. Acta* **1976**, *59*, 1233. Erman, M. B.; Aul'chenko, I. S.; Kheifits, L. A.; Dulova, V. G.; Novikov, J. N.; Vol'pin, M. E. *Tetrahedron Lett.* **1976**, 2981.
(134) Birdwhistell, K. R.; Boucher, T.; Ensminger, M.; Harris, S.; Johnson, M.; Toporek, S. *Organometallics* **1993**, *12*, 1023.
(135) de With, J.; Horton, A. D. *Organometallics* **1993**, *12*, 1493.
(136) Togni, A. *Organometallics* **1990**, *9*, 3106. Togni, A.; Rist, G.; Rihs, G.; Schweiger, A. *J. Am. Chem. Soc.* **1993**, *115*, 1908.
(137) Choudary, B. M.; Reddy, P. N. *J. Chem. Soc., Chem. Commun.* **1993**, 405.
(138) Saito, T.; Itoh, A.; Oshima, K.; Nozaki, H. *Tetrahedron Lett.* **1979**, 3519.
(139) Schrock, R. R.; Parshall, G. W. *Chem. Rev.* **1976**, *76*, 243. Ho, T.-L. *Synthesis* **1979**, 1. Sheldon, R. A.; Kochi, J. K. *Metal-Catalyzed Oxidations of Organic Compounds*; Academic Press: New York, 1981. Freeman, F. In *Organic Syntheses by Oxidation with Metal Compounds*; Mijs, W. J., de Jonge, C. R. H. I., Eds.; Plenum Press: New York, 1986; Chapter 1. Pons, J.-M.; Santelli, M. *Tetrahedron* **1988**, 44, 4295. Rehder, D.; Gailus, H. *Trends Organomet. Chem.* **1994**, *1*, 397. Iqbal, J.; Bhatia, B.; Nayyar, N. K. *Chem Rev.* **1994**, *94*, 519. Dalko, P. I. *Tetrahedron* **1995**, *51*, 7579.

CR960014G