ARTICLES

Organorhenium Chemistry

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As organometallic chemists have delved into the chemistry of rhenium, an amazing variety of unusual stable organorhenium compounds have been synthesized and novel reaction pathways have been uncovered. The broad range of stable organorhenium compounds can be traced to the availability of oxidation states from −III to VII and to the high strength of bonds to rhenium. New types of reaction mechanism are seen in response to the reluctance of rhenium to form coordinatively unsaturated complexes.

Rhenium, the last of the nonradioactive elements, was not discovered until 1925 (*1*). It is one of the three rarest elements in the earth's crust (0.0007 parts per million) and is isolated from the flue ash of molybdenum smelters. The organometallic chemistry of rhenium was little explored until recently, in part because common starting materials for rhenium chemistry are moderately expensive [\$5 per gram for Re_2O_7 and \$8 per gram for $Re_2(CO)_{10}$] and in part because rhenium has found only limited use in catalysis (Re-Pt mixtures are used in the catalytic reforming of petroleum, and Re_2O_7–$SnMe_4$–Al_2O_3 has been used as a heterogeneous catalyst for the metathesis of functionalized olefins).

In the past 10 years, there has been an explosive growth in the organometallic chemistry of rhenium as research groups from around the world have synthesized and isolated an astounding array of stable organorhenium compounds. There are three characteristics of rhenium that make its chemistry distinctive. First, the high strength of bonds made by rhenium to other elements stabilizes ordinarily reactive species and makes possible the isolation of normally unstable structural types. Second, the huge range of oxidation states available to rhenium has made it possible to isolate organometallic derivatives ranging in oxidation state from −III in $Re(CO)_4^{3-}$ to VII in $C_5Me_5ReO_3$ (Me, methyl). Third, the reluctance of rhenium to form coordinatively unsaturated complexes enhances the stability of rhenium intermediates and gives rise to unusual reaction mechanisms. These characteristics are shared by other transition metals, particularly those in the third transition series, but they are particularly pronounced for rhenium.

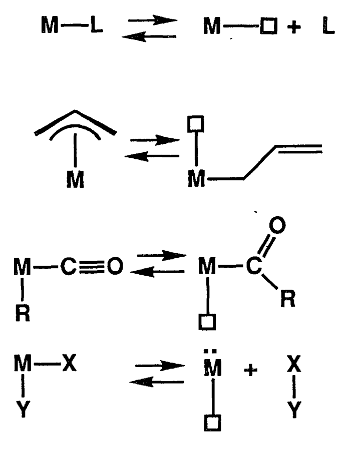
In this article, recent advances in organorhenium chemistry are highlighted that showcase some of the current trends in organometallic chemistry, including the concept of concerted organometallic reactions that avoid high-energy coordinatively unsaturated metal complexes, the preparation of novel π-propargyl complexes, the observation of agostic metal alkyls in which C–H bonds interact with a metal center, the use of chiral-at-metal complexes, the chemistry of compounds with multiple bonds between metals, the isolation of high-valent organometallic complexes, and the role of metals in the catalysis of oxidation reactions and of olefin metathesis reactions.

Concerted Organometallic Reactions

In concerted organic reactions, such as the Diels-Alder reaction between conjugated dienes and alkenes that produces cyclohexenes, two carbon-carbon bond-forming processes are combined into a single step to avoid the intervention of a high-energy diradical intermediate. In concerted organometallic reactions, two elementary processes are combined to avoid the intervention of a high-energy coordinatively unsaturated intermediate. In both cases, evidence for a concerted process comes from the observation of higher reaction rates and lower activation barriers than observed in related reactions that cannot proceed by concerted processes.

For low oxidation state transition metals, there is a strong tendency to form complexes with filled valence shells having 18 electrons (*2*). Organometallic reactions often involve elementary steps in which a high-energy 16–valence electron intermediate with a vacant coordination site is generated or in which such an intermediate is converted to a more stable 18–valence electron product. Examples of elementary processes that generate high-energy intermediates with vacant coordination sites (depicted as M–□) include ligand dissociation, π-allyl to σ-allyl conversion, alkyl migration to CO, and reductive elimination (Scheme 1; M, metal; L, ligand; R, alkyl group or other organic species; and X and Y, atomic species such as oxygen). For metals such as rhenium in the third transition series, metal-to-ligand bond strengths are particularly strong and there are high activation barriers for generation of intermediates with vacant coordination sites that do not take full advantage of the metal's bonding capabilities.

We recently reported the unusually facile rearrangement of the allyl vinyl rhenium complex **1** to the allyl vinyl ketone complex **2** and proposed a mechanism in which two consecutive concerted organometallic rearrangements occur (Scheme 2) (*3*). In contrast, the methyl vinyl rhenium complex **3** was stable for hours at 90°C. A key to understanding the mechanism of formation of **2** was the observation that the isopropyl allyl rhenium complex **4** rearranged to the stable η^3-allyl acyl complex **5**, which did not undergo reductive elimination to give a ketone. A second important observation came from a deuterium labeling study which showed that **1-d** with a deuterium label on the sp^3 allyl carbon rearranged to **2-d**, which had a deuterium label on the sp^2 allyl carbon. The net result of the conversion of **1** to **2** is the coupling of the allyl and vinyl groups to CO with coordination of both carbon-carbon double bonds to rhenium. The allyl vinyl ketone complex **2** has an interesting geometry in which the alkene ligands are "crossed." The double bond of the allyl ligand is roughly parallel to the plane of the cyclopentadienyl ligand, whereas the vinyl ligand coor-



Scheme 1. Some elementary organometallic reactions that generate or consume vacant sites.

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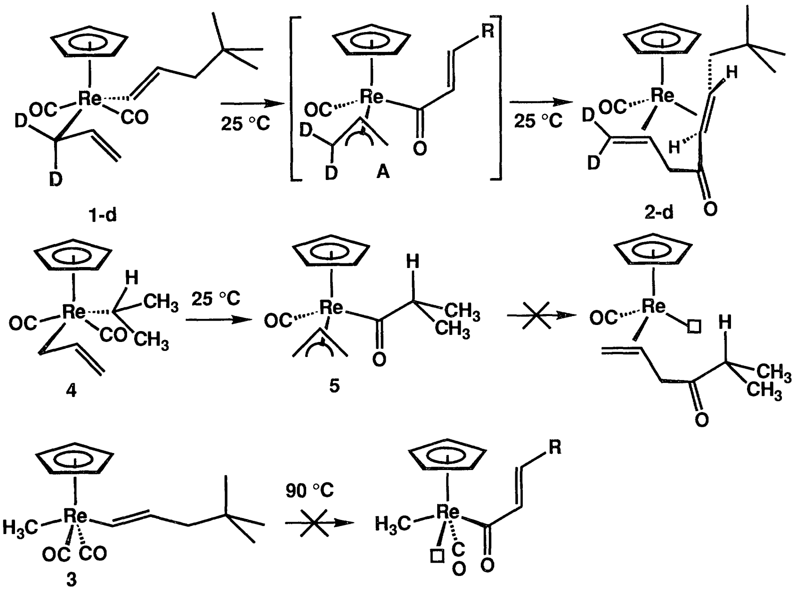
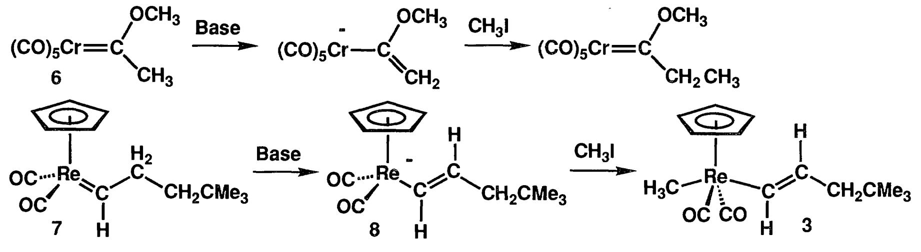


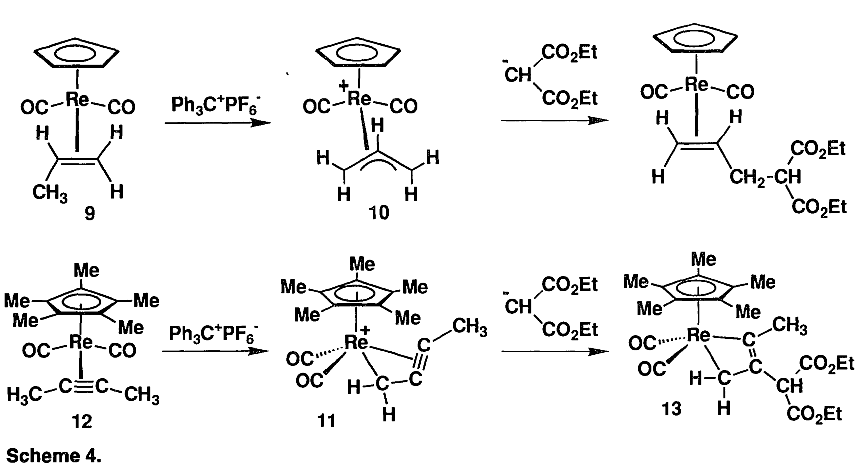
Scheme 2.

dinates roughly perpendicular to that plane.

In each of the two consecutive concerted organometallic rearrangements we have proposed in the conversion of 1 to 2 (3), two steps are combined to avoid the generation of a high-energy coordinatively unsaturated intermediate; one of the steps would normally generate a vacant coordination site, whereas the other would consume a vacant coordination site. In the first concerted reaction, the migration of a vinyl group to CO is assisted by conversion of a σ-allyl to a π-allyl group to produce the proposed reactive intermediate **A**. Such an assisted migration is not possible for the very thermally stable methyl vinyl complex 3; an unassisted migration would have led to a high-energy 16-electron intermediate that was coordinatively unsaturated. In the second concerted reaction, the reductive elimination of the allyl and acyl groups from the proposed intermediate **A** is assisted by coordination of the vinyl double bond. Vinyl coordination is readily achieved only from the *s-trans* conformation of the unsaturated acyl group; this explains the unusual parallel-perpendicular coordination of the double bonds of allyl vinyl ketone complex 2. Such an assisted reductive elimination is not possible for the isopropyl substituted acyl allyl complex 5; an unassisted elimination would have led to a high-energy 16-electron coordinatively unsaturated intermediate. The free energy barrier for the concerted organometallic reactions involved in the conversion of 1 to 2 via **A** is more than 6 kcal mol^{-1} lower than the barriers for decomposition of either 3 or 5.



Scheme 3.



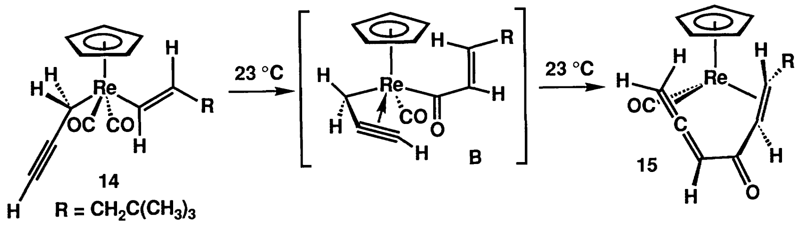
Scheme 4.

Rhenium is effective at stabilizing normally reactive species. For example, low oxidation state d^6 metal carbene complexes such as $(CO)_5Cr{=}C(OCH_3)CH_3$ (6) generally require an electron-donating methoxy or amino substituent for kinetic stabilization, but the alkyl-substituted rhenium carbene complex 7 is stable above room temperature (4). Deprotonation of low oxidation state metal carbene complexes generates vinyl anions that are readily alkylated at carbon (Scheme 3) (5). In contrast, the vinyl anion 8 generated by deprotonation of rhenium carbene complex 7 underwent alkylation at rhenium to generate alkyl vinyl rhenium complexes (3). This difference in regiochemistry of alkylation is a reflection of rhenium's ability to stabilize both the d^6 Re(I) starting material and the formally oxidized d^4 Re(III) product.

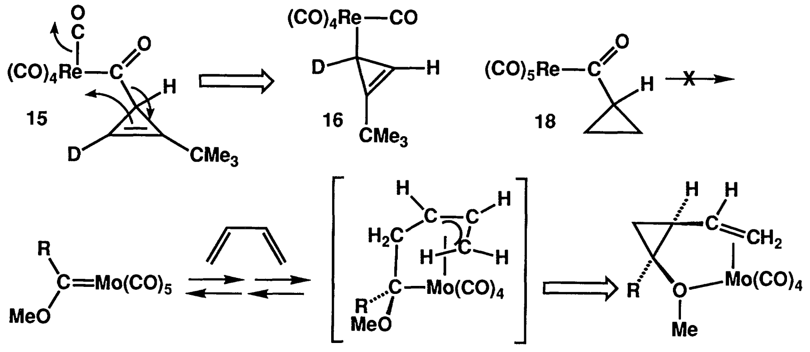
Another example of rhenium's ability to stabilize different oxidation states is seen in the reaction of rhenium(I) propene complex 9 with the hydride abstracting agent $(C_6H_5)_3C^+$, which leads to the formation of the Re(III) π-allyl complex 10. Like most cationic π-allyl complexes, 10 reacts with nucleophiles at a terminal allyl carbon to produce an elaborated rhenium alkene complex (Scheme 4; Ph, phenyl; Et, ethyl) (6).

The ease of formation and stability of π-allyl complex 10 encouraged us to attempt the synthesis of the more strained triple-bond analog, the π-propargyl complex 11. Indeed, hydride abstraction from rhenium alkyne complex 12 led to the isolation of the stable π-propargyl complex 11 in spite of its apparent angle strain (7). Remarkably, 11 reacts with nucleophiles at the central carbon of the π-propargyl ligand to produce metallacyclobutene complexes such as 13 (Scheme 4). Recently, other simple π-propargyl complexes of molybdenum, osmium, tungsten, ruthenium, and iron have been reported (8).

To explore the possibility that a σ- to π-propargyl rearrangement might assist the migration of an alkyl group to CO in a



Scheme 5.



Scheme 6. Reactions suggested to occur via a concerted mechanism are indicated by the symbol ⇨.

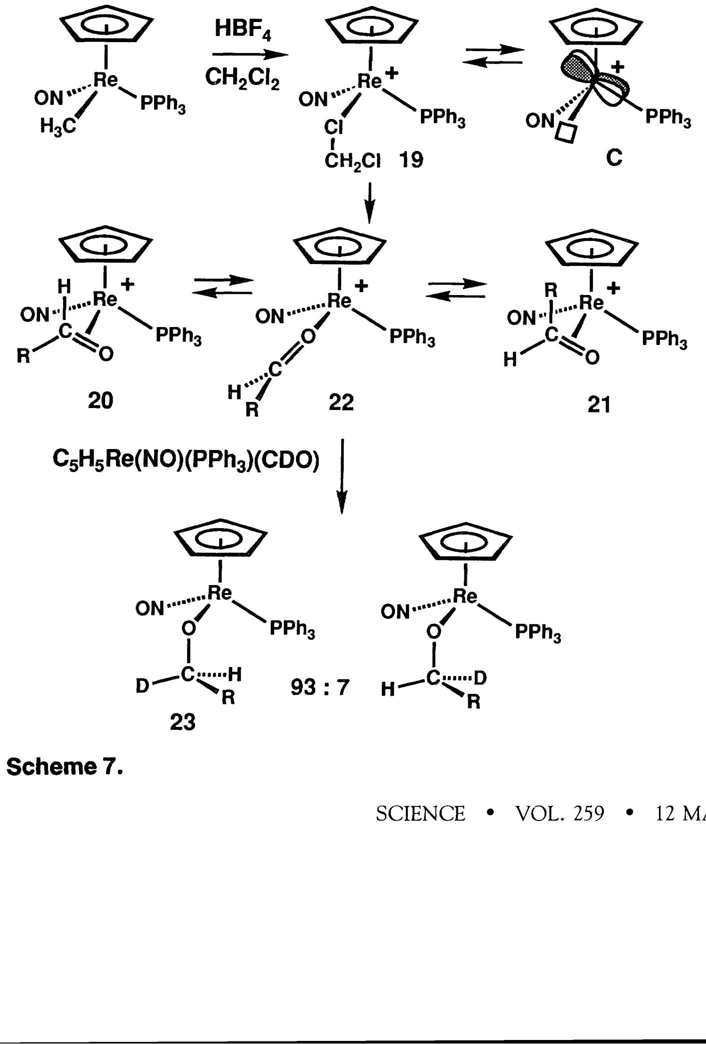
concerted organometallic reaction, we synthesized the vinyl σ-propargyl rhenium complex **14** by alkylation of rhenium vinyl anion **8** with propargyl bromide, BrCH$_2$C≡CH (*9*). Rapid rearrangement of **14** occurred at room temperature to initially produce the allenyl vinyl ketone complex **15** (Scheme 5). In spite of the apparent strain of the π-propargyl ligand in intermediate **B**, σ- to π-propargyl rearrangement is about as effective as σ- to π-allyl rearrangement in promoting vinyl migration to CO. The concerted nature of the alkyl to acyl migration and of the σ- to π-propargyl rearrangement avoids the intervention of a high-energy coordinatively unsaturated intermediate. The π-propargyl ligand promises to become increasingly important in organometallic chemistry.

Well-documented examples of concerted organometallic reactions in which elementary steps are combined to avoid a high-energy coordinatively unsaturated intermediate are still rare (Scheme 6). Hughes and co-workers proposed that the decarbonylation of the acyl rhenium complex **16** to cyclopropenyl complex **17** occurred via concerted loss of CO and cyclopropenyl migration to rhenium, based both upon the much faster reaction of the unsaturated cyclopropenyl compound **16** compared with the saturated cyclopropyl compound **18** and upon the allylic rearrangement of the cyclopropenyl unit; the concerted mechanism avoids a high-energy five-coordinate rhenium acyl intermediate (*10*). Harvey and Lund recently observed a high preference for formation of *cis* vinyl methoxy cyclopropanes from the reaction of dienes with methoxy carbene complexes; reductive elimination from an alkyl π-allyl intermediate concerted with methoxy coordination was proposed to explain the stereochemical preference (*11*).

σ- and π-Complexes of Aldehydes and Ketones

Gladysz and co-workers have exploited pseudotetrahedral "chiral-at-rhenium" C$_5$H$_5$Re(NO)(PPh$_3$)L$^+$ complexes to develop enantioselective syntheses and to probe the intimate details of the mechanisms of organometallic reactions. Because of the high strength of bonds to rhenium, the 16–valence electron fragment C$_5$H$_5$Re(NO)(PPh$_3$)$^+$ (**C**) binds an additional two-electron ligand very tightly. In addition to acting as a σ-acceptor, **C** is also a strong π-donor via its highest occupied molecular orbital (HOMO), a *d*-orbital perpendicular to the Re–N–O axis. The preferred coordination geometry of ligands on **C** maximizes overlap between the *d* orbital HOMO of **C** and the π* acceptor orbital on the unsaturated ligand and minimizes steric interactions with the large PPh$_3$ and medium-sized C$_5$H$_5$ ligands. This combination of electronic and steric effects is responsible for the efficient transmission of the chirality of **C** to new ligand-based chiral centers.

A key starting material for the preparation of C$_5$H$_5$Re(NO)(PPh$_3$)L$^+$ complexes is the very labile methylene chloride adduct C$_5$H$_5$Re(NO)(PPh$_3$)(ClCH$_2$Cl)$^+$BF$_4^-$ (**19**) formed by the low-temperature reaction of C$_5$H$_5$Re(NO)(PPh$_3$)CH$_3$ with HBF$_4$·Et$_2$O in CH$_2$Cl$_2$ (*12*). Substitution of other ligands for CH$_2$Cl$_2$ occurs readily at −40°C and proceeds with retention of stereochemistry at rhenium (Scheme 7). The second-order kinetics seen for RCN substitution for CH$_2$Cl$_2$ are consistent either with an asso-



Scheme 7.

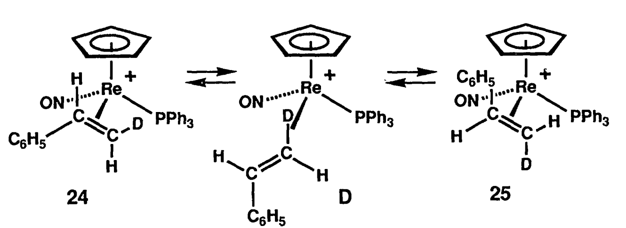
ciative mechanism involving a 20-electron transition state or with reversible CH_2Cl_2 dissociation to give the pyramidal 16-electron intermediate **C**, which is trapped in a rate-determining step by RCN.

Unsaturated organic molecules are activated toward nucleophilic attack by coordination to transition metals. Gladysz has carried out systematic studies of the binding of aldehydes and ketones to **C** and of the reactivity of the complexed carbonyl compounds. For aliphatic aldehydes such as phenylacetaldehyde, only a single diastereomer of the π-complexed aldehyde (**20**, R = $CH_2C_6H_5$) was observed by low-temperature nuclear magnetic resonance (NMR) and infrared spectroscopy (Scheme 7) (*13*). X-ray crystallography showed that the aldehyde C=O bond was aligned approximately parallel to the Re–P bond, which maximizes overlap between the *d* orbital HOMO at rhenium and the π* orbital of the aldehyde.

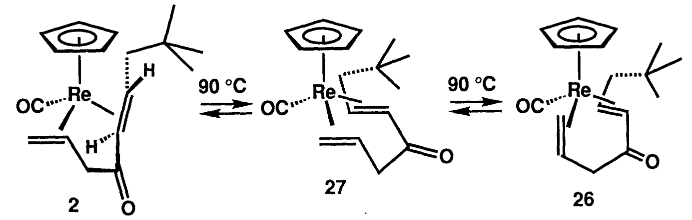
For ketones such as acetophenone, only a σ-complex similar to that depicted in **22** was observed by spectroscopy (*14*). X-ray crystallography showed that the carbonyl group and the NO ligand were approximately coplanar and that the larger phenyl group was *anti* to rhenium. This conformation maximizes overlap between the *d* orbital HOMO at rhenium and the π* orbital of the ketone and minimizes steric interactions with the phenyl group. The dichotomy between preferential π-bonding of aldehydes and σ-bonding of ketones was attributed to the greater bulk of ketones, which disfavors π-bonding, and to the greater π-acidity of aldehydes.

For aromatic aldehydes such as 4-methoxybenzaldehyde, two diastereomeric π-complexes **20** and **21** (R = C_6H_4-4-OCH_3) and a σ-complex **22** were observed by ^{31}P NMR at −137°C in a 58:14:28 ratio (Scheme 7) (*15*). Two-dimensional ^{31}P NMR experiments gave a ^{31}P chemical exchange correlation map that revealed that the two π-complexes **20** and **21** interconvert intramolecularly via the σ-complex **22**. For various substituted aldehydes, the barriers for interconversion of π-isomers varied from 10 to 15 kcal mol^{-1}.

Coordinated aliphatic aldehyde complexes such as **20** (R = $CH_2C_6H_5$) were readily reduced by the deuterated rhenium formyl complex $C_5H_5Re(NO)(PPh_3)(CDO)$ to give a 93:7 mixture of the diastereomeric rhenium alkoxide complexes **23** (Scheme 7) (*13*). Because only a single diastereomer of **20** was observable by NMR, the formation of two diastereomers of **23** suggests that reduction may occur via a σ-aldehyde complex in equilibrium with the π-complex. The stereoselectivity of the reduction is readily explained by hydride attack from the face of the aldehyde opposite the large PPh_3 ligand in the σ-complex **22**.



Scheme 8.



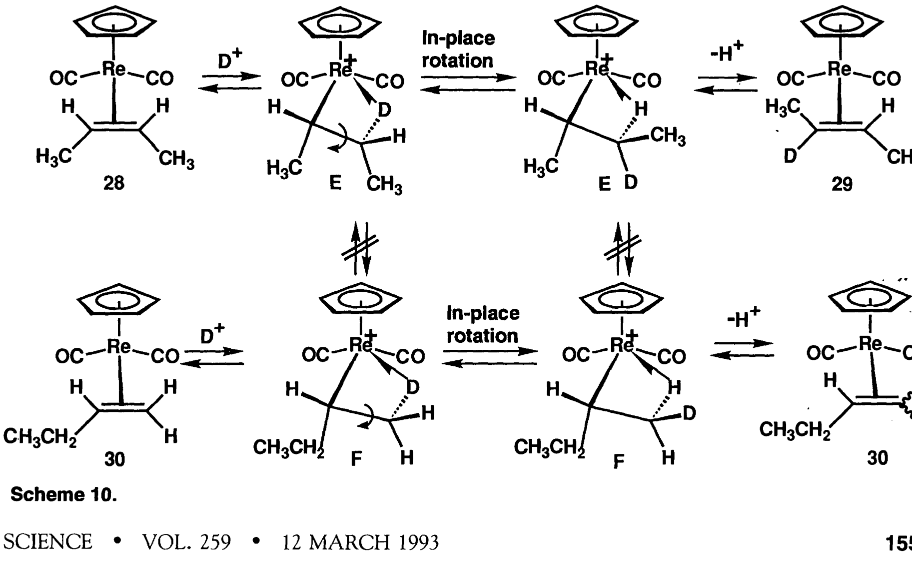
Scheme 9.

Coordinated methyl ketones are also reduced with stereoselectivities that match or exceed those obtained with other chiral hydride reductants (*15*). A variety of methods have been developed for removing the alkoxide ligand and for isolating a recyclable rhenium product with retention of stereochemistry.

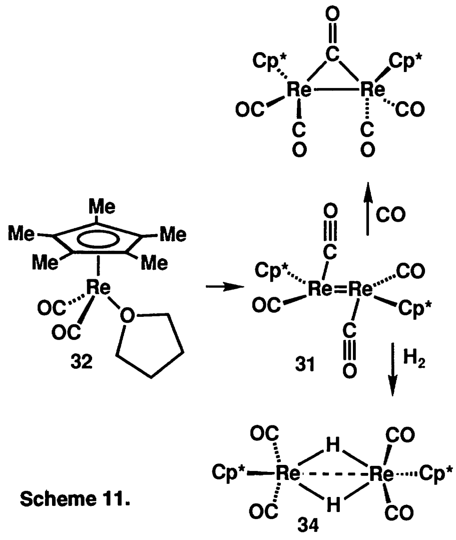
σ- and π-Complexes of Alkenes

Chiral transition metal catalysts are now extensively used for the elaboration of achiral alkenes to optically active organic molecules. When alkenes coordinate to chiral metal fragments, two π-diastereomers that differ in the alkene enantioface bound to the metal can be formed. The interconversion of these π-diastereomers plays a key role in asymmetric transformations and often occurs via reversible alkene dissociation. Recent studies by Peng and Gladysz of chiral rhenium alkene complexes have uncovered an unprecedented intramolecular pathway for interconversion of diastereomers (*16*).

Reaction of alkenes with the CH_2Cl_2 complex **19** initially produces 2:1 mixtures of diastereomeric alkene complexes such as **24** and **25** (Scheme 8). The alkene C=C bond is aligned parallel to the Re–P bond, which gives optimum overlap of the donor *d* orbital on rhenium and the acceptor π* alkene orbital. Upon heating at 100°C, isomerization to a 90:10 mixture of **24**:**25** took place. No exchange with deuterated alkenes or with $P(C_6D_5)_3$ was seen up to 150°C. Retention of configuration at Re and the absence of scrambling of *E*/*Z* deuterium labels ruled out a number of intramolecular mechanisms. A kinetic deuterium isotope effect of 1.64 (k_H/k_D, where *k* is the rate constant) for the (*E*)-CHD=CHC_6H_5 complex suggested the involvement of a C–H bond in the isomerization. Gladysz and Peng proposed a mechanism involving movement of rhenium through the π-nodal plane of the alkene via a carbon-hydrogen "σ-bond complex" (*16*). The interaction of C–H bonds with metals is so weak (<10 kcal mol^{-1}) that C–H σ-bond complexes are normally observed only as part



Scheme 10.



Scheme 11.

of a chelate system that is sometimes referred to as an agostic C–H–M complex. The intervention of a carbon-hydrogen "σ-bond complex" avoids formation of the high-energy coordinatively unsaturated intermediate **C**. An alternative mechanism involving a vinyl hydride oxidative addition product has not been rigorously excluded.

We recently discovered another case in which rhenium traverses alkene enatiofaces without alkene dissociation. When a solution of the "parallel-perpendicular" allyl vinyl ketone complex **2** was heated at 90°C, a 1:2 equilibrium mixture of **2** and an isomeric "perpendicular-parallel" complex **26** in which the opposite enantiofaces of the diene were complexed to rhenium slowly formed (Scheme 9) (*17*). In addition, ~5% of another isomer, possibly the "parallel-parallel" complex **27**, was observed. We suggest that this isomerization may proceed via a carbon-hydrogen "σ-bond complex" because the rate of equilibration was unaffected by added ^{13}CO or PMe_3 and because no products derived from a coordinatively unsaturated intermediate were observed.

A carbon-hydrogen "σ-bond complex" was also found to be involved in the acid-catalyzed isomerization and deuterium exchange reactions of rhenium alkene complexes (*18*). CF_3CO_2H catalyzed the isomerization of the *cis*-2-butene rhenium complex **28** to a 45:55 equilibrium mixture of **28** and the *trans*-2-butene complex **29** (Scheme 10). Isomerization of **28** catalyzed by CF_3CO_2D initially gave only *trans*-2-butene complex **29** monodeuterated at the vinyl position. It seemed curious that the postulated 2-butyl rhenium intermediate **E** did not deprotonate to give the 1-butene complex **30**. Treatment of **30** with excess CF_3CO_2D led only to rapid exchange of deuterium into the terminal vinyl position and slower exchange into the secondary vinyl position. These results require the intervention of two different (2-butyl)rhenium intermediates, **E** and **F**, because no interconversion of 1-butene and 2-butene complexes was observed. To explain these observations, we proposed that the two intermediates fail to interconvert because of an unusually strong agostic interaction between a C–H bond and rhenium. An "in-place rotation" of the agostic alkyl group can account for the *cis-trans* isomerization and deuterium exchange (*19*). In-place rotation and deprotonation was found to occur several thousand times faster than the agostic interaction was broken to give a coordinatively unsaturated intermediate.

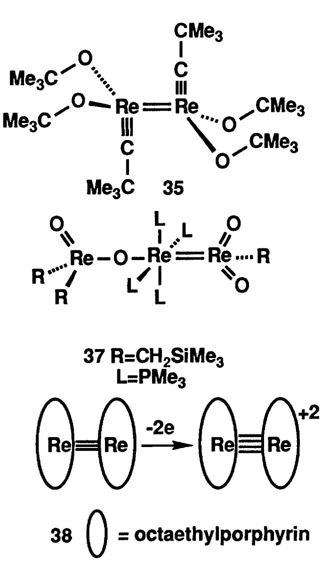
Rhenium-Rhenium Double Bonds

Historically, rhenium has played a central role in the understanding of metal-metal multiple bonding. In 1965, Cotton first recognized the existence of a quadruple bond in the $Re_2Cl_8^{2-}$ ion (*20*). The eclipsed geometry and short 2.24 Å Re–Re distance were explained in terms of one σ, two π, and one δ bond. In the past few years, several compounds with unusual Re–Re double bonds have been discovered.

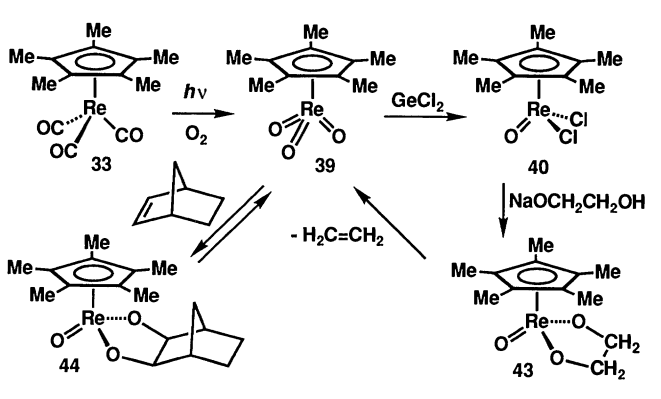
In a serendipitous discovery, we found that $C_5Me_5(CO)_2Re{=}Re(CO)_2C_5Me_5$ (**31**) was formed quantitatively from $C_5Me_5Re(CO)_2(THF)$ (**32**) (Scheme 11; THF, tetrahydrofuran; Cp, cyclopentadienyl) (*21*). Previously, solutions of **32** and $C_5Me_5Re(CO)_3$ (**33**) prepared by photolysis of **33** in THF had been used in synthesis but pure **32** had never been isolated (*22*). For use in the preparation of pure rhenium-alkene and alkyne complexes, we isolated **32** as a yellow solid by addition of hexane to a concentrated solution of the photolysis mixture. When solid yellow **32** was stored for 1 week in a glove box, it was cleanly converted to dark green solid **31**.

The x-ray crystal structure of **31** shows that the 2.72 Å Re=Re double bond is supported only by semibridging carbonyl ligands; **31** is a rare example of a formal dimer of a 16–valence electron d^6 metal fragment. The Re=Re double bond can be described in terms of $\sigma^2\pi^4\delta^2\delta^{*2}\pi^{*2}$ metal-metal bonding; the C_5Me_5 group and the semibridging carbonyl groups serve to break the degeneracy of the π* orbitals. Although **31** is thermally stable to more than 100°C, it is kinetically extremely reactive: addition of CO occurs within seconds at −80°C to produce $C_5Me_5(CO)_2Re(\mu\text{-}CO)Re(CO)_2C_5Me_5$. Dihydrogen also reacts with **31** within seconds at −80°C to produce the new dirhenium dihydride $C_5Me_5(CO)_2Re(\mu\text{-}H)_2Re(CO)_2C_5Me_5$ (**34**) (*21*). Upon heating at 100°C, **34** releases H_2 and reforms **31**. Green and Mountford reported the only previous example of the reversible thermal addition of H_2 to a metal-metal multiple bond in their studies of $[W(C_5H_4R)Cl_2(\mu\text{-}H)]_2$ (*23*).

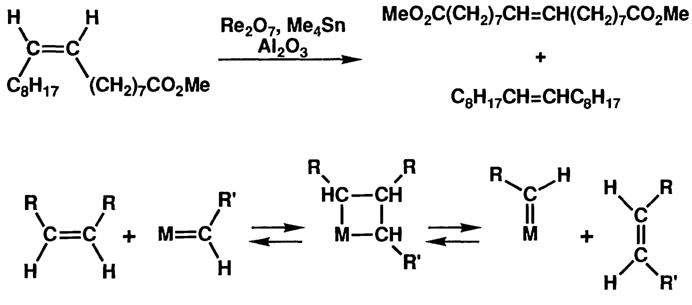
Schrock and co-workers recently characterized the unusual rhenium complex $[Re(C\text{-}t\text{-}Bu)(O\text{-}t\text{-}Bu)_2]_2$ **35**, which contains a very rare "unsupported" metal-metal double bond (Scheme 12) (*24*). Species with metal multiple bonds often have bridging ligands that "support" the metal-metal in-



Scheme 12.



Scheme 13.



Scheme 14.

teraction; **35** is the formal dimer of a 12–valence electron d^2 fragment. The 2.34 Å Re–Re double-bond distance of **35** is substantially shorter than in **31**; this difference can be attributed to the higher oxidation state of **35** and to the $\sigma^2\pi^2$ formulation of the double bond. Unsupported metal-metal double bonds have been reported previously for macrocyclic complexes such as [Ru(octaethylporphyrin)]$_2$ (*25*) and **37** (*26*). Collman and co-workers have reported an unsupported Re≡Re triple bond ($\sigma^2,\pi^4,\delta^2,\delta^{*2}$) in [Re(octaethylporphyrin)]$_2$ (**38**) (*27*). Oxidation of **38** produced a dication with a quadruple bond (σ^2,π^4,δ^2).

High Oxidation State Complexes

Rhenium has played a central role in the development of high oxidation state organometallic chemistry (*28*). Organometallic chemists trained to rigorously exclude oxygen from their reactions were amazed by the report of Herrmann and co-workers that $C_5Me_5ReO_3$ (**39**) could be obtained in high yield by photooxidation of $C_5Me_5Re(CO)_3$ (**33**) (Scheme 13) (*22*). The complex **39** is an air and water stable yellow solid that is sublimeable and stable to 250°C. It was very surprising that Re(VII) was compatible with otherwise easily oxidized π-aromatic ligands. This compound is a versatile starting material; **39** is readily reduced to $C_5Me_5ReOCl_2$ (**40**) by treatment with $GeCl_2$ (*29*) or alkylated and reduced to $C_5Me_5Re(O)Me_2$ (**41**) by reaction with Me_2Zn (*30*). In turn, **41** was converted to the tetramethyl derivative $C_5Me_5ReMe_4$, the initial example of an organorhenium (V) compound without heteroatom ligands (*31*).

The dioxametallacyclopentane complex **43**, related to complexes obtained from the OsO_4 oxidation of alkenes, was obtained by Herrmann *et al.* from reaction of dichloride **40** with the sodium salt of ethylene glycol (Scheme 13) (*32*). When **43** was heated at 100°C, ethylene was eliminated and the trioxo complex **39** was formed. Gable and Phan recently discovered that norbornene reacts reversibly with the trioxo complex **39** to form the isomeric dioxametallacyclopentane complexes (**44**) (*33*). Studies of these dioxarhenacyclopentane complexes as models for OsO_4 alkene oxidation should provide interesting mechanistic insights.

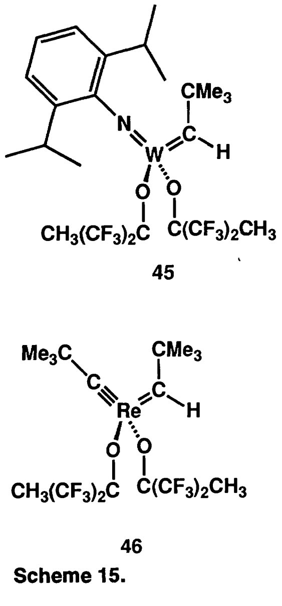
Rhenium Olefin and Acetylene Metathesis Catalysts

In the olefin metathesis reaction, alkene carbon-carbon double bonds are cleaved and remade in new ways (Scheme 14) (*34*). Mechanistic studies established that alkylidene units are exchanged in a nonpairwise manner via reversible reaction of alkenes with metal-alkylidene complexes. Organometallic complexes in their highest oxidation states are normally essential for olefin metathesis (*35*). A heterogeneous rhenium-based metathesis catalyst prepared from Re_2O_7, Al_2O_3, and Me_4Sn was one of the first catalysts found to be effective for the metathesis of functionalized alkenes such as methyl oleate.

Recent work from Herrmann's group has shown that CH_3ReO_3 on acidic Al_2O_3-SiO_2 is a very active catalyst for metathesis of functionalized alkenes at room temperature (*36*). When CD_3ReO_3 was used, CD_2=CHR products were obtained. The mode of generation of the required Re=CD_2 catalyst remains obscure.

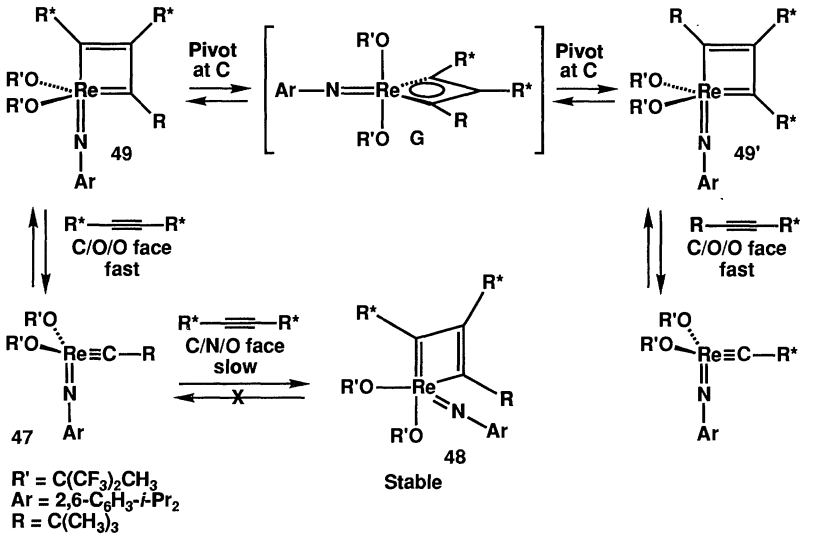
By carefully surveying a wide range of tungsten alkylidene complexes, Schrock's group found that W(CHR)(NR′)(OR″)$_2$ complexes (**45**) with bulky amido groups and electron-withdrawing alkoxy groups were very active metathesis catalysts (Scheme 15) (*37*). Since Re≡CR and W=NR are isoelectronic units, Schrock synthesized Re(CHR)(CR)(OR″)$_2$ (**46**) as a potential metathesis catalyst and found that it was effective for the metathesis of both 2-pentene and methyl oleate (*38*).

The metathesis of alkynes proceeds by reversible reaction of metal alkylidyne com-


45

46

Scheme 15.



R′ = C(CF$_3$)$_2$CH$_3$
Ar = 2,6-C$_6$H$_3$-*i*-Pr$_2$
R = C(CH$_3$)$_3$

Scheme 16.

plexes ($M\equiv CR$) with alkynes to produce metallacyclobutadienes. Schrock's group has made a series of stable rhenium alkylidyne compounds related to **47** that illustrate the complexities of the mechanism of alkyne metathesis (Scheme 16) (39). When the alkoxide and alkylidyne ligands have small substituents, an irreversible reaction with alkynes produces stable metallacycles **48** with an apical alkoxy ligand; no alkyne metathesis is seen. Complex **47** having large alkoxy and alkylidyne substituents was unusual in that it effectively catalyzed metathesis of alkynes with bulky substituents. Both alkylidyne complexes similar to **47** and an isomeric metallacycle with an apical imido ligand were observed during catalysis.

Schrock and co-workers have proposed that for complexes with relatively small substituents on the alkoxy and alkylidyne ligands, electronically preferred attack of the alkyne occurs on the C/N/O face of the pseudotetrahedral complex to produce the stable metallacycle **48** and no catalysis is seen (39). However, for bulky catalysts and alkynes, the alkyne attacks the less hindered C/O/O face of the pseudotetrahedral catalyst **47** to give the reactive metallacycle **49**. Isomerization of **49** to the related metallacycle **49′**, which also has an apical imido group, proceeds through intermediate **G** by two Berry pseudorotations. A new alkyne is then eliminated from **49′** by the microscopic reverse of the initial addition. Occasionally, alkyne addition to the C/N/O face of **47** occurs to produce the stable metallacycle **48** and catalysis ceases. This explanation requires that metallacycle **48** be much more thermodynamically stable than **49** and that conversion of **49** to **48**, which could occur by a Berry pseudorotation about an oxygen pivot, be very slow.

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Turning Down the Heat: Design and Mechanism in Solid-State Synthesis

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Solid-state compounds have historically been prepared through high-temperature solid-solid reactions. New mechanistic understanding of these reactions suggests possible routes to metastable compositions and structures as well as to thermodynamically stable, low-temperature phases that decompose at higher temperatures. Intermediate-temperature synthetic techniques, including flux and hydrothermal methods, as well as low-temperature intercalation and coordination reactions, have recently been developed and have been used to prepare unprecedented materials with interesting electronic, optical, and catalytic properties. The trend in modern solid-state synthesis resembles increasingly the approach used in small-molecule chemistry, in the sense that attention to reaction mechanism and the use of molecular building blocks result in an ability to prepare new materials of designed structure.

The birth and development of useful technologies often hinge on the availability of solid-state materials with appropriate physical and chemical properties. Forty years ago, the preparation of pure semiconductors as single crystals led to a complete transformation of the electronics industry. Today, new high-temperature ceramic superconductors, nonlinear optical solids and thin films, supermagnetic alloys, and "nanophase" catalytic materials also promise to initiate sweeping changes in relevant technologies, including communications, computing, transportation, and chemical manufacturing, to name the most obvious.

Although many of these key solid-state materials have been discovered the old-fashioned way (by accident), rational synthesis is now playing an increasingly important role. The interplay between structural chemistry, physical measurement, and theory is today sufficiently refined that it is often possible to predict a priori the structure and

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