

Mechanism of Rearrangement of an Allylvinylrhenium Complex to an (Allyl vinyl ketone)rhenium Complex: Role of Concerted Organometallic Reactions in Avoiding High-Energy Coordinatively Unsaturated Intermediates

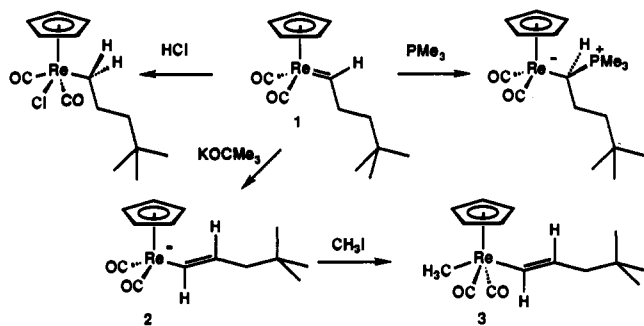
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Abstract: Deprotonation of $C_5H_5(CO)_2Re=CHCH_2CH_2CMe_3$ (**1**) with $KOCMe_3$ produced the vinylrhenium anion $K^+C_5H_5(CO)_2Re[(E)-CH=CHCH_2CMe_3]^-$ (**2**), which reacted with MeI at the rhenium center to produce *trans*- $C_5H_5(CO)_2Re(CH_3)[(E)-CH=CHCH_2CMe_3]$ (**3**). Reaction of **2** with allyl bromide led to a similar allylvinylrhenium complex *trans*- $C_5H_5(CO)_2Re(CH_2CH=CH_2)[(E)-CH=CHCH_2CMe_3]$ (**4**). However, unlike methylvinylrhenium complex **3** which was kinetically very stable, the allylvinylrhenium compound **4** reacted rapidly at room temperature to produce the (allyl vinyl ketone)rhenium complex $C_5H_5(CO)Re(\eta^2, \eta^2-CH_2=CHCH_2COCH=CHCH_2CMe_3)$ (**5**), which was characterized spectroscopically and by X-ray crystallography. The conversion of **4** to **5** was not affected by added PMe_3 . Net inversion of allylic regiochemistry was observed in the conversion of deuterated allylvinylrhenium complex **4- αd_2** to **5- γd_2** . The allylisopropylrhenium compound *trans*- $C_5H_5(CO)_2Re(CH_2CH=CH_2)[CH(CH_3)_2]$ (**9**) rearranged to give the stable η^3 -allyl isobutyryl complex $C_5H_5(CO)Re(\eta^3-CH_2CHCH_2)[COCH(CH_3)_2]$ (**10**), which was resistant to reductive elimination to a ketone. A mechanism involving two consecutive concerted organometallic reactions in avoiding high-energy coordinatively unsaturated intermediates is proposed.

We recently reported that the rhenium carbene complex $C_5H_5(CO)_2Re=CHCH_2CH_2CMe_3$ (**1**) displays unusual amphiphilic reactivity: both nucleophiles and electrophiles added to the carbene carbon.¹ For example, PMe_3 added to **1** to produce



$C_5H_5(CO)_2ReCH(PMe_3)CH_2CH_2CMe_3$ and HCl added to **1** to produce *cis*- $C_5H_5(CO)_2Re(Cl)CH_2CH_2CH_2CMe_3$. Deprotonation of **1** with $KOCMe_3$ produced the vinylrhenium anion (\approx carbene anion) $K^+C_5H_5(CO)_2Re[(E)-CH=CHCH_2CMe_3]^-$ (**2**),¹ in a reaction similar to that of electrophilic carbene complexes.² Unlike anions of electrophilic carbene complexes which undergo alkylation at the β -vinyl carbon,³ $K^+C_5H_5(CO)_2Re[(E)-CH=CHCH_2CMe_3]^-$ (**2**) reacted with MeI at the rhenium center to produce *trans*- $C_5H_5(CO)_2Re(CH_3)[(E)-CH=CHCH_2CMe_3]$ (**3**).¹ Here we report that reaction of **2** with allyl bromide led to a similar allylvinylrhenium complex $C_5H_5(CO)_2Re(CH_2CH=CH_2)[(E)-CH=CHCH_2CMe_3]$ (**4**). However, unlike methylvinylrhenium complex **3** which was kinetically very stable, the allylvinylrhenium compound **4** reacted

rapidly at room temperature to produce the (allyl vinyl ketone)rhenium complex $Cp(CO)Re(\eta^2, \eta^2-CH_2=CHCH_2COCH=CHCH_2CMe_3)$ (**5**).⁴ Detailed mechanistic studies of this dramatic acceleration of ketone formation by the allyl ligand have led us to propose a mechanism that involves two consecutive concerted organometallic reactions that each combine two elementary steps to avoid the intervention of a high-energy coordinatively unsaturated intermediate.

Results

Generation of Vinylrhenium Anion $C_5H_5(CO)_2Re[(E)-CH=CHCH_2CMe_3]^-$ (2**).** Deprotonation of the rhenium carbene complex $C_5H_5(CO)_2Re=CHCH_2CH_2CMe_3$ (**1**) with $KOC(CH_3)_3$ in THF produced the rhenium vinyl anion complex $K^+C_5H_5(CO)_2Re[(E)-CH=CHCH_2CMe_3]^-$ (**2**) as a pale yellow solid. In the 1H NMR spectrum of **2** in CD_3CN , the large 16.2-Hz coupling between the α and β vinyl protons at δ 7.44 and 5.48 established the *trans* relationship of the vinyl protons. The 0.8 ppm upfield shift of the C_5H_5 resonance of anionic complex **2** (δ 4.91) compared with that of the neutral carbene complex **1** (δ 5.75) is consistent with an increase in electron density at rhenium upon deprotonation. The reaction of **2** with mild protic acids such as CH_3OH led to regeneration of carbene complex **1**.⁵

Synthesis of the Kinetically Stable Methylvinylrhenium *trans*- $C_5H_5(CO)_2Re(CH_3)[(E)-CH=CHCH_2CMe_3]$ (3**).** In an attempt to generate new, elaborated carbene complexes, the reaction of the carbene anion **2** with alkylating agents was examined. In contrast to the reaction of **2** with a protic acid, addition of electrophilic alkylating agents occurred at rhenium to generate neutral *trans*-dialkylrhenium complexes. For example, methylation of **2** with CH_3I gave *trans*- $C_5H_5(CO)_2Re(CH_3)[(E)-CH=CHCH_2CMe_3]$ (**3**) as an air-stable yellow solid, which was isolated by chromatography on silica gel and vacuum sublimation at 65 °C.

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In the ^1H NMR spectrum of **3**, the large 15.7-Hz coupling between the vinyl protons at δ 6.74 (dt, $J = 15.7, 1.2$ Hz) and 4.77 (dt, $J = 15.7, 7.2$ Hz) established the trans geometry of the double bond. The relative intensities of the two CO bands in the IR spectrum of **3** at 2009 (m) and 1935 (s) cm^{-1} established the trans relationship of the carbonyl groups.⁶ For a trans carbonyl complex with an interligand angle $>90^\circ$, the higher energy symmetric stretch is weaker than the lower energy asymmetric stretch. For a cis carbonyl complex with an interligand angle $<90^\circ$, the higher energy symmetric stretch has greater intensity. Both the equivalence of the methylene protons at δ 1.96 in the ^1H NMR spectrum and the equivalence of the CO resonances at δ 199.0 in the ^{13}C NMR of **3** are consistent with a trans relationship of the carbonyl groups and of the alkyl groups.

The alkylation of the vinylrhenium anion at the metal center rather than at the β -vinyl carbon is unusual. Most vinylmetal complexes (and anions of electrophilic metal carbene complexes) undergo alkylation at the β -vinyl carbon.³ For example, alkyl halides,² epoxides,⁷ and aldehydes⁸ react with the $(\text{CO})_5\text{Cr}(\text{C}(\text{OCH}_3)=\text{CH}_2)^-$ at the β -vinyl carbon. Similarly, $\text{C}_5\text{H}_5(\text{NO})(\text{PPh}_3)\text{ReCH}=\text{C}(\text{CH}_3)_2$ was methylated by $\text{CH}_3\text{SO}_3\text{F}$ at the β -vinyl carbon to give the rhenium carbene complex $[\text{C}_5\text{H}_5(\text{NO})(\text{PPh}_3)\text{Re}=\text{CHC}(\text{CH}_3)_3]^+\text{FSO}_3^-$.⁹ The tendency of vinylrhenium anion **2** to undergo alkylation at the metal center is probably related to the high kinetic and thermodynamic stability of $\text{Cp}(\text{CO})_2\text{ReR}_2$ systems.¹⁰ Conversely, the failure of anions of chromium carbene complexes to react with electrophiles at the metal center is probably related to the instability of $(\text{CO})_5\text{CrR}_2$ systems.

On being heated at 90°C in CD_3CN , **3** slowly decomposed ($k = 2.9 \times 10^{-5} \text{ s}^{-1}$, $t_{1/2} = 6.6$ h, $90.0 \pm 0.2^\circ\text{C}$, $\Delta G^\ddagger = 28.9 \text{ kcal mol}^{-1}$) to form a mixture of uncharacterized complexes. The decomposition of **3** occurred somewhat more rapidly in the presence of 0.35 M PMe_3 ($k = 1.4 \times 10^{-4} \text{ s}^{-1}$, $t_{1/2} = 1.4$ h, $90.0 \pm 0.2^\circ\text{C}$, $\Delta G^\ddagger = 27.8 \text{ kcal mol}^{-1}$). The stability of **3** is similar to that of $\text{C}_5\text{H}_5(\text{CO})_2\text{Re}(\text{CH}_3)_2$,¹⁰ which survived chromatography and sublimation at 45°C and decomposed at 150 – 155°C .

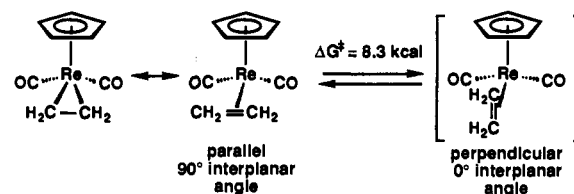
Synthesis of the Kinetically Reactive Allylvinylrhenium Complex *trans*- $\text{C}_5\text{H}_5(\text{CO})_2\text{Re}(\text{CH}_2\text{CH}=\text{CH}_2)[(\text{E})\text{-CH}=\text{CHCH}_2\text{CMe}_3]$ (4**).** The reaction of **2** with allyl bromide also led to alkylation at rhenium and produced the allylvinylrhenium complex *trans*- $\text{C}_5\text{H}_5(\text{CO})_2\text{Re}(\text{CH}_2\text{CH}=\text{CH}_2)[(\text{E})\text{-CH}=\text{CHCH}_2\text{CMe}_3]$ (**4**). In the ^1H NMR spectrum of **4**, resonances at δ 6.73 (dt, $J = 16.0, 2.5$ Hz, $\text{ReCH}=\text{CH}$), 5.78 (dt, $J = 17.0, 10.0$ Hz, $\text{ReCH}=\text{CH}$), and 1.97 (dd, $J = 10.0, 2.0$ Hz, $\text{ReCH}=\text{CHCH}_2$) established the presence of a trans vinyl ligand and resonances at δ 6.00 (m, $\text{ReCH}_2\text{CH}=\text{CH}_2$), 4.66 (dm, $J = 18.0, \text{ReCH}_2\text{CH}=\text{CHH}$), 4.44 (dd, $J = 12.5, 3.5$ Hz, $\text{ReCH}_2\text{CH}=\text{CHH}$), and 2.55 (br d, $J = 10.0$ Hz, $\text{ReCH}_2\text{CH}=\text{CH}_2$) established the presence of an η^1 -allyl ligand. The NMR equivalence of the CH_2 protons in each of the two different methylene groups of **4** and the relative intensities of the two CO bands in the IR spectrum⁶ of **4** at 2007 (s) and 1934 (vs) cm^{-1} established the trans relationship between the allyl and vinyl ligands.

Surprisingly, **4** rearranged rapidly in CD_3CN to produce the (allyl vinyl ketone)rhenium complex $\text{C}_5\text{H}_5(\text{CO})\text{Re}(\eta^2, \eta^2\text{-CH}_2=\text{CHCH}_2\text{COCH}=\text{CHCH}_2\text{CMe}_3)$ (**5**). This transformation involves the coupling of a carbonyl ligand with both the vinyl and the allyl groups and coordination of both carbon-carbon double bonds to rhenium. The rate of conversion of 0.05 M **4** to **5** (k

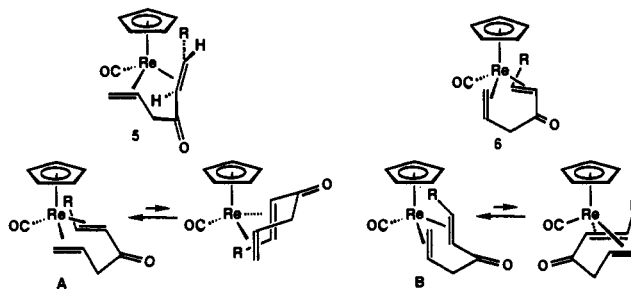
$= 5.0 \times 10^{-4} \text{ s}^{-1}$, $t_{1/2} = 23$ min, 25°C , $\Delta G^\ddagger = 21.9 \text{ kcal mol}^{-1}$) was followed by ^1H NMR using benzene as an internal standard, and linear first-order rate plots were obtained to over 90% conversion. In an effort to trap possible coordinatively unsaturated intermediates, the rearrangement of **4** to **5** was studied in the presence of 0.36 M PMe_3 . The rate of isomerization was essentially unchanged ($k = 4.7 \times 10^{-4} \text{ s}^{-1}$, $t_{1/2} = 24$ min, 23°C), and no new products were observed.

Infrared and NMR spectroscopy established the basic structure of **5**. The IR spectrum of **5** indicated the presence of a single CO ligand [1925 (s) cm^{-1}] and a ketone carbonyl group [1675 (m) cm^{-1}]. In the ^1H NMR of **5**, the allyl and vinyl ligands gave rise to complex overlapping separate **4** and **5** spin systems that were completely analyzed with the aid of multiple single-frequency decoupling experiments. The 8.5-Hz coupling between the trans vinyl hydrogens of the complexed vinyl group of **5** is smaller than that seen for noncomplexed double bonds. The trans geometry of the complexed vinyl group and the precise coordination mode of the diene fragment of **5** were established by a single-crystal X-ray study.

In $\text{Cp}(\text{CO})_2\text{M}(\text{alkene})$ complexes, the preferred orientation of the alkene C=C bond is parallel to the plane of the Cp ring.¹¹ The preference for this geometry is best understood in terms of a metallacyclopropane resonance structure that resembles the stable 4-legged piano stool geometry of $\text{Cp}(\text{CO})_2\text{ReMe}_2$. Rotation of the alkene ligand in $\text{Cp}(\text{CO})_2\text{Re}(\text{CH}_2=\text{CH}_2)$ has been studied by dynamic NMR spectroscopy at low temperature.¹² The low alkene rotational barrier ($\Delta G^\ddagger = 8.3 \text{ kcal mol}^{-1}$) indicates that a "perpendicular" alkene geometry is only slightly less stable than the "parallel" geometry. To more quantitatively discuss the geometry of $\text{Cp}(\text{CO})_2\text{Re}(\text{alkene})$ complexes, we focus attention on the angle between the plane defined by the Cp centroid, Re, and the center of the alkene C=C bond and the plane defined by Re and the C=C bond. We will refer to two extreme geometries: a parallel geometry (90° interplanar angle) and a perpendicular geometry (0° interplanar angle).



There are four possible (allyl vinyl ketone)rhenium diastereomers that differ in whether the two alkene units are coordinated in a parallel or perpendicular geometry. These complexes differ with respect to which alkene enantiofaces are coordinated to Re. The four possible isomers obtainable from **4** are the parallel-perpendicular isomer **5**, the perpendicular-parallel isomer **6**, the parallel-parallel isomer **A**, and the perpendicular-perpendicular isomer **B**, which are shown in idealized conformations as follows:



Several "rotamers" of these diastereomers are possible; the

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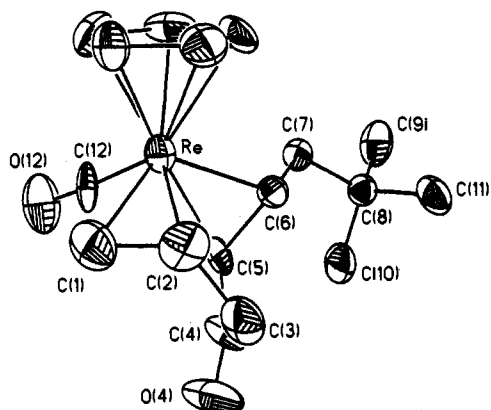


Figure 1. X-ray crystal structure of $C_5H_5(CO)Re(\eta^2, \eta^2-CH_2=CHCH_2-COCH=CHCH_2CMe_3)$ (**5**).

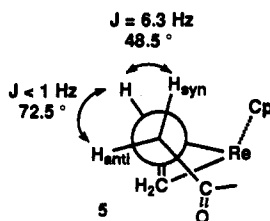
Table I. Selected Bond Lengths (Å) and Angles (deg) for $C_5H_5(CO)Re(\eta^2, \eta^2-CH_2=CHCH_2-COCH=CHCH_2CMe_3)$ (**5**)

Re-C(1)	2.196(21)	C(2)-C(3)	1.513(28)
Re-C(2)	2.246(19)	C(3)-C(4)	1.481(31)
Re-C(5)	2.243(15)	C(4)-O(4)	1.201(29)
Re-C(6)	2.188(17)	C(4)-C(5)	1.531(27)
Re-C(12)	1.890(17)	C(5)-C(6)	1.416(21)
C(1)-C(2)	1.417(29)		
C(1)-C(2)-C(3)	120.8(18)	C(5)-C(6)-C(7)	119.2(12)
C(2)-C(3)-C(4)	109.7(17)	C(3)-C(4)-O(4)	125.3(21)
C(3)-C(4)-C(5)	114.7(18)	O(4)-C(4)-C(5)	119.7(20)
C(4)-C(5)-C(6)	121.7(15)		

conformations seen in crystal structures or that appear sterically less strained from examination of models are depicted.

The structure of **5** was determined by X-ray crystallography (Figure 1; Table I). An interesting feature is the parallel-perpendicular conformation of the allyl vinyl ketone ligand. That is, the allyl double bond is approximately parallel to the plane defined by the cyclopentadienyl ring (82.5° interplanar angle) while the vinyl double bond is approximately perpendicular (8.6° interplanar angle). This type of crossed dialkene coordination has been observed in platinum complexes of the constrained diene 5-methylenecycloheptene.¹³ In the case of **5**, molecular models suggest that the two carbon bridge between the two alkenes does not constrain the system to a parallel-perpendicular geometry. Indeed, the perpendicular-parallel geometry of **6**, the parallel-parallel geometry of **A**, and even the perpendicular-perpendicular geometry of **B** appear sterically accessible. The observation detailed below that **5** isomerizes to an equilibrium mixture of **5** and **6** at elevated temperature indicates that the formation of the parallel-perpendicular isomer **5** is kinetically controlled.

In the X-ray crystal structure of **5**, the dihedral angles between the central allylic proton and the allylic protons α to the carbonyl



group were 48.5 and 72.5° . In the 1H NMR spectrum of **5**, only one of these allylic protons at δ 2.00 (dd, $J = 16.3, 6.3$ Hz) showed significant coupling to the adjacent $CH=C$ proton at δ 2.10 (m), while the other allylic proton at δ 1.66 (d, $J = 16.3$ Hz)

had <1 Hz coupling to the same proton. On the basis of the expected angular dependence of coupling constants,¹⁴ the large 6.3-Hz coupling can confidently be assigned to the proton with a 48.5° dihedral angle, while the negligible 1-Hz coupling is assigned to the proton with a 72.5° dihedral angle. The angular dependence of coupling constants to allylic protons should be useful in future assignments of the stereochemistry of substituted allylic systems when X-ray data are unavailable.

Inversion of Allylic Regiochemistry in Formation of Allyl Vinyl Ketone Complexes. The contrast between the rapid rearrangement of allylvinylrhenium complex **4** to allyl vinyl ketone complex **5** and the kinetic stability of methylvinylrhenium complex **3** suggested that the allyl group assisted in the migrations to CO. Two possible roles for the acceleration by the allyl ligand were initially considered. Migration of the allyl group to CO with allylic inversion could produce an acyl derivative in which the allylic double bond is coordinated to rhenium; this would require an inversion of regiochemistry in a labeled allyl system. Alternatively, the migration of the vinyl ligand of **4** to CO might be aided by a concerted $\eta^1-\eta^3$ rearrangement of the allyl ligand. This might lead to either retention or inversion of the allyl regiochemistry, depending on the details of the allyl rearrangement. Both of these alternatives would avoid the formation of high-energy intermediates and are consistent with our inability to trap unsaturated intermediates with trimethylphosphine.

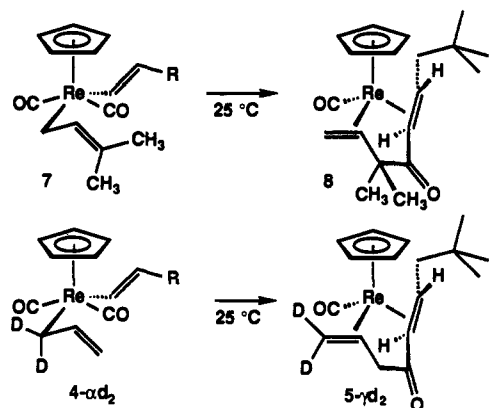
A dimethyl label was first employed to investigate the regiochemistry of the conversion of allylvinylrhenium compounds to (allyl vinyl ketone)rhenium complexes. The reaction of vinyl anion complex **2** with 1-bromo-3-methyl-2-butene proceeded with retention of allylic regiochemistry to produce *trans*- $C_5H_5(CO)_2Re(CH_2CH=CMe_2)[(E)-CH=CHCH_2CMe_3]$ (**7**). Complex **7** rearranged with a half-life of 10 min at room temperature to a single new complex, $C_5H_5(CO)Re(\eta^2, \eta^2-CH_2=CHCMe_2COCH=CHCH_2CMe_3)$ (**8**), with inversion of allyl regiochemistry.

The assignment of the structure of **8** with the gem dimethyl group α to the carbonyl is based on its 1H and ^{13}C NMR spectra. In the 1H NMR spectrum of **8**, resonances for the central, cis, and trans protons of the allyl fragment were observed at δ 2.52 (dd, $J = 10.5, 8.5$ Hz), δ 2.18 (dd, $J = 8.5, 3.1$ Hz), and δ 1.79 (dd, $J = 10.5, 3.1$ Hz). This coupling pattern would have been radically different if the gem dimethyl group was at the terminus of the allyl unit. In the ^{13}C NMR spectrum, four resonances with large J_{CH} couplings consistent with sp^2 hybridization were observed at δ 74.6 (d, $J = 160$ Hz) and δ 42.2 (d, $J = 150$ Hz), assigned to the vinyl ligand, and at δ 37.1 (d, $J = 160$ Hz) and δ 16.4 (t, $J = 155$ Hz), assigned to the central and terminal allyl carbons, respectively. If the product had contained a gem dimethyl group γ to the ketone, only three resonances with large J_{CH} couplings consistent with sp^2 hybridization would have been observed.

Since dimethyl substitution might have biased the regiochemistry of the conversion of allylvinylrhenium compound **7** to (allylvinyl ketone)rhenium complex **8**, a deuterium-labeled system was also studied. The reaction of vinylrhenium anion **2** with excess 3,3-dideuterio-3-chloropropene (96% d_2) led to the formation of *trans*- $C_5H_5(CO)_2Re(CD_2CH=CH_2)[(E)-CH=CHCH_2CMe_3]$ (**4- ad_2**) with 91% retention of allylic regiochemistry as shown by 1H NMR spectroscopy. At room temperature, **4- ad_2** rearranged to $C_5H_5(CO)Re(\eta^2, \eta^2-CD_2=CHCH_2COCH=CHCH_2CMe_3)$ (**5- γd_2**) in which 89% of the deuterium was located on the terminal carbon of the allyl unit as shown by 1H NMR spectroscopy. Therefore, after 9% loss of regiochemistry during the formation of **4- ad_2** , the rearrangement of **4- ad_2** to **5- γd_2** occurred with nearly complete inversion of allylic regiochemistry.

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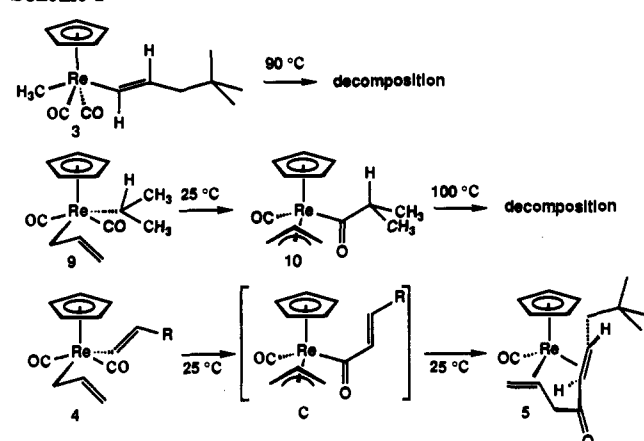


Rearrangement of an Allylisopropylrhenium Complex. The contrast between the high kinetic stability of methylvinylrhenium complex **3** and the rapid rearrangement of the allylvinylrhenium complexes **4** and **7** led us to investigate an allylalkylrhenium complex *trans*-C₅H₅(CO)₂Re(CH₂CH=CH₂)[CH(CH₃)₂] (**9**) to probe the role of the vinyl ligand. Reaction of the rhenium ethylidene complex C₅H₅(CO)₂Re=CHCH₃¹⁵ in THF with LiCuMe₂ produced the isopropylrhenium anion Li⁺-C₅H₅(CO)₂ReCH(CH₃)₂⁻, which reacted with excess allyl bromide to give *trans*-C₅H₅(CO)₂Re(CH₂CH=CH₂)[CH(CH₃)₂] (**9**). In the ¹H NMR of **9**, resonances assigned to the η¹-allyl ligand were observed at δ 5.91 (m, CH₂CH=CH₂), 4.57 (dm, *J* = 18.7, CH₂CH=CHH), 4.36 (dd, *J* = 10.4, 3.9 Hz, CH₂-CH=CHH), and 2.45 (br d, *J* = 9.8 Hz, CH₂CH=CH₂) and resonances assigned to the isopropyl ligand were observed at δ 2.86 (septet, *J* = 7.9 Hz, CHMe₂) and 1.5 (d, *J* = 8.8 Hz, CH(CH₃)₂). The observation of equivalent methyl resonances and equivalent methylene resonances in the ¹H NMR spectrum and the relative intensities of the two CO bands in the IR spectrum⁶ at 1999 (s) and 1922 (vs) cm⁻¹ is consistent with the assignment of *trans* carbonyl groups in **9**.

(η¹-Allyl)isopropylrhenium complex **9** rearranged slowly (*t*_{1/2} = 2.5 d, 23 °C, Δ*G*[‡] = 25 kcal mol⁻¹) to produce the (η³-allyl)acylrhenium complex C₅H₅(CO)₂Re(η³-CH₂CHCH₂)-[COCH(CH₃)₂] (**10**) (Scheme I). The IR spectrum of **10** indicated the presence of a single CO ligand (1925 cm⁻¹) and an acyl ligand (1595 cm⁻¹). In the ¹H NMR spectrum of **10**, resonances assigned to the five different hydrogens of the η³-allyl ligand appeared at δ 3.98 (ddt, *J* = 9.5, 8.5, 5.7 Hz, central H), 2.59 (dd, *J* = 9.7, 0.8 Hz, anti H), 2.05 (dd, *J* = 8.9, 0.6 Hz, anti H'), 2.49 (ddd, *J* = 5.7, 3.2, 1.0 Hz, syn H), and 2.27 (dd, *J* = 5.9, 3.2 Hz, syn H'). The diastereotopic methyl groups of the acyl ligand appeared as two doublets (*J* = 6.7 Hz) at δ 0.75 and 0.68 coupled to the methine proton at δ 2.93 (septet, *J* = 6.7 Hz). In the ¹³C NMR spectrum of **10**, a resonance at δ 255.6 was assigned to the acyl carbon and a resonance at δ 205.4 was assigned to the CO ligand. The allyl ligand gave rise to resonances at δ 81.2 (central), 44.1, and 23.2 (terminal). The transformation of **9** to **10** involves isopropyl migration to CO concerted with η¹- to η³-allyl rearrangement. No coupling of the acyl and η³-allyl ligands of **10** occurred. Such a reductive coupling would have generated a vacant coordination site at rhenium.

A second η³-allyl acyl rhenium isomer, **11**, was observed in 5–30% amounts in various isomerizations of **9**. The major isomer **10** was isolated by preparative thin-layer chromatography. Only a very small amount of impure **11** was isolated by preparative thin-layer chromatography. Since the η³-allyl ligand of transition metal complexes may adopt either an *exo* or *endo* configuration relative to the cyclopentadienyl ring, we suggest that **10** and **11** are *exo* and *endo* isomers. Isolated samples of **10** did not undergo interconversion to **11** on standing at room temperature for 4 days.

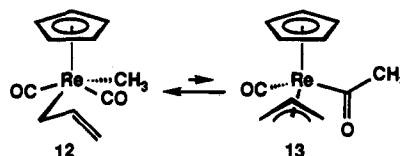
Scheme I



The high-temperature ¹H NMR spectrum of a 3:1 mixture of **10**:**11** showed no broadening of the central allyl proton resonances of either isomer, and the ratio of **10**:**11** did not change over the temperature range from 23 to 97 °C. These results indicate that any interconversion of **10** and **11** occurs very slowly on the NMR time scale. The high thermal stability of **10** and **11** (*t*_{1/2} > 6 h, 97 °C) indicates a barrier to decomposition of greater than 29 kcal mol⁻¹.

No NOE was observed between the cyclopentadienyl ring and any of the protons of the η³-allyl ligand of either **10** or **11**; however, a significant 7% NOE enhancement was observed for the methine resonance of **10** when the cyclopentadienyl resonance was irradiated. This suggests that the acyl ligand adopts the *anti* conformation in **10**, with the methyl groups oriented away from the ring. We are unable to assign *exo* or *endo* configurations to **10** and **11**. Because the *exo* conformation is generally observed to be the thermodynamically more stable isomer for cyclopentadienyl(η³-allyl)metal complexes, we have drawn **10** in an *exo* geometry but no isomeric assignment is intended.

Allylmethylrhenium *trans*-C₅H₅(CO)₂Re(CH₂CH=CH₂)(CH₃) (**12**). The rhenium allyl methyl complex *trans*-C₅H₅(CO)₂Re(CH₂CH=CH₂)(CH₃) (**12**) was prepared by the reaction of the methyl anion complex¹⁶ Li⁺C₅H₅(CO)₂ReCH₃⁻ with excess allyl bromide in CH₃CN at room temperature. Unlike (η¹-allyl)-isopropylrhenium complex **9** which rearranged to (η³-allyl)-acylrhenium complex **10**, (η¹-allyl)methylrhenium complex **12** slowly reacted at room temperature (*t*_{1/2} ≈ 60 h) to give a ~7:1 equilibrium mixture of **12** and a new isomer tentatively assigned



as (η³-allyl)acylrhenium complex C₅H₅(CO)Re(COCH₃)(η³-CH₂CHCH₂) (**13**). When the mixture was warmed to 65 °C, no further production of **13** was observed. When **12** was heated at 120 °C in toluene-*d*₈, it slowly decomposed to a complex mixture of uncharacterized products. Due to the small amount of **13** present in the equilibrium mixture, the resonances due to the η³-allyl ligand of **13** in the ¹H NMR were not easily observed or assigned. The cyclopentadienyl resonance of **13** appeared at δ 5.53 and the acetyl resonance appeared at δ 2.13; a small band at 1614 cm⁻¹ (5% of the intensity of the asym ReCO stretch of **12**) was tentatively assigned to the acyl group of **13**. Attempts to isolate **13** were unsuccessful.

(15) Casey, C. P.; Nagashima, H. *J. Am. Chem. Soc.* **1989**, *111*, 2352.(16) Casey, C. P.; Wang, Y.; Petrovich, L. M.; Underiner, T. L.; Hazin, P. N.; Desper, J. M. *Inorg. Chim. Acta* **1992**, *198–200*, 557.

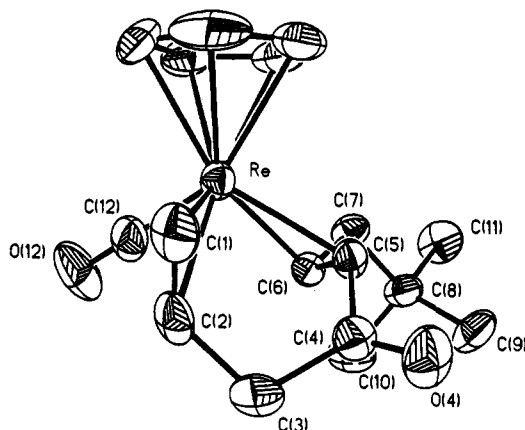
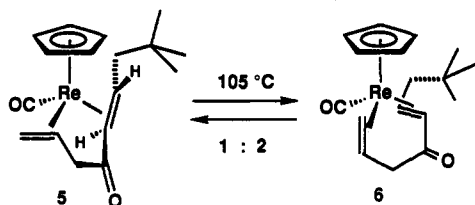


Figure 2. X-ray crystal structure of $C_5H_5(CO)Re(\eta^2,\eta^2-CH_2=CHCH_2-COCH=CHCH_2CMe_3)$ (**6**).

Apparently, the equilibrium between a (η^1 -allyl)alkylrhenium complex and the isomeric (η^3 -allyl)acylrhenium complex depends strongly on the nature of alkyl group migrating to CO. For the isopropyl compound, the η^3 -allyl acyl complex is favored at equilibrium while the η^1 -allyl alkyl complex is favored for the methyl analog. We suggest that migration of the bulkier isopropyl group to CO produces a favored less crowded acyl complex. In the reversible reaction of dimethyl sulfoxide with $C_5H_5(CO)_2-FeR$ which produces $C_5H_5(CO)(DMSO)FeCOR$, the rate of isopropyl migration to CO was 200 times faster than methyl migration and the equilibrium constant was 31 times greater for isopropyl migration than for methyl migration.¹⁷

Thermolysis of (Allyl vinyl ketone)rhenium Complex 5. When an acetonitrile solution of **5** was heated at 100 °C, the slow formation of an isomeric complex, $C_5H_5(CO)Re(\eta^2,\eta^2-CH_2=CHCH_2COCH=CHCH_2CMe_3)$ (**6**), was observed by ¹H NMR.



The reaction slowly ($t_{1/2} \approx 2.5$ days) reached a 1:2 equilibrium ratio of **5**:**6**. During the course of the equilibration of **5**, another small Cp resonance at δ 5.18, possibly due to the parallel-parallel diastereomer **A**,¹⁸ grew to $\sim 9\%$ of the total Cp intensity and then decreased to a steady state of $\sim 4\%$. When the two isomers were separated by preparative TLC and then heated separately in acetonitrile at 105 °C for 2 weeks, the same equilibrium ratio of **5**:**6** was observed in addition to $\sim 4\%$ of the Cp resonance at δ 5.18.

The similarity of the IR and ¹H and ¹³C NMR spectra of **5** and **6** indicated that the compounds were isomers. An X-ray crystal structure analysis of **6** indicated that it was a perpendicular-parallel isomer (Figure 2; Table II). The allyl double bond is approximately perpendicular to the cyclopentadienyl plane (10.2° interplanar angle as defined earlier), while the vinyl double bond is approximately parallel to the cyclopentadienyl ligand (82.1° interplanar angle). Overall, the formation of **6** from **5** can be accomplished by coordination of Re to the opposite enantiofaces of both the allyl and the vinyl double bonds. Detailed studies of the mechanism of the rearrangement of **5** to **6** will be described in a future paper.

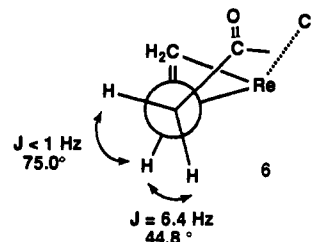
(17) Cotton, J. D.; Crisp, G. T.; Latif, L. *Inorg. Chim. Acta* **1981**, *47*, 171.

(18) A parallel-parallel isomer of $Cp(CO)Re[\eta^2,\eta^2-CH_2=CHCH_2(CO)CH=CHCH_2CMe_3]$ has been isolated from rearrangement of $C_5H_5(CO)_2Re(CH_2CH=CHCH_3)[(E)-CH=CHCH_2CMe_3]$: Casey, C. P.; Slough, G. A. Unpublished results.

Table II. Selected Bond Lengths (Å) and Angles (deg) for $C_5H_5(CO)Re(\eta^2,\eta^2-CH_2=CHCH_2COCH=CHCH_2CMe_3)$ (**6**)

Re-C(1)	2.186(12)	C(2)-C(3)	1.508(16)
Re-C(2)	2.295(12)	C(3)-C(4)	1.528(12)
Re-C(5)	2.199(8)	C(4)-O(4)	1.211(13)
Re-C(6)	2.226(8)	C(4)-C(5)	1.450(17)
Re-C(12)	1.881(10)	C(5)-C(6)	1.445(12)
C(1)-C(2)	1.411(15)		
C(1)-C(2)-C(3)	121.3(9)	C(5)-C(6)-C(7)	119.1(7)
C(2)-C(3)-C(4)	107.5(9)	C(3)-C(4)-O(4)	121.9(11)
C(3)-C(4)-C(5)	114.0(8)	O(4)-C(4)-C(5)	123.6(9)
C(4)-C(5)-C(6)	122.6(8)		

In the X-ray crystal structure of **6**, the dihedral angles between the central allylic proton and the allylic protons α to the carbonyl



group were 75.0 and 44.8°. In the ¹H NMR of **6**, the allylic protons α to the ketone appeared as part of an ABX pattern at δ 2.06 ($J_{AB} = 15.2$ Hz, $J_{AX} = 6.4$ Hz) and 1.99 ($J_{gem} = 15.2$ Hz, $J_{BX} < 1$ Hz). The large difference in coupling constants of the allyl protons to the central proton of the allyl unit is readily understood in terms of the conformation of the allyl group found in the X-ray structure. The large 6.3-Hz coupling can confidently be assigned to the proton with a 44.8° dihedral angle, while the negligible <1-Hz coupling is assigned to the proton with a 75.0° dihedral angle.

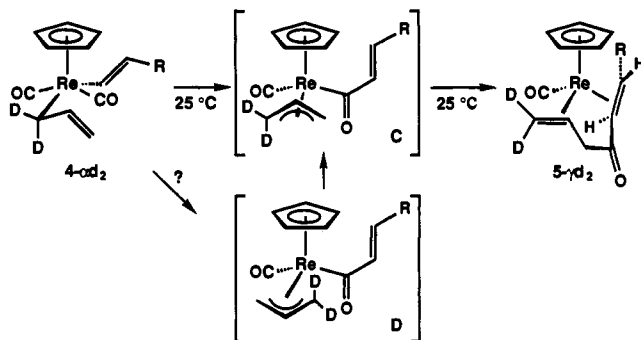
Discussion

The remarkably rapid rearrangement of allylvinylrhenium complex **4** to (allyl vinyl ketone)rhenium complex **5** stands in stark contrast to the high kinetic stability of the closely related methylvinylrhenium complex **3** and requires a special role for the allyl group in promoting the rearrangement. The free energy barrier for rearrangement of **4** to **5** ($t_{1/2} = 23$ min, 25 °C, $\Delta G^\ddagger = 21.9$ kcal mol⁻¹) is much lower than the free energy barrier for decomposition of **3** either in the absence of added ligands ($t_{1/2} = 6.6$ h, 90.0 °C, $\Delta G^\ddagger = 28.9$ kcal mol⁻¹) or in the presence of 0.35 M PMe_3 ($t_{1/2} = 1.4$ h, 90.0 °C, $\Delta G^\ddagger = 27.8$ kcal mol⁻¹). Thus, the allyl group of **4** assists rearrangement to **5** by lowering the free energy barrier by more than 6 kcal mol⁻¹. Similarly, comparison of the free energy of activation for isopropyl migration to CO in the conversion of **9** to **10** ($t_{1/2} = 60$ h, 23 °C, $\Delta G^\ddagger \approx 25$ kcal mol⁻¹) with the free energy barrier for decomposition of **3** indicates that the allyl group assists isopropyl migration to CO.

Any mechanism for the rearrangement of **4** to **5** must account for the dramatic acceleration by the allyl ligand, as well as the five additional key experimental results summarized as follows: (1) The conversion of **4** to **5** was not affected by added PMe_3 . (2) Net inversion of allylic regiochemistry was observed in the conversion of deuterated allyl vinyl rhenium complex **4-*ad*₂** to **5-*gd*₂**. (3) The allyl vinyl ketone is coordinated in a parallel-perpendicular configuration in the kinetically formed isomer **5**. (4) The allylisopropylrhenium compound **9** rearranged to give the stable η^3 -allyl isobutyryl complex **10**, which was resistant to reductive elimination to a ketone. (5) Interconversion of *exo*- and *endo*-(η^3 -allyl)rhenium isomers **10** and **11** was slow at room temperature. These observations place severe constraints on any mechanistic proposal for the rearrangement of **4** to **5**. The only mechanism we have devised which is fully consistent with these

constraints is the series of two consecutive concerted reactions shown in Scheme I.

In the first step, the migration of the vinyl group to CO is assisted by a simultaneous η^1 - to η^3 -allyl rearrangement which generates the intermediate (η^3 -allyl)acylrhenium complex C. The



facile rearrangement of the allylisopropylrhenium compound **9** to the stable η^3 -allyl isobutyryl complex **10** provides an excellent model for this reaction step. The concerted nature of the conversion of **4** to C avoids the intervention of a high-energy coordinatively unsaturated intermediate and is consistent with the kinetic stability of methylvinylrhenium compound **3** and with the failure to trap unsaturated intermediates during the conversion of **4** to **5** in the presence of PMe_3 .

In our more detailed description of the conversion of **4** to intermediate C, we propose that the terminal carbon of the allyl ligand swings toward the incipient acyl ligand to generate an *exo* η^3 -allyl unit. An *exo* configuration of the η^3 -allyl group is required in the formation of the parallel-perpendicular conformation of **5**. The allyl ligand must swing toward the acyl ligand to account for the inversion of allyl ligand regiochemistry observed in the isomerization of $4\text{-}ad_2$. We cannot rigorously exclude an alternative mechanism in which the allyl ligand swings away from the incipient acyl ligand to generate an *endo* intermediate **D**, which then undergoes *endo* to *exo* isomerization to C prior to reductive elimination to **5**. However, since *exo*-*endo* isomerization of the η^3 -allyl group is probably slow relative to reductive elimination to **5**, we propose the direct formation of *exo* intermediate C. Slow rates of *exo*-*endo* allyl isomerization were observed for the (η^3 -allyl)isobutyrylrhenium complexes **10** and **11** and for *exo*- and *endo*- $\text{Cp}^*(\text{CO})\text{Re}(\text{H})(\eta^3\text{-CH}_2\text{CHCH}_2)$ studied by Zhuang and Sutton.¹⁹

The second step in our proposed mechanism for the conversion of **4** to **5** is also a concerted organometallic reaction in which the reductive coupling of the *exo* η^3 -allyl ligand to the acyl ligand is assisted by the simultaneous coordination of the vinyl double bond to rhenium. The formation of a high-energy coordinatively unsaturated intermediate is avoided by combining the reductive coupling with concerted alkene complexation. The concerted nature of this coupling step is consistent with the thermal stability of (η^3 -allyl)isobutyrylrhenium complex **10** which fails to undergo reductive elimination in the absence of available assistance from alkene complexation. The free energy barrier for the overall conversion of **4** to **5** via intermediate C ($\Delta G^\ddagger = 21.9 \text{ kcal mol}^{-1}$) is 7 kcal mol^{-1} less than the barrier for decomposition of **10** ($t_{1/2} > 6 \text{ h}$, 97°C , $\Delta G^\ddagger > 29 \text{ kcal mol}^{-1}$).

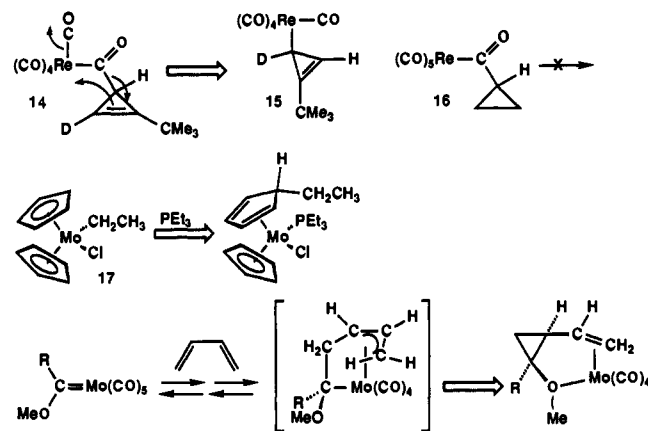
In our more detailed description of the conversion of intermediate C to **5**, we propose that the reductive elimination occurs from the *anti*, *s-trans* conformation of the unsaturated acyl ligand. This conformation minimizes the distance between rhenium and the β -carbon of the vinyl group of the enone ligand and accounts for the kinetic formation of parallel-perpendicular isomer **5**. The observation of an NOE between the C_5H_5 ligand and the methine proton of **10** is consistent with the accessibility of *anti* acyl conformers.

(19) Zhuang, J.-M.; Sutton, D. *Organometallics* **1991**, *10*, 1516.

Concerted organometallic reactions are very unusual but may be much more common than is currently recognized. Concerted organometallic reactions may prove particularly important in the chemistry of third-row transition metals because of the difficulty of generating vacant coordination sites on such metals. For example, the activation energy for CO loss from $\text{Cr}(\text{CO})_6$, $\text{Mo}(\text{CO})_6$, and $\text{W}(\text{CO})_6$ increases from 35.3 to 30.0 to 44.5 kcal mol^{-1} .²⁰ Similarly, alkyl migration to CO occurs much more readily for $(\text{CO})_5\text{MnCH}_3$ than for $(\text{CO})_5\text{ReCH}_3$,²¹ and substitution reactions of $(\text{CO})_5\text{M}(\text{THF})$ become progressively more associative in the series Cr, Mo, W.²²

A large number of elementary organometallic reactions such as ligand dissociation, alkyl migration to CO, η^3 - to η^1 -allyl conversion, and reductive elimination generate a vacant coordination site. An equally large number of elementary organometallic reactions constitute the reverse of these processes and consume vacant coordination sites. In principle, combining a step which would normally generate a vacant coordination site into a single concerted reaction can avoid the formation of a high-energy intermediate with a vacant coordination site and thereby lower the activation barrier of a reaction. We are currently designing molecules capable of undergoing concerted organometallic reactions.

Well-documented examples of concerted organometallic reactions in which elementary steps are combined to avoid a high-energy coordinatively unsaturated intermediate are rare, and the evidence for the concerted nature of the reactions is often sparse.^{23,24} Hughes proposed that the conversion of **14** to **15**



occurred via concerted loss of CO and cyclopropenyl migration to rhenium on the basis of both the much faster reaction of the unsaturated cyclopropenyl compound **16** compared with the saturated cyclopropyl compound **14** and the allylic rearrangement of the cyclopropenyl unit;²⁵ the concerted mechanism avoids a high-energy 5-coordinate rhenium acyl intermediate. (In the reactions shown, an open arrow \Rightarrow is used to indicate a proposed

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(21) (a) Collman, J. P.; Hegedus, L. S.; Norton, J. R.; Finke, R. G. *Principles and Applications of Organotransition Metal Chemistry*; University Science Books: Mill Valley CA, 1987; Chapter 6. (b) Berke, H.; Hoffmann, R. *J. Am. Chem. Soc.* **1978**, *100*, 7224.

(22) Wieland, S.; van Eldik, R. *Organometallics* **1991**, *10*, 3110.

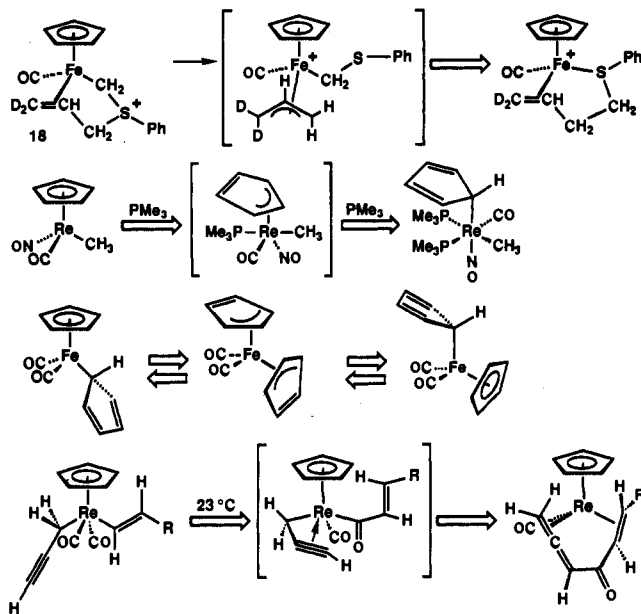
(23) We are preparing a review of concerted organometallic reactions and would appreciate hearing about other examples.

(24) Bergman and Wax reported kinetic evidence that alkyl migration to CO in $\text{CpMo}(\text{CO})_3\text{CH}_3$ was accelerated by the nucleophilic solvent THF and suggested addition of THF to Mo concerted with alkyl migration to CO.⁶ This interpretation is now in question since Halpern has obtained evidence for nucleophile-catalyzed alkyl to acyl migration involving nucleophile addition to a coordinated CO:⁶ (a) Wax, M. J.; Bergman, R. G. *J. Am. Chem. Soc.* **1981**, *103*, 7028. (b) Webb, S. L.; Giandomenico, C. M.; Halpern, J. *J. Am. Chem. Soc.* **1986**, *108*, 345.

(25) (a) DeSimone, D. M.; Desrosiers, P. J.; Hughes, R. P. *J. Am. Chem. Soc.* **1982**, *104*, 4842. (b) Desrosiers, P. J.; Hughes, R. P. *J. Am. Chem. Soc.* **1981**, *103*, 5593.

concerted organometallic reaction.) Green proposed that ethyl migration to the Cp ring of **17** was assisted by PEt_3 attack at Mo.²⁶ Harvey 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 η^3 -allyl intermediate concerted with methoxy coordination was proposed to explain the stereochemical preference.²⁷

Barefield has observed an interesting rearrangement of iron complex **18** and proposed a concerted reductive elimination and



sulfur coordination.²⁸ Cotton observed the rapid interchange of the η^1 - C_5H_5 and η^3 - C_5H_5 rings of $(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2(\eta^1\text{-C}_5\text{H}_5)$ by temperature-dependent NMR studies;²⁹ this interchange may occur by simultaneous slippage of both rings to generate a bis η^3 - C_5H_5 intermediate. We proposed that η^5 - to η^3 - C_5H_5 ring slippage of $\text{Cp}(\text{CO})(\text{NO})\text{ReCH}_3$ was induced by nucleophilic attack of PMe_3 based on the rate dependence on $[\text{PMe}_3]$ even at very high concentrations.³⁰ We recently reported that η^1 - to η^3 -propargyl rearrangement can promote alkyl migration to CO in a manner similar to η^1 - to η^3 -allyl rearrangements reported here.³¹

Reactions facilitated by flexible electron donor ligands can be considered as a separate class of reactions distinct from concerted organometallic reactions. Examples of this type would include reactions in which alkynes change from $2e^-$ to $4e^-$ donors or in which oxo ligands undergo a change from $4e^-$ to $6e^-$ donors. Wulff recently suggested that coupling of a carbene ligand with CO to give a vinyl ketene might be promoted by a coordinated alkyne changing from a $2e^-$ to a $4e^-$ donor.³² Goddard has suggested a special role for oxo ligands in promoting carbene alkene coupling at a metal center by donating extra electrons to the metallacycle product.³³ We believe it is useful to distinguish between this type of minor bonding change and the more drastic changes in bonding that occur during conversions such as η^1 - to η^3 -allyl rearrangement during which the number of centers bonded to the metal changes.

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(27) Harvey, D. F.; Lund, K. P. *J. Am. Chem. Soc.* 1991, 113, 8916.

(28) Barefield, E. K.; McCarten, P.; Steiger, G. E. Private communication.

(29) Bennett, M. J., Jr.; Cotton, F. A.; Davison, A.; Faller, J. W.; Lippard, S. J.; Morehouse, S. M. *J. Am. Chem. Soc.* 1966, 88, 4371.

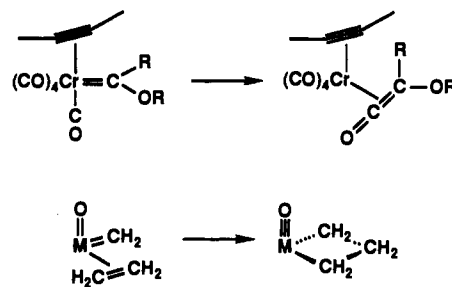
(30) (a) Casey, C. P.; Jones, W. D. *J. Am. Chem. Soc.* 1980, 102, 6154.

(b) Casey, C. P.; O'Connor, J. M.; Haller, K. J. *J. Am. Chem. Soc.* 1985, 107, 1241.

(31) Casey, C. P.; Underiner, T. L.; Vosejka, P. C.; Gavney, J. A., Jr.; Kiprof, P. *J. Am. Chem. Soc.* 1992, 114, 10826.

(32) Bos, M. E.; Wulff, W. D.; Miller, R. A.; Chamberlin, S.; Brandvold, T. A. *J. Am. Chem. Soc.* 1991, 113, 9293.

(33) Rappé, A. K.; Goddard, W. A., III. *J. Am. Chem. Soc.* 1980, 102, 5114.



Experimental Section

General Methods. ^1H NMR spectra were obtained on Bruker WP200, WP270, or AM500 spectrometers. $^{13}\text{C}\{^1\text{H}\}$ NMR spectra were obtained on a Bruker AM500 spectrometer (126 MHz). Infrared spectra were measured on a Mattson Polaris (FT) spectrometer. Mass spectra were determined on a Kratos MS-80. Elemental analyses were performed by Galbraith Laboratories, Inc. (Knoxville, TN).

Diethyl ether, hexane, and THF were distilled from purple solutions of sodium and benzophenone immediately prior to use. Dichloromethane, CD_2Cl_2 , acetonitrile, and CD_3CN were dried over P_2O_5 or CaH_2 and distilled prior to use. Air-sensitive materials were manipulated in an inert-atmosphere glovebox or by standard Schlenk techniques. Thermolysis reactions in acetonitrile at 105°C (~ 2 atm) were carried out in sealed thick-walled NMR tubes or in thick-walled glass tubes equipped with extended tip Teflon valves.

trans-Cp(CO)₂Re(CH₃)(E-CH=CHCH₂CMe₃) (3). A mixture of $\text{K}^+\text{Cp}(\text{CO})_2\text{Re}[(E)\text{-CH=CHCH}_2\text{CMe}_3]^- (2)^1$ (90 mg, 0.20 mmol) and MeI (0.31 mmol) in CH_3CN (20 mL) was stirred at room temperature for 5 min. CH_3CN was evaporated under vacuum, and the residue was dissolved in CH_2Cl_2 (5 mL), filtered through a Celite plug, and concentrated. Preparative TLC (silica gel, 1:10 diethyl ether:hexane) gave a band ($R_f = 0.5$) from which **3** (51 mg, 60%) was isolated as pale yellow microcrystals. Analytically pure material was obtained by sublimation (65°C , 0.001 mmHg): ^1H NMR (200 MHz, CD_3CN) δ 6.74 (dt, $J = 15.7, 1.2$ Hz, ReCH), 5.21 (s, C_5H_5), 4.77 (dt, $J = 15.7, 7.2$ Hz, ReCH=CH), 1.96 (dd, $J = 7.2, 1.1$ Hz, ReCH=CHCH₂), 0.85 (s, $\text{C}(\text{CH}_3)_3$), 0.67 (s, ReCH₃); ^{13}C NMR (126 MHz, CD_3CN) δ 199.0 (s, CO), 143.6 (d, $J = 149$ Hz, ReCH), 105.7 (d, $J = 146$ Hz, ReCH=CH), 91.1 (d, $J = 183$ Hz, C_5H_5), 54.7 (t, $J = 128$ Hz, CH_2), 32.2 (s, $\text{C}(\text{CH}_3)_3$), 29.6 (q, $J = 127$ Hz, $\text{C}(\text{CH}_3)_3$), -23.5 (q, $J = 135$ Hz, ReCH₃); IR (CH_2Cl_2) 2009 (m), 1935 (s) cm^{-1} ; HRMS calcd for $\text{C}_{15}\text{H}_{21}\text{O}_2\text{Re}$ m/e 420.1099, found m/e 420.1124. Anal. Calcd for $\text{C}_{15}\text{H}_{21}\text{O}_2\text{Re}$: C, 42.94; H, 5.04. Found: C, 43.04; H, 5.02.

trans-Cp(CO)₂Re(CH₂CH=CH₂)(E-CH=CHCH₂CMe₃) (4). CD_3CN and excess allyl bromide (0.1 mL, 0.2 mmol) were condensed into an NMR tube containing $\text{K}^+\text{Cp}(\text{CO})_2\text{Re}[(E)\text{-CH=CHCH}_2\text{CMe}_3]^- (2)^1$ (10 mg, 0.02 mmol). The mixture was warmed to room temperature for 5 min. Unreacted allyl bromide and CD_3CN were evaporated under vacuum to give a yellow oil. The oil was dissolved in CH_2Cl_2 , and the mixture was filtered through a short column of silica gel to give **4** containing about 20% of rearrangement product **5**. Because **4** rearranges rapidly at room temperature to **5**, it was not possible to obtain **4** completely free of **5**: ^1H NMR (200 MHz, CD_3CN) δ 6.73 (dt, $J = 16.0, 2.5$ Hz, ReCH=CH), 6.00 (m, $\text{ReCH}_2\text{CH=CH}_2$), 5.78 (dt, $J = 17.0, 10.0$ Hz, ReCH=CH), 5.15 (s, C_5H_5), 4.66 (dq, $J = 18.0, 3.5$ Hz, $\text{ReCH}_2\text{-CH=CHH}$), 4.44 (dd, $J = 12.5, 3.5$ Hz, $\text{ReCH}_2\text{CH=CHH}$), 2.55 (d, $J = 10.0$ Hz, ReCH_2), 1.97 (dd, $J = 10.0, 2.0$ Hz, ReCH=CHCH₂), 0.87 (s, $\text{C}(\text{CH}_3)_3$); IR (CH_2Cl_2) 2007 (s) and 1934 (vs) cm^{-1} .

Cp(CO)Re(η^2 , η^2 -CH₂=CHCH₂COCH=CHCH₂CMe₃) (5). A mixture of $\text{K}^+\text{Cp}(\text{CO})_2\text{Re}[(E)\text{-CH=CHCH}_2\text{CMe}_3]^- (2)$ (100 mg, 0.23 mmol) and allyl bromide (1.50 mmol) in CH_3CN (20 mL) was stirred at room temperature for 10 min, and excess allyl bromide and CH_3CN were evaporated under vacuum to give crude **4**. Cleaner conversion of **4** to **5** was seen when excess allyl bromide was removed before thermal rearrangement. The residue of crude **4** was dissolved in CH_3CN , and the mixture was stirred overnight at room temperature. CH_3CN was evaporated under vacuum, and the residue was dissolved in CH_2Cl_2 . The solution was filtered through a Celite plug and evaporated to give **5** (100 mg, 100%) as a yellow oil. Analytically pure **5** was obtained as a fine yellow powder by trituration of the oil with hexane: ^1H NMR (500 MHz, CD_2Cl_2) δ 4.92 (s, C_5H_5), 3.38 (ddd, $J = 10.7, 8.6, 2.2$ Hz, COCH=CH), 2.58 (d, $J = 8.5$ Hz, COCH=CH), 2.1 (m, 2 H, $\text{COCH}_2\text{CH=CHH}$), 2.00 (dd, $J = 16.2, 6.3$ Hz, COCHH), 1.97 (dd,

$J = 13.5, 2.2$ Hz, COCH=CHCHH), 1.66 (d, $J = 16.3$ Hz, COCHH), 1.59 (dd, $J = 9.9, 2.7$ Hz, COCH₂CH=CHH), 0.98 (s, C(CH₃)₃), 0.72 (dd, $J = 13.5, 10.6$ Hz, COCH=CHCHH) (single-frequency decoupling rigorously established all reported ¹H chemical shifts and coupling constants); ¹³C NMR (126 MHz, CD₃CN) δ 212.8 (s) and 208.2 (s) (Re-CO, R-CO-R'), 85.7 (d, $J = 183$ Hz, C₃H₅), 73.9 (d, $J = 160$ Hz), and 41.4 (d, $J = 151$ Hz) (COCH=CH), 57.3 (t, $J = 122$ Hz, CH₂C-(CH₃)₃), 35.3 (s, C(CH₃)₃), 34.1 (t, $J = 127$ Hz, COCH₂), 29.5 (q, $J = 127$ Hz, C(CH₃)₃), 13.8 (d, $J = 160$ Hz, COCH₂CH), 12.8 (t, $J = 160$ Hz, COCH₂CH=CH₂); IR (CH₂Cl₂) 1925 (s), 1675 (m) cm⁻¹; HRMS calcd for C₁₇H₂₃ReO₂ m/e 446.1256, found m/e 446.1261. Anal. Calcd for C₁₇H₂₃ReO₂: C, 45.82; H, 5.20. Found: C, 46.09; H, 5.10.

CH₂=CHCD₂Cl. A solution of acryloyl chloride (18.03 g, 0.19 mol) in diethyl ether (100 mL) was added dropwise to a slurry of LiAlD₄ (5.00 g, 0.12 mol, Aldrich) in diethyl ether (250 mL).³⁴ The mixture was cooled to 0 °C and quenched by successive addition of 6 mL of H₂O, 6 mL of 15% aqueous NaOH, and 6 mL of H₂O. A granular precipitate was removed by filtration, and the filtrate was dried (Na₂SO₄) and distilled to give CH₂=CHCD₂OH (bp 86–95 °C, 3.70 g, 31%) as a clear liquid. ¹H NMR (200 MHz, CDCl₃): δ 5.90 (dd, $J = 17.0, 9.7$ Hz, CH₂=CH), 5.18 (dd, $J = 17.0, 1.5$ Hz, CHH=CH), 5.06 (dd, $J = 9.7, 1.5$ Hz, CHH=CH), 3.12 (s, OH).

A mixture of PPPh₃ (17.26 g, 66 mmol) and CH₂=CHCD₂OH (3.68 g, 61 mmol) in 20 mL CCl₄ was stirred overnight at room temperature.³⁵ Distillation gave CH₂=CHCD₂Cl (bp 45–55 °C, 2.87 g, 60%, 87% pure by gas chromatography) as a clear liquid. Pure CH₂=CHCD₂Cl was obtained by preparative gas chromatography (20% SE-30, 35 °C). ¹H NMR (200 MHz, C₆D₆): δ 5.57 (dd pentets, $J = 17.5, 10.0, 2.0$ Hz, CH₂=CH), 4.92 (dd, $J = 18.0, 3.0$ Hz, CHH=CH), 4.80 (dd, $J = 10.0, 3.0$ Hz, CHH=CH), 3.5 (0.04 H, residual CDHCl).

Cp(CO)Re(η², η²-CH₂=CHCH₂COCH=CHCH₂CMe₃) (6). A CH₃CN solution of **5** (100 mg, 0.22 mmol) was heated at 90 °C for 21 d until ¹H NMR showed an equilibrium 34:66 mixture of **5**:**6**. Preparative TLC (silica gel, 60:40 hexane:Et₂O) gave a band ($R_f = 0.34$) from which **6** (40 mg, 40%) was isolated as a yellow oil and a second band ($R_f = 0.12$) from which **5** was recovered: ¹H NMR (CD₂Cl₂, 500 MHz) δ 5.07 (s, C₃H₅), 3.27 (ddd, $J = 11.2, 9.1, 2.2$ Hz, COCH=CH), 2.83 (br d, $J = 7.3$ Hz, COCH₂CH=CHH), 2.70 (d, $J = 9.1$ Hz, COCH=CH), 2.42 (m, COCH₂CH=CH₂), 2.16 (dd, $J = 13.5, 2.1$ Hz, CHHCH₂), 2.09 (dd, $J = 15.2, 6.4$ Hz, COCHHCH=CH₂), 1.99 (d, $J = 15.2$ Hz, COCHHCH=CH₂), 1.85 (br d, $J = 9.8$ Hz, COCH₂CH=CHH), 0.96 (s, CMe₃), 0.86 (dd, $J = 13.4, 11.1$ Hz, CHHCH₂Me₃) (single-frequency decoupling rigorously established all reported ¹H chemical shifts and coupling constants); ¹³C NMR (126 MHz, CD₃CN) δ 212.1 and 206.3 (CO's), 84.7, (C₃H₅), 56.3 (COCH=CH), 54.8 (CH₂CMe₃), 41.1 (COCH=CH) and 39.9 (COCH₂CH=CH₂), 34.0 (CMe₃), 33.9 (COCH₂CH=CH₂), 29.5 (CMe₃), 22.4 (COCH₂CH=CH₂); IR (CH₂Cl₂) 1923 (s), 1662 (w) cm⁻¹; HRMS calcd for C₁₇H₂₃ReO₂ m/e 446.1256, found m/e 446.1269.

X-ray Crystal Structures of 5 and 6. Suitable crystals of **5** were grown by slow evaporation of a diisopropyl ether solution of **5** at -20 °C. Suitable crystals of **6** were grown by slow evaporation of a diisopropyl ether solution of **5** at room temperature. The structures of **5** and of **6** were solved by direct methods on a Nicolet P3f diffractometer (Table III). In full-matrix least-squares refinements using SHELXTL PLUS/1989,³⁶ all non-hydrogen atoms were refined independently with anisotropic thermal parameters.

trans-Cp(CO)₂[(CH₃)₂C=CHCH₂][Re(E-CH=CHCH₂CMe₃) (7). CD₃CN and excess 1-bromo-3-methyl-2-butene (0.1 mL, 0.2 mmol) were condensed into an NMR tube containing K⁺Cp(CO)₂Re-[(E)-CH=CHCH₂CMe₃]⁻ (**2**) (10 mg, 0.02 mmol). After 5 min at room temperature, unreacted 1-bromo-3-methyl-2-butene and CD₃CN were evaporated under vacuum to produce **7** as a yellow oil. Because **7** rearranges rapidly at room temperature to **8**, the ¹H NMR was taken immediately after preparation. ¹H NMR (200 MHz, CD₃CN): δ 6.73 (dt, $J = 16.7, 1.2$ Hz, ReCH=CH), 5.74 (dt, $J = 15.6, 7.2$ Hz, ReCH=CH), 5.42 (t septets, $J = 8.7, 1.3$ Hz, ReCH₂CH), 5.19 (s, C₃H₅), 2.54 (d, $J = 8.6$ Hz, ReCH₂), 1.70, 1.66 (singlets, ReCH₂CH=C(CH₃)₂), 0.85 (s, C(CH₃)₃).

Cp(CO)Re(η², η²-CH₂=CHC(CH₃)₂COCH=CHCH₂CMe₃) (8). A mixture of K⁺Cp(CO)₂Re-[(E)-CH=CHCH₂CMe₃]⁻ (**2**) (18 mg, 0.041 mmol) and 1-bromo-3-methyl-2-butene (0.41 mmol) in CH₃CN (3 mL)

Table III. Crystal Structure Data for **5** and **6**

	5	6
empirical formula	C ₁₇ H ₂₃ O ₂ Re	C ₁₇ H ₂₃ O ₂ Re
color; habit	yellow block	yellow block
cryst size (mm)	0.5 × 0.4 × 0.4	0.4 × 0.5 × 0.5
cryst system	orthorhombic	triclinic
space group	Pbca	Pī
unit cell dimens (Å, deg)	$a = 15.544(4)$ $b = 11.478(3)$ $c = 18.712(7)$	$a = 8.776(4)$ $b = 8.877(3)$ $c = 11.553(4)$ $\alpha = 81.43(3)$ $\beta = 72.00(3)$ $\gamma = 70.57(3)$
$V(\text{Å}^3)$	3338.6(16)	806.2(5)
peaks to determine cell	22	18
2θ range of cell peaks (deg)	5.00, 23.00	5.00, 24.00
Z	8	2
fw	445.6	445.6
$D(\text{calc})$ (g cm ⁻³)	1.773	1.835
absn coeff (mm ⁻¹)	7.377	7.638
$F(000)$	1728	432
$R(F)$ (%)	5.41	3.06
$R_w(F)$	6.41	3.88

was stirred at room temperature for 10 min, and excess alkyl bromide and CH₃CN were evaporated under vacuum to give crude **7**. Cleaner rearrangement of **7** to **8** was seen when excess 1-bromo-3-methyl-2-butene was removed. The residue of crude **7** was dissolved in CH₃CN, and the mixture was stirred overnight at room temperature. CH₃CN was evaporated under vacuum, the residue was dissolved in CH₂Cl₂ (0.2 mL), and the mixture was placed on the top of a 10 × 100 mm silica gel flash chromatography column. The yellow band was eluted with CH₂Cl₂. Evaporation of solvent gave **8** (18 mg, 94%) as a yellow crystalline solid: ¹H NMR (200 MHz, CD₃CN) δ 5.00 (s, C₃H₅), 3.58 (ddd, $J = 11.2, 9.0, 2.2$ Hz, COCH=CH), 2.57 (d, $J = 9.0$ Hz, COCH=CH), 2.52 (dd, $J = 10.5, 8.5$ Hz, COC(CH₃)₂CH), 2.18 (dd, $J = 8.5, 3.1$ Hz, COC(CH₃)₂CH=CHH), 2.01 (dd, $J = 13.5, 2.2$ Hz, COCH=CHCHH), 1.79 (dd, $J = 10.5, 3.1$ Hz, COC(CH₃)₂CH=CHH), 1.04, 0.97 (singlets, diastereotopic COC(CH₃)₂), 0.88 [s, C(CH₃)₃], 0.63 (dd, $J = 13.4, 10.5$ Hz, COCH=CHCHH); ¹³C NMR (126 MHz, CD₃CN) δ 211.7 (s) and 210.3 (s) (Re-CO, R-CO-R'), 86.2 (d, $J = 178$ Hz, C₃H₅), 74.6 (d, $J = 160$ Hz) and 42.2 (d, $J = 150$ Hz) (COCH=CH), 58.8 (t, $J = 127$ Hz, CH₂C(CH₃)₃), 43.5 (s, COC(CH₃)₂), 37.1 (d, $J = 159$ Hz, COC(CH₃)₂CH), 35.4 (s, C(CH₃)₃), 29.7 (q, $J = 127$ Hz, C(CH₃)₃), 29.3 (q, $J = 132$ Hz), and 26.2 (q, $J = 132$ Hz) (diastereotopic COC(CH₃)₂), 16.4 (t, $J = 155$ Hz, C(CH₃)₂CH=CH₂); IR (CH₂Cl₂) 1920 (s), 1670 (m) cm⁻¹; HMRS calcd for C₁₉H₂₇ReO₂ m/e 474.1569, found m/e 474.1573.

trans-Cp(CO)₂Re(CH₂=CHCH₂)[CH(CH₃)₂] (9). LiCu(CH₃)₂ prepared by stirring CH₃Li (0.78 mmol) and CuI (78 mg, 0.41 mmol) in THF at -20 °C was cooled to -78 °C and added to a stirred suspension of Cp(CO)₂Re=CHCH₃ (125 mg, 0.37 mmol) in THF (10 mL) at -78 °C. The mixture was stirred for 10 min at room temperature and filtered. THF was evaporated under vacuum to give Li⁺Cp(CO)₂ReCH(CH₃)⁻ as a brown residue, which was used without further purification. ¹H NMR (200 MHz, CD₃CN): δ 4.86 (s, C₃H₅), 1.47 (d, $J = 7.1$ Hz, ReCH(CH₃)₂), CH(CH₃)₂ resonance not resolved due to very broad lines. No other prominent Cp signals were observed by ¹H NMR.

CD₃CN and excess allyl bromide (0.2 mL, 0.4 mmol) were condensed into an NMR tube containing LiCp(CO)₂ReCH(CH₃)⁻. After 5 min at room temperature, unreacted allyl bromide and CD₃CN were evaporated under vacuum to produce **9** as a dark brown oil. **9** rearranged to **10** at room temperature with $t_{1/2} \sim 2.5$ d. ¹H NMR of **9** (200 MHz, CD₃CN): δ 5.91 (m, ReCH₂CH=CH₂), 5.04 (s, C₃H₅), 4.57 (dq, $J = 18.7, 3.9$ Hz, ReCH₂CH=CHH), 4.36 (dd, $J = 10.4, 3.9$ Hz, ReCH₂CH=CHH), 2.86 (septet, $J = 7.9$ Hz, ReCH(CH₃)₂), 2.45 (d, $J = 9.8$ Hz, ReCH₂), 1.5 (d, $J = 8.8$ Hz, ReCH(CH₃)₂); IR (CH₂Cl₂) 1999 (s), 1922 (vs) cm⁻¹.

Cp(CO)(η²-CH₂CHCH₂)ReCOCH(CH₃)₂ (10). Crude **9**, prepared by reaction of Li⁺Cp(CO)₂ReCH(CH₃)⁻ (0.37 mmol) and allyl bromide (1.85 mmol) in CH₃CN followed by evaporation of solvent and excess allyl bromide, was dissolved in 10 mL CH₃CN, and the mixture was stirred for 10 days at room temperature. (Cleaner rearrangement of **9** to **10** was seen when excess allyl bromide was removed before thermal rearrangement.) Preparative TLC (silica gel, 0.15:0.5:1.0 diethyl ether:CH₂Cl₂:hexane) gave a band ($R_f = 0.25$) from which **10** (44 mg, 30%

(34) Schuetz, R. D.; Millard, F. W. *J. Org. Chem.* 1959, 24, 297.(35) Snyder, E. I. *J. Org. Chem.* 1972, 37, 1466.

(36) SHELXTL PLUS/1989, Siemens Analytical X-ray Instruments, Inc., Madison, WI 53719.

based on $\text{Cp}(\text{CO})_2\text{Re}=\text{CHCH}_3$ was isolated as a yellow oil: ^1H NMR (500 MHz, CD_3CN) δ 5.53 (s, C_5H_5), 3.98 (ddt, $J = 9.5, 8.5, 5.7$ Hz, CH_2CHCH_2), 2.93 [septet, $J = 6.7$ Hz, $\text{CH}(\text{CH}_3)_2$], 2.59 (dd, $J = 9.7, 0.8$ Hz, CH_2CHCH_2), 2.49 (ddd, $J = 5.7, 3.2, 1.0$ Hz, CH_2CHCH_2), 2.27 (dd, $J = 5.9, 3.2$ Hz, CH_2CHCH_2), 2.05 (dd, $J = 8.9, 0.6$ Hz, CH_2CHCH_2), 0.75 (d, $J = 6.7$ Hz, $\text{CH}(\text{CH}_3)(\text{CH}_3)$), 0.68 (d, $J = 6.7$ Hz, $\text{CH}(\text{CH}_3)(\text{CH}_3)$) (single-frequency decoupling rigorously established all reported chemical shift and coupling constants); ^{13}C NMR (126 MHz, CD_3CN) δ 255.6 (s, $\text{COCH}(\text{CH}_3)_2$), 205.4 (s, $\text{Re}-\text{CO}$), 90.1 (d, $J = 181$ Hz, C_5H_5), 81.2 (d, $J = 171$ Hz, CH_2CHCH_2), 58.2 (d, $J = 131$ Hz, $\text{COCH}(\text{CH}_3)_2$), 44.1 (t, $J = 156$ Hz, CH_2CHCH_2), 23.2 (t, $J = 151$ Hz, CH_2CHCH_2), 19.5 (q, $J = 126$ Hz, $\text{COCH}(\text{CH}_3)(\text{CH}_3)$), 18.5 (q, $J = 129$ Hz, $\text{COCH}(\text{CH}_3)(\text{CH}_3)$); IR (CH_2Cl_2) 1925 (s), 1595 (m) cm^{-1} ; HRMS calcd for $\text{C}_{13}\text{H}_{17}\text{ReO}_2$ m/e 392.0786, found m/e 392.0800.

trans- $\text{C}_5\text{H}_5(\text{CO})_2\text{Re}(\text{CH}_2\text{CH}=\text{CH}_2)(\text{CH}_3)$ (**12**). CH_3CN and a 5-fold excess of allyl bromide were condensed onto $\text{Li}^+\text{C}_5\text{H}_5(\text{CO})_2\text{ReCH}_3^-$ (57 mg, 0.15 mmol)¹⁶ at -78 °C. The mixture was warmed to room temperature, and after 10 min solvent and excess allyl bromide were evaporated under high vacuum. The residue was chromatographed on silica gel (1:1 hexane:ether) to give **12** as a pale yellow oil: ^1H NMR (200 MHz, CD_3CN) δ 6.05 (ddt, $J = 16.7, 9.8, 8.4$ Hz, $\text{CH}_2\text{CH}=\text{CH}_2$), 5.08 (s, C_5H_5), 4.63 (dq, $J = 16.7, 1.2$ Hz, $\text{CH}_2\text{CH}=\text{CHH}$), 4.38 (dd, $J =$

9.8, 1.8 Hz, $\text{CH}_2\text{CH}=\text{CHH}$), 2.56 (dd, $J = 8.4, 1.2$ Hz, $\text{CH}_2\text{CH}=\text{CH}_2$), 0.74 (s, ReCH_3); ^{13}C $\{^1\text{H}\}$ NMR (68 MHz, C_6D_6) δ 198.6 ($\text{Re}-\text{CO}$), 147.6 ($\text{CH}=\text{CH}_2$), 107.0 ($\text{CH}=\text{CH}_2$), 90.4 (C_5H_5), 35.5 (CH_2), 8.3 (CH_3); IR (CH_2Cl_2) 1996 (s), 1917 (vs) cm^{-1} . HRMS: Calcd for $\text{C}_{13}\text{H}_{17}^{187}\text{ReO}_2$ m/e 392.0786, not observed; $\text{M} - \text{CH}_3^+$, calcd m/e 349.0239, obsd m/e 349.0197 (9%); $\text{M} - \text{CO}^+$, calcd m/e 366.0524, obsd m/e 366.0517 (100%); $\text{M} - \text{C}_3\text{H}_5$, calcd m/e 323.0082, obsd m/e 323.0057 (94%).

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Supplementary Material Available: For **5** and **6**, tables of structure determination data, positional and anisotropic thermal parameters for non-hydrogen atoms, selected interatomic distances and angles, and idealized atomic parameters for hydrogen atoms (12 pages); tables of observed and calculated structure factor amplitudes (16 pages). Ordering information is given on any current masthead page.