for intermediates traversed in the ligand substitution processes by a cluster-opening ligand addition mechanism that is amazingly similar to those observed for **1** and **3**.[1a] We feel that the isolation and characterization of **1** and **3** provide strong support for the viability and importance of such bond cleavage mechanisms for ligand substitution processes in metal cluster complexes.

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Supplementary Material Available: For all four of the structural analyses, tables of hydrogen atom positional parameters and anisotropic thermal parameters (27 pages); listings of structure factor amplitudes (58 pages). Ordering information is given on any current masthead page.

Rearrangement of a Propargyl Vinyl Rhenium Complex to a Rhenium Allenyl Vinyl Ketone Complex

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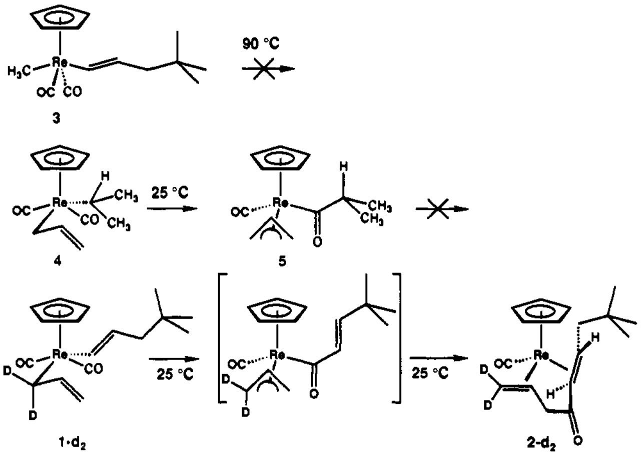
Abstract: An η^1- to η^3-propargyl rearrangement promotes vinyl migration to CO in *trans*-$C_5H_5(CO)_2Re(CH_2C{\equiv}CH)((E)\text{-}CH{=}CHCH_2CMe_3)$ (**7**) which eventually leads to the formation of allenyl vinyl ketone complex $C_5H_5(CO)Re(\eta^2,\eta^2\text{-}H_2C{=}C{=}CHCOCH{=}CHCH_2CMe_3)$ (**8**). This allenyl vinyl ketone complex **8** undergoes additional transformations at room temperature leading to the diastereomeric allenyl vinyl ketone complex $C_5H_5(CO)Re(\eta^2,\eta^2\text{-}H_2C{=}C{=}CHCOCH{=}CHCH_2CMe_3)$ (**9**) by complexation of rhenium to the opposite face of the vinyl group and to the π-allyl σ-vinyl rhenium complex $C_5H_5(CO)Re[\eta^3(exo,syn)\text{-}H_2CCHCHCOCH{=}CCH_2CMe_3]$ (**10**) by a net [1,5] hydrogen migration. Upon heating at 105 °C, allenyl vinyl ketone complex **9** rearranged to the isomeric π-allyl σ-vinyl rhenium complex $C_5H_5(CO)Re[\eta^3(endo,syn)\text{-}H_2CCHCHCOCH{=}CCH_2CMe_3]$ (**11**). When the first formed π-allyl σ-vinyl rhenium complex **10** was heated at 105 °C, it first rearranged to allenyl vinyl ketone complex **9** and then to the more stable π-allyl σ-vinyl rhenium complex **11**. Two different mechanisms can account for the interconversion of allenyl vinyl ketone complexes with π-allyl σ-vinyl rhenium complexes. One involves a [1,5] sigmatropic hydrogen shift over the unsaturated organic fragment and the second involves transfer of hydrogen via a rhenium hydride intermediate.

Introduction

We recently reported the unusually facile rearrangement of the allyl vinyl rhenium complex $C_5H_5(CO)_2Re(CH_2CH{=}CH_2)((E)\text{-}CH{=}CHCH_2CMe_3)$ (**1**) to the allyl vinyl ketone complex $C_5H_5(CO)Re(\eta^2,\eta^2\text{-}H_2C{=}CHCH_2COCH{=}CHCH_2CMe_3)$ (**2**).[1,2] In contrast, the methyl vinyl rhenium complex *trans*-$C_5H_5(CO)_2Re(CH_3)((E)\text{-}CH{=}CHCH_2CMe_3)$ (**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 *trans*-$C_5H_5(CO)_2Re(CH_2CH{=}CH_2)(CHMe_2)$ (**4**) rearranged to the stable η^3-allyl acyl complex $C_5H_5(CO)Re(exo\text{-}\eta^3\text{-}CH_2CHCH_2)(COCHMe_2)$ (**5**), which did not undergo reductive elimination to give a ketone. A second important observation came from a deuterium labeling study which showed that $C_5H_5(CO)_2Re(CD_2CH{=}CH_2)((E)\text{-}CH{=}CHCH_2CMe_3)$ (**1**-*d*) with deuterium label on the sp^3 allyl carbon rearranged to $C_5H_5(CO)Re(\eta^2,\eta^2\text{-}D_2C{=}CHCH_2COCH{=}CHCH_2CMe_3)$ (**2**-*d*) which had deuterium 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. 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, while the vinyl ligand coordinates roughly perpendicular to that plane.[3]

Scheme I



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(1) Casey, C. P.; Vosejpka, P. C.; Gavney, J. A., Jr. *J. Am. Chem. Soc.* **1990**, *112*, 4083.

(2) The rhenium allyl vinyl ketone complex **2** contains three stereogenic centers: the rhenium, the enantioface of the allyl ligand, and the enantioface of the enone ligand. The kinetically formed isomer is the *RRR* (*SSS*) diastereomer. The rhenium allyl vinyl ketone complex **6** is the *RSS* (*SRR*) diastereomer, which corresponds to bonding of the rhenium atom to the opposite enantiofaces of the alkene ligands from **2**.

(3) The angle between the plane defined by the Cp centroid, Re, and the alkene centroid and the plane defined by Re and the two carbons of the alkene is 90° for a "parallel" conformation and 0° for a "perpendicular" conformation. (In the "parallel" conformation the alkene C=C bond is parallel to the plane of the Cp ring.)

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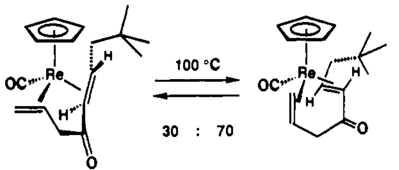
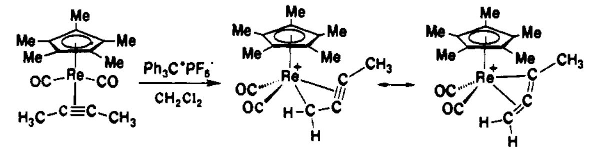
We have proposed that the conversion of **1** to **2** occurs by two consecutive concerted organometallic rearrangements.[1] In each of these rearrangements, two steps are combined to avoid the generation of a high energy coordinatively unsaturated intermediate; one of the steps would normally generate a vacant coordination site while 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. Such an assisted migration is not possible for the very thermally stable methyl vinyl complex **3**. In the second concerted reaction, the reductive elimination of the allyl and acyl groups 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**.



2 **6**

When the kinetically formed allyl vinyl ketone complex **2** was heated at 100 °C for 3 weeks, equilibration with a second allyl vinyl ketone diastereomer $C_5H_5(CO)Re(\eta^2,\eta^2\text{-}H_2C{=}CHCH_2COCH{=}CHCH_2CMe_3)$ (**6**) (**1**:**6** = 30:70) occurred.[2,4] The crystal structure of **6** showed that the allyl and vinyl ligands were again coordinated in a "crossed" fashion; however, in **6**, the *vinyl* ligand is coordinated roughly parallel to the plane of the cyclopentadienyl ligand, while the *allyl* ligand is coordinated perpendicular to that plane. We have shown that **6** is formed from **1** without the intervention of a trappable coordinatively unsaturated intermediate. Labeling studies showed that the isomerization was accomplished by inverting the face of both double bonds coordinated to the metal. It could not be determined whether this occurred via intermediates having the ketone group coordinated in place of an alkene or whether it occurred via agostic vinyl CH intermediates similar to those proposed by Gladysz in the racemization of $C_5H_5(NO)(Ph_3P)Re(CH_2{=}CHCH_3)^+$.[5]

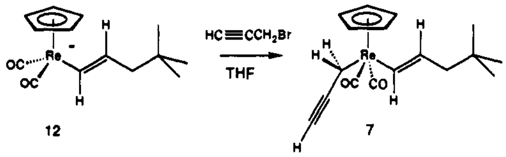
We are interested in the generality of concerted organometallic reactions in which steps are combined to avoid the generation of a high energy coordinatively unsaturated intermediate. In particular, we have focused our attention on the role of ligands which can increase their hapticity to avoid the generation of a vacant coordination site. The propargyl ligand was chosen in this investigation because of its similarity to the allyl ligand and because of the ease of synthesis of a variety of metal propargyl complexes. While π-propargyl complexes are far less common and probably less stable than π-allyl complexes, a growing number of π-propargyl complexes have been reported recently.[6] For example, we recently prepared the stable π-propargyl rhenium complex $C_5Me_5(CO)_2Re(\eta^3\text{-}CH_2C{\equiv}CCH_3)^+PF_6^-$ by hydride abstraction from $C_5Me_5(CO)_2Re(CH_3C{\equiv}CCH_3)$.[7]



To test whether an η^1- to η^3-propargyl rearrangement might promote the migration of organic ligands to CO in a manner analogous to that of an allyl ligand, we prepared the propargyl vinyl complex *trans*-$C_5H_5(CO)_2Re(CH_2C{\equiv}CH)((E)\text{-}CH{=}CHCH_2CMe_3)$ (**7**). Here we report that an η^1- to η^3-propargyl rearrangement promotes the migration of the vinyl ligand to CO and the formation of allenyl vinyl ketone complex $C_5H_5(CO)Re(\eta^2,\eta^2\text{-}H_2C{=}C{=}CHCOCH{=}CHCH_2CMe_3)$ (**8**). This allenyl vinyl ketone complex **8** undergoes additional transformations leading to a diastereomeric allenyl vinyl ketone complex **9** and to π-allyl σ-vinyl rhenium complexes $C_5H_5(CO)Re[\eta^3(exo,syn)\text{-}H_2CCHCHCOCH{=}CCH_2CMe_3]$ (**10**) and $C_5H_5(CO)Re[\eta^3(endo,syn)\text{-}H_2CCHCHCOCH{=}CCH_2CMe_3]$ (**11**). The formation of these π-allyl σ-vinyl rhenium complexes is the result of extremely facile reversible [1,5] hydrogen shifts of the allenyl vinyl ketone complexes.

Results

Synthesis of a σ-Propargyl Vinyl Rhenium Complex. Reaction of excess propargyl bromide with the nucleophilic vinyl rhenium complex $K^+C_5H_5(CO)_2Re[(E)\text{-}CH{=}CHCH_2CMe_3)]^-$ (**12**)[1] in THF resulted in alkylation at rhenium[8] to produce *trans*-$C_5H_5(CO)_2Re(CH_2C{\equiv}CH)((E)\text{-}CH{=}CHCH_2CMe_3)$ (**7**) in >90% yield by ^1H NMR. In the ^1H NMR of **7**, resonances assigned to the propargyl ligand were observed at δ 2.2 (d, J = 2.5 Hz) for the methylene protons and at δ 2.15 (m) for the acetylenic proton. These NMR observations clearly exclude S_N2' attack which would have produced a $ReCH{=}C{=}CH_2$ σ-allenyl unit. Resonances assigned to the σ-vinyl ligand of **7** were observed as doublets of triplets at δ 6.7 (dt, J = 15.2, 1.1 Hz) for the proton α to rhenium and at δ 5.8 (dt, J = 15.2, 7.0 Hz) for the proton β to rhenium. The 15.2-Hz coupling of the vinyl protons establishes the trans geometry of the carbon–carbon double bond. The NMR equivalence of the CH_2 protons of the allylic (δ 1.99) and propargylic (δ 2.2) groups is consistent with the assignment of a trans arrangement of the hydrocarbyl groups attached to rhenium. If **7** were a cis complex, different chemical shifts would be expected for the diastereotopic protons on each of these CH_2 groups. The IR spectrum of **7** exhibited two metal carbonyl stretches at 2024 and 1959 cm^{-1} with an integrated intensity ratio of 1:2.07. An angle of 110° between the carbonyl ligands of **7** was calculated from these relative intensities using the formula $[I_{sym}/I_{asym} = \cot^2(\theta/2)]$.[9] This angle is consistent with the formulation of **7** as a trans dialkyl complex.



12 **7**

Rearrangement of σ-Propargyl Vinyl Complex 7. In contrast to the stability of methyl vinyl rhenium compound **3**,[1] which was stable below 90 °C where it began to decompose slowly, propargyl vinyl rhenium complex **7** was kinetically unstable at 23 °C and rearranged over 4 h to give a 1:1.3 ratio of two new complexes, $C_5H_5(CO)Re[\eta^2(1,2),\eta^2(5,6)\text{-}H_2C{=}C{=}CHCOCH{=}CHCH_2CMe_3]$ (**9**) and $C_5H_5(CO)Re[\eta^3(exo,syn)\text{-}H_2C\text{-}$

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(6) (a) Krivykh, V. V.; Taits, E. S.; Petrovskii, P. V.; Struchkov, Y. T.; Yanovskii, A. I. *Mendeleev Commun.* **1991**, 103. (b) Gotzig, J.; Otto, H.; Werner, H. *J. Organomet. Chem.* **1985**, *287*, 247. (c) Jia, G.; Rheingold, A. L.; Meek, D. W. *Organometallics* **1989**, *8*, 1378. (d) Bianchini, C.; Peruzzini, M.; Zanobini, F.; Frediani, P.; Albinati, A. *J. Am. Chem. Soc.* **1991**, *113*, 5453. (e) McMullen, A. K.; Selegue, J. P.; Wang, J.-G. *Organometallics* **1991**, *10*, 3421. (f) Field, L. D.; George, A. V.; Hambley, T. W. *Inorg. Chem.* **1990**, *29*, 4565. (g) Hills, A.; Hughes, D. L.; Jimenez-Tenorio, M.; Leigh, G. J.; McGeary, C. A.; Rowley, A. T.; Bravo, M.; McKenna, C. E.; McKenna, M.-C. *J. Chem. Soc., Chem. Commun.* **1991**, 522. (h) For an excellent review of σ-propargyl metal compounds see: Wojcicki, A.; Shuchart, C. E. *Coord. Chem. Rev.* **1990**, *105*, 35.

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(8) In reactions of **12** with electrophiles, addition to the β-vinyl carbon was observed only for addition of H$^+$. Casey, C. P.; Vosejpka, P. C.; Askham, F. A. *J. Am. Chem. Soc.* **1990**, *112*, 3713 and references therein.

(9) Cotton, F. A.; Wilkinson, G. *Advanced Inorganic Chemistry*, 4th ed.; John Wiley & Sons: New York, 1980; p 1074.

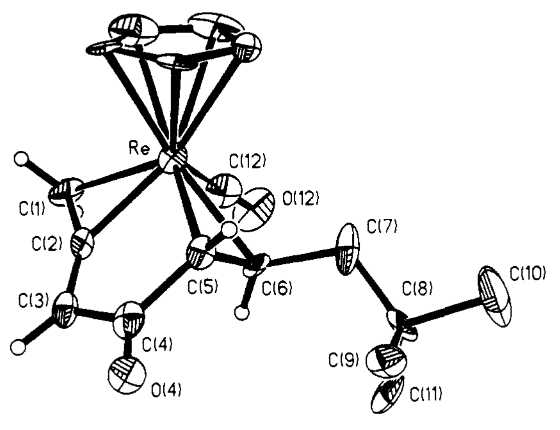
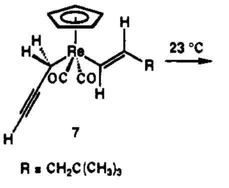


Figure 1. X-ray crystal structure of $C_5H_5(CO)Re[\eta^2(1,2),\eta^2(5,6)$-$H_2C{=}C{=}CHCOCH{=}CHCH_2CMe_3]$ (**9**).

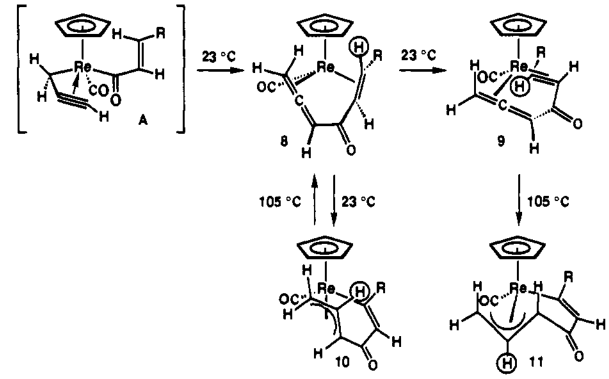
Table I. Selected Bond Lengths (Å) and Angles (deg) for $C_5H_5(CO)Re[\eta^2(1,2),\eta^2(5,6)$-$H_2C{=}C{=}CHCOCH{=}CHCH_2CMe_3]$ (**9**)

Re–C(1)	2.215 (16)	C(1)–C(2)	1.402 (17)
Re–C(2)	2.052 (13)	C(2)–C(3)	1.337 (16)
Re–C(5)	2.212 (12)	C(3)–C(4)	1.466 (23)
Re–C(6)	2.274 (12)	C(4)–O(4)	1.215 (15)
		C(4)–C(5)	1.527 (19)
		C(5)–C(6)	1.411 (17)
C(1)–C(2)–C(3)	153.6 (15)	C(5)–C(6)–C(7)	122.5 (14)
C(2)–C(3)–C(4)	111.4 (13)	C(3)–C(4)–O(4)	127.1 (13)
C(3)–C(4)–C(5)	111.6 (11)	O(4)–C(4)–C(5)	121.2 (14)
C(4)–C(5)–C(6)	118.7 (12)		

$\overline{CHCHCOCH{=}C}CH_2CMe_3]$ (**10**), which were isolated by TLC in 77% combined yield.



R = $CH_2C(CH_3)_3$



The minor isomer **9** was characterized spectroscopically as an allenyl vinyl ketone complex and its precise coordination geometry was determined by X-ray crystallography (see below). It was somewhat surprising that **9** was the only allenyl vinyl ketone complex isolated from rearrangement of **7** since its diastereomer, **8**, is closely related to the kinetically formed allyl vinyl ketone complex **2**.[10]

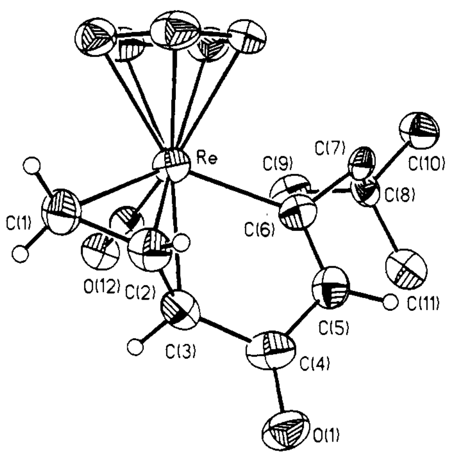


Figure 2. X-ray crystal structure of $C_5H_5(CO)\overline{Re[\eta^3(exo,syn)\text{-}H_2CCHCHCOCH{=}C}CH_2CMe_3]$ (**10**).

Table II. Selected Bond Lengths (Å) and Angles (deg) for $C_5H_5(CO)\overline{Re[\eta^3(exo,syn)\text{-}H_2CCHCHCOCH{=}C}CH_2CMe_3]$ (**10**)

Re–C(1)	2.240 (12)	C(1)–C(2)	1.439 (16)
Re–C(2)	2.152 (11)	C(2)–C(3)	1.409 (14)
Re–C(3)	2.287 (10)	C(3)–C(4)	1.500 (16)
Re–C(6)	2.155 (11)	C(4)–O(1)	1.222 (12)
		C(4)–C(5)	1.461 (16)
		C(5)–C(6)	1.351 (13)
C(1)–C(2)–C(3)	111.2 (9)	C(5)–C(6)–C(7)	111.3 (9)
C(2)–C(3)–C(4)	121.1 (10)	C(3)–C(4)–O(1)	122.1 (10)
C(3)–C(4)–C(5)	110.1 (8)	O(1)–C(4)–C(5)	127.6 (11)
C(4)–C(5)–C(6)	117.2 (10)		

The X-ray crystal structure of **9** showed several interesting features (Figure 1, Table I). The distance from the rhenium to the central carbon of the allene ligand [2.052 (13) Å] is 0.163 Å shorter than the distance from rhenium to the terminal carbon of the allene ligand [2.215 (16) Å]. The uncoordinated double bond of the allene ligand is bent away from rhenium, with a $CH_2{=}C{=}CH$ angle of 153.6 (15)°. The allene and the ketone groups are nearly coplanar; the torsion angle of the $C{=}CHC{=}O$ unit is 170.5°.

The structure observed for the rhenium η^2-allene fragment of **9** is similar to structures observed in other transition metal allene complexes. For example, the $C{=}C{=}C$ angle about the central carbon of η^2-allene complexes varies from 134.5° in $ReCl(\eta^2$-$CH_2{=}C{=}CHPh)(dppe)$[11] to 158° in $Rh(PPh_3)_2(I)(CH_2{=}C{=}CH_2)$.[12] The distance from the metal to the central carbon of an allene ligand is typically 0.05 to 0.19 Å shorter than the distance from the metal to the terminal carbon.[13] This has been attributed to overlap between a filled d orbital on the metal and both of the unoccupied orthogonal π^* orbitals of the central carbon.[13,14]

In the IR spectrum of **9**, a single metal CO stretch was observed at 1922 cm^{-1}. A weaker band at 1634 cm^{-1} was assigned to the enone carbonyl stretch. In the ^{13}C NMR spectrum of **9**, a resonance at δ −9.0 (which gave an inverted peak in a DEPT-135 experiment) was assigned to the terminal, coordinated carbon of the allenyl ligand ($=CH_2$). Similar upfield ^{13}C NMR shifts were observed for the coordinated methylene carbons of the allene complexes $C_5H_5(CO)_2Re(\eta^2$-$H_2C{=}C{=}CH_2)$ (δ − 10.6)[15] and $C_5H_5(i\text{-}Pr_3P)Rh(\eta^2$-$H_2C{=}C{=}CHCH_3)$ (δ − 1.95).[16]

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[10] The kinetically formed allyl vinyl ketone complex **2** has the 5*re*, 6*re* face of the enone bonded to the *R* rhenium center. Allenyl vinyl ketone complex **8** also has the 5*re*, 6*re* face of the enone bonded to the *R* rhenium center. The diastereomer **9**, isolated from the rearrangement of **7**, has the 5*si*, 6*si* face of the enone bonded to the *R* rhenium center; this is similar to allyl vinyl ketone complex **6** which has the 5*si*, 6*si* face of the enone bonded to the *R* rhenium center.

[11] Hughes, D. L.; Pombeiro, A. J. L.; Pickett, C. J.; Richards, R. L. *J. Chem. Soc., Chem. Commun.* **1984**, 992.

[12] Kashiwagi, T.; Yasuoka, N.; Kasai, N.; Kukudo, M. *J. Chem. Soc., Chem. Commun.* **1969**, 317.

[13] Bowden, F. L.; Giles, R. *Coord. Chem. Rev.* **1976**, *20*, 81.

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[15] Casey, C. P.; Underiner, T. L., unpublished observations.

[16] Wolf, J.; Werner, H. *Organometallics* **1987**, *6*, 1164.

Prior to obtaining an X-ray structure of **9**, two different deuterium labeling experiments were carried out to define the course of the rearrangement and to assist in the assignment of the ^1H NMR spectrum of **9**. In the first, the vinyl rhenium anion **12** was treated with $DC{\equiv}CCH_2Br$[17] to produce rearrangement product $C_5H_5(CO)Re[\eta^2(1,2),\eta^2(5,6)\text{-}H_2C{=}C{=}CDCOCH{=}CHCH_2CMe_3]$ (**9**-*3d*) in which the allenic methine position was deuterated. In the ^1H NMR of **9**-*3d*, only the resonance at δ 7.01 assigned to the internal allenic proton had diminished intensity. In a second deuterium labeling study, reaction of α-deuterated vinyl anion complex $K^+C_5H_5(CO)_2Re[(E)\text{-}CD{=}CHCH_2CMe_3)]^-$ (**12**-*d*)[18] with propargyl bromide produced the allenyl vinyl ketone complex $C_5H_5(CO)Re[\eta^2(1,2),\eta^2(5,6)\text{-}H_2C{=}C{=}CHCOCD{=}CHCH_2CMe_3]$ (**9**-*5d*) in which the α-vinyl carbon was deuterated. Only the resonance at δ 4.20 assigned to the α-proton of the enone fragment displayed diminished intensity.

The ^1H NMR spectrum of **10** indicated that it was not an allenyl vinyl ketone complex. The X-ray crystal structure revealed it to be the π-allyl σ-vinyl rhenium complex, $C_5H_5(CO)Re[\eta^3\text{-}(exo,syn)\text{-}H_2CCHCHCOCH{=}CCH_2CMe_3]$ (**10**) (Figure 2 and Table II). The η^3-allyl group of **10** is rotated 56.3° from an idealized exo geometry.[19] This rotation is required to accommodate the chelate ring to the σ-vinyl unit. The observed geometry is close to that proposed for the transition state for η^3-allyl rotation in metal complexes. Legdzins[20] observed a similar geometry for the chelated η^3-allyl ligand of $C_5H_5(NO)Mo(\eta^3exo\text{-}Me_2CCHCHCMe_2CMe_2O)$. The central allyl carbon of **10** is directed toward the σ-vinyl group and is proximal to the cyclopentadienyl group. Examination of models of **10** and of the kinetically formed allenyl vinyl ketone complex $C_5H_5(CO)Re(\eta^2,\eta^2\text{-}H_2C{=}C{=}CHCOCH{=}CHCH_2CMe_3)$ (**8**) indicates that these isomers are related by a net [1,5] hydrogen shift.

The spectroscopic data for **10** are fully consistent with its formulation as a π-allyl σ-vinyl rhenium complex. The IR spectrum of **10** displayed one metal CO band at 1897 cm^{-1} and a weaker band at 1647 cm^{-1} assigned to the unsaturated ketone group. In the ^{13}C NMR spectrum of **10**, resonances at δ 201.4 and 199.9 were assigned to the metal carbonyl and the ketone carbonyl, and a resonance at δ 188.8 was assigned to the vinyl carbon bound to rhenium. A DEPT-135 experiment aided the assignment of the remaining signals. A positive peak at δ 149.9 was assigned to the vinyl CH β to rhenium. Positive peaks at δ 86.9 and 69.2 were assigned to the two CH carbons of the π-allyl ligand and an inverted peak at δ 19.8 was assigned to the CH_2 carbon of the π-allyl ligand.

In the ^1H NMR spectrum of **10**, the π-allyl ligand gave rise to a strongly coupled four-spin system. The central allyl proton appeared at δ 5.18 (ddd, J = 9.7, 9.4, 5.7 Hz) coupled to two anti protons at δ 4.28 and 1.65 (J = 9.7 and 9.4 Hz) and to a syn proton at δ 2.18 (J = 5.7 Hz). The vinyl proton of the enone appeared as a doublet (J = 1.2 Hz) at δ 7.00, coupled weakly to a diastereotopic methylene proton at δ 2.60 (dd, J_{gem} = 13.2 Hz, J = 1.2 Hz).

Deuterium labeling was used to follow the course of the rearrangement and to aid in ^1H NMR assignments. Reaction of the vinyl anion complex **12** with $DC{\equiv}CCH_2Br$[17] led to the formation of $C_5H_5(CO)Re[\eta^3(exo,syn)\text{-}H_2CCHCDCOCH{=}C\text{-}CH_2CMe_3]$ (**10**-*3d*). In the ^1H NMR of **10**-*3d*, only the resonance at δ 4.28 assigned to the π-allyl proton α to the ketone had diminished intensity. Reaction of the α-deuterio vinyl anion complex $K^+C_5H_5(CO)_2Re[(E)\text{-}CD{=}CHCH_2CMe_3)]^-$ (**12**-*d*)[18] with excess propargyl bromide produced $C_5H_5(CO)Re[\eta^3\text{-}(exo,syn)\text{-}H_2CCHCHCOCD{=}CCH_2CMe_3]$ (**10**-*5d*). Only the ^1H NMR resonance at δ 7.00 assigned to the vinyl proton β to rhenium of **10**-*5d* showed diminished intensity.

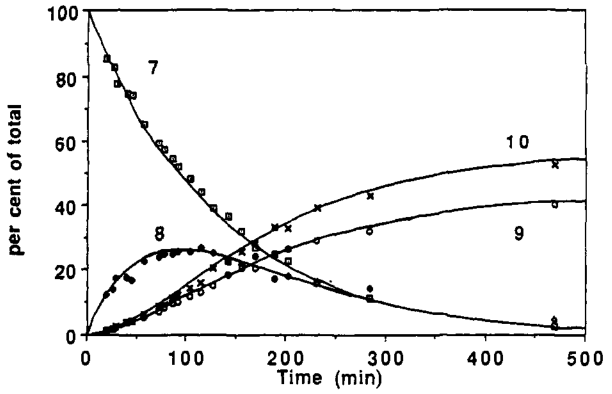

Figure 3. Kinetics of the conversion of **7** to **8**, **9**, and **10**. Curves were calculated using the GEAR program.

Observation of a Transient Intermediate in the Rearrangement of 7. The kinetics of the rearrangement of **7** to **9** and **10** was studied by ^1H NMR spectroscopy at 23 °C. A linear plot of ln [**7**] vs time established a first-order rate law for the disappearance of **7**. The rate constant for disappearance of **7** was found to be $1.29 \pm 0.01 \times 10^{-4}$ s^{-1} ($\Delta G^‡ = 22.6 \pm 0.1$ kcal mol^{-1} at 23 ± 0.5 °C) which corresponds to a half-life of 89 min.

In the course of monitoring the conversion of **7** to **9** and **10**, an intermediate complex $C_5H_5(CO)Re(\eta^2,\eta^2\text{-}H_2C{=}C{=}CHCOCH{=}CHCH_2CMe_3)$ (**8**) was also observed. The relative concentration of **8** reached a maximum of 25% after 100 min at 23 °C and then gradually disappeared with further production of **9** and **10**.

The identity of **8** could not be determined unambiguously by spectroscopy due to its low concentration and due to the presence of **7**, **9**, and **10** in the reaction mixture. However, the ^1H NMR spectrum of **8** was very similar to the ^1H NMR spectrum of allenyl vinyl ketone complex **9** and we considered that **8** might be a diastereomer of **9** differing in the enone enantioface complexed to rhenium. The structure proposed for **8** is closely related to the kinetically formed allyl vinyl ketone complex **2**.[10] A signal at δ 7.10 (m) was assigned to the internal allene proton of **8**. This signal was coupled to two one-proton resonances at δ 2.70 (dd, J = 8.5, 2.0 Hz) and 2.50 (dd, J = 8.5, 2.0 Hz), which were assigned to the terminal allene protons of **8**. The enone ligand of **8** exhibited a one-proton resonance at δ 3.65 (br d, J = 8.8 Hz) for the α-proton and a one-proton resonance at δ 2.35 (dd, J = 11.0, 8.8 Hz) for the β-proton. The methylene protons were not located and were presumably obscured by the signals due to **7**, **9**, or **10**.

The kinetics of the conversion of **7** to **8**, **9**, and **10** was modeled using the computer program GEAR[21] (Figure 3). The best fit to the experimental data employed a model in which **7** was converted to intermediate **8** ($k = 1.29 \pm 0.01 \times 10^{-4}$ s^{-1}, $\Delta G^‡ = 22.6 \pm 0.1$ kcal mol^{-1} at 23 ± 0.5 °C) which was then converted to both **9** ($k = 1.04 \times 10^{-4}$ s^{-1}, $\Delta G^‡ = 22.7$ kcal mol^{-1}) and **10** ($k = 1.36 \times 10^{-4}$ s^{-1}, $\Delta G^‡ = 22.6$ kcal mol^{-1}). There was an induction period for the formation of both **9** and **10** and the ratio of **9**:**10** did not vary significantly over the course of the reaction. Therefore, **8** is the immediate precursor of both **9** and **10**.

Rearrangement of Allenyl Vinyl Ketone Complex 9. When a solution of **9** in CD_3CN was heated at 105 °C, no formation of π-allyl isomer **10** was observed by ^1H NMR. Instead, clean

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(17) Ollis, W. D.; Sutherland, I. O.; Thebtaranonth, Y. *J. Chem. Soc., Perkin Trans. 1* **1981**, 1981.

(18) $K^+C_5H_5(CO)_2Re[(E)\text{-}CD{=}CHCH_2CMe_3]^-$ (**12**-*d*) was prepared by deprotonation of $C_5H_5(CO)_2Re{=}CDCH_2CH_2CMe_3$ with potassium *tert*-butoxide.[8]

(19) The dihedral angle of the C_5H_5 centroid, Re, allyl centroid, central allyl carbon is 0° in an idealized exo allyl geometry and 180° in an idealized endo geometry. Although the structure of **10** is not that of an idealized exo π-allyl ligand, the dihedral angle observed for **10** is 56°, and it is best described as a distorted exo isomer. The dihedral angle observed for **11** is 176.9°, and it is best described as a slightly distorted endo isomer.

(20) Christensen, N. J.; Legzdins, P.; Trotter, J.; Yee, V. C. *Organometallics* **1991**, *10*, 4021.

(21) Weigert, F. J.; McKinney, R. J. "GEAR" PC3003, Project SERAPHIM, Department of Chemistry, University of Wisconsin-Madison, Madison, WI 53706, 1991.

Table III. Selected Bond Lengths (Å) and Angles (deg) for $C_5H_5(CO)Re[\eta^3(endo,syn)\text{-}H_2CCHCHCOCH{=}CCH_2CMe_3]$ (**11**)

Re–C(1)	2.240 (9)	C(1)–C(2)	1.418 (12)
Re–C(2)	2.177 (8)	C(2)–C(3)	1.398 (13)
Re–C(3)	2.217 (7)	C(3)–C(4)	1.518 (11)
Re–C(6)	2.168 (7)	C(4)–O(4)	1.214 (9)
		C(4)–C(5)	1.448 (11)
		C(5)–C(6)	1.358 (10)
C(1)–C(2)–C(3)	113.6 (8)	C(5)–C(6)–C(7)	122.6 (7)
C(2)–C(3)–C(4)	122.0 (7)	C(3)–C(4)–O(4)	122.5 (7)
C(3)–C(4)–C(5)	111.4 (6)	O(4)–C(4)–C(5)	126.1 (7)
C(4)–C(5)–C(6)	117.7 (7)		

formation of a single new complex, the π-allyl σ-vinyl ketone complex $C_5H_5(CO)Re[\eta^3(endo,syn)\text{-}H_2CCHCHCOCH{=}C\text{-}CH_2CMe_3]$ (**11**) was observed with a half-life of approximately 15 h at 105 °C ($k = 1.31 \pm 0.01 \times 10^{-5}\ s^{-1}$, $\Delta G^{\ddagger} = 30.8 \pm 0.1$ kcal mol^{-1} at 105 ± 1 °C).

The structure of **11** was established spectroscopically and confirmed by X-ray crystallography. The ^{13}C NMR spectrum of **11** was very similar to that of **10**. Two resonances at δ 208.2 and 206.1 were assigned to the CO and ketone carbonyl, and a resonance at δ 187.8 was assigned to the vinyl carbon bound to rhenium. A DEPT-135 experiment allowed assignment of the remaining signals. A positive peak at δ 137.9 was assigned to the vinyl CH β to rhenium. The π-allyl ligand gave rise to positive peaks at δ 89.1 and 63.9 for the two CH allyl carbons and an inverted signal at δ 22.0 for the CH_2 allyl carbon.

In the ^1H NMR of **11**, the π-allyl ligand gave rise to a strongly coupled four-spin system. The central proton appeared as a distorted triplet of doublets at δ 4.41 with a 5.4 Hz coupling to a syn proton at δ 2.38 and with 7.4 and 8.0 Hz couplings to two anti protons at δ 3.32 and 2.28, respectively. The presence of *two large* couplings for the central proton established the syn relationship of the ketone carbonyl to the proton on the central position of the π-allyl ligand. When **9**-*3d* was heated at 105 °C for 2 days, only the δ 3.32 resonance assigned to the anti, internal π-allyl proton of $C_5H_5(CO)Re[\eta^3(endo,syn)\text{-}H_2CCHCDCOCH{=}C\text{-}CH_2CMe_3]$ (**11**-*3d*) had diminished intensity. The vinyl proton of the enone fragment appeared as a multiplet at δ 6.46; the far downfield shift of this proton is similar to that seen for the related proton of complex **10**. The infrared spectrum of **11** exhibited a strong band at 1939 cm^{-1} for the metal CO stretch and a weaker band at 1639 cm^{-1} for the enone carbonyl. These data clearly establish that **11** is a π-allyl vinyl ketone complex. The formation of **11** is the net result of a [1,5] hydrogen migration from the coordinated vinyl ligand of **9** to the *bottom* face of the central carbon of the allenyl ligand.

The X-ray crystal structure of **11** (Figure 4 and Table III) confirms that **11** is a π-allyl σ-vinyl rhenium complex similar to **10**. The π-allyl ligand of **11** is distorted only slightly from an idealized endo geometry (the allyl group is rotated only 3.1°).[19] In contrast, the exo π-allyl ligand of **10** was rotated 56° from its idealized geometry; this distortion may be responsible for the lower thermodynamic stability of **10** compared to **11** (see below). Similarly, Legdzins observed greater distortion of the exo than of the endo isomer of $C_5H_5(NO)Mo(\eta^3exo\text{-}Me_2CCH\text{-}CHCMe_2CMe_2O)$.[20] $CHCMe_2CMe_2O)$.[20]

Rearrangement of π-Allyl σ-Vinyl Rhenium Complex 10. When a solution of the exo π-allyl isomer **10** was heated at 105 °C for 5 days, a clean conversion to the endo π-allyl isomer **11** was observed. When the isomerization of **10** to **11** was monitored by ^1H NMR, the formation of an intermediate, the allenyl vinyl ketone complex **9**, was observed. The disappearance of **10** followed first-order kinetics ($k = 1.75 \pm 0.08 \times 10^{-4}\ s^{-1}$, $t_{1/2} = 85$ min at 105 ± 1 °C, $\Delta G^{\ddagger} = 28.8 \pm 0.1$ kcal mol^{-1}) and allenyl vinyl ketone complex **9** was formed as the major product. Upon further heating at 105 °C, **9** was slowly converted to **11**. The rearrangement of **10** to **9** constitutes a rare example of the generation of an allene by a net [1,5] hydrogen shift.[22]

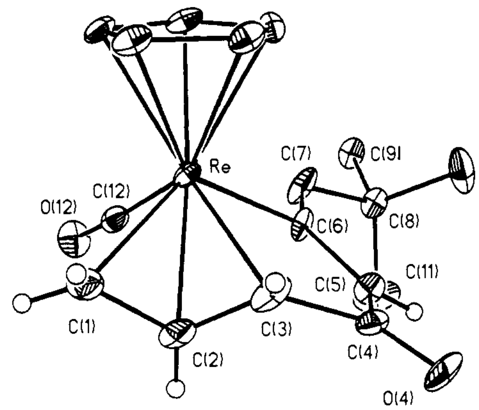


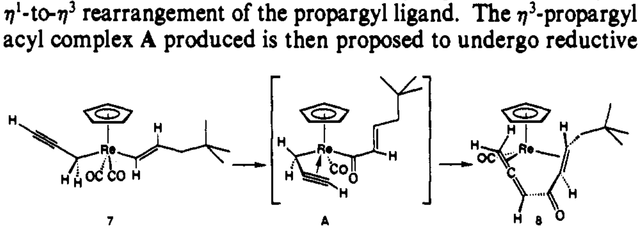
Figure 4. X-ray crystal structure of $C_5H_5(CO)Re[\eta^3(endo,syn)\text{-}H_2CCHCHCOCH{=}CCH_2CMe_3]$ (**11**).

The conversion of a 1:1.3 mixture of **9**:**10** to **11** was carried out in a 2:1 mixture of CD_3CN:CD_3OD at 105 °C for 3 days. The ^1H NMR of **11** showed no measureable incorporation of deuterium.

Discussion

Propargyl Assistance of Vinyl Migration to CO. The free energy of activation for the rearrangement of propargyl vinyl rhenium complex **7** to the allenyl vinyl ketone complex **8** ($\Delta G^{\ddagger} = 22.6$ kcal mol^{-1} at 23 °C) is much lower than that for thermal decomposition of methyl vinyl rhenium complex **3** ($\Delta G^{\ddagger} \approx 30$ kcal mol^{-1} at 90 °C).[1] Thus the η^1- to η^3-propargyl rearrangement of **7** assists the migration of the vinyl group to CO by lowering the activation barrier by at least 7 kcal mol^{-1}. The ability of the propargyl group of **7** to assist the migration of a vinyl group to CO is similar to that of the allyl group of allyl vinyl rhenium complex **1**. Rearrangement of propargyl rhenium complex **7** occurred at 23 °C with a half-life of 89 min, compared with a half-life of 10 min for the rearrangement of allyl vinyl rhenium complex **1**.[1] An increasing number of reports of once rare η^3-propargyl complexes have begun to appear, indicating that η^3-propargyl ligands are reasonably stable units. Recent examples of η^3-propargyl complexes include $C_5Me_5(CO)_2Re(\eta^3\text{-}CH_2C{\equiv}CCH_3)^+$,[7] $(Me_3P)_4Os(\eta^3\text{-}PhC{\equiv}CC{=}CHPh)^+$,[6b] and $C_6Me_6(CO)_2Mo(\eta^3\text{-}CH_2C{\equiv}CH)^+BF_4^-$.[6a]

We propose that the rearrangement of propargyl vinyl rhenium complex **7** to allenyl vinyl ketone complex **8** occurs by an initial migration of the vinyl ligand to a carbonyl ligand, assisted by an η^1-to-η^3 rearrangement of the propargyl ligand. The η^3-propargyl acyl complex **A** produced is then proposed to undergo reductive coupling of the η^3-propargyl and α,β-unsaturated acyl ligands concerted with coordination of the vinyl group via an s-trans, anti acyl conformer. Coordination of the vinyl double bond is most readily achieved from this conformation and leads directly to the allenyl vinyl ketone complex **8** in which the enone C=C double bond is alligned approximately perpendicular to the cyclopentadienyl ring.[3] This proposed geometry is similar to that observed in the X-ray structure of the kinetically formed allyl vinyl ketone complex **2**.[1]



Interconversion of Isomeric Allenyl Vinyl Ketone Complexes. The rapid room temperature isomerization of the initially formed

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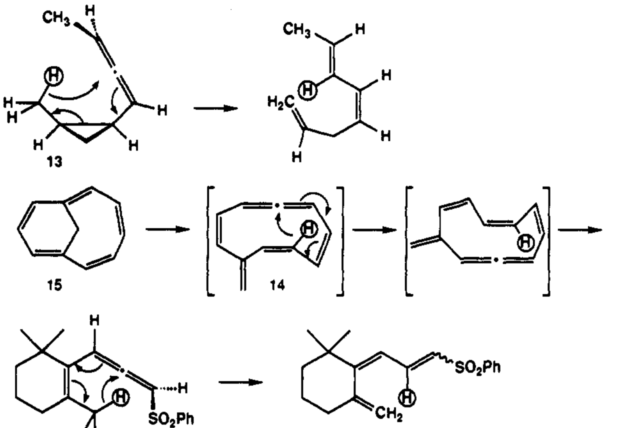
(22) (a) Hopf, H. In *Chemistry of the Allenes*; Landor, S. R., Ed.; Academic Press: New York, 1982; Vol. 2, p 265. (b) Palenzuela, J. A.; Elnagar, H. Y.; Okamura, W. H. *J. Am. Chem. Soc.* **1989**, *111*, 1770.

(23) Minter, D. E.; Fonken, G. J. *Tetrahedron Lett.* **1977**, 4149.

allenyl vinyl ketone complex **8** to the more stable diastereomeric allenyl vinyl ketone complex **9** involves a net migration of rhenium from one alkene enantioface to the other. A similar but slower transformation was seen in the case of the conversion of the initially formed allyl vinyl ketone complex **2** to its diastereomer **6** upon heating at 100 °C for 3 weeks.[4] We do not understand the reasons for the more facile isomerization of the allenyl ketone complex **8**. The X-ray crystal structure of **9** shows that the enone fragment is coordinated in a roughly "parallel" orientation[3] relative to the cyclopentadienyl ring just as in the case of the isomerized allyl vinyl ketone complex **6**. We do not know whether these isomerizations involve intermediates having the ketone group coordinated in place of an alkene or whether they occur via agostic vinyl CH intermediates similar to those proposed by Gladysz for the racemization of $C_5H_5(NO)(Ph_3P)Re(CH_2{=}CHCH_3)^+$.[5]

Mechanism of Rearrangement to π-Allyl σ-Vinyl Rhenium Complexes. The rearrangement of allenyl vinyl ketone complexes **8** and **9** to π-allyl σ-vinyl rhenium complexes **10** and **11** respectively involves an unprecedented net [1,5] hydrogen shift. Examination of molecular models for the initially formed allenyl vinyl ketone complex **8** shows that the β-CH bond of the enone fragment is held in close proximity to the central carbon of the allene ligand. This geometry is poised for an extremely facile hydrogen migration over the face of the complexed ketone nearest the cyclopentadienyl ligand to the central carbon of the allenyl unit which generates the exo π-allyl ligand of **10**. Similarly, examination of the crystal structure of the allenyl vinyl ketone complex **9** shows that the β-CH bond of the enone fragment is poised over the face of the complexed ketone remote from the cyclopentadienyl ligand. Hydrogen migration from this geometry would lead to the formation of the endo π-allyl unit of **11**.

Two different mechanisms for the net [1,5] hydrogen shift can be considered. The first is a [1,5] sigmatropic hydrogen migration along the π-system of the ketone; the second involves an insertion of rhenium into a vinyl CH bond followed by hydride migration from the metal to the central carbon of the complexed allene.

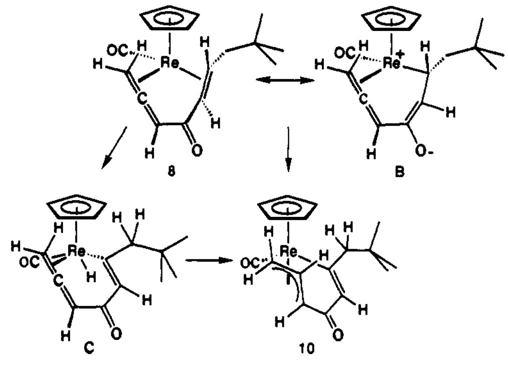


The rearrangement of **8** to **10** involves a net [1,5] hydrogen shift to the central carbon of a complexed allene. Examples of thermal [1,5] hydrogen shifts to the central carbon of allenes include the rearrangement of allenyl methyl cyclopropane **13**[23] and an sp² to sp [1,5] hydrogen shift of the proposed intermediate allene **14** in the isomerization of homoazulene **15**.[24]

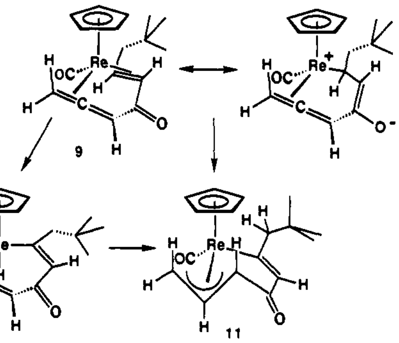
The sigmatropic rearrangement of **8** to **10** might be enhanced by interaction of rhenium with the β-carbon of the enone as depicted in resonance structure **B** which emphasizes the allylic arrangement of the migrating hydrogen relative to the conjugated π system containing the allene. The migration can then be envisioned as a [1,5] sigmatropic hydrogen shift in a vinyl allene-like unit (Scheme II).

[1,5] sigmatropic hydrogen migrations of vinyl allenes are well precedented.[25] Okamura studied [1,5] hydrogen shifts in vinyl allenes of molecules related to vitamins A and D and correlated the rates of the [1,5] hydrogen shifts with the distance separating the termini of the hydrogen migration.[26] The rearrangement of **8** to **10** ($\Delta G^{\ddagger} = 22.6$ kcal mol^{-1}) is one of the most facile [1,5] hydrogen shifts reported for a vinyl allene. Okamura's sulfone-substituted vinyl allene **16** has a similar barrier ($\Delta G^{\ddagger} = 22.7$ kcal mol^{-1}) for a [1,5] hydrogen shift.[27]

Scheme II



Scheme III



An alternative pathway for the hydrogen migration involves rhenium hydride intermediates. Insertion of rhenium into the β-CH bond of the enone **8** would produce the hydrido allenyl vinyl ketone rhenium(III) intermediate (**C**) in which the hydride ligand occupies a position in a four legged piano stool geometry between the vinyl and allene units. Hydride addition to the central carbon of the coordinated allene leads to exo π-allyl vinyl rhenium complex **10**. Insertion of rhenium into the β-CH bond of the isomeric enone **9** would produce a hydrido allenyl vinyl ketone rhenium(III) intermediate in which the hydride ligand occupies a position in a four legged piano stool trans to the allene group. Hydride addition to the central carbon of the allene might occur from the face opposite the cyclopentadienyl ligand to produce the endo π-allyl vinyl rhenium complex **11**; a transition state similar to the trigonal bipyramidal geometry **D** might be envisioned (Scheme III). This less favorable geometry could explain the higher temperature required for rearrangement of **8** to **10** (105 °C) than for rearrangement of **7** to **9** (23 °C).

Since the proposed rhenium hydride intermediates **C** and **D** would be expected to be mildly acidic, we looked for H–D exchange with CD_3OD during the conversion of a mixture of **9** and **10** to **11**. The fact that no deuterium incorporation into **11** was observed indicates that if rhenium hydride intermediates are formed they do not undergo rapid H–D exchange. This experiment also rules out mechanisms involving enol intermediates that would be expected to undergo very rapid H–D exchange.[28]

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(24) Scott, L. T.; Erden, I. *J. Am. Chem. Soc.* **1982**, *104*, 1147.

(25) Okamura, W. H. *Acc. Chem. Res.* **1983**, *16*, 81 and references therein.

(26) Wu, K.-M.; Midland, M. M.; Okamura, W. H. *J. Org. Chem.* **1990**, *55*, 4381.

(27) Shen, G.-Y.; Tapia, R.; Okamura, W. H. *J. Am. Chem. Soc.* **1987**, *109*, 7499.

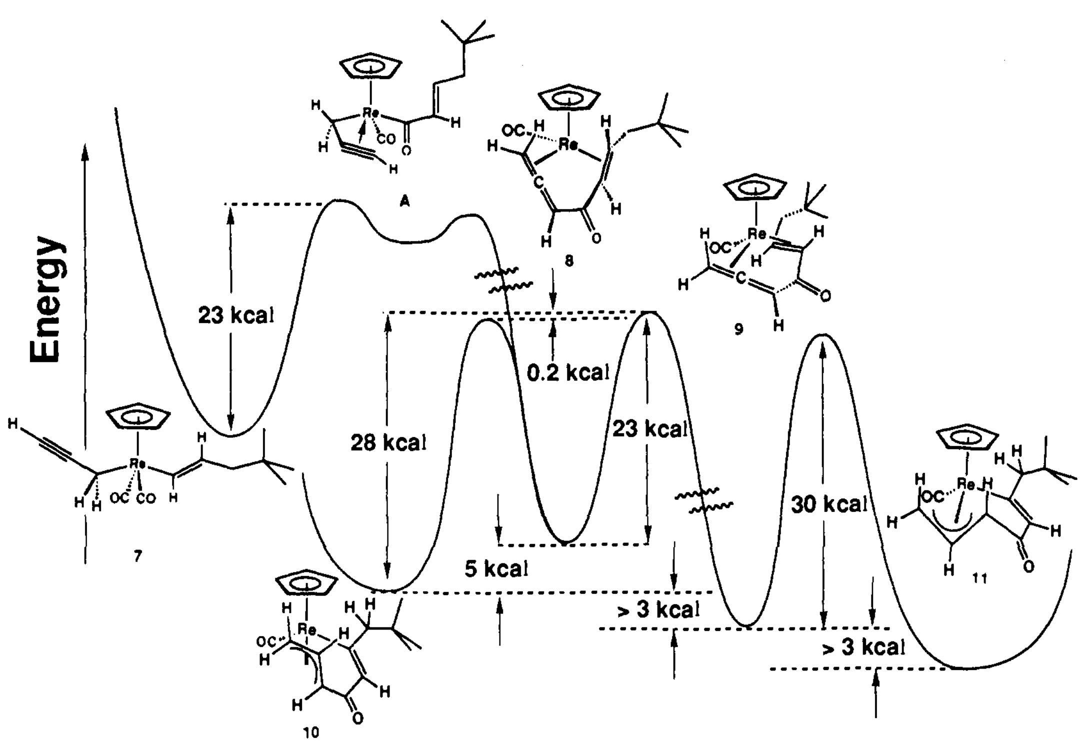

Figure 5. Free energy diagram for the overall isomerization of 7 to 11.

The geometries proposed for direct sigmatropic [1,5] hydrogen shift and for rearrangement via rhenium hydrides are very similar. They differ primarily in whether hydrogen slides along the carbon π-system or makes a brief stop at the metal center. Our experimental evidence does not allow a distinction to be made between the two mechanisms.

Potential Energy Diagram for the Formation and Reactions of Allenyl Vinyl Ketone Complexes. On the basis of free energies of activation calculated from kinetic studies, we have constructed the energy surface relating complexes **7**, **8**, **9**, **10**, and **11** shown in Figure 5. The partitioning of the initially formed allenyl vinyl ketone complex **8** between the isomeric allenyl vinyl ketone complex **9** and exo π-allyl σ-vinyl rhenium complex **10** establishes the 0.2 kcal mol^{-1} difference in activation energies for formation of **9** and **10**. The barrier for conversion of π-allyl σ-vinyl rhenium complex **10** to **9** (probably via **8**) is 5 kcal mol^{-1} higher than the barrier for conversion of **8** to **10** and establishes the 5 kcal mol^{-1} energy difference between **8** and **10**. The fact that none of the exo π-allyl σ-vinyl rhenium complex **10** is observed during the conversion of allenyl vinyl ketone complex **9** to endo π-allyl σ-vinyl rhenium complex **11** implies that **9** is favored over **10** at equilibrium by a factor of at least 100 and establishes that **9** is at least 3 kcal mol^{-1} more stable than **10**. The fact that the conversion of **9** to **11** goes to completion implies that **11** is at least 3 kcal mol^{-1} more stable than **9**.

This analysis highlights three large energy differences. First, the allenyl vinyl ketone complex **9** is ≥8 kcal mol^{-1} more stable than the isomeric kinetically formed allenyl vinyl ketone complex **8**. Examination of molecular models gave little insight into this dramatic energy difference. Second, the barrier to [1,5] hydrogen shift is 7 kcal mol^{-1} lower for conversion of **8** to **10** than for conversion of **9** to **11**. Examination of molecular models for a [1,5] sigmatropic hydrogen shift did not reveal any noticeable differences; but the rate difference can be understood if **9** rearranges to **11** via the high energy trigonal bipyramidal rhenium hydride intermediate D. Third, the endo π-allyl σ-vinyl rhenium complex **11** is ≥6 kcal mol^{-1} more stable than the isomeric kinetically formed exo π-allyl σ-vinyl rhenium complex **10**. The distortion of the exo π-allyl complex **10** explains its relative instability compared with the less distorted endo π-allyl complex **11**.

Experimental Section

General. ^{1}H NMR spectra were obtained on Bruker WP200, WP270, or AM500 spectrometers. ^{13}C{^{1}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. Propargyl bromide (Aldrich) was dried over $MgSO_4$ 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*-$C_5H_5(CO)_2Re(CH_2C{\equiv}CH)((E)\text{-}CH{=}CHCH_2CMe_3)$ (7).** Excess propargyl bromide (0.9 mmol) was condensed into a stirred solution of $K^+C_5H_5(CO)_2Re[(E)\text{-}CH{=}CHCH_2CMe_3)]^-$ (**12**)[1] (20 mg, 0.045 mmol) in THF at −78 °C to give a yellow solution. Upon gradual warming to 25 °C, the solution turned orange and a white precipitate formed. After 10 min, solvent and the excess propargyl bromide were evaporated. The orange oil was taken up in CH_2Cl_2 and filtered through Celite. The orange solution was evaporated and the orange oil was examined by ^{1}H NMR in CD_3CN. The ^{1}H NMR spectrum showed that **7** (90%) was the major species present along with small amounts of rearrangement products **8**, **9**, and **10**. Complex **7** was not isolated due to its instability. ^{1}H NMR (CD_3CN, 200 MHz) δ 6.7 (dt, J = 15.2, 1.1 Hz, $ReCH{=}CH$), 5.8 (dt, J = 15.2, 7.0 Hz, $ReCH{=}CH$), 5.28 (s, C_5H_5), 2.2 (d, J = 2.5 Hz, $ReCH_2C{\equiv}CH$), 2.15 (m, J = 2.5 Hz, $ReCH_2C{\equiv}CH$), 1.99 (dd, J = 7.0, 1.1 Hz, CH_2CMe_3), 0.86 (s, CMe_3); IR (CH_2Cl_2) 2024 (m), 1959 (s) cm^{-1}.

$C_5H_5(CO)Re[\eta^2(1,2),\eta^2(5,6)\text{-}\overline{H_2C{=}C{=}CHCOCH{=}CHCH_2CMe_3}]$ (9) and $C_5H_5(CO)Re[\eta^3(\textit{exo,syn})\text{-}H_2CCHCHCOCH{=}CCH_2CMe_3]$ (10). A solution of $K^+C_5H_5(CO)_2Re[(E)\text{-}CH{=}CHCH_2CMe_3)]^-$ (**12**)[1] (220 mg, 0.495 mmol) and propargyl bromide (8.9 mmol) in 25 mL of

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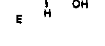
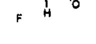
(28) Intermediates such as **E** (suggested by a referee) and **F** are excluded by this experiment.



E



F

Table IV. Crystal Structure Data for **9**, **10**, and **11**

	9	**10**	**11**
empirical formula	$C_{17}H_{21}O_2Re$	$C_{17}H_{21}O_2Re$	$C_{17}H_{21}O_2Re$
color; habit	yellow plate	yellow block	yellow block
crystal size, mm	0.2 × 0.4 × 0.5	0.6 × 0.7 × 0.7	0.5 × 0.5 × 0.6
crystal system	triclinic	monoclinic	monoclinic
space group	$P\bar{1}$	$P2(1)/c$	$P2(1)/n$
unit cell dimens			
a, Å	6.8995 (10)	8.821 (8)	8.678 (2)
b, Å	10.348 (2)	12.620 (9)	16.198 (3)
c, Å	11.191 (2)	13.188 (10)	10.845 (2)
α, deg	82.83 (3)		
β, deg	88.03 (3)	91.30 (3)	90.22 (3)
γ, deg	76.29 (3)		
vol, Å^3	770.2 (2)	1468 (2)	1524.4 (5)
peaks to determine cell	15	20	20
2θ range of cell peaks	5.80, 25.25	7.81, 25.76	9.42, 29.68
Z	2	4	4
formula wt	443.5	443.5	443.5
density (calcd), g/cm^3	1.913	2.007	1.933
abs coeff, mm^{-1}	7.994	8.390	8.078
F(000)	428	856	856
R(*F*), %	5.26	4.77	3.57
wR(*F*), %	6.07	5.59	4.69

THF was stirred at 25 °C for 12 h. Solvent was evaporated under vacuum, and the orange residue was dissolved in a minimum amount of CH_2Cl_2. Preparative TLC (silica gel, 1:1:1 hexane:diethyl ether:dichloromethane) gave a band ($R_f = 0.19$) from which **9** (80 mg, 36%) was isolated as a pale yellow powder and a slower moving band ($R_f = 0.06$) from which **10** (90 mg, 41%) was isolated as a bright yellow oil.

Single crystals of **9** suitable for X-ray analysis were obtained by slow evaporation of an acetonitrile solution of **9**. Single crystals of **10** (mp 142–147 °C dec) suitable for X-ray analysis were obtained by slow cooling of a CD_3CN solution of **10** to −15 °C.

9: ^1H NMR (CD_2Cl_2, 200 MHz) δ 7.01 (m, $H_2C{=}C{=}C\textit{H}$), 5.39 (s, C_5H_5), 4.20 (dd, *J* = 10.0, 1.0 Hz, $COC\textit{H}{=}CH$), 2.51 (ddd, *J* = 12.6, 10.0, 2.2 Hz $COCH{=}C\textit{H}$), 2.48 (dd, *J* = 8.5, 1.8 Hz, $C\textit{H}H{=}C{=}CH$), 2.19 (dd, *J* = 13.3, 2.2 Hz, $C\textit{H}HCMe_3$), 1.97 (dd, *J* = 8.5, 1.8 Hz, $CH\textit{H}{=}C{=}CH$), 0.98 (s, CMe_3), 0.91 (dd, *J* = 13.3, 12.6 Hz, $CH\textit{H}CMe_3$). $^{13}C\{^1H\}$ NMR (126 MHz, CD_2Cl_2) δ 212.8, 206.6, 204.6 (CO's and $H_2{=}\textit{C}{=}CH$); 114.6 ($H_2C{=}C{=}\textit{C}H$); 89.5 (C_5H_5); 66.5 ($COCH{=}\textit{C}H$); 61.3 ($COC\textit{C}H{=}CH$); 54.3 ($\textit{C}H_2CMe_3$); 34.7 ($\textit{C}Me_3$); 29.4 ($C\textit{Me}_3$); −9.0 ($\textit{C}H_2{=}C{=}CH$). IR (CH_2Cl_2) 1922 (s), 1634 (w) cm^{-1}. HRMS calcd for $C_{17}H_{21}O_2Re$ 444.1099, found 444.1126. Anal. Calcd for $C_{17}H_{21}O_2Re$: C, 46.03; H, 4.77. Found: C, 45.92; H, 4.38.

10: ^1H NMR (CD_2Cl_2, 200 MHz) δ 7.00 (d, *J* = 1.2 Hz, $ReC{=}CH$), 5.21 (s, C_5H_5), 5.18 (ddd, *J* = 9.7, 9.4, 5.7 Hz, η^3-$CH_2C\textit{H}CHCO$), 4.28 (br d, *J* = 9.7 Hz, η^3-$CH_2CHC\textit{H}CO$), 2.68 (d, *J* = 13.2 Hz, $C\textit{H}HCMe_3$), 2.60 (dd, *J* = 13.2, 1.2 Hz, $CH\textit{H}CMe_3$), 2.18 (dd, *J* = 5.7, 1.8 Hz, η^3-$C\textit{H}HCHCHCO$, syn H), 1.65 (ddd, *J* = 9.4, 2.0, 0.5 Hz, η^3-$CH\textit{H}CHCHCO$, anti H), 1.03 (s, CMe_3). $^{13}C\{^1H\}$ NMR (126 MHz) δ 201.4, 199.9 (CO); 188.8 ($Re\textit{C}{=}CH$); 149.9 ($ReC{=}\textit{C}H$); 88.0 (C_5H_5); 86.9 (η^3-$CH_2\textit{C}HCHCO$); 69.2 (η^3-$CH_2CH\textit{C}HCO$); 62.7 ($\textit{C}H_2CMe_3$); 33.8 ($\textit{C}Me_3$); 31.0 ($C\textit{Me}_3$); 19.8 (η^3-$\textit{C}H_2CHCHCO$). IR (CH_2Cl_2) 1897 (s), 1647 (w) cm^{-1}. HRMS calcd for $C_{17}H_{21}O_2Re$ 444.1099, found 444.1112. Anal. Calcd for $C_{17}H_{21}O_2Re$: C, 46.03; H, 4.77. Found: C, 46.01; H, 4.57.

Kinetics of the Rearrangement of 7 to 8, 9, and 10. A sample of **7** was prepared by treatment of **12** (7 mg, 0.016 mmol) with excess propargyl bromide in THF. Volatiles were removed under vacuum, and the resulting orange residue was dissolved in CH_2Cl_2 and filtered through Celite. CH_2Cl_2 was evaporated under vacuum and the residue was dissolved in CD_2Cl_2 and monitored by ^1H NMR. As **7** disappeared with a half-life of 89 min, a transient intermediate $C_5H_5(CO)Re[\eta^2(1,2),\eta^2(5,6)$-$H_2C{=}C{=}CHCOCH{=}CHCH_2CMe_3]$ (**8**) was observed and reached a maximum concentration of 25% after 100 min. ^1H NMR signals assigned to **8** include δ 7.10 (m, $H_2C{=}C{=}C\textit{H}$), 5.30 (s, C_5H_5), 3.65 (br d, *J* = 8.8 Hz, $C\textit{H}{=}CHCH_2CMe_3$), 2.70 (dd, *J* = 8.5, 2.0 Hz, $C\textit{H}H{=}C{=}CH$), 2.50 (dd, *J* = 8.5, 2.0 Hz, $CH\textit{H}{=}C{=}CH$), 2.35 (dd, *J* = 11.0, 8.8, 2.0 Hz, $CH{=}C\textit{H}CH_2CMe_3$); the signals for the methylene protons were not seen and are presumably obscured by signals from **7**, **9**, and **10**. Relative concentrations of each of the species observed in the rearrangement were measured by integration of well-resolved one-proton resonances for **7** (δ 6.70), **8** (δ 7.10), **9** (δ 4.28), and **10** (δ 4.20).

$C_5H_5(CO)Re[\eta^3$(*endo,syn*)-$H_2CCHCHCOCH{=}CCH_2CMe_3]$ (11). A CD_3CN solution of **9** (10 mg, 0.02 mmol) in a sealed NMR tube was heated at 105 °C for 4 days. Clean conversion to a single new complex, $C_5H_5(CO)Re[\eta^3$(*endo,syn*)-$H_2CCHCHCOCH{=}CCH_2CMe_3]$ (**11**), was observed. The extent of isomerization of **9** was monitored by ^1H NMR (~50% after 15 h and 90% after 3 days). **11** was also prepared directly from rhenium vinyl anion **12** and propargyl bromide. Excess propargyl bromide (1.5 mmol) was added to a THF solution of **12** (65 mg, 0.15 mmol). After 5 min, excess propargyl bromide and THF were evaporated under vacuum to give an orange residue which was dissolved in CH_2Cl_2 and filtered through Celite. Solvent was evaporated from the resulting orange solution under vacuum and the residue was dissolved in CH_3CN (3 mL) and heated at 105 °C under nitrogen for 5 days. ^1H NMR analysis of an aliquot showed >95% conversion to **11**. Solvent was evaporated under vacuum and the residue was dissolved in a minimum of CH_2Cl_2. **11** was isolated by preparative TLC (silica gel, 2:1 Et_2O:hexane, $R_f = 0.06$) as a pale tan powder (60 mg, 92%). Single crystals of **11** (mp 180–181 °C dec) suitable for X-ray analysis were obtained by slow cooling of a CD_3CN solution of **11** to −15 °C. ^1H NMR (200 MHz, CD_3CN) δ 6.46 (dd, *J* = 1.5, 1.4 Hz, $ReC{=}C\textit{H}$), 5.36 (s, C_5H_5), 4.41 (td, *J* = 7.8, 5.4 Hz, η^3-$CH_2C\textit{H}CHCO$), 3.32 (dt, *J* = 7.4, 0.9 Hz, η^3-$CH_2CHC\textit{H}CO$), 2.68 (dd, *J* = 17.9, 1.4 Hz, $C\textit{H}HCMe_3$), 2.38 (d, *J* = 5.4 Hz, η^3-$C\textit{H}HCHCHCO$), 2.34 (dd, *J* = 17.9, 1.5 Hz, $CH\textit{H}CMe_3$), 2.28 (dt, *J* = 8.0, 0.8 Hz, η^3-$CH\textit{H}CHCHCO$), 0.97 (s, CMe_3). $^{13}C\{^1H\}$ (126 MHz, CD_3CN) δ 208.2, 206.1 (CO's); 187.8 ($Re\textit{C}{=}C$); 137.9 ($ReC{=}\textit{C}$); 89.1 (η^3-$CH_2\textit{C}HCH$), 88.3 (C_5H_5); 64.8 ($\textit{C}H_2CMe_3$); 63.9 (η^3-$CH_2CH\textit{C}H$); 33.5 ($\textit{C}Me_3$); 30.9 ($C\textit{Me}_3$); 22.0 (η^3-$\textit{C}H_2CHCH$). IR (CH_2Cl_2) 1939 (s), 1639 (w) cm^{-1}. HRMS calcd for $C_{17}H_{21}O_2Re$ 444.1099, found 444.1098. Anal. Calcd for $C_{17}H_{21}O_2Re$: C, 46.03; H, 4.77. Found: C, 45.88; H, 4.88.

Conversion of $C_5H_5(CO)Re[\eta^3$(*exo,syn*)-$H_2CCHCHCOCH{=}CCH_2CMe_3]$ (10) to $C_5H_5(CO)Re[\eta^3$(*endo,syn*)-$H_2CCHCHCOCH{=}CCH_2CMe_3]$ (11). A CD_3CN solution of **10** (20 mg, 0.05 mmol) in a sealed NMR tube was heated at 105 °C for 5 days. Complete conversion to $C_5H_5(CO)Re[\eta^3$(*endo,syn*)-$H_2CCHCHCOCH{=}CCH_2CMe_3]$ (**11**) was observed. The rearrangement was monitored by ^1H NMR spectroscopy and the initial formation of allenyl vinyl ketone complex **9** (50% after 80 min) was observed, followed by slow conversion of **9** to **11** over 5 days.

X-ray Crystallographic Determinations and Refinements. Each crystal was mounted on a thin glass fiber and placed in a cold N_2 stream. Intensity data were obtained with graphite-monochromated Mo Kα radiation on a Siemens P3/F diffractometer. Unit cell determinations were based upon 15 to 20 well-centered reflections; axial photographs were taken to verify lattice lengths and unit cell symmetry. The intensities of standard reflections showed no significant variations during the entire collection of data. Empirical absorption corrections[29] were applied to each data set. Crystallographic computations were carried out with SHELXTL PLUS[30] on VAX computers. Initial positions for Re atoms were found by direct methods. The other non-hydrogen atoms were

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(29) Empirical absorption corrections based upon ψ-scan measurements at different azimuthal angles.

(30) SHELXTL-PLUS, Siemens Analytical X-Ray Instruments, Inc.

obtained from successive Fourier difference maps coupled with isotropic least-squares refinement. Hydrogen atoms were modeled in idealized positions with fixed isotropic thermal parameters. Final Fourier difference maps exhibited no unusual features. A summary of crystal structure data is given in Table IV.

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Supplementary Material Available: Tables of data collection parameters, positional and anisotropic thermal parameters for non-hydrogen atoms, selected interatomic distances and angles, and idealized atomic parameters for hydrogen atoms for **9**, **10**, and **11** (24 pages); listing of observed and calculated structure factor amplitudes for **9**, **10**, and **11** (24 pages). Ordering information is given on any current masthead page.

A New Family of Mesoporous Molecular Sieves Prepared with Liquid Crystal Templates

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Abstract: The synthesis, characterization, and proposed mechanism of formation of a new family of silicate/aluminosilicate mesoporous molecular sieves designated as M41S is described. MCM-41, one member of this family, exhibits a hexagonal arrangement of uniform mesopores whose dimensions may be engineered in the range of ~15 Å to greater than 100 Å. Other members of this family, including a material exhibiting cubic symmetry, have been synthesized. The larger pore M41S materials typically have surface areas above 700 m^2/g and hydrocarbon sorption capacities of 0.7 cc/g and greater. A templating mechanism (liquid crystal templating—LCT) in which surfactant liquid crystal structures serve as organic templates is proposed for the formation of these materials. In support of this templating mechanism, it was demonstrated that the structure and pore dimensions of MCM-41 materials are intimately linked to the properties of the surfactant, including surfactant chain length and solution chemistry. The presence of variable pore size MCM-41, cubic material, and other phases indicates that M41S is an extensive family of materials.

Introduction

Two classes of materials that are used extensively as heterogenous catalysts and adsorption media are microporous (pore diameters $\leq \sim 20$ Å) and mesoporous (~20–500 Å) inorganic solids.[1] The utility of these materials is manifested in their microstructures which allow molecules access to large internal surfaces and cavities that enhance catalytic activity and adsorptive capacity. A major subclass of the microporous materials is molecular sieves. These materials are exemplified by the large family of aluminosilicates known as zeolites in which the micropores are regular arrays of uniformly-sized channels.[2] Considerable synthetic effort has been devoted to developing frameworks with pore diameters within the mesoporous range, the largest synthesized to date being $AlPO_4$-8,[3] VPI-5,[4] and cloverite[5] which have pore diameters within the 8–13 Å range. Cacoxenite, a natural ferroaluminophosphate, has been structurally characterized as having ~14 Å channels that approach the mesoporous size range.[6] Mesoporous materials are typically amorphous or paracrystalline solids, such as silicas[7] or transitional aluminas[8] or modified layered materials such as pillared clays and silicates.[9-13] The pores in these materials are generally irregularly spaced and broadly distributed in size.[10] Despite these efforts, mesoporous molecular sieves with regular, well-defined channel systems have remained elusive.

Recently, a new family of mesoporous molecular sieves designated as M41S has been discovered.[14] MCM-41, one of the members of this extensive family of mesoporous sieves, possesses a hexagonal array of uniform mesopores, MCM-41 has been synthesized with uniform channels varying from approximately 15 Å to greater than 100 Å in size. The larger pore materials typically have surface areas above 700 m^2/g and hydrocarbon

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(1) IUPAC Manual of Symbols and Terminology, Appendix 2, Part 1, Colloid and Surface Chemistry, *Pure Appl. Chem.* **1972**, *31*, 578.

(2) See, for example: (a) Meier, W. M.; Olson, D. H. *Atlas of Zeolite Structure Types*, 3rd. ed. revised; Butterworth-Heineman & Co.: Guildford, 1992. (b) Szostak, R. *Molecular Sieves Principles of Synthesis and Identification*; Van Nostrand Reinhold: New York, 1989.

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