Kinetic Addition of Nucleophiles to η^3-Propargyl Rhenium Complexes Occurs at the Central Carbon to Produce Rhenacyclobutenes

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Abstract: Kinetic addition of nucleophiles occurs at the center carbon of η^3-propargyl rhenium complexes to produce rhenacyclobutenes. Reaction of $P(CH_3)_3$ with $C_5Me_5(CO)_2Re[\eta^3\text{-}CH_2C{\equiv}CC(CH_3)_3]^+BF_4^-$ (**3a**) gave the metallacyclobutene $C_5Me_5(CO)_2ReCH_2C(PMe_3){=}CC(CH_3)_3{}^+BF_4^-$ (**4a**), which was characterized by X-ray crystallography. Malonate and acetylide nucleophiles reacted with $C_5Me_5(CO)_2Re[\eta^3\text{-}CH_2C{\equiv}CCH_3]^+PF_6^-$ (**3b**) to give metallacyclobutene complexes. Pyridine added to the central propargyl carbon of **3b** at low temperature to produce the metastable metallacyclobutene $C_5Me_5(CO)_2ReCH_2C(NC_5H_5){=}CCH_3{}^+PF_6^-$ (**14b**) which rearranged to the η^2-allene complex $C_5Me_5(CO)_2Re[\eta^2\text{-}H_2C{=}C{=}C(NC_5H_5)CH_3]^+PF_6^-$ (**15K**) at room temperature. 4-(Dimethylamino)pyridine (DMAP) added to the central carbon of the *tert*-butyl-substituted η^3-propargyl complex **3a** below −38 °C to give the rhenacyclobutene complex $C_5Me_5(CO)_2ReCH_2C\text{-}(NC_5H_4NMe_2){=}CC(CH_3)_3{}^+BF_4^-$ (**22a**) which rearranged to the η^2-alkyne complex $C_5Me_5(CO)_2Re[\eta^2\text{-}(CH_3)_3\text{-}CC{\equiv}CCH_2NC_5H_4NMe_2]^+BF_4^-$ (**23**) at room temperature. Reaction of water with $C_5Me_5(CO)_2Re[\eta^3\text{-}CH_2C{\equiv}CH]^+BF_4^-$ (**3c**) gave the hydroxyallyl complex $C_5Me_5(CO)_2Re[\eta^3\text{-}CH_2C(OH)CH_2]^+BF_4^-$ (**29**) by a process proposed to involve nucleophilic addition of water to the central propargyl carbon of **3c** followed by protonation of the metallacyclobutene intermediate.

Introduction

η^3-Propargyl transition metal complexes are the triple-bond analogues of the well-studied η^3-allyl complexes,[1] which have found great utility in organic synthesis. η^3-Propargyl metal complexes may be involved as transient intermediates in catalytic cycles,[2,3] and have recently been detected and isolated. Since Werner's first report of the isolation of an η^3-propargyl metal complex in 1985,[4] there have been rapid developments in the synthesis and detection of η^3-propargyl metal complexes.[5]

Syntheses of η^3-propargyl metal complexes often parallel those of η^3-allyl metal complexes (Scheme 1). Synthetic methods include protonation of η^2-propargyl alcohol complexes,[6] halide abstraction from η^1-propargyl or η^1-allenyl metal halide complexes,[7] reaction of metal halides with propargyl nucleophiles,[8] reaction of propargyl ether complexes with Lewis acids,[9] addition of a metal acetylide to a vinylidene,[4,10] rearrangement of η^1-homopropargyl metal complexes,[11] and oxidative addition of propargyl halides or tosylates to metal complexes.[12]

Our group has extended the η^2-propargyl alcohol complex protonation methodology to the regiospecific synthesis of a variety of rhenium η^3-propargyl complexes (Scheme 2).[13] In addition, we have developed hydride abstraction from rhenium η^2-alkyne complexes as a new route to η^3-propargyl complexes.[13,14] These methods have proven to be versatile and reliable ways of synthesizing η^3-propargyl compounds.

In a preliminary communication, we reported that nucleophiles attacked the center carbon atom of the η^3-propargyl ligand.[14] Here, we report the scope of these nucleophilic additions and more complete studies of their regiochemistry.

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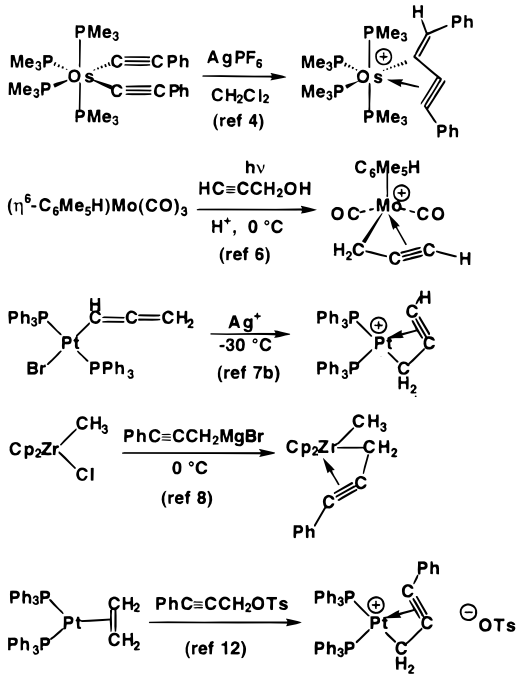
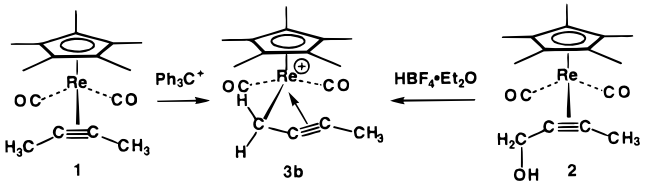
Scheme 1

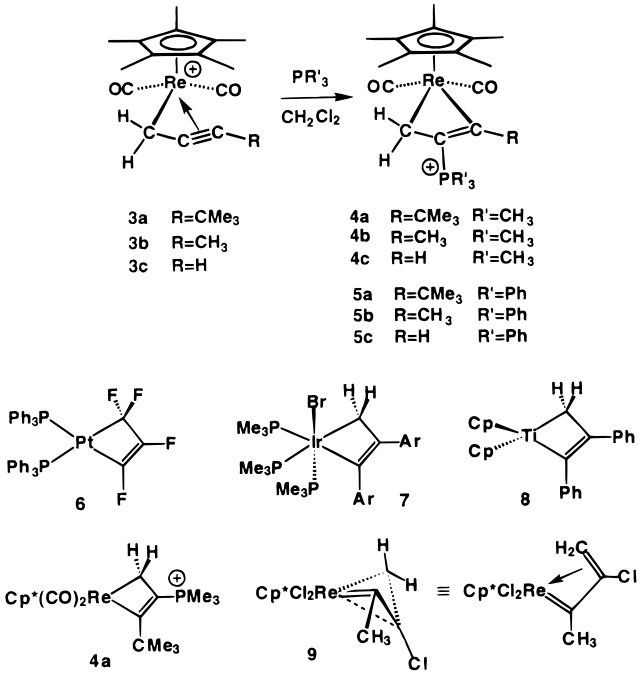


Scheme 2



We have found that while kinetic addition of nucleophiles occurs at the center carbon of the η^3-propargyl ligand to give rhenacyclobutene complexes, this addition is sometimes reversible and can be followed by addition at either of the other two metal-bound carbon atoms to give η^2-allene or η^2-alkyne complexes. In addition, we report that η^3-allyl complexes can be obtained by protonation of the metallacyclobutenes derived from nucleophilic attack at the center carbon of the η^3-propargyl complexes.

Scheme 3



Results

Metallacyclobutenes from Addition of Nucleophiles to η^3-Propargyl Complexes. The kinetic addition of phosphorus, carbon, and nitrogen nucleophiles to the central carbon of η^3-propargyl complexes gives high yields of rhenacyclobutene complexes. These complexes were completely characterized by spectroscopy and in one case by X-ray crystallography.

PMe_3 Addition to $C_5Me_5(CO)_2Re[\eta^3$-$CH_2C{\equiv}CC(CH_3)_3]^+$-$BF_4^-$ (3a). Excess PMe_3 was vacuum-transferred into a yellow solution of $C_5Me_5(CO)_2Re[\eta^3$-$CH_2C{\equiv}CC(CH_3)_3]^+BF_4^-$ (**3a**) in CH_2Cl_2 at −78 °C, and the sample was examined immediately by ^{1}H NMR spectroscopy at −53 °C. The only species observed was the phosphine-substituted rhenacyclobutene complex $C_5Me_5(CO)_2ReCH_2C(PMe_3){=}CC(CH_3)_3{}^+BF_4^-$ (**4a**) (Scheme 3). Evaporation of solvent and excess PMe_3 led to the isolation of **4a** as an air-stable yellow powder in quantitative yield. The structure of **4a** was established spectroscopically and confirmed by X-ray crystallography.

Spectral signatures for rhenacyclobutenes include (a) two low-frequency ^{1}H NMR resonances for the diastereotopic $ReCH_2$ protons with a 11−13 Hz geminal coupling, (b) ^{13}C NMR resonances for the $ReCH_2$ carbon at very low frequency (near δ −25), and (c) ^{13}C NMR resonances for the Re*C*=C carbon near δ 170 and for the ReC=*C* carbon near δ 120 (Table 1). In the ^{1}H NMR spectrum of **4a**, the diastereotopic $ReCH_2$ protons were observed at δ 1.52 and 0.18, with a large 12 Hz geminal coupling. The ^{13}C NMR resonance of the $ReCH_2$ carbon appeared at very low frequency at δ −28.3. Similar NMR parameters have been observed for other metallacyclobutenes; Thorn assigned a ^{1}H NMR resonance at δ 1.16 and a ^{13}C NMR resonance at δ −18.0 to the for $IrCH_2$ group in $(PMe_3)_3$-$BrIrCH_2C(p$-tolyl)=C(p-tolyl).[15] The ^{13}C NMR resonances of the alkene carbons of **4a** appeared at δ 178.3 (J_{PC} = 6 Hz) for Re*C*=CP and at δ 120.8 (J_{PC} = 15 Hz) for ReC=*C*P. Two strong carbonyl bands were observed at 1994 and 1914 cm^{-1} in the IR spectrum of **4a** in THF.

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Table 1. Characteristic Spectroscopic Data of Rhenacyclobutenes[a]

	^{1}H NMR (δ)		^{13}C NMR (δ)			
compd	C*H*$_2$C=C	other	^{13}CH$_2$C=C	CH$_2$^{13}C=C	CH$_2$C=^{13}C	IR ν_{CO} (cm^{-1})
4a	1.52, 0.18[b]		−28.3[i]	120.8	178.3	1994, 1914
	J_{gem} = 12 Hz			J_{PC} = 15 Hz	J_{PC} = 6 Hz	
4b	1.45, 0.30[c]		−31.7[j]	128.0	157.7	1991, 1915
	J_{gem} = 11.5 Hz			J_{PC} = 33.2 Hz		
4c	1.36, 0.09[b]	=*C*H 8.18	−27.0[i]	138.0	142.8	1994, 1914
	J_{gem} = 13 Hz	J_{PH} = 12 Hz		J_{PC} = 38 Hz		
5a	1.51, 0.30[b]		−27.2[i]	115.9	178.0	1993, 1914
	J_{gem} = 13 Hz			J_{PC} = 15 Hz	J_{PC} = 5 Hz	
5b	1.52, 0.17[d]		−26.8[i]	120.4	168.9	1993, 1919
	J_{gem} = 12 Hz			J_{PC} = 20 Hz		
5c	1.86, 0.81[e]	=*C*H 8.32	−27.3[j]	133.9	154.7	1994, 1914
	J_{gem} = 12 Hz	J_{HP} = 11 Hz		J_{PC} = 19 Hz		
10b	1.54, 0.28[b]		−30.0[k]	131.0	179.1	1999, 1926
	J_{gem} = 12 Hz			J_{PC} = 14 Hz		
11b	1.37, 0.20[g]		−21.7	128.0	150.2	1981, 1905
	J_{gem} = 11 Hz					
12b	2.00, 0.50[f]		−25.7[l]	119.0	140.3	1979, 1903
	J_{gem} = 11 Hz					
13b	1.79, 0.66[b]					
	J_{gem} = 12 Hz					
14b	obscd, 0.62[d]					
	J_{gem} = 12 Hz					
16b	obscd, 0.61[d]					
	J_{gem} = 13 Hz					
18c	1.72, 0.58[h]					
	J_{gem} = 12 Hz	=*C*H 7.41	−26.0[m]	111.3	185.7	
22a	1.80, 0.34[h]					
	J_{gem} = 12 Hz		−17.7[m]	105.6	140.9	

[a] ^{1}H and ^{13}C NMR resonances were referenced to solvent peaks. IR spectra were recorded in THF and displayed strong bands of approximately equal intensity. [b] At 300 MHz in CD_2Cl_2. [c] At 200 MHz in CD_2Cl_2. [d] At 500 MHz in CD_2Cl_2. [e] At 500 MHz in acetone-d_6. [f] At 200 MHz in THF-d_8. [g] At 200 MHz in C_6D_6. [h] At 360 MHz in CD_2Cl_2. [i] At 125 MHz in CD_2Cl_2. [j] At 125 MHz in CD_2Cl_2. [k] At 75 MHz in acetone-d_6. [l] At 125 MHz in THF-d_8. [m] At 90 MHz in CD_2Cl_2.

Table 2. Selected Bond Lengths (Å) and Bond Angles (deg) for $C_5Me_5(CO)_2ReCH_2C(PMe_3)$=$CC(CH_3)_3^+BF_4^-$ (**4A**)

Bond Lengths (Å)			
Re−C(1)	1.92 (1)	C(1)−C(2)	1.52 (1)
Re−C(3)	2.19 (1)	C(3)−C(7)	1.51 (2)
C(2)=C(3)	1.33 (1)	C(2)−P(1)	1.79 (1)
Bond Angles (deg)			
C(1)−Re−C(3)	61.2 (3)	Re−C(3)−C(2)	93.3 (6)
Re−C(1)−C(2)	100 (1)	C(2)−C(3)−C(7)	129 (1)
C(1)−C(2)−C(3)	104 (1)	C(11)−Re−C(12)	81.0 (4)

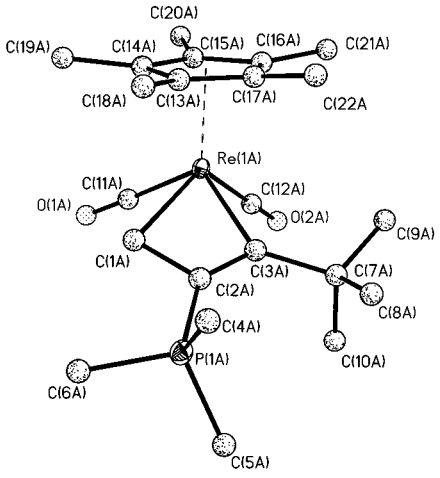

Figure 1. X-ray Structure of $C_5Me_5(CO)_2ReCH_2C(PMe_3)$=*C*C-$(CH_3)_3^+BF_4^-$ (**4a**).

The metallacyclobutene formulation of **4a** was confirmed by X-ray crystallography (Table 2, Figure 1). The metallacycle atoms Re−C(1)−C(2)−C(3) are nearly coplanar. The mean deviation from planarity is 0.039 Å, and Re is only 0.27 Å out of the plane defined by the three carbons. The ring is slightly puckered with the plane of the three carbons tilted 8.1° toward the Cp* ring relative to the C(1)−Re−C(2) plane. The 104 (1)° C−C=C angle of the metallacyclobutene ring of **4a** is similar to those observed for other third-row metallacycles: 104.7 (7)° for $(PPh_3)_2Pt(C_3F_4)$ (**6**)[16] and 106.1 (5)° for $(PMe_3)_3$-(Br)$IrCH_2C$(*p*-tolyl)=C(*p*-tolyl) (**7**).[15] The analogous angle in Tebbe's first-row metallacycle $(C_5H_5)_2TiCH_2C(Ph)$=C(Ph) (**8**)[17] is 112.8 (6)°. Bond length comparisons of **4a** and other metallacyclobutenes show remarkable consistency (Table 3). All of the metallacycles have a shorter M−C distance to the formally sp^2 carbon than to the sp^3 carbon.

Table 3. Structural Comparison of Bond Lengths (Å) for Metallacyclobutenes

	4a	**6**	**7**	**8**
M−C(1)	1.92(1)	2.04(1)	2.13(1)	2.10(1)
M−C(3)	2.19(1)	2.30(1)	2.17(1)	2.12(1)
C(1)−C(2)	1.52(1)	1.47(1)	1.53(1)	1.54(1)
C(2)=C(3)	1.33(1)	1.35(1)	1.34(1)	1.34(1)

Metallacyclobutenes and η^3-vinylcarbene complexes are valence isomers. The η^3-vinylcarbene provides two more valence electrons to the metal center than a metallacyclobutene. Compared with nearly planar metallacyclobutenes, η^3-vinylcarbene complexes have geometries more similar to π-allyl complexes with the metal center strongly interacting with all

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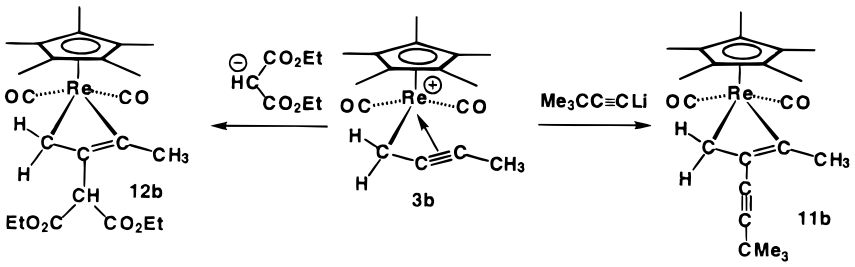
Scheme 4



three carbon centers. Several η^3-vinylcarbene complexes have been characterized by X-ray crystallography,[18,19] including the rhenium complex $C_5Me_5Cl_2Re[\eta^3\text{-}C(CH_3)CCl{=}CH_2]$ (**9**),[20] which can be compared directly to **4a**. In contrast to the near planarity of **4a**, rhenium lies 1.7 Å above the plane of the carbons of the η^3-vinylcarbene ligand of **9** and all three carbons are bonded to Re. In contrast to the low-frequency ^{1}H NMR resonances and large geminal coupling observed for the $ReCH_2$ protons of **4a**, the diastereotopic protons of **9** appear at δ 4.31 and 3.27, with a small 3 Hz geminal coupling, consistent with sp^2 hybridization. A short Re=C distance of 1.97 Å in **9** and a δ 265 ^{13}C NMR resonance provide support for a vinylcarbene formulation.

Addition of PMe_3 to the methyl-substituted η^3-propargyl complex $C_5Me_5(CO)_2Re[\eta^3\text{-}CH_2C{\equiv}CCH_3]^+BF_4^-$ (**3b**) and to the unsubstituted η^3-propargyl complex $C_5Me_5(CO)_2Re[\eta^3\text{-}CH_2C{\equiv}CH]^+BF_4^-$ (**3c**) also proceeded by phosphine attack at the central propargyl carbon and led to the formation of rhenacyclobutenes. For example, when excess PMe_3 was added to a yellow solution of **3b** in CH_2Cl_2, a white precipitate formed gradually over 30 min at room temperature. The rhenacyclobutene $C_5Me_5(CO)_2ReCH_2C(PMe_3){=}CCH_3^+BF_4^-$ (**4b**) was isolated as a white powder in 72% yield. The low-frequency ^{1}H NMR resonances of the diastereotopic $ReCH_2$ protons at δ 1.45 and 0.3 (J_{gem} = 12 Hz) and the low-frequency ^{13}C NMR resonance of the $ReCH_2$ carbon at δ −31.7 helped to establish the presence of the metallacyclobutene substructure of **4b**. Similarly, addition of PMe_3 to $C_5Me_5(CO)_2Re[\eta^3\text{-}CH_2C{\equiv}CH]^+BF_4^-$ (**3c**) gave a 93% yield of $C_5Me_5(CO)_2ReCH_2C(PMe_3){=}CH^+BF_4^-$ (**4c**), which was characterized spectroscopically (Table 1).

PPh_3 also added to the central carbon of η^3-propargyl complexes **3a**−**c** to produce rhenacyclobutenes. When solid PPh_3 was added to a yellow CD_2Cl_2 solution of **3a** at room temperature, ^{1}H NMR spectroscopy revealed the formation of a single new product $C_5Me_5(CO)_2ReCH_2C(PPh_3){=}CC(CH_3)_3^+BF_4^-$ (**5a**) with the resonances characteristic of a rhenacyclobutene (Table 1). Complex **5a** was isolated as a light yellow powder in 91% yield. Similarly, addition of PPh_3 to **3b** and **3c** led to the isolation of $C_5Me_5(CO)_2ReCH_2C(PPh_3){=}CCH_3^+BF_4^-$ (**5b**) in 46% yield and $C_5Me_5(CO)_2ReCH_2C(PPh_3){=}CH^+BF_4^-$ (**5c**) in 91% yield.

Trimethyl phosphite added to the central carbon of η^3-propargyl complex **3b** to give the rhenacyclobutene complex $C_5Me_5(CO)_2ReCH_2C[P(OMe)_3]{=}CCH_3^+BF_4^-$ (**10b**) as a yellow solid in 55% yield. The $ReCH_2$ unit of **10b** gave rise to two doublet of quartet resonances (J_{gem} = 12 Hz, ^5J = 2 Hz) at δ 1.54 and 0.28 in the ^{1}H NMR spectrum and to a low-frequency resonance in the $^{13}C\{^1H\}$ NMR spectrum at δ −30.0 (d, J_{PC} = 9 Hz).

Rhenacyclobutenes from Reaction of η^3-Propargyl Complexes with Carbon Nucleophiles. The methyl-substituted η^3-propargyl complex **3b** reacted with carbon nucleophiles to form metallacyclobutene complexes.[21] When $LiC{\equiv}CC(CH_3)_3$ was added to a yellow THF solution of $C_5Me_5(CO)_2Re[\eta^3\text{-}CH_2C{\equiv}CCH_3]^+PF_6^-$ (**3b**), an orange-red solution was produced in less than 10 min. Chromatography led to the isolation of the neutral rhenacyclobutene $C_5Me_5(CO)_2ReCH_2C[C{\equiv}CC(CH_3)_3]{=}CCH_3$ (**11b**) in 47% yield as a dark orange-red liquid (Scheme 4). The rhenacyclobutene structure was established by the observation of ^{1}H NMR resonances for the diastereotopic $ReCH_2$ protons of **11b** at δ 1.37 and 0.20 (J_{gem} = 11 Hz) and a low-frequency ^{13}C NMR resonance at δ −21.7 (Table 1). Similarly, addition of solid $NaCH(CO_2Et)_2$ to a THF solution of **3b** led to the isolation of $C_5Me_5(CO)_2ReCH_2C[CH(CO_2Et)_2]{=}CCH_3$ (**12b**) in 56% yield as a red-orange oil. In addition to characteristic resonances for a rhenacyclobutene (Table 1), the ^{13}C NMR spectrum of **12b** exhibited resonances for two diastereotopic Et groups. Complexes **11b** and **12b** were thermally less stable than the phosphine-substituted metallacyclobutenes and decomposed in solution at room temperature over several days to give predominantly η^3-allyl complexes. (The reactivity of rhenacyclobutenes toward acid will be described below.)

Addition of excess *tert*-butyl isocyanide to a CD_2Cl_2 solution of **3b** at −78 °C led to the immediate formation of a bright yellow solution whose ^{1}H NMR spectrum at −55 °C was consistent with formation of the rhenacyclobutene $C_5Me_5(CO)_2ReH_2CC(C{\equiv}NCMe_3){=}CCH_3^+PF_6^-$ (**13b**). In particular, two doublets of quartets were observed at δ 1.76 and 0.63 (J_{gem} = 11 Hz, ^5J = 2 Hz). When the solution was warmed above 5 °C, further reaction with excess isocyanide ensued, leading to an unidentified mixture of products. Species **13b** was isolated as an orange solid by evaporation of volatile material under high vacuum at 0 °C.

Addition of malonates and acetylides to the *tert*-butyl-substituted and unsubstituted η^3-propargyl complexes **3a** and **3c** failed to give observable rhenacyclobutenes under conditions that worked adequately for the methyl-substituted η^3-propargyl complex **3b**. The unsubstituted η^3-propargyl complex **3c** decomposed to uncharacterizable products upon warming solutions containing either sodium diethyl malonate or $LiC{\equiv}CC(CH_3)_3$. Due to its thermal instability above −20 °C, **3c** apparently decomposes before nucleophilic attack occurs. The *tert*-butyl-substituted η^3-propargyl complex **3a** is not only thermally sensitive but also failed to react with these carbon nucleophiles to produce rhenacyclobutenes. ^{1}H NMR spectra

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(20) (a) Herrmann, W. A.; Fischer, R. A.; Herdtweck, E. *Angew. Chem., Int. Ed. Engl.* **1987**, *26*, 1263. (b) Fischer, R. A.; Fischer, R. W.; Herrmann, W. A.; Herdtweck, E. *Chem. Ber.* **1989**, *122*, 2035.

(21) Extension of this methodology to the *tert*-butyl-substituted and the unsubstituted propargyl complexes **3a** and **3c** was unsuccessful.

Scheme 5

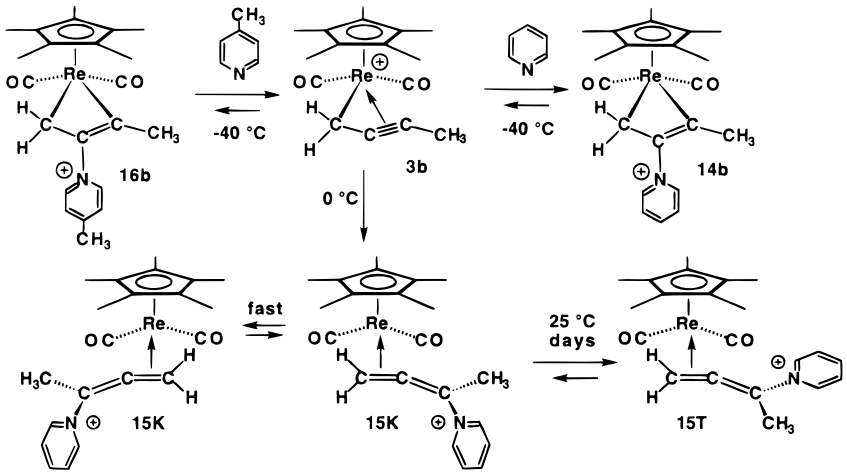


Table 4. Characteristic Spectroscopic Data of Rhenium Allene Complexes[a]

	^{1}H NMR (δ)		^{13}C NMR (δ)			
compd	H_2C=C=CRR′	other	$H_2{}^{13}$C=C=CRR′	H_2C=^{13}C=CRR′	H_2C=C=^{13}CRR′	IR ν_{CO} (cm^{-1})
15K	1.94, 1.19[b] J_{gem} = 8 Hz	R = Me 2.59	−1.7[e]	148.1	132.0	1983, 1911
15T	1.91, 1.19[b] J_{gem} = 8 Hz	R = Me 2.73	−2.9[e]	153.8	125.7	1997, 1914
17	1.5 (br)[b]	R = Me 2.59				
19	2.16, 1.44[c] J_{gem} = 9 Hz	R = Me 2.23	3.4[f]	147.0	123.0	1979, 1909
20	1.69, 0.89[c] J_{gem} = 7 Hz	R = Me 2.37	0.0[g]	142.2	99.0	1975, 1906
21	1.74, 0.95[c] J_{gem} = 8 Hz	R = Me 2.25	−1.0[g]	140.6	111.9	

[a] ^{1}H and ^{13}C NMR resonances were referenced to solvent peaks and observed at ambient temperature unless otherwise noted. IR spectra were recorded in THF, and displayed strong bands of approximately equal intensity. [b] At 500 MHz in CD_2Cl_2. [c] At 500 MHz in CD_2Cl_2, −40 °C. [d] At 300 MHz in CD_2Cl_2. [e] At 125 MHz in CD_2Cl_2, −60 °C. [f] At 125 MHz in CD_2Cl_2. [g] At 75 MHz in CD_2Cl_2.

of the reaction mixtures showed no reaction between **3a** and the nucleophile over a day at room temperature. Perhaps steric hindrance from the *tert*-butyl group of **3a** prevents nucleophilic addition.

Kinetic Formation of Metallacyclobutenes from Addition of Nitrogen Nucleophiles to η^3-Propargyl Complexes. At low temperature, nitrogen nucleophiles kinetically add to the central carbon of η^3-propargyl complexes to give rhenacyclobutenes. Upon warming, the rhenacyclobutenes dissociated the nitrogen nucleophile which then re-added to the η^3-propargyl complex at one of the terminal sites to give either an allene or an alkyne complex.

Addition of excess pyridine to a CD_2Cl_2 solution of **3b** at −78 °C followed by warming to −40 °C resulted in the rapid formation of the metallacyclobutene complex $C_5Me_5(CO)_2ReCH_2C(NC_5H_5)$=$CCH_3{}^+PF_6{}^-$ (**14b**) (Scheme 5). The ^{1}H NMR spectrum of **14b** at −40 °C provided evidence of the formation of a metallacyclobutene. Resonances were observed at δ 2.29 (br s, CH_3), 1.97 (s, C_5Me_5), and 0.62 (dq, shoulders not resolved, J = 12, 2 Hz, Re−C*H*H); the other Re−CH*H* resonance was not observed and is presumably buried under the C_5Me_5 resonance.

Conversion of a Metallacyclobutene to an Allene Complex. When the CH_2Cl_2 solution of **14b** was warmed to room temperature, formation of a >10:1 ratio of η^2-allene complexes $C_5Me_5(CO)_2Re[\eta^2$-H_2C=C=$C(NC_5H_5)CH_3]^+PF_6^-$ (**15K** and **15T**) was observed (Scheme 5). Addition of ether brought about the precipitation of the allene complexes which were isolated in 61% yield. The mass spectrum (LSIMS) showed a peak at 510, consistent with addition of pyridine to the π-propargyl complex **3b**. The ^{1}H NMR spectrum of **15K** at −40 °C had resonances for inequivalent terminal allene protons at δ 1.94 and 1.18 (dq, shoulders not resolved, J = 8, 2 Hz, 1H each) and a triplet CH_3 resonance (J = 2 Hz) at δ 2.64 in addition to resonances for C_5Me_5 and bound pyridine. At room temperature, the resonances for the inequivalent terminal allene protons coalesced to a broad feature at δ 1.6. This coalescence is due to interchange of the environments of the CH_2=C=C protons by rotation about the Re−allene bond. In the coupled ^{13}C NMR spectrum, the $^{13}CH_2$=C=C resonance appeared at δ −1.70 (t, J = 164 Hz), the CH_2=^{13}C=C resonance at δ 148.8 (s), and the CH_2=C=^{13}C resonance at 133.2 (s). These resonances are characteristic of allene complexes (Table 4).

Slow equilibration of the kinetically formed >10:1 mixture of allene complexes **15K**:**15T** occurred over several weeks ($t_{1/2}$ ≈ 14 d) to give a final 1:9 ratio of **15K**:**15T**. The spectroscopic properties of thermodynamically favored complex **15T** were very similar to those of the kinetically favored isomer **15K**. The low-temperature (−60 °C) ^{1}H NMR spectrum of **15T** showed the decoalescence of two methylene protons at δ 1.91 and 1.18 (br d, J = 8 Hz). The $^{13}C\{^1H\}$ NMR spectrum of **15T** exhibited a resonance at δ −2.9, assigned to the $^{13}CH_2$=C=C carbon.

To determine whether the conversion of the metallacycle **14b** to allene complex **15K** occurs via an intra- or intermolecular mechanism, the conversion of the pyridine substituted metallacycle **14b** was carried out in the presence of 4-picoline. Excess 4-picoline was added to a CD_2Cl_2 solution of **14b** at

−78 °C. Inspection of the ^{1}H NMR spectrum at −40 °C showed the complete disappearance of **14b** and formation of a new material (**16b**) having resonances for a bound 4-picoline ligand and a new ReC*H*H resonance at δ 0.61 (br d, J_{gem} = 13 Hz) characteristic of a metallacyclobutene. Apparently, loss of pyridine is rapid and reversible at −40 °C. This provides a dissociative mechanism for exchange of 4-picoline for pyridine at the metallacyclobutene stage. When the solution was warmed to room temperature, a complicated mixture of η^2-allenyl products incorporating both pyridine and 4-picoline was observed. Resonances attributed to one isomer of the 4-picoline η^2-allene adduct $C_5Me_5(CO)_2Re[\eta^2$-$H_2C{=}C{=}C(p$-CH_3-$C_5H_5N)$-$CH_3]^+PF_6^-$ (**17**) were seen.

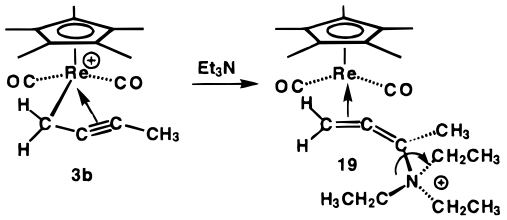
To determine whether the interconversion of allene isomers **15K** and **15T** occurs intramolecularly or by a dissociative mechanism through η^3-propargyl complex **3b**, the equilibration of an initial 2:1 mixture of **15K**:**15T** was carried out in the presence of a 3-fold excess of 4-picoline. After 24 h at room temperature, no formation of 4-picoline η^2-allene adduct **17** was seen by ^{1}H NMR spectroscopy and isomerization to a 1:2 mixture of **15K**:**15T** had taken place. After 5 days, only **15T** was seen and no 4-picoline adducts were observable. This experiment establishes that conversion of **15K** to **15T** is intramolecular and that formation of the allene complexes from η^3-propargyl complex **14b** is irreversible.

The similarity of the spectra of **15K** and **15T** requires that these isomers differ only in the relative stereochemistry at the allene terminus. We cannot assign the absolute stereochemistry of the two allene complexes. However, examination of molecular models indicates that attack on an η^3-propargyl complex should occur preferentially from the side opposite the metal. It is more difficult to assess which isomer is more thermodynamically stable, but since the C=C=C angle in allene complexes is about 140°,[22] the isomer with pyridine syn to rhenium may be more stable. The stereochemistry of the kinetic isomer is arbitrarily drawn as having pyridine anti to rhenium. The intramolecular rearrangement of allene complex **15K** to **15T** probably occurs by migration of rhenium from the less-substituted allene π-bond to the more-substituted allene π-bond and then back to the opposite enantioface of the less-substituted allene π-bond.[23]

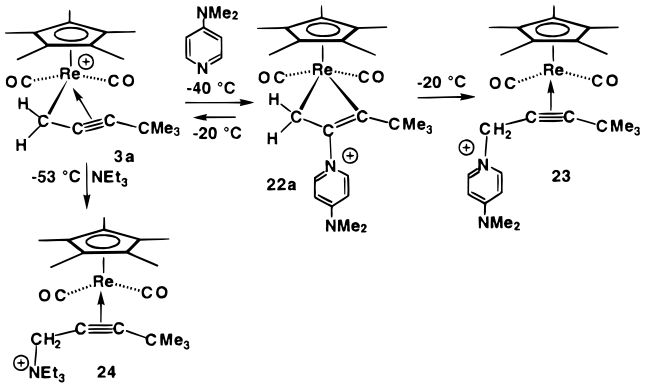
Pyridine added to the central carbon of the unsubstituted η^3-propargyl complex **3c** below −43 °C to give the metallacyclobutene $C_5Me_5(CO)_2ReCH_2C(NC_5H_5){=}CH^+PF_6^-$ (**18c**) as the only observable product (Table 1). This metallacycle decomposed when warmed to −20 °C to give a mixture of more than 10 C_5Me_5-containing products.

The reaction of NEt_3 with η^3-propargyl complex **3b** at room temperature led to the isolation of a single isomer of the allene complex $C_5Me_5(CO)_2Re[\eta^2$-$H_2C{=}C{=}C(NEt_3)CH_3]^+PF_6^-$ (**19**) as a yellow powder in 60% yield (Scheme 6). A key spectral feature that led to the assignment of the allenyl structure of **19** was the appearance of a low-frequency ^{13}C NMR resonance at δ 3.4 for the $^{13}CH_2{=}C{=}C$ carbon. At −47 °C, rotation of the allene ligand was frozen out and separate resonances were seen for the two $CH_2{=}C{=}C$ protons at δ 2.16 and 1.44 (each a broad doublet, J_{gem} = 9 Hz, 1H). Surprisingly, the NEt_3 resonances

Scheme 6



Scheme 7



broadened at −47 °C, suggesting the possibility of a fluxional process involving inequivalent Et groups. Further cooling of the solution to −80 °C resulted in the decoalescence of the NEt_3 peaks into three distinct CH_3 peaks between δ 0.92 and 1.27 (each a broad triplet) and six diastereotopic CH_2 resonances between δ 3.21 and 3.65 (all multiplets). Remarkably, rotation about the C−NR_3 bond has been frozen out at −80 °C.

The solution of **19** was monitored over several weeks at room temperature but no evidence for a second allene isomer (as seen for the pyridine case) was observed. We do not know whether the NEt_3 group is syn or anti to rhenium, but the observation of a slow NEt_3 rotation suggests that the NEt_3 group is in a very crowded environment. The NEt_3 group is arbitrarily drawn anti to rhenium.

Halide attack on the methyl-substituted η^3-propargyl complex **3b** also led to the formation of allene complexes. Addition of Ph_4PBr to a CD_2Cl_2 solution of **3b** led to the isolation of $C_5Me_5(CO)_2Re[\eta^2$-$H_2C{=}C{=}C(Br)CH_3]$ (**20**) in 60% yield. Similarly, reaction of Ph_4PCl with **3b** gave $C_5Me_5(CO)_2Re[\eta^2$-$H_2C{=}C{=}C(Cl)CH_3]$ (**21**) in 58% yield. The ^{1}H and ^{13}C NMR spectra of **20** and **21** support their formulation as allene complexes (Table 4).

Conversion of a Metallacyclobutene to an Alkyne Complex. The *tert*-butyl-substituted η^3-propargyl complex **3a** was attacked by 4-(dimethylamino)pyridine (DMAP) at the central propargyl carbon below −38 °C to give the rhenacyclobutene complex $C_5Me_5(CO)_2ReCH_2C(NC_5H_4NMe_2){=}CC(CH_3)_3^+BF_4^-$ (**22a**). This compound was characterized by its ^{1}H and ^{13}C NMR spectra (Table 1).

When warmed to −20 °C, **22a** rearranged to give the alkyne complex $C_5Me_5(CO)_2Re[\eta^2$-$(CH_3)_3CC{\equiv}CCH_2NC_5H_4NMe_2]^+$-$BF_4^-$ (**23**) which was isolated as a stable yellow solid in 96% yield (Scheme 7). In the ^{1}H NMR spectrum of **23**, the diastereotopic propargyl protons of the CH_2N group appeared as two doublets at δ 5.45 and 5.09 with a geminal coupling of 16 Hz. Rotation about the rhenium−alkyne bond of this sterically crowded alkyne is evidently slow at room temperature. The observation of two carbonyl resonances at δ 209.6 and 208.3 in the $^{13}C\{^1H\}$ NMR spectrum provide further evidence for slow rotation about the rhenium−alkyne bond. The ^{13}C

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Table 5. Characteristic Spectroscopic Data of Rhenium Alkyne Complexes[a]

compd	^{1}H NMR (δ)		^{13}C NMR (δ)		
	CH_2C≡C	^{13}CH_2C≡C	CH_2^{13}C≡C	CH_2C≡^{13}C	IR ν_{CO} (cm^{-1})
23	5.45, 5.09[c] J_{gem} = 16 Hz	66.0[f]	71.6	101.3	1950, 1867
24	4.48, 4.24[b] J_{gem} = 16 Hz				1949, 1865
25	3.97, 3.58[b] J_{gem} = 16 Hz	25.2[f] J_{PC} = 51 Hz	57.8 J_{PC} = 12 Hz	97.0	1951, 1869
26	4.03, 3.71[b] J_{gem} = 16 Hz	27.1[f] J_{PC} = 50 Hz	61.3 J_{PC} = 9 Hz	96.5	1951, 1868
(C_5Me_5)(CO)$_2$Re[η^2-(CH_3)$_3$CC≡CCH_2OH]	4.72, 4.60[c] J_{gem} = 15 Hz	59.0[f]	77.0	96.3	1945, 1863
(C_5Me_5)(CO)$_2$Re(η^2-CH_3C≡CCH_2OH)[13]	4.69, 4.41[d] J_{gem} = 10 Hz	59.2[g]	75.9	76.5	1950, 1862
(C_5Me_5)(CO)$_2$Re(η^2-HC≡CCH_2OH)[13]	4.57, br s[e]	59.1[g]	89.4	64.9	1951, 1867

[a] ^{1}H and ^{13}C NMR resonances were referenced to solvent peaks. IR spectra were recorded in THF and displayed strong bands of approximately equal intensity. [b] At 360 MHz in CD_2Cl_2. [c] At 300 MHz in CD_2Cl_2. [d] At 300 MHz in C_6D_6. [e] At 200 MHz in in C_6D_6. [f] At 90 MHz in CD_2Cl_2. [g] At 125 MHz in C_6D_6.

NMR resonances of the propargyl unit provide a distinctive spectral signature for this class of compounds (Table 5) that allows them to be readily distinguished from metallacyclobutenes and allene complexes. The two alkyne carbons appeared at δ 101.3 and 71.6 (C≡*C*), and the CH_2N resonance appeared at δ 66.0.

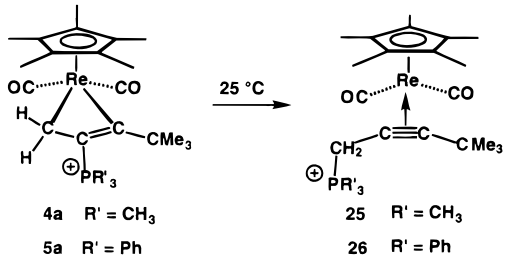
The conversion of metallacyclobutene **22a** to alkyne complex **23** can be explained by dissociation of DMAP from **22a** to regenerate η^3-propargyl complex **3a**, followed by re-addition of DMAP to the terminal CH_2 carbon of the propargyl complex to produce the alkyne complex **23**. Apparently, the bulky *tert*-butyl substituent prevents attack at the C≡C-CMe_3 terminal carbon which would have produced a sterically crowded allene complex.[24]

The addition of NEt_3 to *tert*-butyl-substituted η^3-propargyl complex **3a** at −53 °C led directly to the alkyne complex $C_5Me_5(CO)_2Re[\eta^2$-$(CH_3)_3CC{\equiv}CCH_2NEt_3]^+BF_4^-$ (**24**) which was stable at room temperature. The structure of **24** was assigned on the basis of characteristic ^{1}H and ^{13}C NMR resonances (Table 5). No metallacyclobutene intermediate was detected even at −53 °C. Apparently, the sterically large Et_3N nucleophile is too large to attack either the C=*C*−CMe_3 terminal carbon or the central carbon of **3a**.

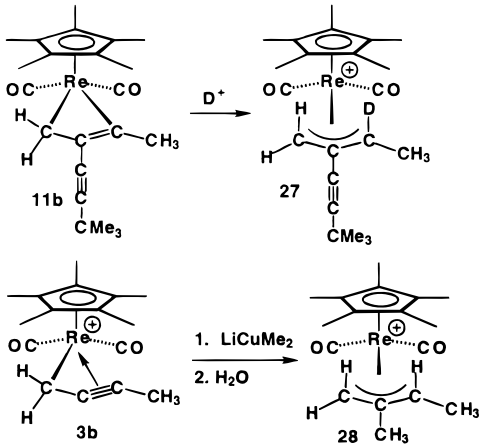
Rearrangement of Phosphorus-Substituted Metallacyclobutenes. The low-temperature rearrangements of nitrogen-substituted metallacyclobutenes led us to explore possible rearrangements of analogous phosphorus-substituted metallacycles. While these phosphorus analogues were stable enough to isolate as solids at room temperature, slow rearrangement of the sterically congested metallacycle $C_5Me_5(CO)_2ReCH_2C$-(PMe_3)=$CC(CH_3)_3^+BF_4^-$ (**4a**) occurred over 2 days in CH_2Cl_2 solution to give the alkyne complex $C_5Me_5(CO)_2Re[\eta^2$-$(CH_3)_3$-$CC{\equiv}CCH_2(PMe_3)]^+BF_4^-$ (**25**) in 90% yield (Scheme 8). The assignment of **25** as an alkyne complex was made spectroscopically (Table 5). Slow rotation about the rhenium−alkyne bond was indicated by the observation of two ^{1}H NMR resonances for the diastereotopic CH_2P hydrogens at δ 3.97 and 3.58 with J_{gem} = 16 Hz.

Similarly, the PPh_3-substituted metallacycle $C_5Me_5(CO)_2$-$ReCH_2C(PPh_3)$=$CC(CH_3)_3^+BF_4^-$ (**5a**) rearranged slowly over 2 days at room temperature to the alkyne complex $C_5Me_5(CO)_2$-$Re[\eta^2$-$(CH_3)_3CC{\equiv}CCH_2(PPh_3)]^+BF_4^-$ (**26**) which was isolated in 96% yield. The observation of two ^{1}H NMR resonances for the diastereotopic CH_2P hydrogens at δ 4.03 and 3.71 with J_{gem} = 16 Hz supported the formulation of **26** as an alkyne complex (Table 5).

Scheme 8



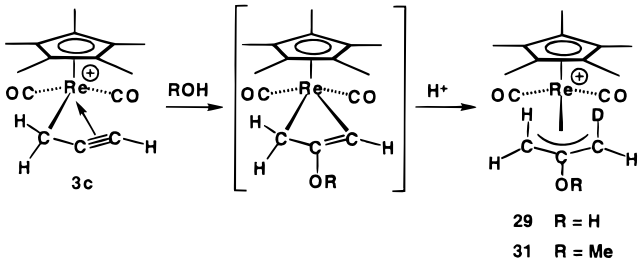
Scheme 9



***η*^{3}-Allyl Complexes from Protonation of Metallacyclobutenes.** The thermal instability of the alkynyl-substituted rhenacyclobutene **11b** was traced in part to protonation by acidic media. When isolated, $C_5Me_5(CO)_2ReCH_2C[C{\equiv}CC$-$(CH_3)_3]$=$CCH_3$ (**11b**) was treated with excess CF_3CO_2H (5 equiv) in CD_2Cl_2 at room temperature, and the cationic η^3-allyl rhenium complex $C_5Me_5(CO)_2Re[\eta^3$-$CH_2C[C{\equiv}CC(CH_3)_3]$-$CHCH_3]^+CF_3CO_2^-$ (**27**) was immediately observed by ^{1}H and ^{13}C NMR spectroscopies (Scheme 9). In the ^{1}H NMR spectrum, resonances at δ 4.05 (d, J_{gem} = 2.5 Hz) and 1.95 (d, J_{gem} = 2.5 Hz) were assigned to syn and anti hydrogens on the same allylic carbon, and a resonance at δ 2.9 (q, J = 9 Hz) was assigned to an anti allylic hydrogen on a terminal allylic carbon bearing a methyl group. The absence of *W*-coupling expected for syn

(24) Reaction of pyridine with the *tert*-butyl-substituted η^3-propargyl complex **3a** *did not produce products with* NMR resonances consistent with the formation of a metallacyclobutene and/or an alkyne complex analogous to the DMAP complexes **22a** or **23**.

Scheme 10



allylic hydrogens on opposite ends of an allylic system was crucial in assigning a syn orientation of the Me group relative to the C≡C(CH_3)$_3$ group on the central allylic carbon. In the ^{13}C NMR spectrum, a carbon resonance at δ 102.8 was assigned to the central allyl carbon and resonances at δ 44.6 and 67.7 were assigned to the unsubstituted and methyl-substituted terminal allyl carbons, respectively. Protonation of metallacycle **11b** with CF_3CO_2D (99%) placed deuterium only on the methyl-substituted allylic carbon of **27**.

When η^3-propargyl complex **3b** was treated with LiC≡CC(CH_3)$_3$ followed by H_2O and CF_3CO_2H, the PF_6^- salt of the η^3-allyl complex was isolated in 45% yield.

In a related reaction, addition of LiCu(CH_3)$_2$ to η^3-propargyl complex **3b** at −78 °C followed by treatment with wet ether led to the isolation of the η^3-allyl complex $C_5Me_5(CO)_2Re[\eta^3$-$CH_2C(CH_3)CHCH_3]^+PF_6^-$ (**28**).

***η*^{3}-Allyl Complexes from Addition of Alcohols to *η*^{3}-Propargyl Complexes.** Addition of water or methanol to η^3-propargyl complexes did not produce observable metallacyclobutenes. Instead, oxygen-substituted η^3-allyl complexes were the first species detected. The formation of these η^3-allyl complexes can be explained by initial attack of the oxygen nucleophile at the central propargyl carbon to give an oxygen-substituted metallacyclobutene followed by protonation of a Re−C bond of the metallacycle (Scheme 10).

Addition of water to a yellow CH_2Cl_2 solution of the unsubstituted η^3-propargyl complex **3c** at 0 °C led to isolation of the 2-hydroxyallyl complex $C_5Me_5(CO)_2Re[\eta^3$-$H_2CC(OH)$-$CH_2]^+BF_4^-$ (**29**) as a red solid in 35% yield. When the reaction was monitored by ^{1}H NMR spectroscopy in CD_2Cl_2 at −20 °C, **29** was observed immediately and no evidence for a metallacyclobutene intermediate was seen. A higher yield (80%) of **29** was obtained by addition of HBF_4·Et_2O to an acetone solution containing propargyl alcohol complex C_5-$Me_5(CO)_2Re(\eta^2$-HC≡$CCH_2OH)$ (**30**)[13] and 0.1 mL of H_2O. This procedure was designed to generate the unsubstituted η^3-propargyl complex **3c** in the presence of H_2O as a trapping agent.

Complex **29** was characterized spectroscopically. The protons on the terminal allyl carbons appeared in the ^{1}H NMR spectrum as AA′XX′ multiplets at δ 4.28 (H_{syn}) and δ 1.89 (H_{anti}) with J_{gem} = 4 Hz, $J_{syn,syn'}$ = 4 Hz, and $J_{anti,anti'}$ = 0 Hz.[25] The ^{13}C NMR spectrum supports the C_s symmetry of **29**: only one carbonyl resonance at δ 195 and one CH_2 resonance at δ 33.3 were observed. η^3-Allyl complexes are often observed as a mixture of exo and endo isomers.[26] The ^{1}H NMR spectrum of **29** in CD_2Cl_2 showed predominantly one compound (9:1). The major compound was assigned the endo configuration on the basis of the observation of a nuclear Overhauser enhancement (NOE) between the C_5Me_5 protons and the H_{anti} protons of the allyl unit, which are proximal in an endo isomer. Saturation of the C_5Me_5 resonance resulted in a 5% NOE enhancement of the H_{anti} resonance and no enhancement of the H_{syn} resonance.

To probe the stereochemistry of water addition to η^3-propargyl complex **3c**, the reaction was repeated using D_2O in place of water. Reaction of **3c** with D_2O in CD_2Cl_2 resulted in the clean formation of $C_5Me_5(CO)_2Re[\eta^3$-$HDCC(OD)CH_2]^+$-BF_4^- (**29-*d*$_2$**) as a red solid in 30% yield (Scheme 10). The chemical shifts of the protons of this complex were very similar to that of the nondeuterated complex **29**. The resonance for H_{syn} appeared at δ 4.27 as a broad doublet (J = 4 Hz) that integrated to 1.7 hydrogens vs the 15 hydrogens of the C_5Me_5 ligand. The H_{anti} resonance was also a broad 4 Hz doublet at δ 1.85. This signal integrated to only 0.9 hydrogens, indicative of the replacement of one of the anti hydrogen atoms by deuterium. These data suggest that the addition of water and D_2O to **3c** occurs stereospecifically to place the additional proton in the anti position of the generated η^3-allyl complex. The same stereochemistry of addition was observed by Wojcicki for addition of MeOH to $(PPh_3)_2Pt(\eta^3$-CH_2C≡$CCH_3)^+$.[7e]

Similarly, when the propargyl alcohol complex **3c** was treated with acid in the presence of methanol, the methoxy-substituted η^3-allyl complex $C_5Me_5(CO)_2Re[\eta^3$-$H_2CC(OCH_3)CH_2]^+BF_4^-$ (**31**) was formed as a red solid in 73% yield. In the ^{1}H NMR spectrum, AA′XX′ multiplets were seen at δ 4.23 for H_{syn} and δ 1.94 for H_{anti}. The endo configuration of the allyl unit was established by the observation of a 15% NOE enhancement of the H_{anti} multiplet upon saturation of the C_5Me_5 resonance.

Discussion

Kinetic Preference for Attack at the Central Carbon of *η*^{3}-Propargyl Rhenium Complexes. Phosphorus, nitrogen, and carbon nucleophiles all attacked the central carbon of η^3-propargyl rhenium complexes to produce rhenacyclobutene complexes. This reactivity pattern stands in contrast to that of η^3-allyl complexes, which "normally" undergo nucleophilic attack at a terminal allyl carbon. Density functional molecular orbital calculations on η^3-propargyl complexes[27] support this mode of attack through both charge control and frontier molecular orbital control.

For nitrogen and phosphorus nucleophiles, the initially formed rhenacyclobutene complexes undergo rearrangement to give products resulting from nucleophilic attack at the two different terminal carbons of the propargyl unit. The addition of pyridine to the central carbon of methyl-substituted η^3-propargyl complex **3b** was found to be reversible. The initially formed metallacyclobutene **14b** reacted with picoline below −40 °C to form the picoline-substituted metallacyclobutene **16b**, presumably by pyridine dissociation to regenerate η^3-propargyl complex **3b**. When warmed to room temperature, the metallacyclobutene **14b** was converted to a thermodynamically more stable allene complex **15K**. The higher stability of allene complexes is reasonable on the basis of the strain inherent in the metallacyclobutene structure. The inability of picoline to exchange with

(25) The NMR shifts are similar to those observed by Sutton for the *endo* rotamer of $C_5Me_5(CO)_2Re(\eta^3$-$CH_2CHCH_2)^+BF_4^-$, whose terminal allyl protons were observed at δ 3.83 (H_{syn}) and δ 1.77 (H_{anti}). (a) Batchelor, R. J.; Einstein, F. W. B.; Zhuang, J.−M.; Sutton, D. *J. Organomet. Chem.* **1990**, *397*, 69. (b) Batchelor, R. J.; Einstein, F. W. B.; He, Y.; Sutton, D. *J. Organomet. Chem.* **1994**, *468*, 183. (c) He, Y.; Batchelor, R. J.; Einstein, F. W. B.; Sutton, D. *J. Organomet. Chem.* **1996**, *509*, 37.

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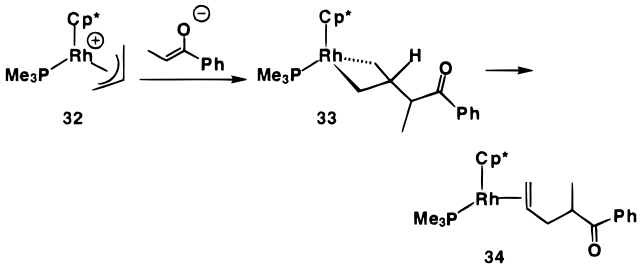
Scheme 11



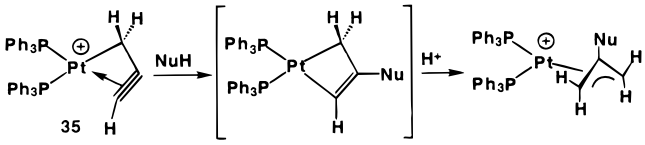
the pyridine bound to allene complex **15K** established the irreversibility of allene complex formation.

The sterically more congested *tert*-butyl-substituted η^3-propargyl complex **3a** was also attacked by nucleophiles at the central propargyl carbon to give metastable metallacyclobutenes. However, the nitrogen- and phosphorus-substituted metallacyclobutenes rearranged to η^2-alkyne complexes instead of η^2-allene complexes. Apparently, attack at the carbon bearing the bulky *tert*-butyl group is strongly disfavored. Thus, when the allene-forming pathway is blocked, nucleophilic attack can occur at the third propargyl carbon to form a lower energy alkyne structure. Again, the greater stability of alkyne complexes compared with that of metallacyclobutenes can be ascribed to ring strain.

Comparison with η^3-Allyl Systems. In contrast to the predominate attack of nucleophiles at the central carbon of η^3-propargyl complexes, the normal mode of attack on nucleophiles is at a terminal carbon of η^3-allyl complexes.[1] Nevertheless, a growing number of examples of nucleophilic attack at the central allyl carbon have been reported for cationic η^3-allyl complexes of Mo,[28] W,[28] Rh,[29] and Pt.[30] In several rare cases, kinetic attack of nucleophiles at the central allyl carbon produced metallacyclobutanes that then rearranged to more stable products of net terminal allyl carbon attack. Stryker and co-workers[31,32] reported that enolate addition to rhodium η^3-allyl complex **32** initially occurred at the central allyl carbon to give metallacyclobutane **33** which subsequently rearranged to alkene complex **34**, the product of terminal carbon attack (Scheme 11).

The regioselectivity of nucleophilic addition to η^3-allyl complexes has been the subject of several theoretical investigations. Davies, Green, and Mingos stressed the importance of *charge control*, and they predicted central-carbon nucleophilic attack on π-allyl complexes with very electron-releasing metal fragments.[33] Curtis and Eisenstein emphasized the role of *frontier orbital control* and pointed out that the energy ordering of the two lowest-lying empty orbitals could affect the regiochemistry of nucleophilic addition to η^3-allyl complexes.[34]

Scheme 12



Bäckvall experimentally confirmed that ligand effects could alter the regiochemistry of nucleophilic addition to η^3-allyl palladium complexes: σ-donor ligands (TMEDA) directed nucleophilic attack toward the central carbon, while π-acceptor ligands (PPh_3) directed attack toward the terminal carbon.[35] Their MP2 ab initio calculations confirmed the ligand dependence of the energy ordering of the two lowest-lying empty orbitals. With σ-donor ligands, the LUMO is localized on the central carbon, but with π-acceptor ligands, the LUMO is localized on the terminal carbons.

Access to Metallacyclobutenes. The addition of nucleophiles to the central carbon of cationic η^3-propargyl rhenium complexes provides a new and efficient way to generate metallacyclobutenes. Other routes to metallacyclobutenes include (1) coupling of alkyne ligands with carbene,[15,17,36] CO,[37,38] and isonitrile ligands,[39] (2) ring opening of cyclopropenes[16,40] and cyclopropenones,[41,42] and (3) rearrangement reactions involving ring contraction of metallacycles.[43]

Addition of Nucleophiles to Other η^3-Propargyl Systems. While other reported nucleophilic additions to η^3-propargyl complexes have not resulted in isolable or even observable metallacyclobutenes, the observed η^3-allyl or η^3-trimethylenemethane products are consistent with initial kinetic attack at the center carbon of the η^3-propargyl ligand. Chen reported that the reaction of $(PPh_3)_2Pt(\eta^3\text{-}H_2CC{\equiv}CH)^+BF_4^-$ (**35**) with a range of nucleophiles generated η^3-allyl complexes (Scheme 12).[44] The Wojcicki group found that the substituted η^3-propargyl platinum complex $(PPh_3)_2Pt(\eta^3\text{-}H_2CC{\equiv}CPh)^+$ (and its palladium analog) reacted with nucleophiles to form η^3-allyl complexes.[12,45] These products are consistent with nucleophilic addition to the central propargyl carbon to form a transient platinacyclobutene, followed by protonation of the metallacyclobutene to give the observed η^3-allyl complexes. We observed a similar reactivity pattern in the reactions of water with the unsubstituted propargyl complex **3c** which led to the isolation of hydroxy-substituted η^3-allyl complex **29**.

Parallel work in the laboratories of Wojcicki and Chen explored the conversion of η^3-propargyl platinum complexes

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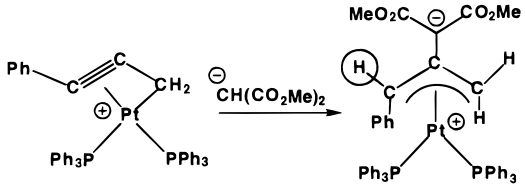
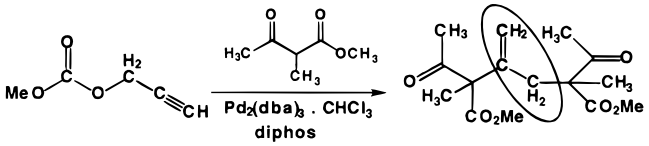
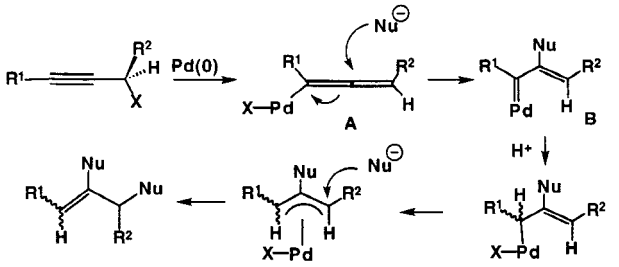
Scheme 13



Scheme 14



Scheme 15

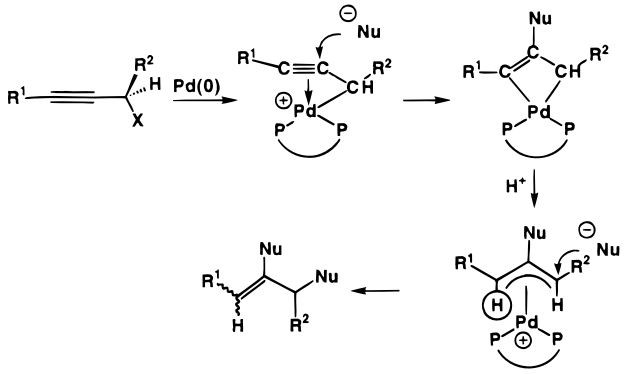


to η^3-trimethylenemethane complexes.[46] The addition of sodium dimethylmalonate to palladium[47] and platinum[48] η^3-propargyl complexes produced η^3-trimethylenemethane (η^3-TMM) complexes (Scheme 13).

Comments on the Mechanism of Palladium-Catalyzed Reactions of Propargyl Carbonates. Tsuji and co-workers have developed many useful palladium-catalyzed reactions of propargyl carbonates.[3] The reactions of carbon nucleophiles with propargyl carbonates produce double nucleophilic addition products where nucleophiles have added to both the central and a terminal carbon of the propargyl unit (Scheme 14). These reactions are related to the well-studied palladium-catalyzed reaction of allyl carbonates with nucleophiles.[49]

In Tsuji's proposed mechanism (Scheme 15), oxidative addition of the propargyl carbonate produces an η^1-allenyl complex (**A**) which is attacked by the first nucleophile at the center allene carbon to produce a palladium carbene complex (**B**) that is then protonated to give a η^1-allyl intermediate. Conversion of the η^1- to an η^3-allyl complex is then followed by addition of a second nucleophile to a terminal allyl carbon. Tsuji has provided convincing evidence for an η^3-allyl intermediate in these double nucleophilic additions. However, both the addition of a nucleophile to the central carbon of an η^1-allenyl complex (**A**) and the protonation of a Pd carbene complex (**B**) at carbon are unprecedented processes. Chen observed nucleophilic attack on a platinum η^1-allenyl complex to occur at the metal;[7c] the η^1-allenyl ligand was found be far less reactive toward nucleophiles than an η^3-propargyl ligand.

Scheme 16



In Stille coupling reactions, vinyl palladium intermediates (which are good models for η^1-allenyl species) react with nucleophiles at the metal center and not at the β-vinyl carbon.[50]

On the basis of the reactivity patterns we have observed for η^3-propargyl complexes, we propose an alternative mechanism for the double nucleophilic addition (Scheme 16). In our proposed mechanism, oxidative addition of the propargyl carbonate leads to an η^3-propargyl intermediate. The first nucleophilic addition occurs to the central carbon of the propargyl ligand to produce a metallacyclobutene. This is followed by a precedented protonation of the metallacyclobutene to generate the same η^3-allyl complex as proposed in Tsuji's mechanism.

Conclusions

A clear picture of the nature of nucleophilic attack on η^3-propargyl complexes is emerging from the results reported by our group and the other groups in this actively researched area. It seems clear that kinetic attack of nucleophiles on the center carbon of the propargyl ligand is almost always favored. After this initial metallacyclobutene-forming attack, subsequent transformations can lead to a variety of products, including η^3-allyl complexes, η^3-trimethylenemethane complexes, η^2-allene complexes, and η^2-alkyne complexes.

Experimental Section

General. For details, see the Supporting Information. $C_5Me_5(CO)_2Re(\eta^2\text{-}HC{\equiv}CCH_2OH)$, $C_5Me_5(CO)_2Re(\eta^3\text{-}H_2CC{\equiv}CH)^+BF_4^-$, and $C_5Me_5(CO)_2Re(\eta^3\text{-}H_2CC{\equiv}CCH_3)^+PF_6^-$ were prepared as described earlier.[13,14]

$C_5Me_5(CO)_2ReCH_2C(PMe_3){=}CC(CH_3)_3^+BF_4^-$ (4a). Excess PMe_3 (0.5 mL) was vacuum transferred into a yellow solution of **3a** (60 mg, 0.105 mmol) in CH_2Cl_2 (1 mL) at −78 °C. The mixture was stirred and allowed to warm to 25 °C over 30 min. Volatiles were evaporated under high vacuum to give **4a** (68 mg, 100%) as a light yellow air-stable solid. ^{1}H NMR (CD_2Cl_2, 300 (MHz): δ 1.98 (s, C_5Me_5), 1.88 (d, J_{PH} = 13 Hz, PMe_3), 1.52 (d, J = 12 Hz, C*H*H), 1.16 [s, $C(CH_3)_3$], 0.18 (d, J = 12 Hz, CH*H*). $^{13}C\{^1H\}$ NMR (CD_2Cl_2, 125 (MHz): δ 212.9 (CO), 212.2 (CO), 178.3 (d, J_{PC} = 6 Hz, *C*=CPMe$_3$), 120.8 (d, J_{PC} = 15 Hz, C=*C*PMe$_3$), 102.8 (C_5Me_5), 41.9 [*C*$(CH_3)_3$], 32.8 [C(*C*$H_3)_3$], 12.1 (d, J_{PC} = 53 Hz, PMe_3), 10.5 (C_5*Me*$_5$), −28.3 (CH_2). IR (THF): 1994 (s), 1914 (s) cm^{-1}. MS (MALDI-TOF) calcd (obsd): for $C_{22}H_{35}O_2PRe^+$ (M^+) 547.19 (547.41), for $C_{21}H_{35}OPRe^+$ (M^+ − CO) 519.20 (519.47), for $C_{19}H_{26}O_2Re^+$ (M^+ − PMe_3) 471.15 (471.41).

X-ray Crystallographic Determination of $C_5Me_5(CO)_2ReCH_2C(PMe_3){=}CC(CH_3)_3^+BF_4^-$ (4a). Single crystals of **4a** suitable

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Table 6. X-ray Crystal Structure Data for $C_5Me_5(CO)_2ReCH_2C(PMe_3)$═$CC(CH_3)_3^+BF_4^-$ (**4A**)

empirical form	$C_{22}H_{35}BF_4O_2PRe$
color; habit	yellow transparent prism
cryst syst	monoclinic
space group	*Cc*
unit cell dimens	$a = 25.6741(2)$ Å
	$b = 11.9960(3)$ Å
	$c = 16.6122(3)$ Å
	$\beta = 101.218(2)°$
vol.	5018.6 Å^3
Peaks to determine cell	8192
θ range of cell peaks	3.0 to 25.0°
Z	8
form wt	635.48
density (calcd)	1.682 Mg/m^3
abs coeff	4.952 mm^{-1}
F(000)	2512
$R(F)^a$	3.16%
wR $(F^2)^a$	7.85%

[a] *R* factors are defined as follows: $R(F) = \{\sum|F_o - kF_c|\}/\sum|F_o|$ and $wR(F^2) = (\{\sum w(F_o^2 - F_c^2)^2\}/\sum[w(F_o^2)^2])^{1/2}$.

for X-ray analysis were obtained by slow diffusion of Et_2O into a saturated CH_2Cl_2 solution of pure compound at room temperature over the course of 3 days. A crystal of **4a** was coated in epoxy and mounted on the tip of a thin glass fiber. Diffraction data were obtained with graphite-monochromated Mo Kα radiation on a Siemens P4/CCD diffractometer at 133 K. Intensity data were collected in the range $1.62 \le \theta \le 25°$ using ϕ scan frames. Standard reflections for the data set showed a maximum variation of 0.32% throughout acquisition. Systematic absences and statistical analyses were consistent with the space group *Cc*. The 11 098 reflections collected produced 5029 independent reflections. The initial positions for Re atoms were found by direct methods, and all non-hydrogen atoms were located from successive difference Fourier maps. All non-hydrogen atoms were refined anisotropically; hydrogen atoms were refined from initial idealized positions with a riding model using isotropic displacement parameters of 1.2× isotropic equivalent of the bonded atom. In the riding model, hydrogens are fixed a set distance and geometry from the heavy atom and "ride" the motions of the heavy atom during refinement. A semiempirical absorption correction from ψ-scans was applied to each data set. Crystallographic computations were performed using the SHELXTL-PLUS[51] software on a Silicon Graphics Indigo computer. Crystallographic data is summarized in Table 6.

$C_5Me_5(CO)_2ReCH_2C(PMe_3)$═$CCH_3^+PF_6^-$ (4b). Excess PMe_3 (10 equiv) was vacuum transferred into a CH_2Cl_2 solution of **3b** (50 mg, 0.087 mmol). A white precipitate gradually formed over 1 h at room temperature. The precipitate was filtered and washed with Et_2O to give **4b** (41 mg, 72%) as a white powder. ^{1}H NMR (acetone-d_6, 200 MHz): δ 2.36 (q, $J = 2$ Hz, CCH_3), 2.05 (s, C_5Me_5), 1.95 (d, $J_{PH} = 14$ Hz, PMe_3), 1.45 (dqd, $J = 12$, 2 Hz, $J_{PH} = 0.7$ Hz, C*H*H), 0.3 (dq, $J = 12$, 2 Hz, CH*H*). ^{13}C NMR (acetone-d_6, 126 MHz): δ 213.5 (s, CO), 207.0 (s, CO), 157.7 (s, ═*C*CH_3), 128.0 (d, $J_{PC} = 33$ Hz, *C*PMe_3), 103.3 (s, *C*$_5Me_5$), 24.8 (q, $J_{CH} = 130$ Hz, ═C*C*H_3), 9.9 (q, $J_{CH} = 128$ Hz, C_5*Me*$_5$), 9.2 (qd, $J_{CH} = 133$ Hz, $J_{PC} = 53.0$ Hz, PMe_3), −31.7 (t, $J_{CH} = 145$ Hz, $ReCH_2$). ^{31}P{^{1}H} NMR (acetone-d_6, 202.5 MHz): δ 3.3 (s, PMe_3). IR (acetone): 1991 (s), 1915 (s) cm^{-1}. Anal. Calcd for $C_{19}H_{29}O_2ReP_2F_6$: C, 35.02; H, 4.49. Found: C, 35.31; H, 4.36.

$C_5Me_5(CO)_2ReCH_2C[C$≡$CC(CH_3)_3]$═CCH_3 (11b). LiC≡$CC(CH_3)_3$ (8 mg, 87 μmol) was added to **3b** (50 mg, 87 μmol) in THF at room temperature. After 10 min, solvent was evaporated under high vacuum, and Et_2O was added. The Et_2O solution was filtered and chromatographed (silica gel, 3:1 hexane/Et_2O) to give **11b** (29 mg, 47% yield, >90% pure by ^{1}H NMR) as a dark orange-red liquid. ^{1}H NMR (THF-d_8, 200 MHz): δ 2.03 (t, $J = 2$ Hz, ═CCH_3), 1.96 (s, C_5Me_5), 1.37 (dq, $J = 11$, 2 Hz, C*H*H), 1.19 [s, $C(CH_3)_3$], 0.20 (dq, J = 11, 2 Hz, CH*H*). ^{13}C{^{1}H} NMR (THF-d_8, 126 MHz): δ 216.9 (CO), 214.2 (CO), 102.4 (C_5Me_5), 150.2 (Re*C*═C), 128.0 (ReC═*C*), 92.2 and 83.1 (C≡C), 31.9 [*C*$(CH_3)_3$], 31.2 [C(*C*$H_3)_3$], 21.1 (═C*C*H_3), 10.1 (C_5*Me*$_5$), −21.7 (CH_2). IR (Et_2O): 1981 (s), 1905 (s) cm^{-1}. HRMS (EI) calcd (obsd) for $C_{22}H_{29}O_2Re$ 512.1728, obsd (512.1731).

$C_5Me_5(CO)_2ReCH_2C[CH(CO_2Et)_2]$═$CCH_3$ (12b). Solid $NaCH(CO_2Et)_2$ (9.5 mg, 52 μmol) dissolved over 10 min as it reacted with **3b** (30 mg, 52 μmol) in THF. Solvent was evaporated under high vacuum, and the residue was dissolved in Et_2O. The solution was filtered and evaporated to give **12b** (30 mg, 54% yield, >90% pure by ^{1}H NMR) as a dark orange-red oil. ^{1}H NMR (C_6D_6, 200 MHz): δ 4.5 [s, C*H*$(CO_2Et)_2$], 4.0 (m, OC*H*$_2CH_3$), 2.1 (t, $J = 2$ Hz, ═CCH_3), 2.0 (dq, $J = 11$, 2 Hz, C*H*H), 1.61 (s, C_5Me_5), 1.0 (m, OCH_2C*H*$_3$), 0.5 (dq, J = 11, 2 Hz, CH*H*). ^{13}C NMR (THF-d_8, 126 MHz): δ 216.9 (s, CO), 214.5 (s, CO), 168.3 (s, CO_2R), 167.4 (s, CO_2R), 140.3 (s, ═*C*CH_3), 119.0 (s, *C*═CCH_3), 102.1 (s, *C*$_5Me_5$), 61.3 (t, $J_{CH} = 149$ Hz, OCH_2), 61.1 (t, $J_{CH} = 144$ Hz, OC′H_2), 59.2 (d, $J_{CH} = 130$ Hz, *C*$H(CO_2Et)_2$), 18.8 (q, $J_{CH} = 125$ Hz, ═C*C*H_3), 14.4 (q, $J = 127$ Hz, OCH_2*C*H_3), 14.2 (q, $J = 127$ Hz, OCH_2*C*′H_3), 10.1 (q, $J = 128$ Hz, C_5*Me*$_5$), −25.7 (t, $J = 141$ Hz, $ReCH_2$): IR (Et_2O) 1979 (s), 1903 (s), 1736 (m) cm^{-1}. HRMS calcd (obsd): for $C_{23}H_{31}O_6Re$ 590.1681 (590.1681).

$C_5Me_5(CO)_2ReCH_2C(NC_5H_5)$═$CCH_3^+PF_6^-$ (14b). Pyridine (2 drops, 0.5 mmol) was added to a resealable NMR tube containing a CD_2Cl_2 solution of **3b** (15 mg, 0.09 mmol) frozen in liquid nitrogen. The tube was evacuated, warmed to −78 °C, inverted several times to mix the components, and placed in a pre-cooled NMR probe at −73 °C. ^{1}H NMR spectra of the bright yellow solution showed the formation of **14b**. ^{1}H NMR (CD_2Cl_2, −53 °C, 500 (MHz): δ 8.51 (d, $J = 6$ Hz, *o*-C_5H_5N), 8.31 (t, $J = 8$ Hz, *p*-C_5H_5N), 8.02 (t, $J = 7$ Hz, *m*-C_5H_5N), 2.29 (br s, CH_3), 1.97 (s, C_5Me_5), 0.62 (dq, $J = 12$, 2 Hz, ═C*H*H), remaining C═CH*H* obscured by C_5Me_5.

$C_5Me_5(CO)_2Re[\eta^2$-H_2C═C═$C(NC_5H_5)CH_3]^+PF_6^-$ (15K) and $C_5Me_5(CO)_2Re[\eta^2$-H_2C═C═$C(CH_3)NC_5H_5]^+PF_6^-$ (15T). Complex **3b** (50 mg, 0.09 mmol) and pyridine (0.54 mmol) were stirred in 5 mL of CH_2Cl_2 for 15 min. Most of the solvent was evaporated from the bright yellow solution, and 10 mL of Et_2O was added. The resulting yellow precipitate was filtered off, washed with Et_2O, and dried under vacuum to give a 10:1 mixture of **15K**/**15T** (36 mg, 61%) as a yellow powder. MS (LSIMS) calcd (obsd): for $C_{21}H_{25}O_2NRe$ 510.1 (510.2). Anal. Calcd for $C_{21}H_{25}O_2NRePF_6$: C, 38.50; H, 3.96. Found: C, 38.20; H, 3.61.

Major Kinetic Isomer 15K. ^{1}H NMR (CD_2Cl_2, −40 °C, 500 MHz): δ 8.73 (d, $J = 6$ Hz, *o*-C_5H_5N), 8.39 (t, $J = 8$ Hz, *p*-C_5H_5N), 8.02 (br t, $J = 8$ Hz, m-C_5H_5N), 2.59 (br s, CH_3), 2.00 (s, C_5Me_5), 1.94 (dq, shoulders not resolved, $J = 9$, 2 Hz, ═C*H*H), 1.19 (dq, shoulders not resolved, $J = 8$, 2 Hz, ═CH*H*). ^{13}C{^{1}H} NMR (CD_2Cl_2, −60 °C, 126 MHz): δ 205.8 (CO), 202.4 (CO), 148.1 (C═*C*═C), 146.1 (br, *p*-C_5H_5N), 143.4 (br, *o*-C_5H_5N), 132.0 (═*C*$(CH_3)NC_5H_5$), 126.9 (*m*-C_5H_5N), 100.1 (*C*$_5Me_5$), 26.4 (CH_3), 9.7 (C_5*Me*$_5$), −2.5 (═CH_2). ^{13}C{^{1}H} NMR (CD_2Cl_2, 22 °C, 126 MHz): δ 204 (br, CO), 148.9 (C═*C*═C), 145.8 (*p*-C_5H_5N), 144.4 (*o*-C_5H_5N), 133.3 (═*C*(CH_3)-NC_5H_5), 128.5 (*m*-C_5H_5N), 101.7 (*C*$_5Me_5$), 26.9 (CH_3), 10.2 (C_5*Me*$_5$), −1.7 (═CH_2). ^{13}C NMR (CD_2Cl_2, 22 °C, 126 MHz): δ 204 (br, CO), 148.8 (s), 145.7 (d, $J = 164$ Hz), 144.4 (d, $J = 176$ Hz), 133.2 (s), 128.5 (d, $J = 189$ Hz), 101.1 (s), 26.9 (q, $J = 139$ Hz), 10.2 (q, $J = 126$ Hz), −1.8 (t, $J = 164$ Hz). IR (THF): 1983 (s), 1911 (s) cm^{-1}.

A solution of **15K** (6 mg, 9.2 μmol) in CD_2Cl_2 solution slowly equilibrated ($t_{1/2} \approx 14$ d) to a 1:9 mixture of **15K**/**15T**. After 2 months, evaporation of solvent gave a yellow solid which was washed with ether to give a 1:9 mixture of **15K**/**15T** (6 mg, 100%).

Minor Kinetic Isomer 15T. ^{1}H NMR (CD_2Cl_2, 213 K, 500 MHz): δ 8.73 (d, $J = 6$ Hz, *o*-C_5H_5N), 8.52 (t, $J = 6$ Hz, *p*-C_5H_5N), 8.09 (br t, $J = 6$ Hz, *m*-C_5H_5N), 2.73 (br s, CH_3), 1.91 (br d, $J = 8$ Hz, ═C*H*H), 1.81 (s, C_5Me_5), 1.19 (br d, $J = 8$ Hz, ═CH*H*). ^{13}C{^{1}H} NMR (CD_2Cl_2, 213 K, 126 (MHz): δ 203.7 (CO), 203.0 (CO), 153.8 (C═*C*═C), 144.0 (br, C_5H_5N), 140.8 (br, C_5H_5N), 126.7 (C_5H_5N), 125.7 (═*C*$(CH_3)NC_5H_5$), 100.1 (*C*$_5Me_5$), 19.9 (CH_3), 9.9 (C_5*Me*$_5$), −2.9 (═CH_2). IR (THF): 1997 (s), 1914 (s) cm^{-1}.

Reaction of $C_5Me_5(CO)_2ReCH_2C(NC_5H_5)$═$CCH_3^+PF_6^-$ (14b) with 4-Picoline. A CD_2Cl_2 solution of **14b** was prepared from pyridine (7 μL, 9 μmol) and **3b** (15 mg, 2.6 μmol) at −78 °C in a resealable

(51) Sheldrick, G. M. SHELXTL Version 5 Reference Manual, 1994; Siemens Analytical X-ray Instruments, 6300 Enterprise Dr., Madison, WI 53719−1173.

NMR tube. ^{1}H NMR spectra at −30 °C showed formation of **14b** along with excess pyridine. 4-Picoline (30 μL, 310 μmol) was added to the solution at −78 °C. ^{1}H NMR spectra at −40 °C showed complete formation of $C_5Me_5(CO)_2ReCH_2C(NC_5H_4$-*p*-$CH_3)$═$CCH_3^+PF_6^-$ (**16b**) along with excess pyridine and 4-picoline. **16b**. ^{1}H NMR (CD_2Cl_2, −40 °C, 500 MHz): δ 8.39 (d, J = 6 Hz, *o*-C_5H_4N), 7.79 (d, J = 6 Hz, *m*-C_5H_4N), 2.58 (s, CH_3), 1.98 (s, C_5Me_5), 0.61 (br d, J = 13 Hz, C*H*H), CH_3 and CH*H* resonances buried under excess 4-picoline and C_5Me_5 resonances.

At 9 °C, new resonances for $C_5Me_5(CO)_2Re[\eta^2$-H_2C═C═C-$(CH_3)(NC_5H_4$-*p*-$CH_3)]^+PF_6^-$ (**17**) grew in slowly. After 8 h at room temperature, volatile materials were evaporated under vacuum and fresh CD_2Cl_2 was added. ^{1}H NMR showed a complex mixture of η^2-allenyl adducts from both pyridine and 4-picoline. For **17**. (CD_2Cl_2, 300 MHz): δ 8.58 (d, J = 7 Hz, *o*-C_5H_4N), 7.82 (d, J = 7 Hz, *m*-C_5H_4N), 2.68 (s, CH_3), 2.59 (s, CH_3), 2.05 (s, C_5Me_5), 1.5 (br, ═C*H*$_2$).

$C_5Me_5(CO)_2Re[\eta^2$-H_2C═C═C$(NEt_3)CH_3]^+PF_6^-$ (19). Addition of NEt_3 (20 mg, 170 μmol) to $C_5Me_5(CO)_2Re(\eta^3$-CH_2C≡$CCH_3)^+PF_6^-$ (55 mg, 9.6 μmol) in CD_2Cl_2 produced a bright yellow solution. Volatile materials were evaporated under vacuum, and the resulting dark yellow solid was washed with Et_2O and dried under vacuum to give $C_5Me_5(CO)_2Re[\eta^2$-H_2C═C═C$(NEt_3)CH_3]^+PF_6^-$ (**19**) (14 mg, 60%) as a yellow powder. ^{1}H NMR (CD_2Cl_2, 24 °C, 500 MHz): δ 3.53 (q, J = 8 Hz, NC*H*$_2$CH$_3$), 2.32 (t, J = 2 Hz, CH_3), 2.04 (s, C_5Me_5), 1.23 (t, J = 8 Hz, NCH$_2$C*H*$_3$), ═CH_2 resonances broadened by allene rotation. The CH_2═ resonances decoalesced at −47 °C. ^{1}H NMR (CD_2Cl_2, −47 °C, 500 MHz): δ 3.4 (br, NC*H*$_2$CH$_3$), 2.23 (br s, CH_3), 2.16 (br d, J_{gem} = 9 Hz, ═C*H*H), 1.96 (s, C_5Me_5), 1.44 (br d, J_{gem} = 9 Hz, ═CH*H*), 1.25 (br, NCH$_2$C*H*$_3$). ^{1}H NMR (CD_2Cl_2, −80 °C, 500 MHz): additional resonances observed for decoalesced Et groups at δ 3.65 (br, 1H), 3.52 (br, 1H), 3.41 (br, 1H), 3.29 (br, 2H), 3.21 (br, 1H), 1.27 (br t, J = 6 Hz, 3H), 1.11 (br t, J = 7 Hz, 3H), 0.92 (br t, J = 5 Hz, 3H). ^{13}C{^{1}H} NMR (CD_2Cl_2, 126 (MHz): δ 203.4 (CO), 147.0 (C═*C*═C), 123.0 (═*C*$(CH_3)NEt_3$), 101.1 (C_5Me_5), 53.2 (N*C*H$_2$CH$_3$), 18.9 (═C(*C*H$_3$)-NEt_3), 10.5 (C_5*Me*$_5$), 8.4 (NCH$_2$*C*H$_3$), 3.4 (═*C*H$_2$). IR (THF): 1979 (s), 1909 (s) cm^{-1}. MS (LSIMS) calcd (obsd): for $C_{22}H_{35}O_2NRe^+$ 532.2 (532.2). Anal. Calcd for $C_{22}H_{35}O_2NRePF_6$: C, 39.05; H, 5.21. Found: C, 39.22; H, 5.17.

$C_5Me_5(CO)_2ReCH_2C(NC_5H_4NMe_2)$═$CC(CH_3)_3^+BF_4^-$ (22a). 4-(Dimethylamino)pyridine (DMAP, 5 mg, 0.040 mmol) was added to a yellow solution of **3a** (20 mg, 0.035 mmol) in CD_2Cl_2 (1 mL) in a resealable NMR tube at −78 °C. The tube was inverted to mix the reactants and immediately inserted into a pre-cooled NMR probe at −38 °C. Complex **22a** was the only product observed by ^{1}H NMR spectroscopy. Rearrangement to **23** occurred at −20 °C. ^{1}H NMR (CD_2Cl_2, 360 MHz, −38 °C): δ 7.74 (d, J = 7 Hz, CHN), 6.77 (d, J = 7 Hz, C*H*CHN), 3.20 (s, NMe_2), 1.99 (s, C_5Me_5), 1.80 (d, J_{gem} = 12 Hz, C*H*H), 0.91 [s, C$(CH_3)_3$], 0.34 (d, J_{gem} = 12 Hz, CH*H*). ^{13}C{^{1}H} NMR (CD_2Cl_2, 90 MHz, −38 °C): δ 214.2, 213.6 (CO); 140.9 (C═*C*DMAP); 155.6, 136.9, 130.4 (DMAP aromatic carbons); 105.6 (*C*═CDMAP), 101.8 (C_5Me_5), 40.3 (NMe_2), 37.5 [*C*$(CH_3)_3$], 32.0 [C(*C*H$_3)_3$], 10.2 (C_5*Me*$_5$), −17.7 (CH_2).

$C_5H_5(CO)_2Re[\eta^2$-$(CH_3)_3CC$≡$CCH_2(NC_5H_4NMe_2)]^+BF_4^-$ (23). A yellow solution of DMAP (10 mg, 38 μmol) and **3a** (17 mg, 35 μmol) in CH_2Cl_2 (5 mL) was stirred at room temperature for 15 min. Volatiles were evaporated under high vacuum, and the resulting yellow residue was washed with 10 mL of diethyl ether to give **23** (25 mg, 96%) as a yellow solid. ^{1}H NMR (CD_2Cl_2, 300 MHz): δ 7.87 (d, J = 7 Hz, NCH), 6.85 (d, J = 7 Hz, NCCH), 5.45 (d, J_{gem} = 16 Hz, C*H*H), 5.09 (d, J_{gem} = 16 Hz, CH*H*), 3.22 (s, NMe_2), 2.02 (s, C_5Me_5), 1.18 [s, C$(CH_3)_3$]. ^{13}C{^{1}H} NMR (CD_2Cl_2, 90 (MHz): δ 209.6, 208.3 (CO); 147.7, 141.2, 141.0 (DMAP aromatic carbons); 101.3 (*C*≡C), 101.1 (C_5Me_5), 71.6 (C≡*C*), 66.0 (CH_2), 40.5 (NMe_2), 33.9 [*C*$(CH_3)_3$], 31.7 [C(*C*H$_3)_3$], 10.7 (C_5*Me*$_5$). IR (THF): 1950 (s), 1867 (s) cm^{-1}. MS (MALDI-TOF) calcd (obsd): for $C_{26}H_{36}O_2N_2Re^+$ (M^+) 593.23 (593.30), for M^+ − CO 565.24 (565.31), for M^+ − DMAP 471.15 (471.29).

$C_5Me_5(CO)_2Re[\eta^2$-$(CH_3)_3CC$≡$CCH_2(PMe_3)]^+BF_4^-$ (25). A CH_2Cl_2 solution of **4a** (50 mg, 0.077 mmol) was stirred at room temperature for 2 days. Volatiles were evaporated under high vacuum, and the yellow residue was washed with 10 mL of diethyl ether to give **25** (45 mg, 90%) as a yellow solid. ^{1}H NMR (CD_2Cl_2, 360 MHz): δ 3.97 (dd, J_{gem} = 16 Hz, J_{PH} = 19 Hz, C*H*HP), 3.58 (dd, J_{gem} = 16 Hz, J_{PH} = 15 Hz, CH*H*P), 2.01 (s, C_5Me_5), 1.92 (d, J_{PH} = 15 Hz, PMe_3), 1.30 (s, C$(CH_3)_3$). ^{13}C{^{1}H} NMR (CD_2Cl_2, 90 MHz): δ 205.9 (CO), 204.8 (CO), 97.0 (*C*≡CCH_2), 100.9 (C_5Me_5), 57.8 (d, J_{PC} = 12 Hz, C≡*C*CH_2), 32.8 [*C*$(CH_3)_3$], 30.7 [C(*C*H$_3)_3$], 25.2 (d, J_{PC} = 51 Hz, *C*H$_2$P), 10.4 (C_5*Me*$_5$). IR (THF): 1951 (s), 1869 (s) cm^{-1}. MS (MALDI-TOF) calcd (obsd): for $C_{22}H_{35}O_2PRe^+$ (M^+) 547.19 (547.38).

$C_5Me_5(CO)_2Re\{\eta^3$-$CH_2C[C$≡$CC(CH_3)_3]CHCH_3\}^+PF_6^-$ (27). H_2O (2 equiv) was vacuum transferred into a THF solution of **3b** (50 mg, 87 μmol). After 10 min at 25 °C, excess CF_3CO_2H (10 equiv) was added, and volatile materials were evaporated under vacuum. The residue was washed with wet Et_2O and filtered to give **27** (26 mg, 45%) as a pale-brown solid. ^{1}H NMR (acetone-d_6, 200 MHz): δ 4.07 (d, J_{gem} = 3 Hz, C*H*H), 2.90 (q, J = 9.0 Hz, C*H*CH$_3$), 2.27 (s, C_5Me_5), 2.11 (d, J = 9 Hz, CHC*H*$_3$), 1.95 (br d, J_{gem} = 3 Hz, CH*H*), 1.24 [s, C$(CH_3)_3$]. ^{13}C{^{1}H} NMR (acetone-d_6, 126 MHz): δ 195.0, 193.1 (CO); 104.9 (C_5Me_5) 102.8 (CH_2C) 90.6, 73.2 (C≡C) 67.7 (*C*HCH$_3$) 44.6 (CH_2) 31.1 [C(*C*H$_3)_3$], 16.9 (CH*C*H$_3$) 10.1 (C_5*Me*$_5$). IR (acetone): 2045 (s), 1990 (s) cm^{-1}.

$C_5Me_5(CO)_2Re[\eta^3$-$H_2CC(OH)CH_2]^+BF_4^-$ (29). Addition of HBF_4·Et_2O (10 μL, 85%) to a yellow solution of $C_5Me_5(CO)_2Re(\eta^2$-HC≡CCH_2OH) (25 mg, 58 μmol) and distilled water (0.1 mL) in acetone (2 mL) produced an orange-red solution. The red precipitate which formed upon addition of Et_2O (15 mL) was separated, washed twice with 10 mL of Et_2O, and dried under vacuum to give **29** (20 mg, 80%) as a red air-stable powder as a 9:1 ratio of endo and exo isomers. ^{1}H NMR (CD_2Cl_2, 300 MHz): endo isomer: δ 8.35 (br s, OH), 4.28 (*AA′*XX′, J_{AX} = −4 Hz, J_{XX} = 4 Hz, H_{syn}),[52] 2.09 (s, C_5Me_5), 1.89 (AA′*XX′*, J_{AX} = 4 Hz, J_{XX} = 4 Hz, H_{anti}). ^{1}H NMR (CD_2Cl_2, 300 MHz) exo isomer: δ 8.35 (br s, OH), 4.07 (m, H_{syn}), 2.05 (s, C_5Me_5), 1.68 (m, H_{anti}). ^{13}C{^{1}H} NMR (CD_2Cl_2, 90 MHz): δ 195.0 (CO), 134.0 (COH), 104.2 (C_5Me_5), 33.3 (CH_2), 10.4 (C_5*Me*$_5$). IR (CH_2Cl_2): 2045 (s), 1986 (s) cm^{-1}. MS (MALDI-TOF) calcd (obsd): for $C_{15}H_{20}O_3Re^+$ 433.09 (433.23).

Reaction of 3c with D_2O. HBF_4·Et_2O (10 μL, 85%) was added to a yellow solution of **30** (20 mg, 46 μmol) in CD_2Cl_2 (1 mL) at room temperature to generate **3c**. D_2O (0.1 mL, excess) was immediately added to the resulting orange solution, which reddened upon mixing. Et_2O (5 mL) was added to precipitate $C_5Me_5(CO)_2Re[\eta^3$-HDCC-$(OD)CH_2]^+BF_4^-$ (**29-*d*$_2$**) as a red solid (7 mg, 30%). ^{1}H NMR (CD_2Cl_2, 300 MHz): δ 4.27 (br d, J = 4 Hz, 1.7 H, H_{syn}), 2.05 (s, 15 H, C_5Me_5), 1.85 (br d, J = 4 Hz, 0.9 H, H_{anti}).

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Supporting Information Available: General experimental methods and experimental details and characterization for $C_5Me_5(CO)_2Re[\eta^2$-$(CH_3)_3CC$≡$CCH_2OH]$, **3a**, **4c**, **5a**, **5b**, **5c**, **10b**, **13b**, **18c**, **20**, **21**, **24**, **26**, **28**, and **31** and X-ray crystallographic data for **4a** (19 pages). An X-ray crystallographic file, in CIF format, is available through the Internet only. See any current masthead page for ordering and Internet access instructions.

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(52) The AA′XX′ pattern was modeled using the program WinDNMR (v.1.4 Reich, H. J. *J. Chem. Educ. Software*, 1996) and is consistent with $J_{AA'}$ = 0 Hz, J_{AX} = 4 Hz, and $J_{XX'}$ = 4 Hz, where "A"is H_{syn} and "X"is H_{anti}. Coupling constants between remote η^3−allyl protons are generally small,[26] and the assignment of the H_{syn}−H_{syn} coupling as larger than the H_{anti}−H_{anti} coupling is consistent with the "W" relative geometry of the syn protons, which is more favorable *for the transmission of coupling information*.