Carbon–Carbon Bond Forming Reactions of Rhenium Enolates with Terminal Alkynes. Evidence for an Alkyne C–H Oxidative Addition Mechanism and Observation of Highly Stereoselective Base-Catalyzed Proton Transfer Reactions in Rhenium Metallacycles

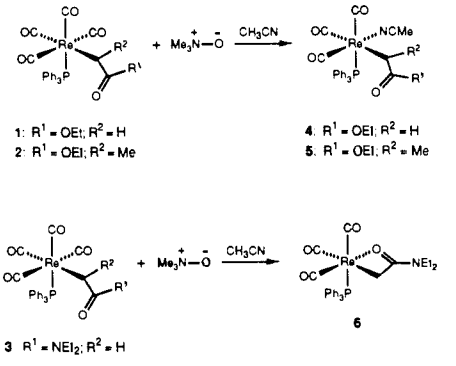
Jeffrey G. Stack, Robert D. Simpson, Frederick J. Hollander, Robert G. Bergman,* and Clayton H. Heathcock*

Contribution from the Department of Chemistry, University of California, Berkeley, California 94720. *Received July 31, 1989*

Abstract: The acetonitrile-substituted complexes *fac*-$(MeCN)(OC)_3(PPh_3)ReCH(R^2)CO(R^1)$ (**4**, R^1 = OEt, R^2 = H; **5**, R^1 = OEt, R^2 = Me) and the chelating amide complex **6** react with terminal alkynes ($R^3C{\equiv}CH$) to afford five-membered metallacycles **7–9**. The metallacycles possess an exocyclic double bond which exists in the less thermodynamically stable *Z* stereochemistry, in which the alkyl group R^3 is oriented proximate to the metal center. These complexes rearrange in the presence of a Lewis base to form the endocyclic isomers **10–12**. The structure of the metallacycle **10g** was determined by a single-crystal X-ray diffraction study. Labeling studies demonstrated that the 1,3-hydrogen shift involved in this rearrangement is intramolecular and stereospecific with respect to the rhenium center, even though it is mediated by an external reagent. Deuterium incorporation into the γ-position of the endo metallacycles can also be induced by base and once again occurs stereospecifically (anti to the phosphine ligand). Treatment of the metallacycles with acid results in removal of the metal and yields the unsaturated esters as a mixture of stereo- and regioisomers. Kinetic studies demonstrated that the reaction of **4** with terminal alkynes involves reversible dissociation of the coordinated acetonitrile to form an unsaturated intermediate **29** (R^1 = CO_2Et). This intermediate reacts faster with more electron-rich alkynes ($HC{\equiv}CCMe_3$) than electron-deficient alkynes ($HC{\equiv}CCO_2Me$) and displays a $R^3C{\equiv}CH/R^3C{\equiv}CD$ kinetic isotope effect k_H/k_D of 2.0. On the basis of these results and information about reactions of related rhenium complexes, we suggest that formation of the metallacycles is best accommodated by the mechanism shown in Scheme VIII: insertion of **29** into the alkyne C–H bond leading to a 7-coordinate rhenium acetylide hydride **31**, 1,3-migration of the hydride to the acetylide β-carbon, providing vinylidene complex **32**, and then migration of the enolate ligand to the α-carbon of the vinylidene group, giving the exo metallacycle.

The insertion of alkynes into transition metal–carbon bonds is a well-documented reaction and has been observed in nearly all of the triads of transition metals. Specific examples are known for molybdenum,[1] chromium,[1a] tungsten,[1,2] manganese,[3] iron,[3c,4] ruthenium,[3c,5] cobalt,[4,6] iridium,[7] nickel,[8] and palladium.[3c,9] Except for a few isolated cases,[8b,c] the reactions of transition-metal alkyls with alkynes require activated (i.e., electron-deficient) alkynes[4a,5a] or prior insertion of coordinated CO[1-3] to facilitate the insertion. We have examined the addition of alkynes to labile rhenium enolate complexes and have found that unactivated terminal alkynes react rapidly under mild conditions to give rhenium oxametallacycles in high yield. Mechanistic evidence suggests that this addition does not occur by the "normal" direct insertion of the alkyne C≡C bond but through an oxidative addition of the alkynyl C—H bond and rearrangement to a highly reactive vinylidene intermediate.

Scheme I



Scheme II

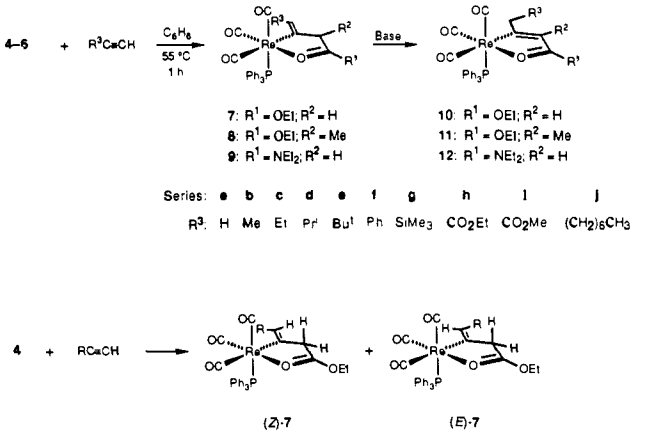


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Table I. Yields of Rhenium Oxametallacycles **7e** and **10–12**

enolate	$R^3C{\equiv}CH$	product	% yield
4	*t*-Bu	**7e**	78
4	H	**10a**	83
4	Me	**10b**	94
4	Et	**10c**	61
4	*i*-Pr	**10d**	72
4	*t*-Bu	**10e**	79
4	Ph	**10f**	79
4	$SiMe_3$	**10g**	81
4	CO_2Et	**10h**	87
4	CO_2Me	**10i**	94
4	$(CH_2)_6CH_3$	**10j**	60
5	Ph	**11a**	65
5	$SiMe_3$	**11b**	77
6	Me	**12**	72

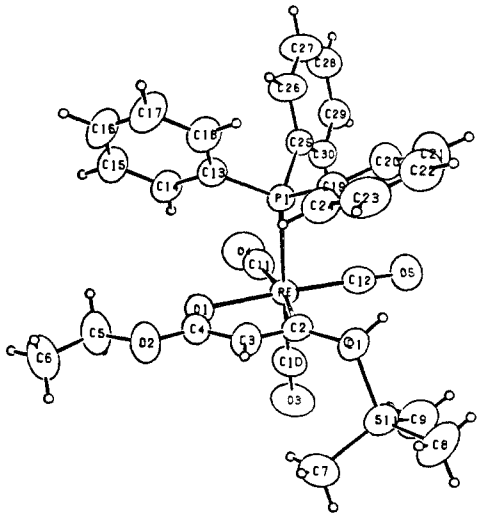

Figure 1. ORTEP diagram of alkyne addition product **10g** with 50% probability thermal ellipsoids. The diagram shows the numbering scheme used in the tables.

Results and Discussion

Synthesis and Characterization. The Ph_3P-substituted ester and amide enolates **1–3** react with trimethylamine *N*-oxide (Me_3NO) in CH_3CN to give labile acetonitrile-coordinated derivatives of the enolates (Scheme I).[10] The esters **1–2** yield nitrile complexes **4–5** whereas the amide oxygen internally coordinates to afford the chelated complex **6**. Despite their reactivity, these complexes can be prepared in high yield and manipulated by using standard benchtop techniques. Heating benzene solutions of **4–6** with a slight excess of many terminal alkynes at 55 °C for 1 h affords exo-oxametallacyclic[11] rhenium complexes **7–9**, as shown in Scheme II. Except where R^3 = Bu^t, these products are unstable with respect to rearrangement to the endocyclic isomers **10–12** and cannot be isolated as pure compounds. For $R^3 = CO_2Et$ and $SiMe_3$, the exo isomers are not observed, due presumably to the increased acidity of the protons α to the chelated carbonyl group. Treatment of the exo products with base (Et_3N or 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU)) allows isolation of the endo complexes **10–12** in high yield as pure compounds. A summary of yields is presented in Table I.

The assigned regiochemistry of the addition to the terminal carbon of the alkyne is consistent with spectral data (vide infra) and has been confirmed by single-crystal X-ray analysis of the trimethylsilyl-substituted metallacycle **10g**. Crystals of **10g** were obtained by slow evaporation of a C_6H_6/heptane solution of the complex at 25 °C. Conditions for data collection are summarized in Table II; details of the structure determination are described in the Experimental Section. An ORTEP diagram and a listing of selected structural parameters can be found in Figure 1 and Table III, respectively. The chelate ring in **10g** exhibits modest delocalization. The C3–C4 distance (1.418 (5) Å) is shortened by ~0.04 Å with respect to an average sp^2–sp^2 distance of 1.46 Å;[12] the C2–C3 distance (1.351 (6) Å) and the C4–O1 distance (1.244 (4) Å) are both lengthened slightly (~0.01–0.02 Å) with respect to typically observed bond lengths.[12] An analogous manganese oxametallacycle has been structurally characterized and has a similar chelate ring;[3a] related tungsten analogues, however, display more pronounced delocalization.[1a,2] The most noteworthy feature of the structure is the short metal–carbon bond in the metallacycle (Re–C2, 2.162 (4) Å) which is almost midway between Re–C_{sp^2} single (~2.22 Å) and double (~2.09 Å) bonds.[13] This type of carbenoid character has also been noted in the manganese and tungsten systems mentioned previously.

As noted above, the exo isomers **7–9** cannot be isolated in most cases, but examination of crude reaction mixtures derived from **4** and $RC{\equiv}CH$ by ^1H NMR spectroscopy indicated the presence of both stereoisomers of complex **7**, as depicted in the second equation in Scheme II. Table IV lists the ratios of *E*/*Z* isomers that range from 78:22 (R = Me) to ≥98:2 (R = Bu^t). We were not able to determine the stereochemistry of the olefin by direct inspection of the ^1H NMR spectra of these complexes; use of homonuclear NOE difference spectroscopy was necessary. The *tert*-butyl complex **7e** was chosen for study because it was obtained

Table II. Summary of Crystallographic Data for **10g**

formula	$2(C_{30}H_{32}O_5PReSi)\cdot C_6H_6$
formula wt	1513.8
crystal system	triclinic
space group	$P\bar{1}$
cell dimensions (298 K)	
a	11.8002 (13) Å
b	12.3649 (13) Å
c	25.608 (3) Å
α	80.556 (9)°
β	84.660 (9)°
γ	63.004 (9)°
V	3283.4 (7) Å^3
Z	2
d_{calcd}	1.53 g cm^{-1}
μ_{calcd}	38.7 cm^{-1}
crystal dimensions	0.31 × 0.32 × 0.35 mm
radiation	Mo Kα (λ = 0.71073 Å)
temp of collection	25 °C
data collection method	ω
2θ scan range	$5° \le 5\theta \le 45°$
reflections measured	$+h, \pm k, \pm l$
scan width ($\Delta\theta$)	0.60 + 0.35 tan θ
scan speed	0.90–6.7° min^{-1}
reflections collected	8563
unique data	8563
unique data obsd ($F^2 > 3\sigma(F^2)$)	7209
variables	709
$R = \sum\|\|F_o\| - \|F_c\|\|/\sum\|F_o\|$	2.14%
$R_w = [\sum w_i(\|F_o\| - \|F_c\|)^2/\sum w_i F_o^2]^{1/2}$	3.07%
GOF	1.574

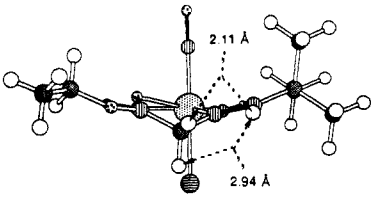

Figure 2. PCMODEL-generated minimum conformation of (*Z*)-**7e**; phenyl rings of Ph_3P ligand omitted for clarity.

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(11) The terms exo and endo are used to refer to the position of the double bond with respect to the metallacyclic ring.

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Table III. Selected Intramolecular Distances and Angles for **10g**[a]

atom 1	atom 2	distance, Å	atom 1	atom 2	atom 3	angle, deg
Re	P	2.471 (1)	P	Re	O1	90.75 (8)
Re	O1	2.191 (2)	P	Re	C2	88.47 (10)
Re	C2	2.162 (2)	P	Re	C10	177.70 (15)
Re	C10	1.938 (4)	P	Re	C11	92.06 (11)
Re	C11	1.949 (7)	P	Re	C12	87.61 (12)
Re	C12	1.888 (6)	O1	Re	C2	75.65 (15)
			O1	Re	C10	91.50 (13)
C10	O3	1.134 (7)	O1	Re	C11	93.16 (12)
C11	O4	1.152 (7)	O1	Re	C12	172.88 (13)
C12	O5	1.165 (7)	C2	Re	C10	92.57 (15)
			C2	Re	C11	168.8 (2)
C1	C2	1.491 (6)	C2	Re	C12	97.4 (2)
C2	C3	1.351 (6)	C10	Re	C11	87.32 (17)
C3	C4	1.418 (5)	C10	Re	C12	90.22 (16)
C4	O1	1.244 (4)	C11	Re	C12	93.82 (16)
C4	O2	1.322 (4)				
O2	C5	1.451 (5)	Re	C10	O3	176.4 (4)
C5	C6	1.458 (7)	Re	C11	O4	177.0 (3)
			Re	C12	O5	177.5 (3)
P	C13	1.824 (4)				
P	C19	1.828 (4)	Si	C1	C2	114.0 (3)
P	C25	1.836 (5)	Re	C2	C1	128.6 (4)
			Re	C2	C3	113.2 (3)
Si	C1	1.897 (4)	C1	C2	C3	118.1 (4)
Si	C7	1.867 (4)	C2	C3	C4	116.0 (3)
Si	C8	1.871 (4)	Re	O1	C4	113.3 (2)
Si	C9	1.859 (5)	O1	C4	O2	120.2 (3)
			O1	C4	C3	121.7 (3)
			O2	C4	C3	118.0 (3)
			C4	O2	C5	118.2 (3)
			O2	C5	C6	109.1 (4)

[a] Esd valves are in parentheses.

Table IV. Ratios of Exocyclic Alkene Isomers in **7b–f**

compd	R	*Z*	*E*
7b	Me	78	22
7c	Et	79	21
7d	Pr^i	88	12
7e	Bu^t	≥98	≤2
7f	Ph	≥98	≤2

as a single isomer. The results of these experiments show a definite NOE between the vinyl proton and *one* of the methylene protons of the ring, indicating that the vinyl proton is proximate to the ring protons, and the *tert*-butyl group is proximate (*Z*) to the metal center. This geometry appears to be more sterically congested than the *E* isomer, with significant interaction of the R group of the alkyne with the metal.

Molecular mechanics calculations, using MMX (modified MM2) parameters,[14] agree with this assumption and estimate the *Z* isomer to be ~3.6 kcal mol^{-1} less stable than the corresponding *E* isomer. The minimized conformation (Figure 2) obtained from these calculations also provide an explanation as to why only *one* of the ring protons exhibits a through-space NOE with the vinyl proton. The intramolecular distances between the two ring protons and the vinyl proton are 2.11 and 2.94 Å, respectively. This is presumably the major conformation in solution, and only one of the ring protons is near enough to interact with the vinyl proton. Additionally, the proton that does not exhibit magnetization transfer to the vinyl proton displays allylic coupling ($J \sim 0.5$–1.0 Hz) with the vinyl proton. The dihedral angle (~90°) between these two protons is in the range of values known to give the observed long-range coupling.[15] The proton that exhibits NOE interaction with the vinyl proton is nearly in the same plane (dihedral angle ~20°) as the vinyl proton and cannot overlap with the π-system; it therefore shows coupling <0.5 Hz.

The structures assigned to the exo- and endocyclic products are also consistent with other observed spectroscopic data. The ^1H NMR spectra of the exocyclic products all display a characteristic vinyl proton in the 6.0–6.5 ppm range (except for R = Ph, in which case the vinyl proton is further downfield and obscured by the aromatic protons of the Ph_3P ligand) as well as diastereotopic methylene protons of the ethyl group of the esters or amide. The product derived from the primary enolates **4** and **6** also displays an AB pattern for the methylene protons which are chemically inequivalent and exhibit typically large geminal (J_{HH} = −19 to −22 Hz) coupling constants for five-membered rings. In the ^{13}C NMR spectrum, the olefinic carbons of the *tert*-butyl-substituted metallacycle **7e** are observed in the normal (i.e., unconjugated) range[16] at 152.98 (α) and 149.95 (β) ppm with ^1H–^{31}P coupling constants of 11.3 and 2.6 Hz, respectively. As expected, the IR stretching frequency of the ester carbonyl is reduced in energy by 43 cm^{-1} relative to **4** due to the coordination to rhenium.

While the spectral properties of the endocyclic complexes **10–12** are similar to those of the exo isomers, some marked differences are observed. In the ^1H NMR spectra of **10** and **12** a vinyl proton is found in the same range as in **7** and **9**; in **11** the methyl group is observed as a doublet (J_{PH} = 1.0 Hz) at 1.50 ppm. Diastereotopic protons are still observed for the ester and amide methylene groups as well as the allylic methylene group, which is now exocyclic. These latter protons are influenced considerably by the electronic nature of the R group of the alkyne, and range from 2.44 for **10a** (R^3 = H) to 4.02 ppm (center of the AB multiplet) for **10f** (R^3 = Ph). The geminal coupling observed for these protons is now in the usual range of −9 to −16 Hz for a freely rotating group. The most noteworthy differences between the exo and endo isomers are found in the ^{13}C NMR and IR spectra. The α-carbon (C2) is observed at unusually low field (227–244 ppm) in the ^{13}C NMR spectra of **10–12**, which is consistent with the short rhenium–carbon bond length described above. Similar low-field ^{13}C NMR resonances have been observed in analogous

(14) The calculations were performed using the PCMODEL program obtained from Serena Software, Box 3076, Bloomington, IN 47402-3076.

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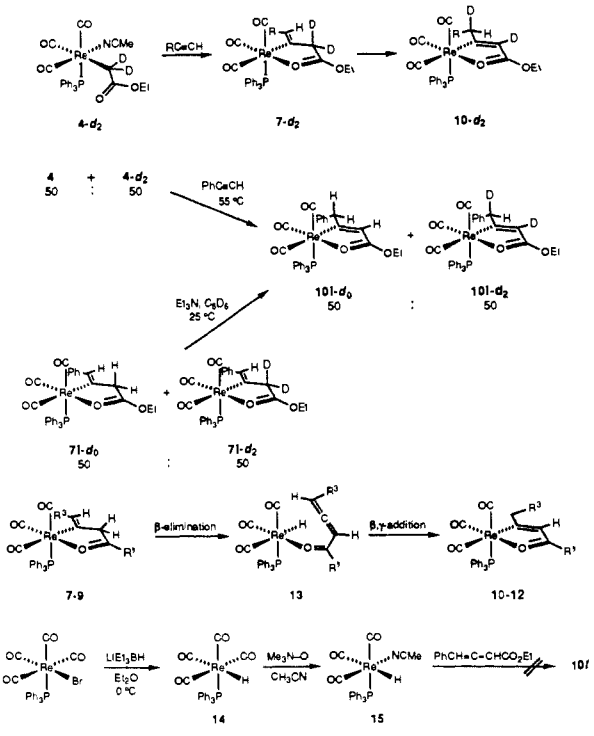
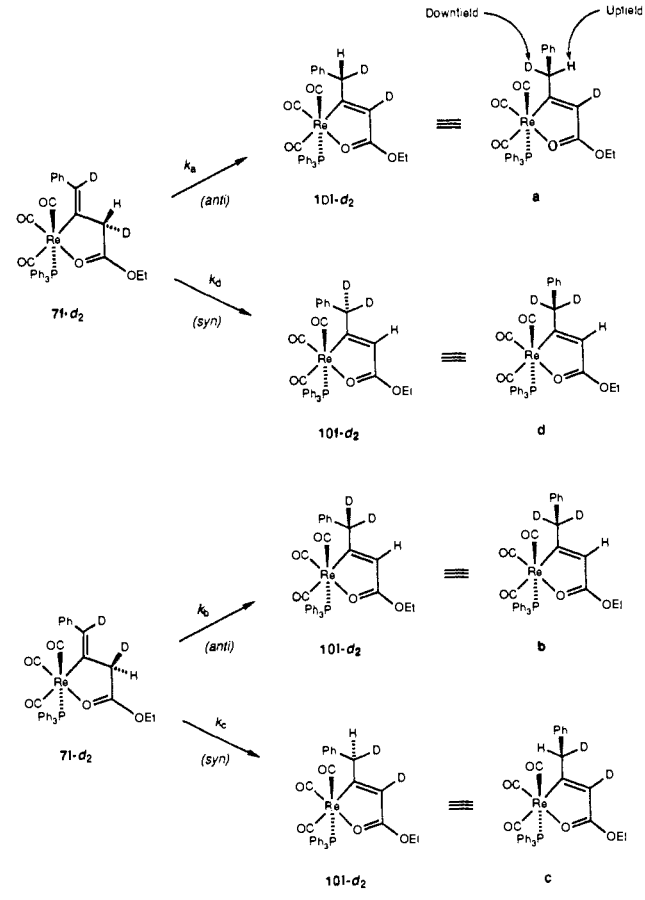
Scheme III



Scheme IV



metal–ring systems.[1a,2,3a] The other olefinic carbons are found between 119 and 124 ppm, only slightly shifted from their usual values of ~128 ppm. Although the organic carbonyls do not display unusual ^{13}C NMR chemical shifts, the IR resonances of these carbonyls are reduced ~150 cm^{-1} for the esters and ~100 cm^{-1} for the amide compound compared with the uncoordinated α,β-unsaturated carbonyl compounds[16] (~1725 and 1665 cm^{-1} for free α,β-unsaturated esters and amides, respectively). Similar values have been obtained upon chelation of α,β-unsaturated esters to manganese.[17]

Isomerization of 7–9 to 10–12. As mentioned earlier, the exocyclic products **7–9** are generally unstable with respect to rearrangement to their corresponding endocyclic isomers **10–12**. The ratio of these materials formed in the reaction of the rhenium enolates with 1-alkynes is erratic and varies with the nature of the alkynyl substituent and the enolate, as well as the reaction medium (including solvent and glassware). Labeling of the enolate methylene protons with deuterium provides additional information about this process. Reaction of **4-d_2** with 1-alkynes gives **7-d_2** and, after rearrangement, **10-d_2**, in which the vinyl proton and only *one* of the exocyclic methylene protons are replaced by deuterium (Scheme III). Addition of PhC≡CH to a 50:50 mixture of **4-d_0** and **4-d_2** in a crossover experiment gave >95% **10f-d_0** and **10f-d_2** (analysis by mass spectroscopy).

The absence of deuterium scrambling in the crossover experiment suggests an *intramolecular* mechanism for the rearrangement. Normally, a suprafacial 1,3-hydrogen transfer is considered a thermally "forbidden" process.[18] However, other possibilities arise with transition metal complexes. One such possible mechanism, shown in Scheme III, involves β-elimination of the chelate ring of **7–9** to yield an allenic carbonyl compound and a rhenium hydride; subsequent M–H insertion of the β,γ-portion of the allene affords the endocyclic product. To test this hypothesis, the complex *fac*-$(MeCN)(Ph_3P)(CO)_3ReH$ (**15**) was investigated as a possible precursor for the putative hydride intermediate **13**. The synthesis of **15** is shown in Scheme III. Addition of $LiEt_3BH$ to *cis*-$(Ph_3P)(CO)_4ReBr$ in Et_2O at 0 °C produced *cis*-$(Ph_3P)(CO)_4ReH$ (**14**) in 61% yield. Reaction of **14** with 1 equiv of Me_3NO in CH_3CN afforded a 78% yield of **15**; interestingly, **15** is a reasonably air-stable solid despite the labile nitrile ligand. When a C_6D_6 solution of **15** was treated with the allenic ester ethyl 4-phenyl-2,3-butadienoate,[19] a reaction occurred, but the expected endocyclic product **10f** was not observed.

Another possible mechanism for the isomerization is a 1,3-hydrogen shift that occurs through external catalysis (which would be more consistent with the erratic rates of this reaction noted above). The rearrangement is in general more facile for certain complexes (R^3 = Ph, $SiMe_3$, CO_2Et) and retarded for others (R^3 = Bu^t). On the basis of increased acidity of the enolate protons in the former complexes, a base-catalyzed process is suggested. The possibility of a base-catalyzed isomerization was demonstrated by repeating the crossover experiment from above with added base. A 50:50 mixture of **4-d_0** and **4-d_2** was allowed to react with PhC≡CH in C_6D_6 at 55 °C for 0.5 h, generating a mixture of **7f-d_0** and **7f-d_2** (Scheme III). Addition of Et_3N resulted in isomerization to the endocyclic products. Analysis of the reaction mixture by mass spectroscopy indicated the presence of only **10f-d_0** and **10f-d_2**; <5% **10f-d_1** could be detected. *The 1,3-hydrogen shift is therefore intramolecular and stereospecific with respect to rhenium, even though it is mediated by an external reagent.*[20] An analogous phenomenon has been demonstrated for organic allyl systems in a series of classic experiments by Cram and co-workers.[21]

The stereospecific nature of the isomerization indicates that there is a high facial preference for the base-catalyzed transfer. Although the most sterically accessible proton would be the one anti to the bulky Ph_3P ligand, the major ground state conformation (as determined by the aforementioned NOE experiment) places

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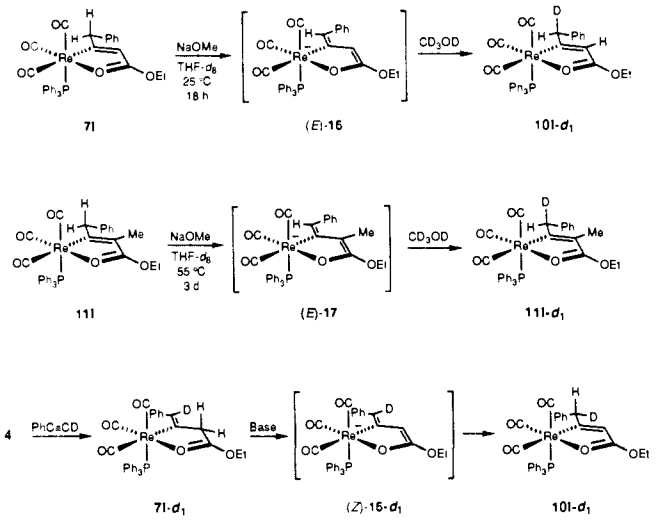
Scheme V



this proton in a pseudo-equatorial position (i.e., the "wrong" conformation for deprotonation). It was not clear to us whether the preference for deprotonation would thus be governed by the ground-state conformation, resulting in syn deprotonation, or by steric factors, resulting in a conformational change to place the anti proton in the necessary pseudo-axial position for deprotonation. To determine which proton was removed at the greatest rate, the following deuterium-labeling experiment was performed and is summarized in Scheme IV.

The monodeuterated enolate **4-d_1** was prepared in the usual manner using $ClCHDCO_2Et$. Reaction of **4-d_1** with PhC≡CD[22] generated a mixture of **7f-d_2** with one deuterium in the vinyl position and the other deuterium equally dispersed between the syn and anti (with respect to the Ph_3P ligand) positions at C3. There are four reaction pathways available for the rearrangement of this mixture with base: anti deprotonation of hydrogen (k_a), anti deprotonation of deuterium (k_b), syn deprotonation of hydrogen (k_c), and syn deprotonation of deuterium (k_d). Treatment of the **7f-d_2** mixture with Et_3N in 7:3 $C_6D_6/CDCl_3$ resulted in deprotonation and rearrangement to a mixture **10f-d_2**. Monitoring of this reaction by ^1H NMR spectroscopy showed that the resonance for anti proton disappeared ~6 times faster than did that for the syn proton and that the upfield proton (due to product a indicated in Scheme IV) in **10f-d_2** appeared at a similar rate. The ratio of the upfield:downfield protons in **10f-d_2** at the completion of the reaction was ~3.5:1. Since both the k_a and k_d pathways result in disappearance of the anti proton resonance, the expression for the ratio of rates of disappearance of the two **7** isomers $[H_{anti\text{-}7}]:[H_{syn\text{-}7}]$ is given in eq 1. The total facial selectivity is defined by the overall rate of anti/syn deprotonation and given in eq 2. The methylene hydrogens in products a and c are the only ones observable by ^1H NMR spectroscopy. Equation 3 gives the a/c ratio in terms of the rate constants shown in Scheme IV. Substitution of the value of 6 measured for eq 1 into eq 3 gives a value of ≥21 for the selectivity for deprotonation of the proton anti to the phosphine (k_a) versus deprotonation syn to the phosphine (k_c) (eq 4).

$$\frac{d[H_{anti}]}{d[H_{syn}]} = \frac{k_a + k_d}{k_b + k_c} \cong 6 \qquad (1)$$

$$\text{total facial selectivity} = \frac{k_a + k_b}{k_c + k_d} \qquad (2)$$

$$\frac{[a]}{[c]} = \frac{k_a}{k_a + k_d}\,\frac{k_b + k_c}{k_c} = \frac{k_a}{k_c}\,\frac{k_b + k_c}{k_a + k_d} \qquad (3)$$

$$3.5 = \frac{k_a}{k_c}\frac{1}{6} \qquad \frac{k_a}{k_c} = 3.5 \times 6 \cong 21 \qquad (4)$$

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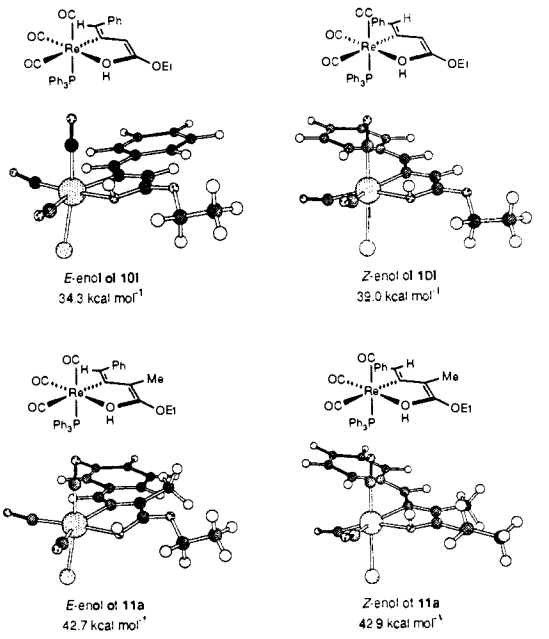


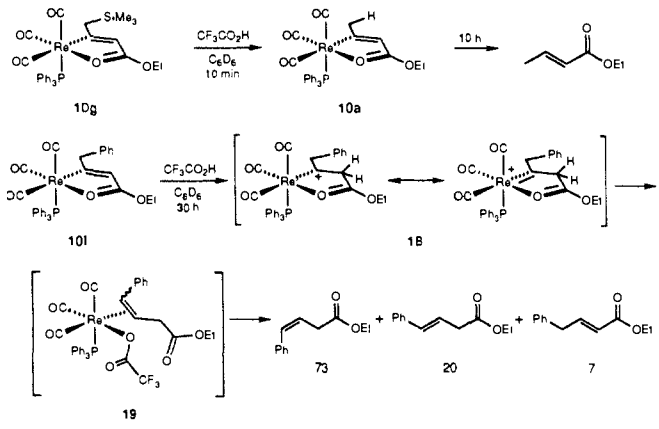
Figure 3. PCMODEL-generated minimum conformations and MMX energies for the enols of **10f** and the *E* enol of **11a**; phenyl rings of the Ph_3P ligands are omitted for clarity.

Reaction of Endo Metallacycles with Base. The chelate ring in **10–12** retains its reactivity as an organic functional group. As in α,β-unsaturated carbonyl compounds, the γ-protons are acidic. Treatment of the phenyl-substituted complex **10f** with a catalytic amount of NaOMe in $CD_3OD/THF\text{-}d_8$ at 25 °C for 18 h results in complete deuterium incorporation at only *one* of the *exo*-methylene positions, as shown in Scheme V. An identical result is obtained for the phenyl-substituted complex **11f** (obtained from the secondary enolate **2**) upon treatment with NaOMe in $CD_3OD/THF\text{-}d_8$, except that the conditions required are more vigorous: 3 days at 55 °C are necessary for complete deuterium incorporation. On the basis of the ^1H NMR chemical shift of the remaining proton (the upfield proton is retained) in both **10f-d_1** and **11f-d_1**, the relative stereochemistry in both compounds is assumed to be *identical*.

The stereospecific deuterium incorporation suggests that only one enolate geometry of **16** and **17** is formed upon deprotonation of either **10f** or **11f** and that the delivery of the deuteron occurs from only one face of the planar enolate system. Since direct determination of the enolate geometry was not possible, an indirect method was devised; this is summarized in Scheme V. The geometries of the exocyclic complexes **7–9** are known and can be used to deduce the geometry of the enolate in the following manner. Treatment of primary enolate **4** with PhC≡CD gives **10f-d_1**, via **7f-d_1**, as a single isomer. In this instance, the ^1H NMR chemical shift of the proton remaining is again the more upfield of the two protons in **10f**, the same as that obtained by deuterium exchange. Assuming that the exchange reaction occurs from the same face (i.e., anti to the Ph_3P ligand) as the deprotonation/protonation sequence (**7f-d_1** → **16-d_1** → **10f-d_1**), the enolate geometries of **16** and **17** generated in the exchange reacion must be opposite (i.e., *E*) to the *Z* enolate generated in the PhC≡CD reaction.

Molecular mechanics calculations provide additional supporting evidence for the proposed enolate geometries. For convenience, the (uncharged) enol forms of **10f** were used in the modeling experiment and are shown in Figure 3. The data obtained from the calculations afford an energy value for the *E* enol of **10f** that is ~4.7 kcal mol^{-1} lower in energy than the value obtained for the *Z* enol, consistent with the results of the deuterium exchange. The calculations also provide a possible explanation for the sluggishness of the exchange reaction for the methyl-substituted derivative. The MMX energy of the *E* enol of **11f** was found to be ~8.4 kcal mol^{-1} higher than that of the *E* enol of **10f**, due to

Scheme VI



increased steric repulsion between the phenyl group and the methyl group on the ring. Presumably, a similar effect is found in the transition state leading to the enolate of **11f** which is of substantially higher energy than that leading to the enolate of **10f**. The MMX energy of the *Z* enol of **11f** is only slightly higher (0.2 kcal mol^{-1}) than that of the *E* enol, but the results of the exchange reaction indicate only one enolate isomer is formed upon deprotonation.

Demetallation with Acid. Cleavage of the metal–carbon bond can be effected under acidic conditions. As shown in Scheme VI, treatment of **10g** with trifluoroacetic acid (TFA) in C_6D_6 results in rapid (10 min) desilylation at 25 °C to give **10a** (identical by ^{1}H NMR spectroscopy to that prepared from **4** and HC≡CH), followed by the slower (10 h, 25 °C) metal–carbon bond cleavage to give ethyl crotonate in 95% yield (determined by ^{1}H NMR spectroscopy). Addition of TFA to **10f** in C_6D_6 results in the formation (30 h, 25 °C) of a mixture of β,γ- and α,β-unsaturated esters: ethyl (*Z*)-4-phenyl-3-propenoate,[23] ethyl (*E*)-4-phenyl-3-propenoate,[24] and ethyl (*E*)-4-phenyl-2-propenoate[25] are detected in a ratio of 73:20:7 and in 92% overall yield by ^{1}H NMR spectroscopy. The formation of these products can be explained by initial protonation of the ring at C3 to generate a cationic carbene complex **18** (Scheme VI). Rearrangement of this species provides an unstable coordinated alkene complex **19** that decomposes to the free alkene. A similar acid-induced demetalation has been reported for analogous manganese oxametallacycles.[3a] Rearrangement of carbene complexes to coordinated alkenes has been observed for cationic rhenium[25] and iron[26] carbenes, as well as for neutral tungsten[27] carbene complexes. The production of the substantial amount of *Z* isomer can be accounted for by the fact that the rearrangement to the alkene complex presumably gives a majority of the more sterically favorable *Z*-alkene complex.

Reactions of Related Rhenium Complexes with Alkynes. Support for the facile addition of C–H bonds to rhenium centers analogous to those in the enolates discussed above was furnished by performing analogous reactions of terminal alkynes with *fac*-(MeCN)(Ph_3P)($CO)_3$ReMe (**21**), prepared in 95% yield by the reaction of *cis*-(Ph_3P)($CO)_4$ReMe[28] (**20**) with 1 equiv of Me_3NO in CH_3CN (Scheme VII). Treatment of a C_6D_6 solution of **21** with RC≡CH at 25 °C resulted in the rapid evolution of CH_4 (as identified in the ^{1}H NMR spectrum) and the formation of the σ-acetylide complexes *fac*-(MeCN)(Ph_3P)($CO)_3$ReC≡CR (**22**). The acetylides are generally unstable and decompose in solution soon after they are formed. Only where R = Bu^t can the product be isolated (83% yield) and characterized.

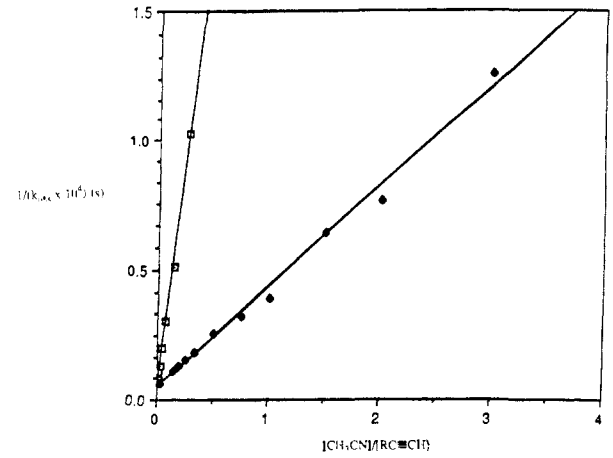
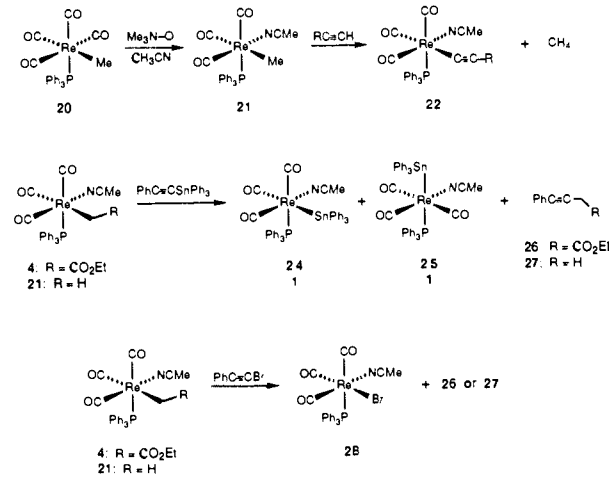


Figure 4. A plot of $1/(k_{obs} \times 10^4)$ versus [MeCN]/[HC≡CR]: (□) R = CO_2Me, r^2 = 0.998; (◇) R = $C(Me)_3$, r^2 = 0.993.

Scheme VII



Finally, oxidative addition processes were observed for other RC≡C—X bonds, and these are shown in Scheme VII as well. In contrast to the internal alkynes described above, PhC≡$CSnPh_3$[29] reacts with **4** at 55 °C, undergoing a C–Sn bond cleavage[30] to give *fac*- and *mer*-(MeCN)(Ph_3P)($CO)_3$ReSnPh_3 (**24**, **25**) and ethyl 4-phenyl-3-butynoate[31] (**26**). The rhenium–tin complexes were formed as a ~1:1 mixture of isomers. The methyl complex **21** also reacts smoothly with PhC≡$CSnPh_3$ to give the coupled product 1-phenylpropyne (**27**) and the rhenium–tin complexes **24** and **25** in 87% and 92% yields (^{1}H NMR spectroscopy), respectively. Finally, addition of PhC≡CBr[32] to C_6D_6 solution of **4** or **21** again results in coupling of the organic fragments to give **26** or **27**, respectively, along with *fac*-(MeCN)-(Ph_3P)($CO)_3$ReBr (**28**), prepared independently by treatment of *cis*-(Ph_3P)($CO)_4$ReBr with Me_3NO/CH_3CN.

Kinetic Studies. The rate of reaction of **4** with acetylenes was determined by UV/vis spectroscopy by following the increase in absorbance at 300 nm due to the formation of the oxametallacycles. The reactions were carried out under pseudo-first-order conditions using at least 10 equiv of alkyne and CH_3CN. Changes in UV/vis spectra during the reaction of **4** and 3,3-dimethyl-1-

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(30) For examples of other alkynyltin oxidative additions, see: (a) Anatova, A. B.; Kolobova, N. E.; Petrovsky, P. V.; Lokshin, B. V.; Obeyzuk, N. S. *J. Organomet. Chem.* **1977**, *137*, 55–67. (b) Cetinkaya, B.; Lappert, M. F.; McMeeking, J.; Palmer, D. E. *J. Chem. Soc., Dalton Trans.* **1973**, 1202–08.
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(32) Eisch, J. J.; Foxton, M. W. *J. Org. Chem.* **1971**, *36*, 3520–26.

Table V. First-Order Rate Constants for the Reaction of **4** with Acetylenes

3,3-Dimethyl-1-butyne Kinetics	[**4**] = 3.4×10^{-4} M
$[CH_3CN]/[t\text{-BuC}{\equiv}CH]$	k_{obs}[a], s^{-1}
0.034	7.91×10^{-5}
0.143	1.31×10^{-4}
0.167	1.57×10^{-4}
0.200	2.56×10^{-4}
0.250	3.10×10^{-4}
0.333	3.85×10^{-4}
0.500	5.40×10^{-4}
0.750	6.37×10^{-4}
1.00	7.52×10^{-4}
1.50	8.35×10^{-4}
2.00	9.16×10^{-4}
3.00	1.64×10^{-3}
Methyl Propynoate Kinetics	[**4**] = 3.09×10^{-4} M
$[CH_3CN]/[HC{\equiv}CCO_2CH_3]$	k_{obs}[a], s^{-1}
0.010	1.09×10^{-3}
0.013	9.62×10^{-4}
0.017	9.09×10^{-4}
0.027	7.49×10^{-4}
0.046	4.84×10^{-4}
0.067	3.28×10^{-4}
0.134	1.96×10^{-4}
0.268	9.74×10^{-5}
1-Nonyne Kinetics	[**4**] = 3.54×10^{-4} M
$[CH_3CN]/[HC{\equiv}C(CH_2)_6CH_3]$	k_{obs}[a], s^{-1}
0.035	2.06×10^{-3}
0.046	1.74×10^{-3}
0.069	1.43×10^{-3}
0.092	1.21×10^{-3}
0.168	1.12×10^{-3}
0.224	8.39×10^{-4}
0.335	7.16×10^{-4}
0.671	3.72×10^{-4}
1.34	2.05×10^{-4}
1-Nonyne-1-*d* Kinetics	[**4**] = 3.41×10^{-4} M
$[CH_3CN]/[DC{\equiv}C(CH_2)_6CH_3]$	k_{obs}[a], s^{-1}
0.036	1.38×10^{-3}
0.048	1.20×10^{-3}
0.072	1.01×10^{-3}
0.096	8.00×10^{-4}
0.134	6.36×10^{-4}
0.204	4.72×10^{-4}
0.272	3.54×10^{-4}
0.408	2.46×10^{-4}
0.817	1.38×10^{-4}
1.63	7.62×10^{-5}

[a] All values ±10%.

Table VI. Extrapolated Rate Constants from Kinetic Studies

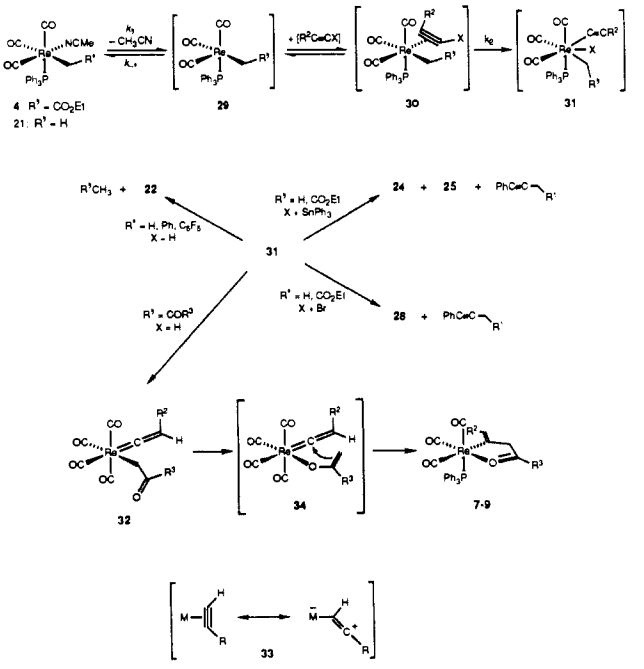
alkyne	k_1,[a] s^{-1}	k_1/k_2[a]
3,3-dimethyl-1-butyne	2.2×10^{-3}	8.4
methyl propynoate	2.0×10^{-3}	75.6
1-nonyne	2.4×10^{-3}	8.0
1-nonyne-*1-d*	1.9×10^{-3}	14.4

[a] All values ±10%.

butyne were monitored, and the accompanying pseudo-first-order plot of ln $(A_\infty - A_t)$ versus time gave the pseudo-first-order rate constant k_{obs}. The values of k_{obs} for a range of concentrations of 3,3-dimethyl-1-butyne at constant concentrations of **4** and CH_3CN are shown in Table V. A plot of $1/k_{obs}$ versus $[CH_3CN]/[HC{\equiv}CCMe_3]$ was linear, as shown in Figure 4.

A similar kinetic study was performed with methyl propynoate. Once again saturation behavior was observed, along with a good linear dependence of $1/k_{obs}$ versus $[CH_3CN]/[HC{\equiv}CCO_2Me]$ (Figure 4). The intercept of $k_1 = 2.2 \times 10^{-3}$ s^{-1} (Table VI) is identical within experimental error to that measured for 3,3-dimethyl-1-butyne.

Scheme VIII



Discussion of Alkyne-Insertion Mechanism. The kinetic data discussed above are consistent with a mechanism involving reversible dissociation of CH_3CN from **4**, to form an unsaturated intermediate **29** ($R^1 = CO_2Et$), followed by irreversible interaction of **29** with alkyne, as shown in Scheme VIII. Applying the steady-state approximation to **29** ($R^1 = CO_2Et$) yields the following rate law:

$$\frac{-d[\mathbf{4}]}{dt} = \frac{k_1k_2[R^2C{\equiv}CH][\mathbf{4}]}{k_2[R^2C{\equiv}CH] + k_{-1}[CH_3CN]} = k_{obs}[\mathbf{4}]$$

$$k_{obs} = \frac{k_1k_2[R^2C{\equiv}CH]}{k_2[R^2C{\equiv}CH] + k_{-1}[CH_3CN]}$$

$$\frac{1}{k_{obs}} = \frac{1}{k_1} + \frac{k_{-1}}{k_1k_2}\frac{[CH_3CN]}{[R^2C{\equiv}CH]}$$

In the case of $R^2C{\equiv}CH$ = 3,3-dimethyl-1-butyne, the mechanism is supported by the linear dependence of $1/k_{obs}$ with $[CH_3CN]/[R^2C{\equiv}CH]$, shown in Figure 4. The extrapolated value of k_1 from the inverse plot gives a value of 2.2×10^{-3} s^{-1} for the rate constant of CH_3CN dissociation from **4**. The slope of the inverse plot gives the selectivity of **29** ($R^1 = CO_2Et$) for either CH_3CN or 3,3-dimethyl-1-butyne; CH_3CN reacts 8.3 times faster with **29** ($R^1 = CO_2Et$) to reform **4**. The higher affinity of the unsaturated intermediate for CH_3CN is in accord with the observation that stable complexes with coordinated alkynes are not formed in this system.

The fact that the reaction of **4** with methyl propynoate gives analogous kinetic behavior and that identical values of k_1 are determined from the intercepts of the two inverse plots (Figure 4) provides strong evidence that the two alkynes react by analogous mechanisms. The rate constants k_1 and k_{-1} are independent of the nature of the alkyne. This allows us to combine the data from both studies to determine that $[k_2(t\text{-BuC}{\equiv}CH)/k_2(MeO_2CC{\equiv}CH)] = 9$. *Thus the intermediate* **29** *($R^1 = CO_2Et$) reacts faster with electron-rich alkynes than with electron-deficient alkynes.*

Isotope Effect. The initial formation of the exocyclic olefin products **7–9**, in which the hydrogen atom and the alkyl substituent reside on the same carbon, requires that rearrangement of the alkyne occurs at some time during the addition reaction. Also, internal alkynes (even activated alkynes such as $MeO_2CC{\equiv}CO_2Me$) fail to give addition products with **4** and lead only to decomposition. These results suggest involvement of the alkyne

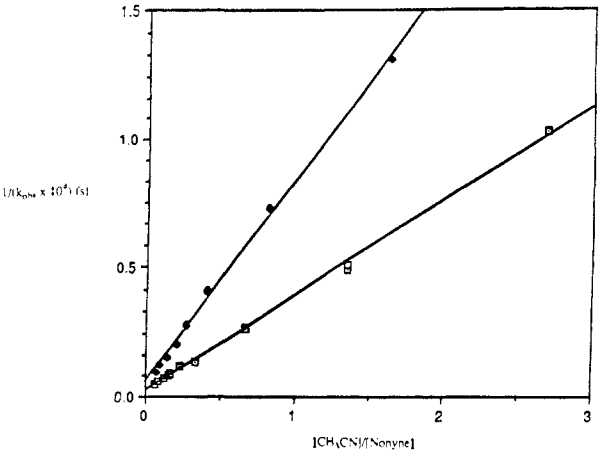


Figure 5. A plot of $1/(k_{obs} \times 10^4)$ versus [MeCN]/[nonyne]: (◇) 1-nonyne-*1-d*, $r^2 = 0.998$; (□) 1-nonyne, $r^2 = 0.998$.

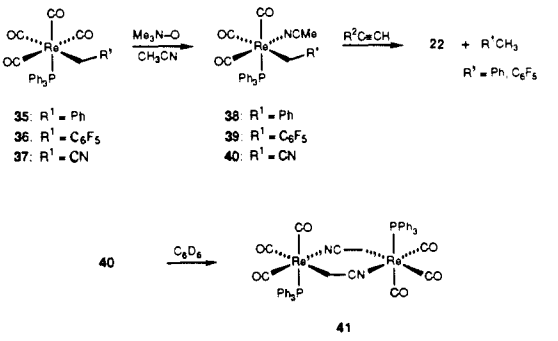
C–H bond in the overall reaction, possibly through a C–H oxidative addition process.

Additional evidence for alkyne C–H bond breaking in the k_2 step is given by the deuterium isotope effects observed in direct kinetic measurements using 1-nonyne and 1-nonyne-d_1. As with the experiments utilizing $Me_3CC{\equiv}CH$ and $MeO_2CC{\equiv}CH$, the deuterated alkynes give linear reciprocal plots. Comparison of the slopes of these plots (Figure 5, Table VI) allows us to compare the relative values of k_2 for reactivity of **29** with a deuterated and protiated alkyne. The value of $k_2^H/k_2^D = 2.0$ determined in this way demonstrates that C–H bond breakage is occurring during the rate-determining step of the reaction. Similarly, a competition study in which **4** was allowed to react with an excess (5 equiv each) of $PhC{\equiv}CH$ and $PhC{\equiv}CD$ gives directly a value of $k_2^H/k_2^D = 2.2$ for this alkyne. Again, this study compares the k_2 steps of the reactions with a deuterated and protiated alkyne. The similarity of these values for the two alkynes suggests that the k_2 step of the reaction is the same for both and that C–H bond breakage is occurring in the two systems.

With this information in hand we propose the overall mechanism outlined in Scheme VIII. Initially, reversible dissociation of CH_3CN from **4** occurs, followed by oxidative addition of rhenium across the C–X bond of the alkyne to afford the seven-coordinate rhenium[30,33] intermediate **31** ($R^1 = CO_2Et$, Me). This oxidative addition step may be preceded by coordination of the alkyne to form alkyne complex **30**. However, if this occurs, the alkyne coordination must be a reversible preequilibrium step because of the presence of a significant isotope effect. Although we have not collected kinetic or isotope data on the methyl rhenium analogue **21**, we assume its reactions begin by a similar sequence proceeding via intermediate **29** (R^1 = Me). Two reaction pathways are available for **31** ($R^1 = CO_2Et$): reductive elimination or rearrangement to vinylidene complex **32**. For the rhenium methyl derivative **31** (R^1 = X = H), reductive elimination of methane is fast, yielding the σ-alkylrhenium complex **22**.[34] When R^1 is an electron withdrawing group, the rhenium–carbon bond is strengthened; when X is either $SnPh_3$ or Br, the Re–X bond is strengthened. In these cases, the reductive elimination of R^1CH_2X is slower than that for methane liberation, and other processes can intervene.

Only in the case of $R^1 = COR^3$ and X = H, does rearrangement of **31** to the vinylidene species **32** occur. The formation of transition metal vinylidene complexes from terminal alkynes and unsaturated metal centers has become an increasingly common

Scheme IX



mode of reactivity.[35] The exact mechanism of the rearrangement is unknown but has been proposed to involve either C–H oxidative addition or a zwitterionic η^1-alkyne complex such as **33**. Even though ab initio calculations predict that the reaction pathway proceeding through the zwitterionic intermediate **33** is of lower energy,[36] the reactions of the rhenium enolate **4** and the rhenium methyl complex **21** with $PhC{\equiv}CX$ (in which a Re—X bond is formed) and the reaction of **21** with $RC{\equiv}CH$ (in which a Re—$C{\equiv}CR$ bond is formed) suggest that oxidative addition of the terminal alkyne linkage across the rhenium center can occur. Our kinetic isotope effects are consistent with either mechanism and cannot distinguish between the two. Coupling of the enolate carbon and the α-carbon of the vinylidene followed by coordination of the carbonyl oxygen leads to the exocyclic addition products **7–9**.

The relative reactivity of unsaturated intermediate **29** with different terminal alkynes is unusual. The more facile reaction of the electron-rich alkyne does not correlate with the expected acidities of the alkynyl C–H bonds,[37] disfavoring a mechanism in which the alkyne acts as an acid and transfers a proton to the metal center. In contrast to our observations, previous reports of alkyne C–H oxidative addition to square planar Ir(I) complexes show that alkyl propionates react to form σ-acetylides,[38] while no net reaction is observed with alkyl substituted alkynes. The earlier authors suggested that this may be a thermodynamic rather than a kinetic effect.[38a] The differing kinetic reactivity in our system may be caused by different K_{eq} values in a reversible precoordination of the alkyne to the rhenium center preceding C–H bond breakage. If this is rapid and reversible, incorporation of this additional step in this mechanism gives a rate law which is kinetically indistinguishable from that derived above. To our knowledge, no neutral η^2-alkyne complexes of rhenium(I) are known except for those containing cyclopentadienyl ligands, and so we cannot say whether the more electron-rich triple bond of 3,3-dimethyl-1-butyne should be a better ligand for the rhenium center. To the best of our knowledge, there have been no other studies of the relative C–H activation reactivities of different alkynes with transition-metal centers.

The exact nature of the enolate/vinylidene carbon–carbon coupling has not been determined. It could occur by direct migratory insertion of enolate carbon to the vinylidene, or through oxygen-bound enolate **34**. While there is no direct evidence for **34**, it is an attractive intermediate for several reasons. *Most*

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(34) The σ-acetylide complexes are formed for all terminal alkynes tried except for methyl propynoate. The structure of this product will be reported in a subsequent publication.

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significantly, the only electron-withdrawing (EWG) substituents on the rhenium-bound alkyl group that give successful carbon—carbon bond forming reactions with 1-alkynes are those that contain a C=O functionality. Other EWGs, such as Ph and C_6F_5 (complexes **38–39**), exhibit a reactivity similar to that of the methyl complex **21**, yielding toluene or $C_6F_5CH_3$, respectively, but at slower rates than **21** (Scheme IX). The nitrile enolate **40**[10] does not interact with 1-alkynes, but instead gives a dimeric product **41** upon dissociation of CH_3CN.

Intervention of the O-bound enolate **34** also provides an explanation for the interesting stereochemical course of the coupling reaction, which leads to the thermodynamically less stable (presumably sterically hindered) *Z* isomers of exocyclic metallacycles **7–9** as kinetic products. As illustrated in Scheme VIII, this stereochemistry is consistent with the enolate carbon in **34** adding to the least hindered face of the vinylidene. Addition of carbon nucleophiles to transition metal vinylidenes is well documented,[35g] especially for cationic $Cp(CO)(L)Fe{=}C{=}CR_2$[39] derivatives. Stereochemical results analogous to ours have been obtained by Reger and co-workers in the addition of higher-order cuprates to unsymmetrical iron vinylidenes.[39b]

Finally, unlike the fairly common migratory insertion reactions of coordinated CO, alkyl migrations to coordinated carbenes and related species are uncommon.[40] These facts, along with the observation that EWG's normally retard the rate of migratory insertion of transition metal alkyl complexes,[41] suggest that the coupling reaction between the enolate and vinylidene fragment occurs through nucleophilic O-bound enolate **34**. Evidence for the nucleophilic nature of oxygen-bound transition metal enolates has been advanced in several instances.[42]

Summary and Conclusions

Labile derivatives of the Ph_3P-substituted rhenium enolates react rapidly with terminal alkynes to give rhenium oxametallacycles. The addition occurs such that the terminal carbon of the alkyne is bound to the metal and a new bond is formed between this carbon and the enolate carbon. The initial chelated β,γ-carbonyl compounds are formed stereoselectively, with the less stable *Z* isomer predominating. These exocyclic products are generally unstable toward rearrangement to the corresponding endocyclic isomers and, except in one instance, cannot be isolated as pure compounds. Treatment of the exocyclic products with base affords the endocyclic isomers in high yield. This exo–endo isomerization has been examined by using deuterium-labeling crossover experiments and was found to occur through an *intramolecular* base-catalyzed 1,3-hydrogen transfer. Additional labeling experiments indicate that the transfer occurs in a stereoselective manner on the face anti to the bulky Ph_3P ligand.

Treatment of the endo oxametallacycles with $NaOMe/CD_3OD$ results in the stereospecific incorporation of only one deuterium in the γ-position of the unsaturated carbonyl system. This exchange reaction suggests that deprotonation occurs from one face, and that only one enolate geometry is formed upon deprotonation. An indirect method was used to determine that the more thermodynamically stable *E* enolate is formed in the exchange reaction. Addition of acid to the endo oxametallacycles affords a mixture of α,β- and β,γ-unsaturated esters through a protonation/elimination sequence.

The mechanism of the alkyne addition reaction has been examined and is proposed to proceed through initial dissociation of the nitrile ligand, followed by an oxidative addition of the terminal alkyne C–H bond to give a key seven-coordinate intermediate. Rearrangement of this intermediate to a reactive vinylidene intermediate and coupling with the enolate fragment affords the observed products. Kinetic studies of this reaction indicate that the rate-limiting step involves reversible dissociation of the nitrile ligand, followed by irreversible alkyne addition. Electron-rich alkynes (3,3-dimethyl-1-butyne) were found to react faster than electron-deficient alkynes. Evidence for the proposed mechanism is provided by an observed primary kinetic isotope effect (k_H/k_D = 2.2), the formation of σ-acetylides upon treatment of a related rhenium methyl complex with 1-alkynes, and the formation of Re—X (X = $SnPh_3$, Br) bonds in the reaction of the enolates or the methyl complex with RC≡CX.

Experimental Section

General. All manipulations involving air-sensitive material were performed under nitrogen or argon by using Schlenk or vacuum line techniques[43] or in a Vacuum Atmospheres HE 43-2 inert-atmosphere glovebox equipped with an HE-493 Dri-Train inert gas purifier.

All solvents were thoroughly dried and degassed before use in all reactions. Tetrahydrofuran (THF) was distilled from Na/benzophenone under a nitrogen atmosphere. Acetonitrile (CH_3CN), benzene (C_6H_6), pentane, and dichloromethane (CH_2Cl_2) were distilled from CaH_2 under a nitrogen atmosphere. Other solvents were reagent grade and were used without purification. All NMR solvents were dried and transferred under vacuum before use: benzene-d_6 (C_6D_6) was stirred over Na/benzophenone; chloroform-*d* ($CDCl_3$) and methylene chloride-d_2 were stirred over P_2O_5. The $Re_2(CO)_{10}$ was used as received from Strem Chemicals; *cis*-$(Ph_3P)(CO)_4ReBr$ was prepared as previously described.[10] Benzyl chloride (Aldrich) was distilled and degassed before use. Methanesulfonyl chloride (Aldrich) was distilled before use. Acetic acid-d_4, 2,3,4,5,6-pentafluorobenzyl alcohol, 37% DCl in D_2O, 1,8-diazabicyclo-[5.4.0]undec-7-ene (DBU), *N*-chlorosuccinimide, and 1.0 M $LiEt_3BH$ in THF were used as received from Aldrich Chemicals. Triphenyltin chloride was used as received from Alfa. Anhydrous trimethylamine *N*-oxide (Me_3NO) was prepared from $Me_3NO{\cdot}2H_2O$ (Aldrich) by azeotropic removal of H_2O with dimethylformamide.[44] Acetylene (Liquid Carbonic) was purified by passing the gas stream through saturated aqueous $NaHSO_3$ and 96% H_2SO_4 and solid NaOH before use. Propyne (Liquid Carbonic) and 1-butyne (Farchan) were used as received. Phenylacetylene, ethynyltrimethylsilane, and ethyl propynoate were obtained from Aldrich; 3-methyl-1-butyne and 3,3-dimethyl-1-butyne were obtained from Farchan. All liquid alkynes were dried over CaH_2, distilled, and/or transferred under vacuum and then degassed before use. Other reagents were used as received.

Solution infrared spectra were recorded in 0.1 mm NaCl sealed cells; IR data are reported as (solvent) cm^{-1} (intensity: vs, very strong; s, strong; m, medium; w, weak), and are calibrated with the 1601-cm^{-1} band of polystyrene. UV/vis spectra were recorded with a Hewlett Packard Model 8450 UV/vis spectrometer in 1.00-cm quartz cells fused to Kontes Vacuum stopcocks. NMR spectra were obtained on instruments constructed by Mr. Rudi Nunlist in the UC Berkeley NMR laboratory that incorporates Cryosystems, Inc. magnets and Nicolet data systems, or on Bruker AM-400 and AM-500 instruments. Data for complex ^1H NMR spin systems are reported in the manner suggested by Jackman and Sternhell.[45] When necessary, coupling constants for these systems were obtained through simulation of the spectra. ^{13}C NMR spectra are referenced by using the ^{13}C resonance of the solvent as an internal standard (C_6D_6, 128.0; $CDCl_3$, 77.0; CD_2Cl_2, 53.8 ppm); all ^{13}C resonances are singlets unless otherwise noted. The ^{31}P NMR (121.5 or 82 MHz) spectra were recorded with proton decoupling and are reported in units of parts per million (δ) downfield from external 85% H_3PO_4. *J* values for all NMR data are reported in hertz. Elemental analyses were carried out by the UC Berkeley College of Chemistry elemental analysis facility. Mass spectra were obtained on AEI MS-12, Finnigan 4000, or Kratos MS-50 spectrometers. Electron-impact mass spectra are reported as the most intense peak of the isotope envelope. Melting points are reported uncorrected.

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Flash column chromatographic separations by the method of Still, Kahn, and Mitra[46] were carried out on silica gel under nitrogen pressure. Solvents for chromatography were reagent grade (Fisher) and were not purified before use.

Ethyl 2-Chloro-2-deuterioacetate. A 25-mL, round-bottomed flask was flushed with Ar, and then 2.50 mL (3.20 g, 20.4 mmol) of ethyl dichloroacetate[47] and 6.35 mL (6.99 g, 23.9 mmol) of tri-*n*-butyltin deuteride[48] were added sequentially by syringe. After a brief induction period, the temperature of the mixture increased slightly and then gradually subsided. After 24 h at ambient temperature, the reaction mixture was dissolved in 30 mL of Et_2O, and this solution was stirred with 30 mL of 2 M aqueous KF for 3 h. The precipitated tri-*n*-butyltin fluoride was filtered and the Et_2O layer was separated, dried over $MgSO_4$, and evaporated (evaporation flask cooled at 0 °C). Vacuum transfer (25 °C, static vacuum) of the residue afforded 2.16 g (86%) of a clear liquid that was >95 atom % D by ^1H NMR. IR ($CHCl_3$): 1757 (s) cm^{-1}. ^1H NMR (250 MHz, $CDCl_3$): δ 1.31 (t, 3, J = 7.1), 4.04 (1:1:1 triplet, 1, J_{HD} = 2.2), 4.26 (q, 2, J = 7.1). ^{13}C NMR (75.5 MHz, $CDCl_3$): δ 13.90, 40.34 (quintet, J_{DC} = 23.2), 62.06, 167.09. Anal. Calcd for $C_4H_6ClDO_2$: C, 38.88; H, 5.71; Cl, 28.69. Found: C, 38.72; H, 5.55; Cl, 28.80.

Ethyl 2-Chloro-2,2-Dideuterioacetate. This procedure is based on that of Harpp and co-workers.[49] A 100-mL, round-bottomed flask containing 5.7 mL (6.48 g, 0.10 mol) of acetic acid-d_4 and 9.0 mL (14.7 g, 0.12 mol) of thionyl chloride was fitted with a water-cooled condenser and was heated at 70 °C for 0.5 h. After this time the evolution of HCl and SO_2 had ceased, and a drying tube containing $CaSO_4$ was placed on the condenser, and the reaction mixture was allowed to cool to ambient temperature. The mixture was treated with 20.0 g (0.15 mol) of *N*-chlorosuccinimide, 3.0 mL (4.89 g, 0.04 mol) of $SOCl_2$, and 7 drops of 37% DCl in D_2O and heated at 85 °C for 2 h. The mixture was allowed to cool to room temperature, the flask was placed in an ice–water bath, 23.5 mL (18.5 g; 0.40 mol) of 100% EtOH was added slowly (*N.B.* vigorous gas evolution), and the mixture was stirred an additional 0.5 h. The liquid was dissolved in 20 mL of pentane and the organic phase was washed repeatedly with saturated aqueous $NaHCO_3$ until CO_2 evolution had ceased and the aqueous layer remained basic to litmus. The organic layer was dried over $MgSO_4$, and the pentane evaporated (evaporation flask cooled at 0 °C). Distillation of this residue at atmospheric pressure, collecting only the second of three fractions, gave 2.70 g (22%) of a clear liquid, bp 138–42 °C, that was >95 atom % D by ^1H NMR. IR ($CHCl_3$): 1759 (s) cm^{-1}. ^1H NMR (250 MHz, $CDCl_3$): δ 1.31 (t, 3, J = 7.1), 4.26 (q, 2, J = 7.1). ^{13}C NMR (75.5 MHz, $CDCl_3$): δ 13.90, 40.34 (quintet, J_{DC} = 23.2), 62.06, 167.09. Anal. Calcd for $C_4H_5ClD_2O_2$: C, 38.88; H, 5.71; Cl, 28.69. Found: C, 38.72; H, 5.55; Cl, 28.80.

2,3,4,5,6-Pentafluoro-2′-[(methylsulfonyl)oxy]toluene. To a stirring solution of 1.99 g (10.1 mmol) of 2,3,4,5,6-pentafluorobenzyl alcohol and 2.10 mL (1.53 g, 15.1 mmol) of Et_3N in 50 mL of CH_2Cl_2 at −15 °C (ethylene glycol/CO_2 bath) was added 860 μL (1.27 g, 11.1 mmol) of methanesulfonyl chloride by syringe over 10 min. After 15 min, the heterogeneous mixture was transferred to a separatory funnel with an additional 10 mL of CH_2Cl_2. The organic layer was washed successively with 25 mL each of ice-cold H_2O, 5% aqueous HCl, saturated aqueous $NaHCO_3$, and saturated aqueous NaCl, dried over $MgSO_4$, and evaporated to give 2.70 g (97%) of a white, crystalline solid, mp 72–73 °C. IR ($CHCl_3$): 1528 (s), 1512 (vs), 1187 (s) cm^{-1}. ^1H NMR (250 MHz, $CDCl_3$): δ 3.09 (s, 3), 5.32 (s, 2). ^{13}C NMR (75.5 MHz, $CDCl_3$): δ 37.82, 57.24, 107.56 (dt, J_{FC} = 16.8, 4.4), 137.84 (dm, J_{FC} = 221.0), 142.46 (dm, J_{FC} = 248.8), 145.74 (dm, J_{FC} = 246.9). Anal. Calcd for $C_8H_5F_5O_3S$: C, 34.79; H, 1.82; S, 11.61. Found: C, 34.64; H, 1.82; S, 11.72.

***cis*-Tetracarbonyl(1-deuterio-2-ethoxy-2-oxoethyl)(triphenylphosphine)rhenium (1-d_1).** This material was prepared in an identical manner with that used for the undeuterated derivative.[10] Sequential reaction of 642 mg (1.00 mmol) of *cis*-$(Ph_3P)(CO)_4ReBr$ in 10 mL of THF with 0.2 M sodium naphthalenide (NaNp) in THF and 200 μL (230 mg, 1.86 mmol) of ethyl 2-chloro-2-deuterioacetate at −78 °C for 1 h and −20 °C for 12 h followed by the usual workup gave 1.24 g of an orange, semisolid residue. Purification of this residue by flash chromatography (97.5:2.5 CH_2Cl_2/Et_2O) afforded 480 mg (74%) of white, crystalline solid, mp 110–112 °C, that was >95 atom % D by ^1H NMR spectroscopy. Mass spectroscopy (EI, m/z 649 (M^+), 183 (base)) indicates the presence of 5% of **1**-d_0. IR ($CHCl_3$): 2100 (s), 2000 (sh), 1987 (vs), 1944 (s), 1669 (m) cm^{-1}. ^1H NMR (250 MHz, C_6D_6): δ 1.16 (t, 3, J = 7.1), 1.79 (d, 1, J_{PH} = 6.8), 4.21 (q, 2, J = 7.1), 6.91–7.01 (m, 9), 7.43–7.50 (m, 6). Anal. Calcd for $C_{26}H_{21}DO_6PRe$: C, 48.14; H, 3.42. Found: C, 48.16; H, 3.46.

***cis*-Tetracarbonyl(1,1-dideuterio-2-ethoxy-2-oxoethyl)(triphenylphosphine)rhenium (1-d_2).** This material was prepared in an identical manner with that used for the undeuterated derivative.[10] Sequential reaction of 962 mg (1.50 mmol) of *cis*-$(Ph_3P)(CO)_4ReBr$ in 10 mL of THF with 0.2 M NaNp in THF and 213 mg (1.71 mmol) of ethyl 2-chloro-2,2-dideuterioacetate at −78 °C for 1 h and −20 °C for 12 h followed by the usual workup gave 1.37 g of an orange, semisolid residue. Purification of this residue by flash chromatography (98:2 CH_2Cl_2/Et_2O) afforded 761 mg of a white solid. Recrystallization of this material from Et_2O at −20 °C gave, in two crops, 612 and 62 mg (69%) of a white, crystalline solid, mp 114–115 °C, that was >95 atom % D by ^1H NMR spectroscopy. Mass spectroscopy (EI, m/z 650 (M^+), 183 (base)) indicates the presence of 5% of **1**-d_1 and no **1**-d_0. IR ($CHCl_3$): 2100 (s), 2003 (sh), 1984 (vs), 1945 (s), 1670 (m) cm^{-1}. ^1H NMR (250 MHz, C_6D_6): δ 1.16 (t, 3, J = 7.1), 4.21 (q, 2, J = 7.1), 6.91–7.01 (m, 9), 7.43–7.50 (m, 6). Anal. Calcd for $C_{26}H_{20}D_2O_6PRe$: C, 48.07; H, 3.41. Found: C, 48.17; H, 3.51.

***fac*-(Acetonitrile)tricarbonyl(1,1-dideuterio-2-ethoxy-2-oxoethyl)(triphenylphosphine)rhenium (4-d_1).** This material was prepared in a manner identical with that used for the undeuterated derivative.[10] Reaction of 324 mg (0.50 mmol) of **1**-d_1 in 20 mL of CH_3CN with 39 mg (0.52 mmol) of Me_3NO in 5 mL of CH_3CN gave 310 mg (94%) of a off-white solid, dec pt >130 °C, as a 1:1 mixture of diastereomers that were not separated. IR (CH_3CN): 2033 (s), 1924 (s), 1893 (s), 1672 (m) cm^{-1}. ^1H NMR (250 MHz, C_6D_6): δ 0.59 (d, 3, J_{PH} = 0.4), 1.29 (t, 3, J = 7.1), 1.45 (d, 1, isomer A, J_{PH} = 8.0), 2.32 (d, 1, isomer B, J_{PH} = 5.7), 4.30 (q, 2, J = 7.1), 6.87–7.01 (m, 9), 7.62–7.69 (m, 6). Anal. Calcd for $C_{27}H_{24}DNO_5PRe$: C, 49.01; H, 3.81; N, 2.12. Found: C, 48.83; H, 3.83; N, 1.99.

***fac*-(Acetonitrile)tricarbonyl(1,1-dideuterio-2-ethoxy-2-oxoethyl)(triphenylphosphine)rhenium (4-d_2).** This material was prepared in an identical manner with that used for the undeuterated derivative.[10] Reaction of 325 mg (0.50 mmol) of **1**-d_2 in 13 mL of CH_3CN with 39 mg (0.52 mmol) of Me_3NO in 4 mL of CH_3CN gave 315 mg (95%) of an off-white solid. IR (CH_3CN): 2030 (s), 1926 (s), 1895 (s), 1673 (m) cm^{-1}. ^1H NMR (250 MHz, C_6D_6): δ 0.54 (d, 3, J_{PH} = 1.2), 1.28 (t, 3, J = 7.1), 4.30 (q, 2, J = 7.1), 6.87–7.01 (m, 9), 7.62–7.69 (m, 6). Anal. Calcd for $C_{27}H_{23}D_2NO_5PRe$: C, 49.01; H, 3.81; N, 2.12. Found: C, 48.83; H, 3.83; N, 1.99.

***fac*-Tricarbonyl[1-ethoxy-5,5-dimethyl-1-oxo-(*Z*)-3-hexenyl-C^3,O](triphenylphosphine)rhenium (7e).** A resealable pressure bottle was charged with a solution of 132 mg (0.20 mmol) of **4** and 50 μL (33 mg, 0.40 mmol) of 3,3-dimethyl-1-butyne in 5.0 mL of C_6H_6. The bottle was sealed and then placed in an oil bath maintained at 55 °C for 1 h. The bottle was opened, the pale yellow solution was passed with a positive pressure of N_2 through a 5 × 1.5 cm column of flash silica gel (premoistened with C_6H_6), and then the column was eluted with 10 mL of C_6H_6. The combined eluate was evaporated with a rotary evaporator to give 109 mg (78%) of pale yellow solid, mp 145–147 °C. IR ($CHCl_3$): 2025 (s), 1921 (s), 1879 (s), 1630 (m) cm^{-1}. ^1H NMR (250 MHz, C_6D_6): δ 0.51 (t, 3, J = 7.2), 1.88 (s, 9), 3.05 (AB, 2, J = −19.8, ν_{AB} = 85.7), 3.22 (ABX_3, 2, J = −10.8, 7.2, ν_{AB} = 31.9), 6.72 (br s, 1), 6.97–7.01 (m, 9), 7.62–7.69 (m, 6). ^{13}C NMR (75.5 MHz, $CDCl_3$): δ 13.63, 31.79, 34.10, 56.05 (d, J = 3.2), 64.07, 128.27 (d, J = 9.6), 130.19 (d, J = 2.0), 132.77 (d, J = 41.2), 133.97 (d, J = 10.9), 149.95 (d, J = 2.6), 152.98 (d, J = 11.3), 189.96, 195.22 (d, J = 68.3), 197.24 (d, J = 6.9), 201.05 (d, J = 7.8). ^{31}P NMR (82 MHz; $CDCl_3$): δ 18.0. Anal. Calcd for $C_{31}H_{32}O_5PRe$: C, 53.06; H, 4.60. Found: C, 53.06; H, 4.59.

General Procedure for the Preparation of Insertion Products 10a–f, 11a, 12. Example Procedure: *fac*-Tricarbonyl(1-ethoxy-1-oxo-2-butenyl-C^3,O)(triphenylphosphine)rhenium (10a). A solution of 66 mg (0.10 mmol) of **4** in 5.0 mL of C_6H_6 was placed in a resealable pressure bottle containing a stirring bar. The bottle was sealed and removed from the glovebox. The bottle was opened under a stream of acetylene admitted by a 22-gauge syringe needle. The needle was then placed in the solution, and acetylene was bubbled through the solution for 5 min. The bottle was resealed, and the mixture was heated at 55 °C with stirring for 1 h. The solution was allowed to cool to ambient temperature and 15 μL (15 mg, 0.10 mmol) of DBU was added. After 0.5 h, the pale yellow solution was passed with a positive pressure of N_2 through a 5 × 1.5 cm column of flash silica gel (premoistened with C_6H_6), and then the column was eluted with 10 mL of C_6H_6. The combined eluate was evaporated in vacuo to give 54 mg (83%) of a pale yellow solid, mp 141–142 °C. IR ($CHCl_3$): 2035 (s), 1928 (s), 1887 (s), 1572 (m) cm^{-1}. ^1H NMR (250

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MHz, C_6D_6): δ 0.69 (t, 3, J = 7.1), 2.44 (s, 3), 3.54 (ABX_3, 2, J = −10.6, 7.1, ν_{AB} = 36.4), 6.47 (m, 1), 6.94–6.99 (m, 9), 7.52–7.60 (m, 6). ^{13}C NMR (75.5 MHz, $CDCl_3$): δ 14.12, 34.66 (d, J = 1.6), 61.98, 121.50 (d, J = 1.7), 128.16 (d, J = 9.7), 130.13 (d, J = 43.3), 133.87 (d, J = 11.0), 185.72, 192.04 (d, J = 59.9), 198.73 (d, J = 8.8), 199.0 (d, J = 7.7), 238.72 (d, J = 9.9). ^{31}P NMR (82 MHz, $CDCl_3$): δ 23.7. Anal. Calcd for $C_{27}H_{24}NO_5PRe$: C, 50.23; H, 3.75. Found: C, 50.48; H, 3.83.

***fac*-Tricarbonyl(1-ethoxy-1-oxo-2-pentenyl-C^3,O)(triphenylphosphine)rhenium (10b).** Reaction of 67 mg (0.10 mmol) of **4** in 4.0 mL of C_6H_6 with propyne (bubbled through the solution for 30 s) using the foregoing method gave upon evaporation of solvent 62 mg (94%) of pale yellow solid, mp 150–151 °C. IR ($CHCl_3$): 2022 (s), 1923 (s), 1881 (s), 1568 (m) cm^{-1}. ^1H NMR (250 MHz, C_6D_6): δ 0.70 (t, 3, J = 7.1), 1.08 (t, 3, J = 7.3), 2.63 (ABX_3, 2, J = −14.7, 7.3, ν_{AB} = 43.8), 3.56 (ABX_3, 2, J = −10.7, 7.1, ν_{AB} = 35.1), 6.52 (br s, 1), 6.94–6.97 (m, 9), 7.50–7.58 (m, 6). ^{13}C NMR (75.5 MHz, $CDCl_3$): δ 13.67, 14.12, 40.69, 62.00, 118.66 (d, J = 1.6), 128.16 (d, J = 9.7), 130.11 (d, J = 1.7), 131.80 (d, J = 43.1), 133.87 (d, J = 11.0), 186.08, 192.21 (d, J = 60.4), 198.59 (d, J = 8.9), 199.10 (d, J = 7.7), 244.02 (d, J = 9.8). ^{31}P NMR (82 MHz, $CDCl_3$): δ 23.6. Anal. Calcd for $C_{28}H_{26}O_5PRe$: C, 50.98; H, 3.97. Found: C, 51.00; H, 3.96.

***fac*-Tricarbonyl(1-ethoxy-1-oxo-2-hexenyl-C^3,O)(triphenylphosphine)rhenium (10c).** Reaction of 66 mg (0.10 mmol) of **4** in 5.0 mL of C_6H_6 with 1-butyne (bubbled through the solution for 30 s) using the foregoing method gave upon evaporation of solvent a white, semi-solid residue. Trituration of this residue with pentane yielded a solid that was collected on a fritted disc and dried in vacuo to give 33 mg of ivory colored powder, mp 139–140 °C. Concentration of the filtrate gave an additional 8 mg of product, for an overall yield of 41 mg (61%). IR ($CHCl_3$): 2025 (s), 1926 (s), 1883 (s), 1572 (m) cm^{-1}. ^1H NMR (250 MHz, C_6D_6): δ 0.70 (t, 3, J = 7.1), 0.87 (t, 3, J = 7.3), 1.67 ($ABMNX_3$, 2, J = −14, 5, 9, 7.3, ν_{MN} = 72), 2.62 ($ABMNX_3$, 2, J = −14, 5, 9, ν_{AB} = 76), 3.55 (ABX_3, 2, J = −10.7, 7.1, ν_{AB} = 34.1), 6.55 (t, 1, J = 0.9), 6.94–6.98 (m, 9), 7.52–7.60 (m, 6). ^{13}C NMR (75.5 MHz, $CDCl_3$): δ 14.12, 14.15, 22.22, 50.01, 61.99, 119.70 (d, J = 1.5), 128.15 (d, J = 9.7), 130.10 (d, J = 1.0), 131.83 (d, J = 43.1), 133.89 (d, J = 11.0), 185.94, 192.22 (d, J = 60.4), 198.52 (d, J = 8.9), 199.08 (d, J = 7.6), 242.87 (d, J = 9.7). ^{31}P NMR (121.5 MHz, $CDCl_3$): δ 23.6. Anal. Calcd for $C_{29}H_{28}O_5PRe$: C, 51.70; H, 4.19. Found: C, 51.66; H, 4.15.

***fac*-Tricarbonyl(1-ethoxy-5-methyl-1-oxo-2-hexenyl-C^3,O)(triphenylphosphine)rhenium (10d).** Reaction of 66 mg (0.10 mmol) of **4** in 5.0 mL of C_6H_6 with 75 μL (50 mg, 0.73 mmol) of 3-methyl-1-butyne (added by syringe) using the foregoing method gave upon evaporation of solvent 63 mg of a semisolid residue. Addition of ~0.5 mL of pentane and cooling at −20 °C for 8 h resulted in the formation of a solid that was collected on a fritted disk, washed with a minimum of pentane, and dried in vacuo to give 50 mg (72%) of a pale yellow solid, mp 143–144 °C. IR ($CHCl_3$): 2026 (s), 1924 (s), 1885 (s), 1573 (m) cm^{-1}. ^1H NMR (250 MHz, C_6D_6): δ 0.70 (t, 3, J = 7.1), 0.91 and 1.03 (2 d, 3, J = 6.4), 2.41 ($ABMX_6$, 1, J_{AM} = 2.8, J_{BM} = 9.7, J_{MX} = 6.4), 2.49 ($ABMX_6$, 2, J = −11.9, 2.8, 9.7, ν_{AB} = 105.5), 3.55 (ABX_3, 2, J = −10.7, 7.1, ν_{AB} = 33.4), 6.54 (d, 1, J = 0.9), 6.94–6.97 (m, 9), 7.53–7.61 (m, 6). ^{13}C NMR (75.5 MHz, $CDCl_3$): δ 14.12, 22.13, 24.04, 27.684, 57.33, 62.01, 121.23 (d, J = 1.9), 128.16 (d, J = 9.6), 130.12, 131.80 (d, J = 43.0), 133.92 (d, J = 10.9), 185.76, 192.26 (d, J = 60.3), 198.33 (d, J = 9.0), 199.11 (d, J = 7.6), 242.49 (d, J = 9.6). ^{31}P NMR (121.5 MHz, $CDCl_3$): δ 23.4. Anal. Calcd for $C_{30}H_{30}O_5PRe$: C, 52.39; H, 4.40. Found: C, 52.18; H, 4.42.

***fac*-Tricarbonyl(1-ethoxy-5,5-dimethyl-1-oxo-2-hexenyl-C^3,O)(triphenylphosphine)rhenium (10e).** Reaction of 67 mg (0.10 mmol) of **4** in 4.0 mL of C_6H_6 with 25 μL (17 mg; 0.20 mmol) of 3,3-dimethyl-1-butyne (added by syringe) using the foregoing method gave upon evaporation of solvent a pale yellow glass. Addition of pentane induced crystallization, and the resulting solid was collected on a fritted disk, washed with a minimum of pentane, and dried in vacuo to give 55 mg (79%) of pale yellow solid, mp 151–152 °C. IR ($CHCl_3$): 2021 (s), 1920 (s), 1884 (s), 1568 (m) cm^{-1}. ^1H NMR (250 MHz, C_6D_6): δ 0.70 (t, 3, J = 7.1), 1.14 (s, 9), 2.70 (AB, 2, J = −12.0, ν_{AB} = 130.4), 3.54 (ABX_3, 2, J = −10.7, 7.1, ν_{AB} = 31.1), 6.60 (d, 1, J = 1.7), 6.96–7.00 (m, 9), 7.55–7.63 (m, 6). ^{13}C NMR (75.5 MHz, $CDCl_3$): δ 14.12, 30.91, 33.14, 60.10, 123.97 (d, J = 1.6), 128.17 (d, J = 9.7), 130.11 (d, J = 1.8), 131.85 (d, J = 42.8), 133.95 (d, J = 10.9), 185.30, 193.09 (d, J = 60.8), 197.96 (d, J = 9.5), 199.47 (d, J = 7.1), 241.51 (d, J = 10.0). ^{31}P NMR (82 MHz, $CDCl_3$): δ 22.9. Anal. Calcd for $C_{31}H_{32}O_5PRe \cdot (0.1\ C_5H_{12})$: C, 53.36; H, 4.72. Found: C, 53.53; H, 4.86. (Prolonged drying under high vacuum did not remove 0.1 equiv of pentane, which was confirmed quantitatively by ^1H NMR.)

***fac*-Tricarbonyl(1-ethoxy-1-oxo-4-phenyl-2-butenyl-C^3,O)(triphenylphosphine)rhenium (10f).** Reaction of 66 mg (0.10 mmol) of **4** in 4.0 mL of C_6H_6 with 25 μL (23 mg, 0.23 mmol) of phenylacetylene (added by syringe) using the foregoing method gave upon evaporation of solvent a yellow glass. Addition of ~1.0 mL of pentane and cooling at −20 °C for 8 h resulted in the formation of a solid that was collected on a fritted disk, washed with a minimum of pentane, and dried in vacuo to give 57 mg (79%) of pale yellow solid, mp 128–130 °C. IR (THF): 2028 (s), 1930 (s), 1892 (s), 1572 (m) cm^{-1}. ^1H NMR (250 MHz, C_6D_6): δ 0.63 (t, 3, J = 7.2), 3.44 (ABX_3, 2, J = −10.7, 7.2, ν_{AB} = 36.9), 4.02 (AB, 2, J = −15.6, ν_{AB} = 65.3), 6.37 (d, 1, J = 0.8), 6.94–7.02 (m, 9), 7.53–7.68 (m, 6). ^{13}C NMR (75.5 MHz, $CDCl_3$): δ 13.98, 53.73, 62.08, 120.76, 128.06, 128.28 (d, J = 9.8), 129.59, 130.21, 131.94 (d, J = 43.2), 133.88 (d, J = 11.0), 140.10, 185.96, 191.54 (d, J = 61.2), 198.46 (d, J = 8.0), 199.12 (d, J = 7.7), 238.62 (d, J = 9.5). ^{31}P NMR (82 MHz, $CDCl_3$): δ 23.3. MS (EI): m/z 722 (M^+), 183 (base). Anal. Calcd for $C_{33}H_{28}O_5PRe$: C, 54.92; H, 3.91. Found: C, 54.88; H, 3.97.

***fac*-Tricarbonyl[1-ethoxy-4-(trimethylsilyl)-1-oxo-2-butenyl-C^3,O]-(triphenylphosphine)rhenium (10g).** A solution of 67 mg (0.10 mmol) of **4** and 30 μL (21 mg, 0.21 mmol) of ethynyltrimethylsilane in 4.0 mL of C_6H_6 was placed in a resealable pressure bottle containing a stir bar. The bottle was sealed and removed from the glovebox, and the mixture was heated at 55 °C with stirring for 2 h. The solution was allowed to cool to ambient temperature and the solvent was evaporated in vacuo. The yellow residue was dissolved in a minimum of C_6H_6 and passed with a positive pressure of N_2 through a 5 × 1.5 cm column of flash silica gel (premoistened with C_6H_6), and then the column was eluted with 10 mL of C_6H_6. Evaporation of the combined eluate in vacuo gave a light yellow glass. Addition of pentane and cooling to −20 °C induced crystallization, and the resulting crystals were collected on a fritted disk, washed with pentane, and dried in vacuo to give 58 mg (81%) of pale yellow solid, mp 133–134 °C. IR ($CHCl_3$): 2030 (s), 1922 (s), 1883 (s), 1556 (m) cm^{-1}. ^1H NMR (250 MHz, C_6D_6): δ 0.24 (s, 9), 0.73 (t, 3, J = 7.2), 2.63 (AB, 2, J = −9.4, ν_{AB} = 29.2), 3.60 (ABX_3, 2, J = −10.8, 7.2, ν_{AB} = 26.4), 6.38 (d, 1, J = 1.6), 6.96–7.01 (m, 9), 7.56–7.64 (m, 6). ^{13}C NMR (51 MHz, $CDCl_3$): δ −0.36, 14.20, 43.76, 61.65, 119.00, 128.11 (d, J = 9.7), 130.11 (d, J = 1.6), 131.83 (d, J = 43.6), 134.01 (d, J = 10.9); 186.19, 193.18 (d, J = 63.5), 197.96 (d, J = 9.1) 199.38 (d, J = 7.4), 242.71 (d, J = 10.0). ^{31}P NMR (82 MHz, $CDCl_3$): δ 23.3. Anal. Calcd for $C_{30}H_{32}O_5PReSi \cdot (0.5\ C_6H_6)$: C, 52.37; H, 4.66. Found: C, 52.21; H, 4.54. (Compound **10g** crystallizes with 0.5 equiv of C_6H_6, as confirmed in the X-ray crystal structure; prolonged drying under high vacuum does not remove the C_6H_6).

***fac*-Tricarbonyl(1,5-diethoxy-1,5-dioxo-2-pentenyl-C^3,O)(triphenylphosphine)rhenium (10h).** A solution of 99 mg (0.15 mmol) of **4** and 30 μL (29 mg, 0.30 mmol) of ethyl propynoate in 4.0 mL of C_6H_6 was placed in a resealable pressure bottle containing a stirring bar. The bottle was sealed and removed from the glovebox, and the mixture was heated at 55 °C with stirring for 2 h. The solution was allowed to cool to ambient temperature, and the solvent was evaporated in vacuo. Purification of the crude material by flash chromatography (C_6H_6) gave 94 mg (87%) of pale yellow crystals, mp 127–128 °C. IR ($CHCl_3$): 2032 (s), 1932 (s), 1890 (s), 1727 (m), 1573 (m) cm^{-1}. ^1H NMR (250 MHz, C_6D_6): δ 0.65 (t, 3, J = 7.1), 1.01 (t, 3, J = 7.1), 3.47 (ABX_3, 2, J = −10.7, 7.1, ν_{AB} = 33.4), 3.62 (AB, 2, J = −15.2, ν_{AB} = 58.0), 4.03 (ABX_3, 2, J = −10.5, 7.1, ν_{AB} = 10.1), 6.75 (d, 1, J = 0.9), 6.94–7.02 (m, 9), 7.51–7.59 (m, 6). ^{13}C NMR (75.5 MHz, $CDCl_3$): δ 14.03, 14.22, 51.96, 60.49, 62.35, 122.58 (d, J = 1.8), 128.29 (d, J = 9.7), 130.23 (d, J = 1.9), 131.43 (d, J = 43.4), 133.80 (d, J = 11.0), 171.32, 185.60, 191.16 (d, J = 59.8), 198.10 (d, J = 9.1), 198.11 (d, J = 7.2), 227.44 (d, J = 10.3). ^{31}P NMR (82 MHz, $CDCl_3$): δ 23.3. Anal. Calcd for $C_{30}H_{28}O_7PRe$: C, 50.20; H, 3.93. Found: C, 50.40; H, 4.02.

***fac*-Tricarbonyl(1-ethoxy-5-methoxy-1,5-dioxo-2-pentenyl-C^3,O)-(triphenylphosphine)rhenium (10i).** A solution of 50 mg (0.076 mmol) of **4** and 11 μL of methyl propynoate in 3.0 mL of C_6H_6 was placed in a reseable pressure bottle. The bottle was sealed and removed from the glovebox and the mixture heated at 55 °C for 1.5 h. The solution was allowed to cool to ambient temperature and the solvent evaporated in vacuo. Purification of the crude material by flash chromatography (20:1 CH_2Cl_2/CH_3CN) afforded 46 mg (86%) of a pale yellow powder, mp 130–133 °C. IR (CH_2Cl_2): 2007 (s), 1929 (s), 1890 (s), 1723 (m), 1578 (m) cm^{-1}. ^1H NMR (300 MHz, C_6D_6): δ 1.04 (t, 3, J = 7.0), 2.91 (s, 3), 3.65 (AB, 2, J = −12, ν_{AB} = 71), 4.04 (m, 2), 6.74 (bs, 1), 6.93–7.02 (m, 9), 7.56–7.50 (m, 6). ^{13}C NMR (75.5 MHz, CD_2Cl_2): δ 14.38, 27.12, 52.44, 53.72, 60.79, 128.71 (d, J = 9.6), 130.73, 131.80 (d, J = 43.6), 134.16 (d, J = 10.9), 171.24, 186.5, 191.73 (d, J = 59.7), 198.48 (d, J = 7.8), 198.62 (d, J = 11.2), 228.46. ^{31}P NMR (121.5 MHz, CD_2Cl_2): δ 23.1. Anal. Calcd for $C_{29}H_{25}O_7PRe$: C, 49.57; H, 3.59. Found: C, 49.59; H, 3.71.

***fac*-Tricarbonyl(1-ethoxy-2-methyl-1-oxo-4-phenyl-2-butenyl-C^3,O)(triphenylphosphine)rhenium (11f).** Reaction of 67 mg (0.10 mmol) of **5** in 5.0 mL of C_6H_6 with 50 μL (46 mg, 0.45 mmol) of phenylacetylene (added by syringe) using the foregoing method gave

upon evaporation of solvent a light yellow glass. Addition of ~1.0 mL of pentane and cooling at −20 °C for 8 h resulted in the formation of a solid that was collected on a fritted disk, washed with a minimum of pentane, and dried in vacuo to give 48 mg (65%) of a pale yellow solid, mp 169–171 °C. IR ($CHCl_3$): 2028 (s), 1974 (s), 1882 (s), 1581 (w) cm^{-1}. ^1H NMR (250 MHz, C_6D_6): δ 0.70 (t, 3, J = 7.1), 1.59 (d, 3, J = 1.5), 3.57 (ABX_3, 2, J = −10.7, 7.1, ν_{AB} = 22.6), 3.94 (AB, 2, J = −11.7, ν_{AB} = 130.7), 6.94–7.00 (m, 10), 7.20–7.25 (m, 2), 7.43–7.56 (m, 8). ^{13}C NMR (75.5 MHz, $CDCl_3$): δ 13.11, 14.17, 48.22, 62.32, 125.68, 126.36, 128.02, 128.18 (d, J = 9.5), 129.61, 130.10 (d, J = 2.2), 131.71 (d, J = 42.4), 133.91 (d, J = 10.9), 139.75, 185.44, 191.40 (d, J = 62.3), 198.20 (d, J = 9.7), 199.17 (d, J = 8.3), 229.11 (d, J = 9.7). ^{31}P NMR (121.5 MHz, $CDCl_3$): δ 24.0. Anal. Calcd for $C_{34}H_{30}O_5PRe$: C, 55.50; H, 4.11. Found: C, 55.84; H, 4.20.

***fac*-Tricarbonyl[1-ethoxy-2-methyl-4-(trimethylsilyl)-1-oxo-2-butenyl-C^3,O](triphenylphosphine)rhenium (11g).** A solution of 68 mg (0.10 mmol) of **5** and 30 μL (21 mg, 0.21 mmol) of ethynyltrimethylsilane in 4.0 mL of C_6H_6 was placed in a resealable pressure bottle containing a stirring bar. The bottle was sealed and removed from the glovebox, and the mixture was heated at 55 °C with stirring for 2 h. The solution was allowed to cool to ambient temperature, the yellow solution was passed with a positive pressure of N_2 through a 5 × 1.5 cm column of flash silica gel (premoistened with C_6H_6), and then the column was eluted with 10 mL of C_6H_6. Evaporation of the combined eluate in vacuo gave 57 mg (77%) of a pale yellow solid, mp 128–131 °C dec. IR ($CHCl_3$): 2023 (s), 1918 (s), 1881 (s), 1569 (w) cm^{-1}. ^1H NMR (250 MHz, C_6D_6): δ 0.29 (s, 9), 0.74 (t, 3, J = 7.1), 1.43 (d, 3, J = 1.5), 2.67 (s, 2), 3.65 (ABX_3, 2, J = −10.8, 7.1, ν_{AB} = 17.4), 6.95–7.00 (m, 9), 7.49–7.57 (m, 6). ^{13}C NMR (75.5 MHz, $CDCl_3$): δ 0.08, 12.78 (d, J = 0.9), 14.29, 39.84, 61.74, 123.00 (d, J = 2.0), 128.07 (d, J = 9.6), 130.04, 131.57 (d, J = 42.5), 133.93 (d, J = 10.9), 184.35, 193.40 (d, J = 61.3), 197.91 (d, J = 9.3), 199.67 (d, J = 7.1), 232.38 (d, J = 10.0). ^{31}P NMR (121.5 MHz, $CDCl_3$): δ 23.2. Anal. Calcd: C, 50.88; H, 4.68. Found: C, 50.87; H, 4.66.

***fac*-Tricarbonyl[1-(N,N-diethylamino)-1-oxo-2-pentenyl-C^3,O](triphenylphosphine)rhenium (12b).** Reaction of 65 mg (0.10 mmol) of **6** in 5.0 mL of C_6H_6 with propyne (bubbled through the solution for 30 s) using the foregoing method gave upon evaporation of solvent 60 mg of a semisolid residue. Addition of pentane resulted in the formation of a solid that was collected on a fritted disk, washed with pentane, and dried in vacuo to give 50 mg (72%) of an ivory colored solid, mp 134–135 °C. IR ($CHCl_3$): 2016 (s), 1912 (s), 1873 (s), 1560 (s) cm^{-1}. ^1H NMR (250 MHz, C_6D_6): δ 0.39 (t, 3, J = 7.1), 0.61 (t, 3, J = 7.1), 1.27 (t, 3, J = 7.3), 2.49 (ABX_3, 2, J = −14.5, 7.3, ν_{AB} = 43.2), 2.68–3.00 (m, 4), 6.36 (d, J = 0.8), 6.97–7.02 (m, 9), 7.55–7.63 (m, 6). ^{13}C NMR (75.5 MHz, $CDCl_3$): δ 13.48, 14.11, 14.30, 40.52, 40.94, 43.90, 119.51 (d, J = 1.4), 127.93 (d, J = 9.5), 129.84 (d, J = 1.6), 132.29 (d, J = 41.5), 134.10 (d, J = 10.9), 181.78, 193.42 (d, J = 64.8), 199.18 (d, J = 9.0), 199.99 (d, J = 7.2), 234.17 (d, J = 10.1). ^{31}P NMR (121.5 MHz, $CDCl_3$): δ 21.6. Anal. Calcd for $C_{30}H_{31}NO_4PRe$: C, 52.47; H, 4.55; N, 2.04. Found: C, 52.44; H, 4.53; N, 2.00.

***cis*-Tetracarbonylhydrido(triphenylphosphine)rhenium (14).** A 50-mL Schlenk flask containing 481 mg (0.75 mmol) of *cis*-$(Ph_3P)(CO)_4ReBr$ and a stirring bar was degassed (2 vacuum/Ar-backfill cycles) and then 15 mL of Et_2O was added. The flask was cooled in an ice–water bath, and 1.30 mL of 1.0 M $LiEt_3BH$ in THF was added by syringe over 5 min. After 2 h at 0 °C, the reaction mixture was quenched with 5 mL of 1 M aqueous NaOH and transferred to a separatory funnel. The layers were separated, and the organic phase was washed with an additional 5 mL of 1 M aqueous NaOH. The combined aqueous layers were extracted with 3 × 5 mL of Et_2O. These extracts were combined with the previous organic phase and then washed with 10 mL of saturated aqueous NaCl and evaporated in vacuo. The resulting yellow residue was rapidly passed with a positive pressure of N_2 through a 3 × 6 cm column of flash silica gel (premoistened with C_6H_6) with 75 mL of C_6H_6. (This step is necessary to remove polar impurities that otherwise result in partial decomposition of the product in the subsequent flash chromatography step.) Evaporation of the C_6H_6 yielded 0.33 g of a yellow-white solid that was purified by flash chromatography (2:1 C_6H_6/hexanes) to give 258 mg (61%) of a white solid, mp 155–156 °C (lit.[50] mp 159–161 °C). IR ($CHCl_3$): 2096 (m), 1988 (sh), 1975 (s), 1962 (sh) cm^{-1}. ^1H NMR (250 MHz, C_6D_6): δ −4.45 (d, 1, J_{PH} = 22.6), 6.93–6.98 (m, 9), 7.45–7.54 (m, 6). ^{13}C NMR (75.5 MHz, $CDCl_3$): δ 128.46 (d, J = 10.2), 130.54 (d, J = 2.1), 133.45 (d, J = 11.5), 133.99 (d, J = 47.8), 188.25 (d, J = 42.4), 189.43 (d, J = 7.4), 189.79 (d, J = 9.9). ^{31}P NMR (121.5 MHz, $CDCl_3$): δ 15.7. Anal. Calcd: C, 47.06; H, 2.87. Found: C, 46.96; H, 2.99.

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***fac*-(Acetonitrile)tricarbonylhydrido(triphenylphosphine)rhenium (15).** To a stirring suspension of 185 mg (0.25 mmol) of **14** in 8.5 mL of CH_3CN was added a solution of 22 mg (0.29 mmol) of Me_3NO in 2.0 mL of CH_3CN. After 2 h, the solvent was concentrated to ~0.5 mL, and the addition of 0.5 mL of hexanes induced crystallization. The solid was collected on a fritted disk, washed with hexanes, and dried in vacuo to give 113 mg (78%) of an off-white, crystalline product, dec pt >125 °C. IR (CH_3CN): 2018 (s), 1918 (s), 1897 (s) cm^{-1}. ^1H NMR (250 MHz, C_6D_6): δ −1.11 (d, 1, J_{PH} = 27.8), 0.40 (s, 3), 6.93–7.03 (m, 9), 7.74–7.82 (m, 6). ^{13}C NMR (75.5 MHz, $CDCl_3$): δ 3.10, 119.74 (d, J = 0.6), 128.35 (d, J = 9.7), 130.32 (d, J = 1.3), 131.44 (d, J = 44.3), 134.05 (d, J = 10.4), 188.17 (d, J = 71.1), 188.59 (d, J = 6.3), 193.17 (d, J = 7.3). ^{31}P NMR (121.5 MHz, $CDCl_3$): δ 15.3. Anal. Calcd: C, 48.08; H, 3.33; N, 2.44. Found: C, 47.85; H, 3.42; N, 2.34.

***fac*-(Acetonitrile)tricarbonylmethyl(triphenylphosphine)rhenium (21).** To a stirred solution of 144 mg (0.25 mmol) of *cis*-$(Ph_3P)(CO)_4ReMe$[28] in 8.0 mL of CH_3CN was added a solution of 20 mg (0.26 mmol) of Me_3NO in 2.0 mL of CH_3CN by syringe. After 1 h at ambient temperature, the consumption of starting material was confirmed by IR spectroscopy. Evaporation of the solvent with a rotary evaporator yielded a white solid. The solid was collected on a fritted disk, washed with pentane, and dried in vacuo to give 140 mg (95%) of a white powder, dec pt >140 °C. (This solid can handled in the air with no apparent decomposition; in solution, however, **21** is moisture sensitive and reacts rapidly with trace amounts of H_2O.) IR (CH_3CN): 2017 (s), 1909 (s), 1878 (s) cm^{-1}. ^1H NMR (250 MHz, C_6D_6): δ 0.16 (d, 3, J = 0.9), 0.25 (d, 3, J = 8.4), 6.87–7.02 (m, 9), 7.67–7.74 (m, 6). ^{13}C NMR (51 MHz, C_6D_6): δ −15.89 (d, J = 8.7), 0.90, 119.39, 128.41 (d, J = 7.8), 129.91, 133.62 (d, J = 41.6), 134.27 (d, J = 10.7), 193.21 (d, J = 7.0), 196.59 (d, J = 67.4), 199.76 (d, J = 9.2). ^{31}P NMR (82 MHz, C_6D_6): δ 20.9. Anal. Calcd for $C_{24}H_{21}NO_3PRe$: C, 48.97; H, 3.60; N, 2.38. Found: C, 49.08; H, 3.62; N, 2.39.

***fac*-(Acetonitrile)tricarbonyl(3,3-dimethyl-1-butynyl)(triphenylphosphine)rhenium (22).** To stirred solution of 59 mg (0.10 mmol) of **21** in 4 mL of C_6H_6 was added 25 μL (17 mg, 0.21 mmol) of 3,3-dimethyl-1-butyne. After 2 h, evaporation of the solvent with a rotary evaporator afforded a pale yellow glass that solidified upon standing for 12 h. This solid was collected on a fritted disk, washed with a minimum of pentane, and dried in vacuo to give 54 mg (83%) of white powder, dec pt > 107 °C. IR (C_6H_6): 2040 (s), 1934 (s), 1905 (s) cm^{-1}. ^1H NMR (250 MHz, C_6D_6): δ 0.20 (d, 3, J = 0.9) 1.30 (s, 9), 6.98–7.10 (m, 9), 7.91–7.98 (m, 6). ^{13}C NMR (75.5 MHz, $CDCl_3$): δ 3.12, 29.07 (d, J = 1.1), 32.30, 92.88 (d, J = 16.9), 118.90, 121.42 (d, J = 3.0), 127.97 (d, J = 9.6), 129.84 (d, J = 1.9), 133.01 (d, J = 43.2), 134.32 (d, J = 5.3), 190.07 (d, J = 65.0), 191.36 (d, J = 7.1), 194.27 (d, J = 8.9). ^{31}P NMR (82 MHz, $CDCl_3$): δ 12.9. Anal. Calcd for $C_{29}H_{27}NO_3PRe$: C, 53.20; H, 4.16; N, 2.14. Found: C, 53.25; H, 4.17; N, 1.73. (Satisfactory analysis for N could not be obtained. Attempts at further purification of **22** resulted in partial decomposition of the material.)

***trans*-Tetracarbonyl(triphenylphosphine)(triphenylstannyl)rhenium (23).** A 50-mL Schlenk flask containing 646 mg (1.01 mmol) of *cis*-$(Ph_3P)(CO)_4ReBr$ and a glass stirring bar was degassed (2 vacuum/Ar backfill cycles) and then 10 mL of THF was added by syringe. The flask was cooled to −78 °C and a solution of NaNp in THF was added via cannula until the green color of the NaNp persisted. After 10 min, a solution of 426 mg (1.11 mmol) of triphenyltin chloride in 1.5 mL of THF was added by syringe. The reaction mixture was maintained at −78 °C for 1 h and then was allowed to warm to room temperature. Evaporation of the solvent gave an orange semisolid residue that was partitioned between H_2O and Et_2O/THF. (The THF is necessary to dissolve the residue). The aqueous layer was separated, and the organic layer was washed with 2 × 10 mL of brine, dried over $MgSO_4$, and concentrated to give 1.05 g of a pale yellow solid. Purification of this solid by flash chromatography (6:1 hexanes/EtOAc, followed by 2:1 hexanes/EtOAc) yielded 547 mg (59%) of an off-white solid, mp 212–214 °C dec. IR ($CHCl_3$): 1970 (s) cm^{-1}. ^1H NMR (250 MHz, C_6D_6): δ 6.89–6.94 (m, 9), 7.13–7.40 (m, 15), 7.96–8.00 (m, 6). ^{13}C NMR (75.5 MHz, $CDCl_3$): δ 127.48, 127.79, 128.70 (d, J = 10.5), 130.58 (d, J = 2.0), 132.59 (d, J = 11.6), 135.48 (d, J = 49.3), 137.07, 144.11, 192.09 (d, J = 6.4). ^{31}P NMR (121.5 MHz, $CDCl_3$): δ 12.1. Anal. Calcd for $C_{40}H_{30}O_4PReSn$: C, 52.76; H, 3.32. Found: C, 53.03; H, 3.40.

***mer*-(Acetonitrile)tricarbonyl(triphenylphosphine)(triphenylstannyl)rhenium (25).** To a rapidly stirred suspension of 137 mg (0.15 mmol) of **23** in 3.5 mL of CH_3CN and 2.5 mL of C_6H_6 was added in one portion a solution of 12 mg (0.16 mmol) of Me_3NO in 1.5 mL of CH_3CN. The heterogeneous mixture gradually became homogeneous within 1 min. After 1 h at ambient temperature, the solvent was evaporated and the residue was triturated with a small portion of hexanes. The resulting solid was collected on a fritted disk, washed with hexanes, and dried in vacuo to give 122 mg (88%) of a white solid, dec pt > 185 °C. IR (CH_3CN):

1933 (s) cm^{-1}. ^1H NMR (250 MHz, C_6D_6): δ 0.10 (br d, 3, J = 1.5), 6.86–7.05 (m, 9), 7.10–7.16 (m, 3), 7.20–7.32 (m, 6), 7.55–7.63 (m, 6), 8.01–8.19 (m, 6). ^{13}C NMR (75.5 MHz, $CDCl_3$): δ 2.10, 122.18, 126.83, 127.53, 128.32 (d, J = 10.0), 129.85, 133.14 (d, J = 11.4), 135.13 (d, J = 45.5), 137.52, 146.72, 199.51 (d, J = 6.2) (low solubility prevented observation of other CO). ^{31}P NMR (82 MHz, C_6D_6): δ 21.6. Anal. Calcd for $C_{41}H_{33}NO_3PReSn$: C, 53.32; H, 3.60; N, 1.52. Found: C, 53.21; H, 3.67; N, 1.49.

***fac*-(Acetonitrile)bromotricarbonyl(triphenylphosphine)rhenium (28).** To a stirred solution of 128 mg (0.20 mmol) of *cis*-$(Ph_3P)(CO)_4ReBr$ in 8 mL of CH_3CN was added a solution of 16 mg (0.21 mmol) of Me_3NO in 2 mL of CH_3CN. After 1 h at ambient temperature, the consumption of starting material was confirmed by IR spectroscopy of the solution. Evaporation of the solvent gave a solid that was collected on a fritted disk, washed with pentane, and dried in vacuo to give 123 mg (94%) of a white, crystalline solid, dec pt > 135 °C. IR (CH_3CN): 2048 (s), 1944 (s), 1919 (s) cm^{-1}. ^1H NMR (250 MHz, C_6D_6): δ 0.26 (d, 3, J_{PH} = 1.2), 6.95–7.00 (m, 9), 7.79–7.86 (m, 6). ^{13}C NMR (75.5 MHz, $CDCl_3$): δ 3.12 (d, J = 0.6), 120.20, 128.29 (d, J = 9.8), 130.30 (d, J = 1.4), 131.54 (d, J = 44.7), 134.06 (d, J = 10.3), 187.59 (d, J = 68.7), 187.99 (d, J = 7.9), 192.73 (d, J = 7.6). ^{31}P NMR (121.5 MHz, $CDCl_3$): δ 12.8. Anal. Calcd for $C_{23}H_{18}BrNO_3PRe$: C, 42.27; H, 2.78; N, 2.14. Found: C, 42.30; H, 2.99; N, 2.01.

***cis*-Benzyltetracarbonyl(triphenylphosphine)rhenium (34).** A 50-mL Schlenk flask containing 640 mg (1.00 mmol) of *cis*-$(Ph_3P)(CO)_4ReBr$ and a glass stirring bar was degassed (2 vacuum/Ar-backfill cycles), and then 7.5 mL of THF was added. The flask was cooled to −78 °C and a 0.2 M solution of NaNp in THF was added by syringe until the green color of the NaNp persisted. After stirring of the mixture for 15 min, 250 μL (275 mg, 2.17 mmol) of benzyl chloride was added by syringe. The reaction mixture was maintained at −78 °C for 3 h, at −20 °C for 12 h, and then allowed to warm to room temperature. The contents of the flask were transferred to a separatory funnel with 20 mL of Et_2O. The organic layer was washed with 20 mL each of H_2O and saturated aqueous NaCl, dried over $MgSO_4$, and evaporated to afford 1.1 g of a yellow solid. Purification of this solid by flash chromatography (7:3 hexanes/C_6H_6) gave 476 mg (73%) of a white solid, mp 179–181 °C. IR ($CHCl_3$): 2088 (m), 1989 (sh), 1974 (vs), 1933 (s) cm^{-1}. ^1H NMR (250 MHz, C_6D_6): δ 2.28 (d, 2, J_{PH} = 6.1), 6.83–7.00 (m, 12), 7.05–7.22 (m, 2), 7.40–7.49 (m, 6). ^{13}C NMR (75.5 MHz, $CDCl_3$): δ 4.71 (d, J = 5.7), 121.24, 125.34, 127.60, 128.67 (d, J = 10.0), 130.69 (d, J = 1.8), 132.53 (d, J = 46.0), 133.32 (d, J = 10.9), 156.21 (d, J = 4.3), 187.50 (d, J = 7.7), 187.96 (d, J = 50.6), 192.36 (d, J = 9.7). ^{31}P NMR (121.5 MHz, $CDCl_3$): δ 11.3. Anal. Calcd for $C_{29}H_{22}O_4PRe$: C, 53.45; H, 3.40. Found: C, 53.69; H, 3.44.

***cis*-Tetracarbonyl(2,3,4,5,6-pentafluorobenzyl)(triphenylphosphine)-rhenium (35).** A 25-mL, round-bottomed flask containing 320 mg (0.50 mmol) of *cis*-$(Ph_3P)(CO)_4ReBr$ and a glass stirring bar was flushed with Ar, and then 4.0 mL of THF was added. The flask was cooled in a −78 °C cold bath, and a 0.2 M solution of NaNp in THF was added by syringe until the green color of the NaNp persisted. After stirring of the mixture for 10 min, a solution of 276 mg (1.00 mmol) of 2,3,4,5,6-pentafluoro-2′-[(methylsulfonyl)oxy]toluene in 1.0 mL of THF was added slowly by syringe. The mixture was maintained at −78 °C for 1 h and then at −20 °C for 12 h. The flask was allowed to warm to room temperature, and the reaction mixture was transferred to a separatory funnel with 10 mL of Et_2O. The organic phase was washed with 10 mL each of H_2O and saturated aqueous NaCl, dried over $MgSO_4$, and evaporated to give 0.60 g of a yellow-orange solid. Purification of this solid by flash chromatography (3.5:1 hexanes/C_6H_6) gave 309 mg (83%) of a white, crystalline solid, mp 150–151 °C. IR ($CHCl_3$): 2097 (m), 1995 (vs), 1984 (vs), 1893 (s) cm^{-1}. ^1H NMR (250 MHz, C_6D_6): δ 1.76 (br d, J_{PC} = 5.0), 6.92–7.01 (m, 9), 7.40–7.47 (m, 6). ^{13}C NMR (75.5 MHz, $CDCl_3$): δ −14.31 (d, J_{PC} = 4.6), 128.84 (d, J_{PC} = 10.1), 129.45–130.07 (m), 130.91 (d, J_{PC} = 1.9), 132.02 (d, J_{PC} = 46.6), 133.18 (d, J_{PC} = 10.9), 135.67 (dm, J_{FC} = 244.4), 137.13 (dm, J_{FC} = 249.3), 142.59 (dm, J_{FC} = 238.8), 186.18 (d, J_{PC} = 7.6), 187.01 (d, J_{PC} = 49.5), 189.85 (d, J_{PC} = 9.6). ^{31}P NMR (121.5 MHz, $CDCl_3$): δ 10.7. Anal. Calcd for $C_{29}H_{15}F_5O_4PRe$: C, 46.97; H, 2.31. Found: C, 46.95; H, 2.32.

***fac*-(Acetonitrile)benzyltricarbonyl(triphenylphosphine)rhenium (37).** To a stirred solution of 260 mg (0.40 mmol) of **34** in 15.0 mL of CH_3CN was added a solution of 32 mg (0.43 mmol) of Me_3NO in 5.0 mL of CH_3CN. After 1 h at ambient temperature, the consumption of starting material was confirmed by IR spectroscopy. Evaporation of the solvent with a rotary evaporator yielded a white solid. The solid was collected on a fritted disk, washed with pentane, and dried in vacuo to give 246 mg (92%) of a white powder, mp 145–147 °C dec. IR (CH_3CN): 2024 (s), 1918 (s), 1889 (s) cm^{-1}. ^1H NMR (250 MHz, C_6D_6): δ 0.26 (d, 3, J_{PH} = 0.8), 2.56 (*AB*X (X = ^{31}P), 2, J_{AB} = −9.9, J_{AX} = 5.2, J_{BX} = 11.3, ν_{AB} = 255.3), 6.75–6.82 (m, 1), 6.91–7.11 (m, 13), 7.63–7.70 (m, 6). ^{13}C NMR (75.5 MHz, $CDCl_3$): δ 2.76, 13.83 (d, J = 6.6), 118.88, 119.82, 126.23, 126.93, 128.32 (d, J = 9.4), 129.97, 132.61 (d, J = 42.1), 133.82 (d, J = 10.7), 156.23 (d, J = 6.1), 191.84 (d, J = 7.3), 194.28 (d, J = 65.8), 198.28 (d, J = 8.8). ^{31}P NMR (121.5 MHz, $CDCl_3$): δ 20.6. Anal. Calcd for $C_{30}H_{25}NO_3PRe$: C, 54.21; H, 3.79; N, 2.11. Found: C, 54.31; H, 3.87; N, 2.08.

***fac*-(Acetonitrile)tricarbonyl(2,3,4,5,6-pentafluorobenzyl)(triphenylphosphine)rhenium (38).** To a stirred suspension of 185 mg (0.25 mmol) of **35** in 8.5 mL of CH_3CN was added a solution of 19.5 mg (0.26 mmol) of Me_3NO in 1.5 mL of CH_3CN. The heterogeneous mixture gradually became homogeneous as **35** was consumed. After 2 h, the solvent was concentrated in vacuo to ~0.5 mL, and the addition of 0.5 mL of hexanes resulted in crystallization. The solid was collected on a fritted disk, washed with hexanes, and dried in vacuo to give 176 mg (93%) of a white, crystalline product, mp 143–146 °C. IR (CH_3CN): 2022 (s), 1919 (s), 1891 (s) cm^{-1}. ^1H NMR (250 MHz, C_6D_6): δ 0.35 (s, 3), 1.55–1.66 (m, 1), 2.24–2.30 (m, 1), 6.87–7.02 (m, 9), 7.63–7.70 (m, 6). ^{13}C NMR (75.5 MHz, $CDCl_3$): δ −1.54 (d, J_{PC} = 5.5), 2.67, 119.80, 128.49 (d, J_{PC} = 9.5), 130.56 (d, J_{PC} = 0.8), 131.36–131.89 (m), 132.17 (d, J_{PC} = 42.6), 133.68 (d, J_{PC} = 10.7), 134.64 (dm, J_{FC} = 236.8), 137.02 (dm, J_{FC} = 246.4), 142.49 (dm, J_{FC} = 237.0), 190.97 (d, J_{PC} = 7.7), 192.71 (d, J_{PC} = 63.7), 196.71 (d, J_{PC} = 8.6). ^{31}P NMR (121.5 MHz, $CDCl_3$): δ 20.6. Anal. Calcd for $C_{30}H_{20}F_5NO_3PRe$: C, 47.75; H, 2.67; N, 1.86. Found: C, 47.56; H, 2.61; N, 1.84.

Complexes characterized by spectroscopic data only:

***fac*-Tricarbonyl(4-ethoxy-4-oxo-1-butenyl-C^2,O)(triphenylphosphine)rhenium (7a).** ^1H NMR (250 MHz, C_6D_6): δ 0.55 (t, 3, J = 7.2), 2.79 (AB, 2, J = −21.6, ν_{AB} = 134.6), 3.21 (*AB*X_3, J = −10.7, 7.2, 2, ν_{AB} = 28.9), 6.01 (m, 1), 6.33 (m, 1), 6.94–7.00 (m, 9), 7.61–7.69 (m, 6).

***fac*-Tricarbonyl[5-ethoxy-5-oxo-(*Z*)-2-pentenyl-C^3,O](triphenylphosphine)rhenium (7b).** ^1H NMR (250 MHz, C_6D_6): δ 0.55 (t, 3, J = 7.2), 2.37 (br d, 3, J = 6.1), 2.85 (AB, 2, J = −20.2, ν_{AB} = 146.4), 3.12–3.37 (m, 2), 6.51–6.58 (m, 1), 6.93–7.02 (m, 9), 7.54–7.68 (m, 6).

***fac*-Tricarbonyl[1-ethoxy-1-oxo-(*Z*)-3-pentenyl-C^3,O](triphenylphosphine)rhenium (7c).** ^1H NMR (250 MHz, C_6D_6): δ 0.54 (t, 3, J = 7.2), 1.37 (t, 3, J = 7.5), 2.88 (AB, 2, J = −20.9, ν_{AB} = 140.5), 2.75–2.88 (m, 2), 3.11–3.33 (m, 2), 6.45 (dt, 1, J = 6.5, 1.0), 6.95–7.03 (m, 9), 7.59–7.67 (m, 6).

***fac*-Tricarbonyl[1-ethoxy-5-methyl-1-oxo-(*Z*)-3-hexenyl-C^3,O](triphenylphosphine)rhenium (7d).** ^1H NMR (250 MHz, C_6D_6): δ 0.54 (t, 3, J = 7.2), 1.37 (d, 3, J = 6.6), 1.44 (d, 3, J = 6.6), 2.91 (AB, 2, J = −19.2, ν_{AB} = 129.8), 3.10–3.30 (m, 3), 6.28 (dd, 1, J = 8.8, 0.5), 6.94–7.01 (m, 9), 7.58–7.66 (m, 6).

***fac*-Tricarbonyl[4-ethoxy-4-oxo-1-phenyl-(*Z*)-1-butenyl-C^2,O](triphenylphosphine)rhenium (7f).** ^1H NMR (250 MHz, $CDCl_3$): δ 1.18 (t, 3, J = 7.2), 3.03 (AB, 2, J = −21.5, ν_{AB} = 152.5), 3.73–4.19 (m, 2), 6.10 (br s, 1), 7.27–7.54 (m, 20). ^{31}P NMR (82 MHz, $CDCl_3$): δ 18.9.

***fac*-Tricarbonyl(1-ethoxy-1-oxo-2-undecene-C^3,O)(triphenylphosphine)rhenium (10j).** IR (C6H6): 2013 (s), 1924 (s), 1889 (s), 1566 (m). ^1H NMR (300 MHz, C_6D_6): δ 0.71 (t, J = 7.2, 3), 0.89 (t, J = 6.5, 3), 1.22–1.34 (m, 8), 1.51–1.64 (m, 2), 1.80–1.93 (m, 2), 2.52–2.84 (m, 2), 3.43–3.65 (m, 2), 6.60 (bs, 1), 6.96–6.98 (m, 9), 7.54–7.61 (m, 6). ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 14.15, 22.70, 25.02, 29.30, 29.53, 29.62, 31.60, 31.91, 47.86, 61.97, 119.68, 128.14 (d, J = 9.6), 130.08 (d, J = 1.39), 131.84 (d, J = 43.4), 133.89 (d, J = 10.9), 185.92, 191.70 (d, J = 60.8), 198.55 (d, J = 8.6), 199.08 (d, J = 7.7), 243.24 (d, J = 9.4). ^{31}P NMR (121.5 MHz, C_6D_6): δ 24.07.

Kinetics of the Reaction of 4 with Alkynes. Standard solutions of **4**, 3,3-dimethyl-1-butyne, and acetonitrile were prepared with the following concentrations: **4**, 3.4 × 10^{-3} M; 3,3-dimethyl-1-butyne, 3.4 × 10^{-2} M and 0.162 M; acetonitrile, 3.4 × 10^{-3} M. Samples were prepared by addition of 1.0 mL of the solution of **4** to a 10.0-mL volumetric flask, addition of the appropriate amounts of 3,3-dimethyl-1-butyne and acetonitrile solutions to the flask, and then dilution to 10 mL. The flask was shaken, then the solution transferred by pipet to the UV/vis cell, and the stopcock closed. The solution was warmed to 35 °C in the temperature-control unit of the UV/vis spectrophotometer. A 5-min equilibrium period was allowed for each sample to come to temperature, and then spectra were recorded at appropriate intervals. Data were collected for at least 3 half-lives for each reaction. The absorbance value at infinite time (A_∞) was calculated by fitting the data to a first-order exponential using a Marquardtian nonlinear least-squares iterative fitting procedure. The observed rate constants (k_{obs}) were then calculated from a plot of the natural logarithm of ($A_\infty - A_t$) versus time. Analogous procedures were used for the other alkynes.

Determination of X-ray Structure for Complex 10g. Clear, colorless crystals of the compound were obtained by slow evaporation from benzene/heptane solution. Some of these crystals were mounted on glass fibers using polycyanoacrylate cement. Preliminary precession photo-

graphs indicated triclinic Laue symmetry and yielded approximate cell dimensions. The crystal used for data collection was then transferred to our Enraf-Nonius CAD-4 diffractometer[51] and centered in the beam. Automatic peak search and indexing procedures yielded a triclinic reduced primitive cell. Inspection of the Niggli values[52] revealed no conventional cell of higher symmetry.

The 8563 unique raw intensity data were converted to structure factor amplitudes and their esd values by correction for scan speed, background, and Lorentz and polarization effects. Inspection of the intensity standards revealed a reduction of 5.5% of the original intensity. The data were corrected for this decay. Inspection of the azimuthal scan data showed a variation $I_{min}/I_{max} = 0.92$ for the average curve. An empirical correction based on the observed variation was applied to the data.

The structure was solved by Patterson methods and refined via standard least-squares and Fourier techniques. The benzene of solvation was discovered in a difference Fourier map after all of the expected atoms in the molecule were discovered. In a difference Fourier map calculated following the refinement of all non-hydrogen atoms with anisotropic thermal parameters, peaks were found corresponding to the positions of most of the hydrogen atoms. Hydrogen atoms were assigned idealized locations and values of B_{iso} approximately 1.3 times the B_{eqv} of the atoms to which they were attached. They were included in structure factor calculations but not refined. Hydrogen atoms for the benzene were not included. Details of the structure determination are given in Table II.[53]

The quantity minimized by the least-squares program was $\sum w(|F_o| - |F_c|)^2$, where w is the weight of a given observation. The p factor, used to reduce the weight of intense reflections, was set to 0.03 throughout the refinement. The analytical forms of the scattering factor tables for the neutral atoms were used and all scattering factors were corrected for both the real and imaginary components of anomalous dispersion.[54]

The structure consists of two independent molecules of the compound and a molecule of benzene packed in the unit cell. While the molecules are similar, they are not identical, having significant differences in the torsion angles, especially in the triphenylphosphine group. Selected bond distances and angles are given in Table III.

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(51) For a description of the X-ray diffraction and analysis protocols used, see: Hersh, W. H.; Hollander, F. J.; Bergman, R. G. *J. Am. Chem. Soc.* **1983**, *105*, 5834-46.

(52) Roof, R. B., Jr. *A Theoretical Extension of the Reduced-Cell Concept in Crystallography*; Publication LA-4038, Los Alamos Scientific Laboratory: Los Alamos, NM, 1969.

(53) The atomic coordinates for this work are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge, CB2 1EW. Any request should be accompanied by the full literature citation for this paper.

(54) Cromer, D. T.; Waber, J. T. *International Tables for X-ray Crystallography*; Kynoch Press: Birmingham, England, 1974; Vol. IV, Table 2.2B.

A Structure–Reactivity Relationship for Base-Promoted Hydrolysis and Methanolysis of Monocyclic β-Lactams

S. Nagaraja Rao and R. A. More O'Ferrall*

Contribution from the Department of Chemistry, University College, Belfield, Dublin 4, Ireland.
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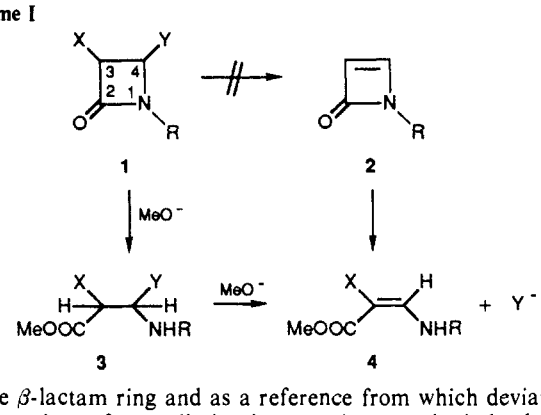
Abstract: A structure–reactivity relationship for base hydrolysis and methanolysis of nearly 50 azetidinones ranging in reactivity over nine powers of 10 is described. Substituents at 3- and 4-positions show similar effects upon reactivity and are correlated by a Taft relationship with $\rho_I = 5$, implying strong activation by electron withdrawal. Substituents at nitrogen show a linear dependence of log k upon the pK_a of the corresponding substituted dimethylamine with $\beta_{lg} = -0.35$. The effects are approximately additive and consistent with rate-determining attack of hydroxide or methoxide ions upon the carbonyl group of the ring. Large positive deviations occur for N–H β-lactams containing a good leaving group at the 4-position, which are subject to competing 1,4-elimination–addition, but there is no evidence of the corresponding 3,4-elimination or of a previously suggested change in the rate-determining step from nucleophilic attack upon the carbonyl group to ring-opening cleavage of the carbon–nitrogen bond. Steric effects lead to negative deviations and slower reactions of *trans*- than *cis*-azetidinones, but the effects are small (less than a factor of 10) unless the ring is heavily substituted, e.g., as in 1-phenyl-3,3-dimethyl-4-phenyl-4-(methylthio)azetidinone, which reacts 65 000 times more slowly than predicted. The accelerating effect of ring fusion on β-lactam reactivity is estimated to be 85-fold for the thiazolidine ring of penicillin and 16-fold for the dihydrothiazine ring of cephalosporins.

In methanolic sodium methoxide, 3-tosyloxy and 3-azido β-lactams bearing a chloro or methylthio leaving group at the 4-position (**1**, X = OTs, N_3; Y = SMe, Cl) have beeen shown to undergo ring opening followed by elimination of HCl or MeSH to form the enamine ester (**4**), as shown in the lower pathway of Scheme I.[1] Similar behavior is observed for a wide range of β-lactam structures, and in the present paper we report a study of these reactions (a) to determine if alternative activating groups at the 3-position induce elimination within the β-lactam ring itself, as in the upper pathway of Scheme I, and (b) to establish a structure–reactivity relationship for the ring-opening reaction.

A structure–reactivity relationship for ring opening can be measured because ring opening (**1** → **3**) is rate determining in Scheme I and the enamine ester product provides a good chromophore for monitoring the reaction.[1] The relationship is of interest both for understanding factors influencing the reactivity of the β-lactam ring and as a reference from which deviations representing a faster elimination reaction may be judged.

Scheme I



Previous studies of structure–reactivity relationships for β-lactam ring opening have been summarized by Page.[2,3] For

(1) Rao, S. N.; More O'Ferrall, R. A. *J. Org. Chem.* In press.

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