Synthesis of η^3-Propargyl Rhenium Complexes

Charles P. Casey,* Anthony D. Selmeczy, John R. Nash, Chae S. Yi, Douglas R. Powell, and Randy K. Hayashi

Contribution from the Department of Chemistry, University of Wisconsin, Madison Wisconsin 53706

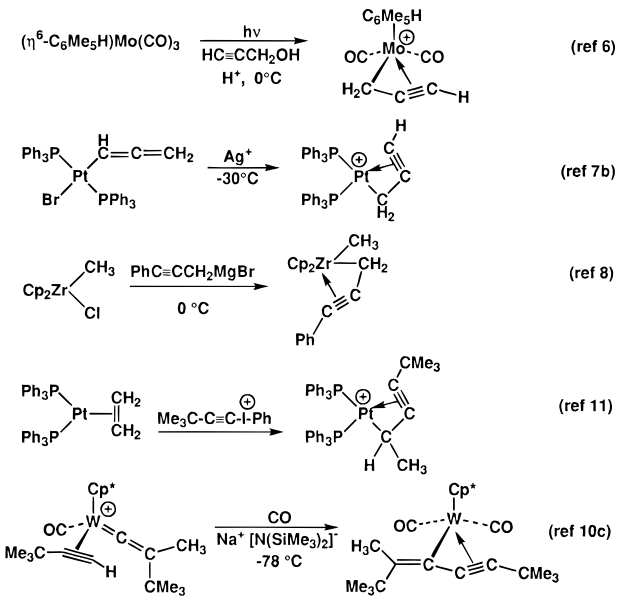
Received February 5, 1996[⊗]

Abstract: Hydride abstraction from η^2-alkyne rhenium complexes $C_5Me_5(CO)_2Re(RC{\equiv}CR')$ (**2**) with $Ph_3C^+PF_6^-$ produces η^3-propargyl complexes $C_5Me_5(CO)_2Re(\eta^3\text{-}CHR''{-}C{\equiv}CR)^+PF_6^-$ (**3**). Successful hydride abstraction to produce η^3-propargyl complexes was observed only for internal acetylenes with a methyl or primary alkyl substituent. An unusual regioselectivity for hydride abstraction was observed: $CH_3CH_2 > CH_3 \gg CH(CH_3)_2$. Hydride abstraction from diethylacetylene complex $C_5Me_5(CO)_2Re(\eta^2\text{-}CH_3CH_2C{\equiv}CCH_2CH_3)$ (**2c**) produced a single stereoisomer of η^3-propargyl complex $C_5Me_5(CO)_2Re(\eta^3\text{-}CH_3CH{-}C{\equiv}CCH_2CH_3)^+PF_6^-$ (**3c**) in which it is suggested that the methyl group is located in the less crowded position anti to the Cp* group. The regio- and stereoselectivity of hydride abstraction can be explained in terms of transition state **A** in which the carbon hydrogen bond being cleaved is antiperiplanar with respect to rhenium and the syn propargylic substituent comes into close contact with the Cp* ligand. Protonation of $C_5Me_5(CO)_2Re(\eta^2\text{-}HC{\equiv}CCH_2OH)$ (**6h**) with $HBF_4{\cdot}Et_2O$ gave $C_5Me_5(CO)_2Re(\eta^3\text{-}CH_2{-}C{\equiv}CH)^+BF_4^-$ (**3h**), which could not be obtained by hydride abstraction from the terminal alkyne complex $C_5Me_5(CO)_2Re(\eta^2\text{-}HC{\equiv}CCH_3)$ (**2h**). Protonation of propargyl alcohol complexes provides a regiospecific synthesis of π-propargyl complexes: protonation of $C_5Me_5(CO)_2Re(\eta^2\text{-}CH_3CH_2C{\equiv}CCH_2OH)$ (**6e**) gave $C_5Me_5(CO)_2Re(\eta^3\text{-}CH_2\text{-}C{\equiv}CCH_2CH_3)^+BF_4^-$ (**3e-BF$_4$**), while protonation of $C_5Me_5(CO)_2Re[\eta^2\text{-}CH_3C{\equiv}CCH(CH_3)OH]$ (**6d**) gave $C_5Me_5(CO)_2Re(\eta^3\text{-}CH_3CH{-}C{\equiv}CCH_3)^+BF_4^-$ (***anti*-3d-BF$_4$**).

π-Propargyl metal complexes[1,2] are the triple bond analogs of π-allyl complexes which have proven to be extremely useful in organic synthesis. In 1992, we developed a synthesis of these apparently highly strained π-propargyl complexes by hydride abstraction from alkyne metal complexes.[3,4] We also found that nucleophiles attack the central carbon of the π-propargyl ligand to produce metallacyclobutene complexes.

Although π-propargyl transition metal complexes had been proposed as intermediates in catalytic cycles,[5] their detection and isolation had proven elusive until recently. Since 1985, a number of stable π-propargyl transition metal complexes have been prepared by various synthetic routes (Scheme 1), including protonation of η^2-propargyl alcohol complexes,[6] halide abstraction from σ-propargyl or σ-allenyl metal halide complexes,[7] reaction of metal halides with propargyl nucleophiles,[8] reaction of propargyl ether complexes with Lewis acids,[9] insertion of a metal acetylide into a vinylidene,[10] and rearrangement of η^1-homopropargyl metal complexes.[11] The reaction of π-propargyl intermediates with malonate nucleophiles has been used as a route to stable trimethylenemethane Pt and Pd complexes.[12]

Scheme 1



Here we report the scope and limitations of hydride abstraction from $C_5Me_5(CO)_2Re$(alkyne) complexes as a route to π-propargyl complexes. In addition, a regiospecific route to π-propargyl complexes by protonation[13] of propargyl alcohol complexes is presented.

[⊗] Abstract published in *Advance ACS Abstracts,* July 1, 1996.

(1) Doherty, S.; Corrigan, J. F.; Carty, A. J.; Sappa, E. *Adv. Organomet. Chem.* **1995**, *37*, 39−130.

(2) Wojcicki, A. *New J. Chem.* **1994**, *18*, 61−8.

(3) Casey, C. P.; Yi, C. S. *J. Am. Chem. Soc.* **1992**, *114*, 6597−6598.

(4) For other examples of hydride abstraction from metal π-complexes, see: (a) Casey, C. P.; Yi, C. S. *Organometallics* **1990**, *9*, 2143. (b) Batchelor, R. J.; Einstein, F. W. B.; Zhuang, J.-M.; Sutton, D. *J. Organomet. Chem.* **1990**, *397*, 69−80. (c) Margulis, T. N.; Schiff, L.; Rosenblum, M. *J. Am. Chem. Soc.* **1965**, *87*, 3269. (d) Fischer, E. O.; Fischer, R. D. *Angew. Chem.* **1960**, *72*, 919.

(5) (a) Keinan, E.; Bosch, E. *J. Org. Chem.* **1986,** *51*, 4006−4016. (b) Wakatsuki, Y.; Yamazaki, H.; Kumegawa, N.; Satoh, T. *J. Am. Chem. Soc.* **1991**, *113*, 9604−9610. (c) Tsuji, J.; Watanabe, H.; Minami, I.; Shimizu, I. *J. Am. Chem. Soc.* **1985**, *107*, 2196−2198. (d) Minami, I.; Tsuji, J.; Watanabe, H.; Yuhara, M. *J. Organomet. Chem.* **1987**, *334*, 225−242.

(6) Krivykh, V. V.; Taits, E. S.; Petrovskii, P. V.; Struchkov, Y. T.; Yanovskii, A. I. *Mendeleev Commun.* **1991**, 103−4.

(7) (a) Blosser, P. W.; Schimpff, D. G.; Gallucci, J. C.; Wojcicki, A. *Organometallics* **1993**, *12*, 1993−5. (b) Huang, T.-M.; Chen, J.-T.; Lee, G.-H.; Wang, Y. *J. Am. Chem. Soc.* **1993**, *115*, 1170−1. (c) Huang, T.-M.; Hsu, R.-H.; Yang, C.-S.; Chen, J.-T.; Lee, G.-H.; Wang, Y. *Organometallics* **1994**, *13* , 3657−3663. (d) Ogoshi, S.; Tsutsumi, K.; Kurosawa, H. *J. Organomet. Chem.* **1995**, *493*, C19-C21. (e) Baize, M. W.; Blosser, P. W.; Plantevin, V.; Schimpff, D. G.; Gallucci, J. C.; Wojcicki, A. *Organometallics* **1996**, *15*, 164−173.

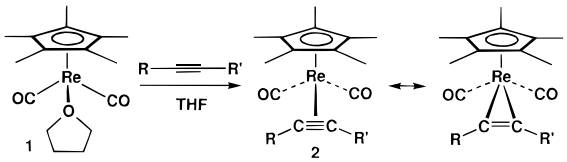
(8) Blosser, P. W.; Gallucci, J. C.; Wojcicki, A. *J. Am. Chem. Soc.* **1993**, *115*, 2994−5.

(9) Weng, W.; Arif, A. M.; Gladysz, J. A. *Angew. Chem., Int. Ed. Engl.* **1993**, *32*, 891−2.

S0002-7863(96)00375-7 CCC: $12.00

Results

All of the routes we have developed for the synthesis of η^3-propargyl rhenium complexes begin with the synthesis of a rhenium alkyne complex from reaction of isolated $C_5Me_5(CO)_2Re(THF)$ (**1**)[14] with an alkyne. The resulting η^2-alkyne complexes are stable yellow solids. X-ray crystal structures of alkyne rhenium complexes show that the alkyne is oriented parallel to the Cp* ring and the substituents on the alkyne carbon are bent back away from rhenium by about 25°.[15] Alkyne rotation about the Re center is slow on the NMR time scale at room temperature (the rotation barrier is typically $\Delta G^{\ddagger} = 16-18$ kcal mol^{-1}).



Synthesis of η^3-Propargyl Rhenium Complexes by Hydride Abstraction from η^2-Alkyne Complexes. In a preliminary communication, we reported that the reaction of $C_5Me_5(CO)_2Re(\eta^2\text{-}CH_3C{\equiv}CCH_3)$ (**2a**) with $Ph_3C^+PF_6^-$ in CH_2Cl_2 produced the stable η^3-propargyl complex $C_5Me_5(CO)_2Re(\eta^3\text{-}CH_2{-}C{\equiv}CCH_3)^+PF_6^-$ (**3a-PF$_6$**) which was isolated as a pale brown solid in 87% yield. The structure of **3a-PF$_6$** was established by spectroscopy since we were unable to obtain single crystals for X-ray diffraction. The ^{1}H NMR spectrum of **3a-PF$_6$** in CD_2Cl_2 exhibited a Cp* resonance shifted to high frequency at δ 2.11, a methyl resonance at δ 2.58 (t, $J = 3$ Hz), and two doublets of quartets at δ 4.38 and 3.32 that were assigned to the inequivalent propargyl hydrogens coupled to each other ($J_{gem} = 10$ Hz) and to the methyl group ($J = 3$ Hz). In the coupled ^{13}C NMR spectrum of **3a-PF$_6$**, two singlets at δ 76.6 and 56.7 were assigned to the quaternary propargyl carbons and a triplet ($J = 170$ Hz) at δ 29.0 was assigned to the terminal propargyl CH_2.

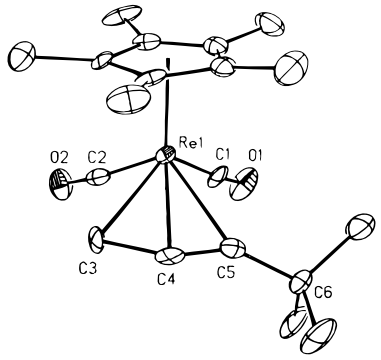
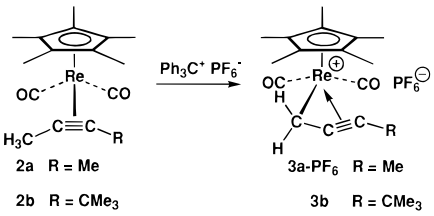


Figure 1. X-ray Structure of $C_5Me_5(CO)_2Re[\eta^3\text{-}CH_2{-}C{\equiv}CC(CH_3)_3]^+PF_6^-$ (**3b**).

Table 1. Selected Bond Lengths (Å) and Bond Angles (deg) for $C_5Me_5(CO)_2Re[\eta^3\text{-}CH_2{-}C{\equiv}CC(CH_3)_3]^+PF_6^-$ (**3b**)

Re−C(3)H$_2$	2.305(7)	C(3)−C(4)−C(5)	152.7(8)
Re−C(4)	2.239(7)	C(4)−C(5)−C(6)	146.9(8)
Re−C(5)CMe$_3$	2.345(8)	C(1)−Re−C(2)	79.2(3)
C(3)H$_2$−C(4)	1.38(1)	Cp*−Re−C(1)	120.6
C(4)≡C(5)	1.26(1)	Cp*−Re−C(2)	119.0
C(5)−C(6)Me$_3$	1.49(1)	Cp*−Re−C(3)	115.1
		Cp*−Re−C(4)	121.7
		Cp*−Re−C(5)	120.7

The large 10-Hz geminal coupling constant of the propargyl methylene protons is characteristic of π-propargyl complexes.[1,2] This coupling is substantially larger than the geminal coupling of the π-allyl CH_2 unit (0−3 Hz)[16] and that of the uncomplexed $=CH_2$ unit of allene metal complexes (~3 Hz), but is similar to that of the complexed $=CH_2$ unit of allene metal complexes (10−11 Hz),[17] and is somewhat smaller than that of the methylene of a σ-propargyl complex (15 Hz).[17]



Reaction of $Ph_3C^+PF_6^-$ with the *tert*-butylmethylacetylene complex $C_5Me_5(CO)_2Re[\eta^2\text{-}CH_3C{\equiv}CC(CH_3)_3]$ (**2b**) also led to hydride abstraction from a methyl group and formation of η^3-propargyl complex $C_5Me_5(CO)_2Re[\eta^3\text{-}CH_2{-}C{\equiv}CC(CH_3)_3]^+PF_6^-$ (**3b**) as a bright yellow powder in 49% yield. In the ^{1}H NMR spectrum of **3b**, doublets ($J = 9.6$ Hz) at δ 4.40 and 3.34 were assigned to inequivalent propargyl protons. In the ^{13}C NMR spectrum, the three propargyl carbons appeared at δ 94.2 (≡*C*CMe$_3$), 60.5 (CH_2*C*≡), and 30.0 (*C*H$_2$C≡).

The structure of **3b** determined by X-ray crystallography has a four-legged piano stool geometry with the η^3-propargyl ligand occupying two of the basal positions (Figure 1, Table 1). The three-carbon propargyl unit is bent [C(3)−C(4)−C(5) = 152.7(8)°] so that all three carbons are at similar distances to rhenium [Re−C(3)H$_2$ (2.305(7) Å), Re−C(4) (2.239(7) Å), Re−C(5)CMe$_3$ (2.345(8) Å)]. The H$_2$C(3)−C(4) distance of 1.38(1) Å is between that of normal C−C single and double bonds and the C(4)−C(5)CMe$_3$ distance of 1.26(1) Å is between that of normal C−C double and triple bonds. These values indicate

(10) (a) Gotzig, J.; Otto, H.; Werner, H. *J. Organomet. Chem.* **1985**, *287*, 247−54. (b) Hills, A.; Hughes, D. L.; Jimenez-Tenorio, M.; Leigh, G. J.; McGeary, C. A.; Rowley, A. T.; Bravo, M.; McKenna, C. E.; McKenna, M.-C. *J. Chem. Soc., Chem. Commun.* **1991**, 522−4. (c) McMullen, A. K.; Selegue, J. P.; Wang, J.-G. *Organometallics* **1991**, *10*, 3421−3; Jia, G.; Rheingold, A. L.; Meek, D. W. *Organometallics* **1989**, *8*, 1378−80. (d) Field, L. D.; George, A. V.; Hambley, T. W. *Inorg. Chem.* **1990**, *29*, 4565−9. (e) Wakatsuki, Y.; Yamazaki, H.; Kumegawa, N.; Satoh, T. *J. Am. Chem. Soc.* **1991**, *113*, 9604−9610. (f) Satoh, J. Y. *J. Am. Chem. Soc.* **1991**, *113*, 9604−9610. (g) Bianchini, C.; Bohanna, C.; Esteruelas, M. A.; Frediana, P.; Meli, A.; Oro, L. A.; Peruzzini, M. *Organometallics* **1992**, *11*, 3837−44. (h) Bianchini, C.; Peruzzini, M.; Zanobini, F.; Frediani, P.; Albinati, A. *J. Am. Chem. Soc.* **1991**, *113*, 5453−4. (i) Albertin, G.; Amendola, P.; Antoniutti, S.; Ianelli, S.; Pelizzi, G.; Bordignon, E. *Organometallics* **1991**, *10*, 2876−2883. (j) Wakatsuki, Y.; Yamazaki, H.; Maruyama, Y.; Shimizu, I. *J. Chem. Soc., Chem. Commun.* **1991**, 261−263. (k) Hughes, D. L.; Jimenez-Tenorio, M.; Leigh, G. J.; Rowley, A. T. *J. Chem. Soc., Dalton Trans.* **1993**, 3151−3162. (l) Alcock, N. W.; Hill, A. F.; Melling, R. P.; Thompsett, A. R. *Organometallics* **1993**, *12* , 641−648.

(11) Stang, P. J.; Crittell, C. M.; Arif, A. M. *Organometallics* **1993**, *12*, 4799−4804.

(12) (a) Su, C.-C.; Chen, J.-T.; Lee, G.-H.; Wang, Y. *J. Am. Chem. Soc.* **1994**, *116*, 4999−5000. (b) Plantevin, V.; Blosser, P. W.; Gallucci, J. C.; Wojcicki, A. *Organometallics* **1994**, *13*, 3651−6.

(13) For related syntheses of π-allyl metal complexes by protonation of allyl alcohol complexes, see: (a) Rosan, A. M. *J. Chem. Soc., Chem. Commun.* **1981**, 311. (b) Krivykh, V. V.; Gusev, O. V.; Rybinskaya, M. I. *J. Organomet. Chem.* **1989**, *362*, 351−362. (c) Rosan, A. M.; Romano, D. M. *Organometallics* **1990**, *9*, 1048−1052.

(14) Casey, C. P.; Sakaba, H.; Hazin, P. N.; Powell, D. R. *J. Am. Chem. Soc.* **1991**, *113*, 8165−8166.

(15) Casey, C. P.; Ha, Y.; Powell, D. R. *J. Organomet. Chem.* **1994**, *472*, 185−193.

(16) Collman, J. P.; Hegedus, L. S.; Norton, J. R.; Finke, R. G. *Principles and Applications of Organotransitionmetal Chemistry*; University Science Books: Mill Valley, 1987; p 177.

(17) Pu, J.; Peng, T.-S.; Arif, A. M.; Gladysz, J. A. *Organometallics* **1992**, *11*, 3232−3241.

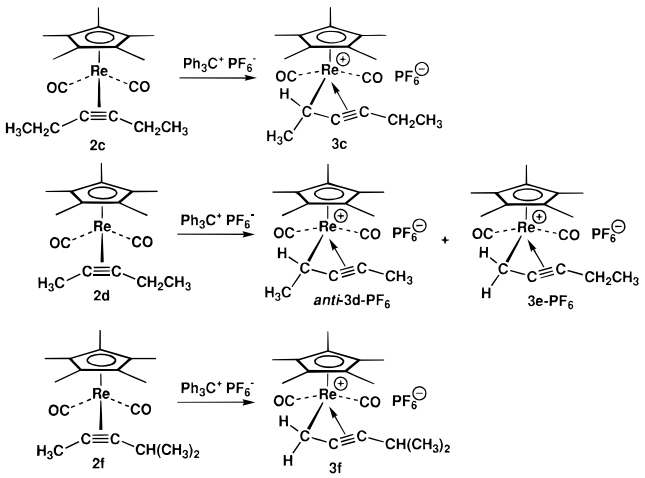
Table 2. Structural Features of η^3-Propargyl Complexes M(η^3-CR_2−C≡CR)

structure	CR_2−C (Å)	C≡C (Å)	C−C−C (deg)	ref
$(C_5H_5)_2(Me)Zr(\eta^3\text{-}CH_2C{\equiv}CPh)$	1.344(5)	1.259(4)	155.4(3)	8
$C_6Me_5H(CO)_2Mo(\eta^3\text{-}CH_2C{\equiv}CH)^+$	1.380(4)	1.236(4)	150.9(3)	6
$(PPh_3)_2Pt(\eta^3\text{-}CH_2C{\equiv}CPh)^+$	1.39(2)	1.23(1)	152(1)	7a
$(PPh_3)_2Pt(\eta^3\text{-}CH(Me)C{\equiv}CCMe_3)^+$	1.390(5)	1.266(5)	154.1(3)	11
$(PPh_3)_2Pd(\eta^3\text{-}CH_2C{\equiv}CPh)^+$	1.385(7)	1.233(7)	154.7(5)	7e
$C_5Me_5(CO)_2Re(\eta^3\text{-}CH_2C{\equiv}CCMe_3)^+$	1.378(12)	1.256(12)	152.7(8)	this work

that both propargyl C−C≡C and allenyl C=C=C resonance structures are important contributors to this η^3-propargyl complex. The 79.2(3)° angle between the carbonyl groups is normal for four-legged piano stool structures.[18]

Two accommodations are apparently made for the steric bulk of the *tert*-butyl substituent: (1) the *tert*-butyl group is bent out of the mean plane of Re and the propargyl carbons and away from the Cp* ligand [the *tert*-butyl carbon is displaced 0.32 Å from the mean plane of Re and the propargyl carbons, and the torsional angle C(3)−C(4)−C(5)−C(6) is 149°]; and (2) the plane of Re and the propargyl carbons is tilted relative to the Cp* ring to reduce the interaction between the *tert*-butyl and Cp* groups [the torsional angle Cp*(centroid)−Re−C(4)−C(5) is 98.1°]. In crystal structures of related η^3-propargyl complexes, the C−C−C propargyl angle ranges from 151° to 155°, the R_2C−C distances range from 1.34 to 1.39 Å, and the C≡CR distances range from 1.22 to 1.27 Å (Table 2).

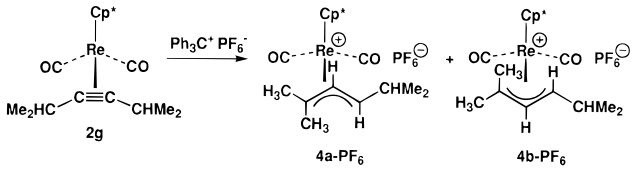
Abstraction of a methylene hydrogen from the 3-hexyne complex $C_5Me_5(CO)_2Re(\eta^2\text{-}CH_3CH_2C{\equiv}CCH_2CH_3)$ (**2c**) occurred readily to produce an η^3-propargyl complex. Reaction of **2c** with $Ph_3C^+PF_6^-$ in CH_2Cl_2 at room temperature gave a single isomer of $C_5Me_5(CO)_2Re(\eta^3\text{-}CH_3CH{-}C{\equiv}CCH_2CH_3)^+PF_6^-$ (**3c**) in 64% isolated yield. The presence of a single propargylic $C_\alpha HR$ group was evident both from the ^{1}H NMR spectrum (δ 4.24) and from the coupled ^{13}C NMR spectrum [δ 49.3 (d, J = 177 Hz)]. The observation of a single diastereomer at C_α suggests a stereochemical preference for hydride abstraction. Based on examination of molecular models, we suggest that the methyl group is located in the less crowded position anti to the Cp* group.



A 2.5:1 regioselective preference for abstraction of a methylene hydrogen over a methyl hydrogen was observed in the reaction of the 2-pentyne complex $C_5Me_5(CO)_2Re(\eta^2\text{-}CH_3C{\equiv}CCH_2CH_3)$ (**2d**). Reaction of **2d** with $Ph_3C^+PF_6^-$ in CH_2Cl_2 at room temperature gave a 2.5:1 mixture of $C_5Me_5(CO)_2Re(\eta^3\text{-}CH_3CH{-}C{\equiv}CCH_3)^+PF_6^-$ (***anti*-3d-PF$_6$**): $C_5Me_5(CO)_2Re(\eta^3\text{-}CH_2\text{-}C{\equiv}CCH_2CH_3)^+PF_6^-$ (**3e-PF$_6$**) in a combined yield of 89%. The major product ***anti*-3d-PF$_6$** exhibited two methyl doublets in the ^{1}H NMR spectrum at δ 2.63 (J = 2 Hz, C≡CCH_3) and 2.05 (J = 7 Hz, CH_3CH) and a multiplet at δ 4.20 for a propargyl methine hydrogen. Again, only a single isomer of **3d** was observed; based on steric arguments, an anti orientation of the methyl group relative to the Cp* group is suggested. The minor product **3e-PF$_6$** displayed inequivalent propargyl resonances at δ 4.41 and 3.34 (each a dt, J = 10, 3 Hz) along with a methyl triplet at δ 1.54 (J = 7 Hz).

A surprising *reversal of regioselectivity* was seen in the reaction of methyl isopropylacetylene complex $C_5Me_5(CO)_2Re[\eta^2\text{-}CH_3C{\equiv}CCH(CH_3)_2]$ (**2f**). Exclusive abstraction of a methyl hydrogen in preference over the methine hydrogen of the isopropyl group was observed. Reaction of **2f** with $Ph_3C^+PF_6^-$ in CH_2Cl_2 at room temperature gave $C_5Me_5(CO)_2Re[\eta^3\text{-}CH_2{-}C{\equiv}CCH(CH_3)_2]^+PF_6^-$ (**3f**) in 37% isolated yield. The material was 80% pure by ^{1}H NMR and contained about 20% of a single unidentified impurity. The ^{1}H NMR spectrum showed inequivalent propargyl resonances at δ 4.40 and 3.35 (each a dd, J = 10, 2 Hz) along with diastereotopic methyl doublets at δ 1.63 and 1.38.

To determine whether hydrogen abstraction from an isopropyl group could be accomplished when no other hydride source is available, the reaction of diisopropyl acetylene complex $C_5Me_5(CO)_2Re[\eta^2\text{-}(CH_3)_2CHC{\equiv}CCH(CH_3)_2]$ (**2g**) was studied. Reaction of **2g** with $Ph_3C^+PF_6^-$ in CH_2Cl_2 at room temperature did not lead to hydride abstraction and formation of an η^3-propargyl complex. Instead, a 1:1 mixture of η^3-allyl complexes $C_5Me_5(CO)_2Re\{\eta^3\text{-}endo,syn\text{-}(CH_3)_2C{-}CH{-}CH[CH(CH_3)_2]\}^+PF_6^-$ (**4a-PF$_6$**) and $C_5Me_5(CO)_2Re\{\eta^3\text{-}exo,syn\text{-}(CH_3)_2C{-}CH{-}CH[CH(CH_3)_2]\}^+PF_6^-$ (**4b-PF$_6$**) was formed in 43% isolated yield. The 1:1 mixture equilibrated over 2 days in CD_2Cl_2 solution to produce a 1.3:1 ratio of **4a-PF$_6$**:**4b-PF$_6$**. The formation of η^3-allyl complexes requires the net addition of H^+ and hydrogen migrations. A 1:1 mixture of the related BF_4^- salts $C_5Me_5(CO)_2Re\{\eta^3\text{-}endo,syn\text{-}(CH_3)_2C{-}CH{-}CH[CH(CH_3)_2]\}^+BF_4^-$ (**4a-BF$_4$**) and $C_5Me_5(CO)_2Re\{\eta^3\text{-}exo,syn\text{-}(CH_3)_2C{-}CH{-}CH[CH(CH_3)_2]\}^+BF_4^-$ (**4b-BF$_4$**) was obtained in 52% isolated yield from protonation of **2g** with HBF_4 in CD_2Cl_2.



The structures of **4a-PF$_6$** and **4b-PF$_6$** were determined spectroscopically. The LSIMS mass spectrum of the mixture showed that the cation peak was one mass unit *larger* than the parent alkyne complex, consistent with proton addition and clearly inconsistent with loss of hydride. The ^{1}H NMR spectrum indicated a 1:1 mixture of **4a-PF$_6$**:**4b-PF$_6$**. A doublet ($J \approx 10$ Hz) and a triplet ($J \approx 10$ Hz) in the δ 3.1−4.0 region were observed for each isomer and are assigned to the central allyl proton and an anti allyl proton. Each isomer also exhibited a

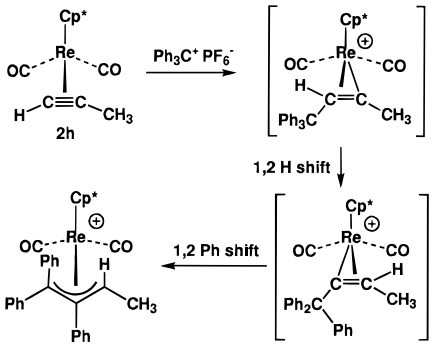
(18) Goldberg, K. I., Bergman, R. G. *J. Am. Chem. Soc.* **1989**, *111*, 1285−1299.

pair of doublets (J = 7 Hz) assigned to diastereotopic methyl groups of the isopropyl group and a pair of inequivalent methyl singlets assigned to the methyl substituents on the η^3-allyl ligand. Based on ^{1}H and ^{13}C NMR chemical shift arguments, the major isomer is assigned an endo,syn geometry and the minor isomer is assigned an exo,syn geometry.

In a competition experiment, 1 equiv of $Ph_3C^+PF_6^-$ was added to a 1:1 mixture of dimethylacetylene **2a** and diisopropylacetylene complexes **2g** in CD_2Cl_2 containing C_6Me_6 as an internal NMR standard. The only product observed was $C_5Me_5(CO)_2Re(\eta^3\text{-}CH_2{-}C{\equiv}CCH_3)^+PF_6^-$ (**3a-PF$_6$**), formed by hydride abstraction from dimethylacetylene complex **2a** in 70% NMR yield. No disappearance of the diisopropylacetylene complex **2g** was observed and none of the η^3-allyl complexes **4a-PF$_6$** and **4b-PF$_6$** were seen.

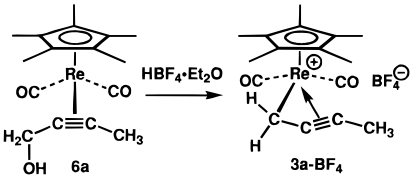
An attempt to prepare the Cp analog of a Cp* η^3-propargyl complex failed. Reaction of $C_5H_5(CO)_2Re(\eta^2\text{-}CH_3C{\equiv}CCH_3)$ (**5**) with $Ph_3C^+PF_6^-$ in CH_2Cl_2 led to a color change from yellow to green, but isolation procedures successful with Cp* analogs gave a black solid with more than 12 Cp resonances between δ 5.3 and 6.0 in the ^{1}H NMR spectrum. Observation of the reaction by ^{1}H NMR spectroscopy at −50 °C also showed multiple Cp resonances. Again, no evidence for clean formation of a π-propargyl complex was obtained.

Synthesis of η^3-Propargyl Rhenium Complexes by Protonation of η^2-Propargyl Alcohol Complexes. Two limitations of the hydride abstraction route to π-propargyl complexes are illustrated by the low regioselectivity of hydride abstraction from 2-pentyne complex **2d** and the failure to abstract a methine hydrogen from the diisopropylacetylene complex **2g**. A further limitation of the hydride abstraction route was discovered in an attempt to synthesize an unsubstituted π-propargyl complex. Attempted hydride abstraction from $C_5Me_5(CO)_2Re(\eta^2\text{-}HC{\equiv}CCH_3)$ (**2h**) using $Ph_3C^+PF_6^-$ led instead to addition of the Ph_3C^+ unit and formation of the 1,1,2-triphenylallyl complex $C_5Me_5(CO)_2Re[\eta^3\text{-}endo,syn\text{-}(CH_3)CH{-}CPh{-}CPh_2]^+PF_6^-$.[19]



To circumvent these limitations, an alternate method of synthesizing π-propargyl complexes by protonation of propargyl alcohol complexes was explored. This method of synthesizing π-propargyl complexes requires a more highly functionalized starting alkyne than is needed for hydride abstraction, but it provides the possibility of controlling regioselectivity in cases where hydride abstraction gives mixtures of products.

$C_5Me_5(CO)_2Re(H_3CC{\equiv}CCH_2OH)$ (**6a**) was synthesized by reaction of $C_5Me_5(CO)_2Re(THF)$ (**1**) with $H_3CC{\equiv}CCH_2OH$. The diastereotopic CH_2 protons were observed as separate signals (d, J = 10 Hz) in the room temperature ^{1}H NMR spectrum, consistent with slow rotation of the ligand on the NMR time scale. In a variable-temperature experiment, the signals were observed to coalesce at 77 °C, with a calculated $\Delta G^{\ddagger}_{rot}$ of 16.9 kcal mol^{-1}. Reaction of $HBF_4{\cdot}Et_2O$ with **6a** in CH_2Cl_2 cleanly produced $C_5Me_5(CO)_2Re(\eta^3\text{-}CH_2{-}C{\equiv}CCH_3)^+BF_4^-$ (**3a-BF$_4$**), which displayed identical NMR and IR spectra to **3a-PF$_6$** generated via hydride abstraction from 2-butyne complex **2a**.



The η^2-propargyl alcohol complex $C_5Me_5(CO)_2Re(\eta^2\text{-}HC{\equiv}CCH_2OH)$ (**6h**) was synthesized as a possible precursor to an unsubstituted π-propargyl complex by reaction of $C_5Me_5(CO)_2Re(THF)$ (**1**) with $HC{\equiv}CCH_2OH$. In contrast to what was observed for **3a**, the CH_2 protons on the complexed ligand were seen as a broad singlet in the ^{1}H NMR spectrum at room temperature, implying free rotation of the ligand to interconvert the two otherwise diastereotopic protons. Cooling of the sample below −16 °C decoalesced the signal into two doublets with a geminal coupling of 16 Hz. From this experiment, $\Delta G^{\ddagger}_{rot}$ for the ligand was determined to be 12.2 kcal mol^{-1}.

6h was also characterized by X-ray crystallography (Table 3, Figure 2). The alkyne carbons of **6h** are aligned nearly parallel to the Cp* ring (the angle between the plane of Re and the two alkyne carbons and the plane of Re, the Cp* centroid, and the midpoint of the complexed C≡C bond is 92.3°). The CH_2OH substituent is nearly in the plane of Re and the C≡C bond (the largest deviation from the mean plane defined by these four atoms is 0.02 Å). The CH_2OH substituent is bent away from Re [the C(3)≡C(2)−C(1) angle is 153° and the Re−C(1) distance is 3.33 Å]. The hydroxyl group is nearly antiperiplanar with respect to Re (the Re−C(2)−C(1)−OH torsional angle is 179.8°).

Treatment of **6h** with $HBF_4{\cdot}Et_2O$ in CD_2Cl_2 at −53 °C led to the clean generation of $C_5Me_5(CO)_2Re(\eta^3\text{-}CH_2{-}C{\equiv}CH)^+BF_4^-$ (**3h**), which was characterized at low temperature by ^{1}H and ^{13}C NMR and IR spectroscopy. In the ^{1}H NMR spectrum

Table 3. Selected Bond Lengths (Å) and Bond Angles (deg) for $C_5Me_5(CO)_2Re(\eta^2\text{-}HC{\equiv}CCH_2OH)$ (**6h**)

Re−C(2)	2.16(1)	C(1)−C(2)−C(3)	153(1)
Re−C(3)H	2.19(1)	C(2)−C(1)−O(1)	114(1)
C(2)≡C(3)	1.23(2)	C(4)−Re−C(5)	83.6(4)
C(1)−C(2)	1.47(2)	Cp*(cent)−Re−C(4)	125
C(1)−O(1)	1.45(2)	Cp*(cent)−Re−C(5)	124
Re−alkyne midpoint	2.09	Cp*(cent)−Re−alkyne midpoint	120

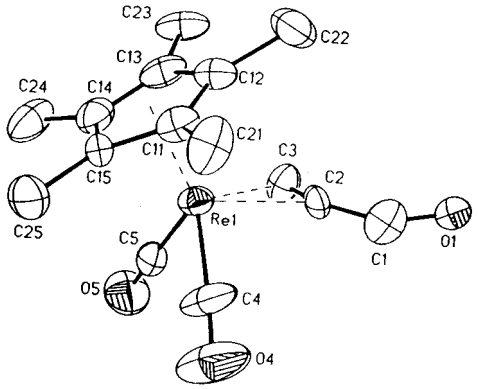
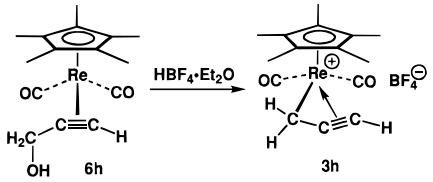


Figure 2. X-ray Structure of $C_5Me_5(CO)_2Re(\eta^2\text{-}HC{\equiv}CCH_2OH)$ (**6h**).

(19) Casey, C. P.; Yi, C. S.; Gavney, J. A. *J. Organomet. Chem.* **1993**, *443*, 111−114.

at −53 °C, the resonances for the complexed propargyl ligand appeared at δ 6.09 (t, J = 2.4 Hz, HC≡), 4.52 (dd, J = 11, 2.4 Hz, C*H*H), and 3.51 (dd, J = 11, 2.4 Hz, CH*H*). The one bond couplings of the H−^{13}C≡ unit (J_{CH} = 232 Hz) and of the ≡C−^{13}CH$_2$ unit (J_{CH} = 170 Hz) seen in the coupled ^{13}C NMR spectrum of **3h** can be used to estimate sp$^{1.2}$ hybridization for the H−C≡ group and sp$^{1.9}$ hydbridization for the −CH$_2$ group.[20] This is consistent with the importance of both propargylic and allenic resonance structures for **3h**.

The unsubstituted η^3-propargyl complex **3h** was isolated at 0 °C and could be handled rapidly at room temperature but decomposed within an hour. In solution, **3h** was stable at 0 °C, but underwent complete decomposition within 30 min at room temperature to produce more than 10 Cp* resonances between δ 1.5 and 2.5 in the ^{1}H NMR spectrum.

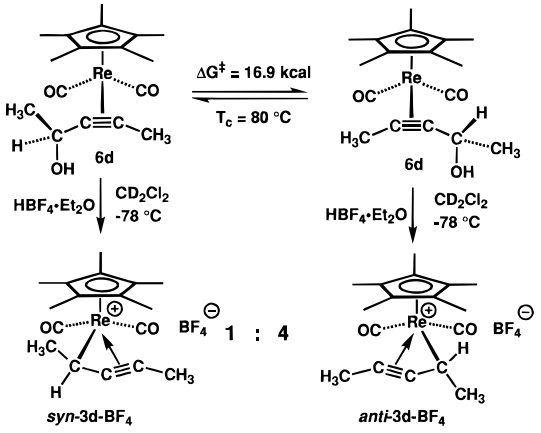


$C_5Me_5(CO)_2Re(\eta^2$-$CH_3CH_2C{\equiv}CCH_2OH)$ (**6e**) was synthesized as a possible precursor to one of the products of the reaction of the 2-pentyne complex **2d** with $Ph_3C^+PF_6^-$. As in the case of **6a**, the CH_2 diastereotopic protons of **6e** were observed as separate doublets. Reaction of **6e** with $HBF_4{\cdot}Et_2O$ in CH_2Cl_2 cleanly gave $C_5Me_5(CO)_2Re(\eta^3$-$CH_2{-}C{\equiv}CCH_2$-$CH_3)^+BF_4^-$ (**3e-BF$_4$**) in 85% yield. **3e-BF$_4$** displayed NMR and IR spectra identical to those of **3e-PF$_6$**.

To synthesize the second product generated via hydride abstraction from **2d**, $C_5Me_5(CO)_2Re[\eta^2$-$CH_3C{\equiv}CCH(CH_3)OH]$ (**6d**) was synthesized. The hydroxyl-bearing carbon in this complex adds another chiral center to the molecule, and **6d** was observed as a 1:1 mixture of diastereomers. The diastereomers can be interconverted by rotation of the alkyne ligand, and the ^{1}H NMR signals for the two compounds coalesced at 80 °C ($\Delta G^{\ddagger}_{rot}$ = 16.9 kcal mol^{-1}). Reaction of **6d** with $HBF_4{\cdot}Et_2O$ in CH_2Cl_2 at room temperature gave yellow-orange $C_5Me_5(CO)_2$-$Re(\eta^3$-$CH_3CH{-}C{\equiv}CCH_3)^+BF_4^-$ (***anti*-3d-BF$_4$**) in 80% isolated yield. The NMR and IR spectra of the complex were the same as those of ***anti*-3d-PF$_6$**, which was assigned an anti orientation of the methyl group relative to the Cp* group based on steric arguments.

The possibility that ***anti*-3d-BF$_4$** is formed by stereospecific acid promoted loss of the hydroxyl group from one of the two rapidly interconverting diastereomers of **6d** needs to be considered. If this is the case, then the observation of an 80% yield of ***anti*-3d-BF$_4$** from a 1:1 mixture of diastereomers of **6d** requires either (1) that interconversion of the diastereomers of **6d** be faster than selective loss of the hydroxyl group from one of the diastereomers or (2) that any ***syn*-3d-BF$_4$** be converted to ***anti*-3d-BF$_4$**.

To gain insight into these stereochemical issues, the protonation of **6d** (0.14 M) with 1 equiv of $HBF_4{\cdot}Et_2O$ in CD_2Cl_2 at −78 °C was monitored by 500 MHz ^{1}H NMR spectroscopy. The color of the solution changed from yellow to purple upon contact with the acid. ^{1}H NMR at −80 °C showed the formation of a 4:1 ratio of ***anti*-3d-BF$_4$** and a second compound assigned as ***syn*-3d-BF$_4$**. The broad C*H*(Me) resonance of the minor product ***syn*-3d-BF$_4$** appeared at higher frequency (δ 5.14) than that of the major isomer ***anti*-3d-BF$_4$** (δ 4.15), while the CH(*Me*) resonance for ***syn*-3d-BF$_4$** appeared at lower frequency (δ 1.71, d, J = 6.4 Hz) than that of the major isomer ***anti*-3d-BF$_4$** (δ 2.00). The $H_3CC{\equiv}$ resonance appeared at δ 2.48 for ***syn*-3d-BF$_4$** compared to δ 2.58 for ***anti*-3d-BF$_4$**. The Cp* resonances of both isomers were coincident at δ 2.02. Upon warming above −20 °C, both the purple color and resonances for the minor product ***syn*-3d-BF$_4$** disappeared while the intensities of the signals for the major product ***anti*-3d-BF$_4$** were unchanged. This is consistent with decomposition of ***syn*-3d-BF$_4$** to unknown products rather than conversion to ***anti*-3d-BF$_4$**.



Since we were unable to prepare π-propargyl complexes by abstraction of a methine hydrogen from an isopropyl group, we have investigated the protonation of propargyl alcohol complexes as a route to such compounds. While protonation of $C_5Me_5(CO)_2Re[\eta^2$-$HC{\equiv}CC(CH_3)_2OH]$ (**6i**) with $HBF_4{\cdot}Et_2O$ in CH_2Cl_2 at room temperature resulted in decomposition (>10 Cp* ^{1}H NMR resonances between δ 1.5 and δ 2.5), protonation of **6i** in CD_2Cl_2 at −80 °C resulted in a purple solution. ^{1}H NMR spectroscopy at −50 °C showed a single major product consistent with the formation of $C_5Me_5(CO)_2Re[\eta^3$-$(CH_3)_2C{-}C{\equiv}CH]^+BF_4^-$ (**3i**). The Cp* resonance appeared at δ 2.02 and a singlet at δ 6.35 was assigned to the HC≡ unit. Resonances for the *gem*-dimethyl group were obscured by the Cp* resonance. Upon warming to −20 °C, the purple color disappeared and decomposition products were observed by ^{1}H NMR spectroscopy.

Discussion

Preferred Synthetic Routes to π-Propargyl Complexes. Two routes to η^3-propargyl rhenium complexes were explored. In cases where hydride abstraction with $Ph_3C^+PF_6^-$ from $C_5Me_5(CO)_2Re(\eta^2$-alkyne) complexes produces a single product, this method is preferred because the starting alkyne complexes can be prepared in higher yield and from less functionalized precursors. These cases include symmetric internal alkynes and unsymmetric internal alkynes where one of the substituents is a secondary or tertiary alkyl group inert to hydride abstraction. The hydride abstraction route, however, has low regioselectivity and fails for terminal alkyne complexes. Protonation of rhenium propargyl alcohol complexes provides a more versatile route to π-propargyl complexes because of its regiospecificity and tolerance of terminal alkynes.

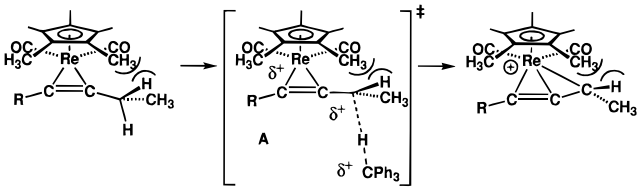
Stereochemistry and Mechanism of Hydride Abstraction. The regioselectivity of hydride abstraction from η^2-alkyne complexes showed the following highly unusual reactivity order: methylene > methyl ≫ methine hydrogen. A 2.5:1 preference for abstraction from an ethyl group compared with

(20) Freibolin, H. *Basic One- and Two-Dimensional NMR Spectroscopy*; VCH: Weinheim, 1993; p 95.

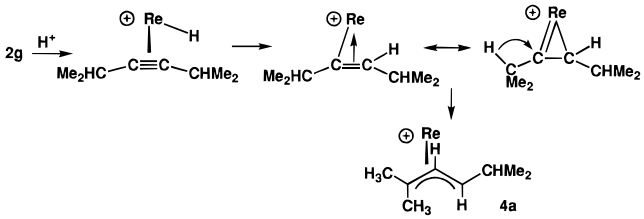
a methyl group was seen in the reaction of methylethylacetylene complex **2d**. This regioselectivity is readily understood since the hydride abstraction generates a cation in which the partial positive charge developing at carbon can be electronically stabilized by the electron donor alkyl substituent. An even greater regioselectivity for hydride abstraction from isopropyl over methyl was anticipated because the two electron donor substituents at the propargylic carbon should be better able to electronically stabilize the developing positive charge. However, in a very surprising reversal of regioselectivity, exclusive hydride abstraction from the methyl group of methylisopropylacetylene complex **2f** was observed.

Hydride abstraction from the ethyl group of either methylethylacetylene complex **2d** or diethylacetylene complex **2c** gave only a single stereoisomer. Based on steric considerations, we suggest that the methyl group is located in the less crowded anti position directed away from the Cp* group in both **3c** and ***anti*-3d-PF$_6$**.

The unusual regioselectivity and stereoselectivity of hydride abstraction can be explained by a transition state **A** in which the carbon−hydrogen bond being cleaved is antiperiplanar with respect to rhenium. In this transition state, the syn propargylic substituent comes into close contact with the Cp* ligand. For abstraction from an ethyl group, one hydrogen must be antiperiplanar to Re and the other hydrogen can occupy the sterically crowded syn position; this leads directly to the *anti*-methyl-substituted product. For isopropyl groups, antiperiplanar hydride abstraction would require a methyl group in the sterically crowded syn position; this transition state is high enough in energy that competing reactions dominate and no hydride abstraction from isopropyl groups is observed. It is interesting to note that the propargylic carbon undergoing hydride abstraction is bent away from Re in the starting η^2-alkyne complex and bent toward Re in the η^3-propargyl complex. In contrast, substituents on this propargylic carbon are bent toward Re in the η^2-alkyne complex and away from Re in the η^3-propargyl complex; these geometric differences largely cancel one another so that the substituents on the propargylic carbon move only slightly closer to Re upon conversion of the η^2-alkyne complex to the η^3-propargyl complex.



In an attempt to force hydride abstraction from an isopropyl group, the reaction of diisopropylacetylene complex **2g** with $Ph_3C^+PF_6^-$ was studied. However, hydride abstraction is so disfavored that an addition of adventitious acid[21] to **2g** occurred instead to give η^3-allyl complexes **4a-PF$_6$** and **4b-PF$_6$**. The formation of these η^3-allyl complexes is suggested to occur via protonation of the complexed acetylene, followed by a 1,2-hydride shift.[22]



Mechanism of Alcohol Protonation Route to π-Propargyl Complexes. The low temperature protonation of the 1:1 mixture of the diastereomers of pent-3-yn-2-ol complex $C_5Me_5(CO)_2Re[\eta^2\text{-}CH_3C{\equiv}CCH(CH_3)OH]$ (**6d**) produced a 4:1 mixture of ***anti*-:*syn*-3d-BF$_4$** [$C_5Me_5(CO)_2Re(\eta^3\text{-}CH_3CH{-}C{\equiv}CCH_3)^+BF_4^-$]. Upon warming to −20 °C, the syn isomer decomposed without any evidence for conversion to the anti isomer. These observations are readily understood in terms of a mechanism similar to that suggested for hydride abstraction. We propose that acid-promoted loss of the hydroxyl group occurs via a transition state in which rhenium and the protonated hydroxyl group are antiperiplanar to one another. Thus, one of the diastereomers of **6d** is poised for formation of sterically uncrowded ***anti*-3d-BF$_4$** in which the methyl group is directed away from the large Cp* ligand. Loss of water from the other diastereomer would produce sterically crowded ***syn*-3d-BF$_4$** with a methyl group jabbed into the vicinity of the Cp* ligand and would be expected to be slower. Apparently, loss of water is slow enough to allow interconversion of the two diastereomers at a rate competitive with loss of water from the precursor of the more strained π-propargyl complex. The sterically more crowded ***syn*-3d-BF$_4$** undergoes decomposition so that only ***anti*-3d-BF$_4$** can be isolated upon workup. No conversion of ***syn*-3d-BF$_4$** to ***anti*-3d-BF$_4$** was seen; indeed, we have found no evidence for rotation of a π-propargyl ligand that would interchange syn and anti positions.

Experimental Section

General. All air-sensitive materials were manipulated under dry nitrogen in a glovebox or by standard high-vacuum and Schlenk techniques. Diethyl ether, THF, toluene, hexane, and benzene were distilled from purple solutions of sodium benzophenone ketyl immediately prior to use.

^{1}H NMR spectra were obtained on Bruker WP200, WP270, AC300, AM360, or AM500 spectrometers. ^{13}C NMR spectra were obtained on Bruker AM360 or AM500 spectrometers. Infrared spectra were measured on Mattson Polaris or Mattson Genesis FT-IR spectrometers. EI mass spectra were determined on a KRATOS MS-80. LSIMS mass spectra were determined on a VG AutoSpec M.

$C_5Me_5(CO)_2Re(THF)$ (1).[14] A solution of $C_5Me_5Re(CO)_3$[23] (1.00 g, 2.46 mmol) in THF (150 mL) was purged with nitrogen in a photolysis cell at 0 °C. The solution was irradiated with a Hanovia medium-pressure mercury lamp for 30 min at 0 °C under a nitrogen purge. When the resulting red-orange solution was concentrated to 2 mL under vacuum in a reversible frit apparatus, a yellow solid precipitated. Additional yellow solid precipitated when hexane (∼40 mL) was vacuum-transferred into the flask at −78 °C. The solid was collected on the frit, washed with cold hexane to remove red hexane-soluble impurities, and dried under vacuum to give **1** (460 mg, 42%) as a bright yellow solid which was stored at −30 °C under nitrogen. ^{1}H NMR (200 MHz, THF-d_8) δ 3.78 (OCH_2), 1.95 (C_5Me_5), 1.81 (OCH_2CH_2). ^{13}C{^{1}H} NMR (126 MHz, toluene-d_8, −80 °C) δ 208.9 (CO), 92.9 (C_5Me_5), 86.4 (OCH_2), 27.3 (OCH_2CH_2), 10.8 (C_5Me_5). IR (THF) 1893 (s), 1823 (s) cm^{-1}.

General Procedure for Preparation of Alkyne Complexes. A solution of $C_5Me_5(CO)_2Re(THF)$ (**1**) and excess alkyne RC≡CR′ (5−15 equiv) in 5 mL of THF was stirred overnight. Volatiles were evaporated under vacuum and the solid residue was chromatographed on silica gel using 3:1 hexanes:Et_2O to give the corresponding rhenium alkyne complex as a yellow solid.

(21) The source of the acid protons is unknown. Trityl cation reacts with water to generate H^+ and Ph_3COH. We cannot rule out the water from the glassware as the proton source, despite our best efforts to maintain dry conditions.

(22) The net 1,2-hydride shift might also occur by β-hydride elimination from the vinyl intermediate to form a metal−hydride−allene complex, followed by addition of hydride to the central carbon.

(23) Patton, A. T.; Strouse, C. E.; Knobler, C. B.; Gladysz, J. A. *J. Am. Chem. Soc.* **1983**, *105*, 5804−5811.

$C_5Me_5(CO)_2Re(CH_3C{\equiv}CCH_3)$ (2a). 2-Butyne (3 mmol) and **1** (254 mg, 0.565 mmol) gave **2a** (210 mg, 85%). ^{1}H NMR (C_6D_6, 200 MHz) δ 2.27 (s, C≡CH_3), 1.68 (s, C_5Me_5). ^{13}C NMR (C_6D_6, 126 MHz) δ 209.2 (s, CO), 99.2 (s, C_5Me_5), 70.6 (s, $C{\equiv}CH_3$), 11.2 (q, J = 130 Hz, C≡CH_3), 10.4 (q, J = 127 Hz, C_5Me_5). IR (Et_2O) 1953 (s), 1868 (s) cm^{-1}. HRMS (EI) Calcd (obsd) for $C_{16}H_{21}O_2Re$ 432.1101 (432.1110). Anal. Calcd for $C_{16}H_{21}O_2Re$: C, 44.53, H, 4.90. Found: C, 44.63; H, 4.63.

$C_5Me_5(CO)_2Re[\eta^2\text{-}CH_3C{\equiv}CC(CH_3)_3]$ (2b). 4,4-Dimethyl-2-pentyne (1 mmol) and **1** (30 mg, 0.067 mmol) gave **2b** (16 mg, 50%). ^{1}H NMR (C_6D_6, 200 MHz) δ 2.28 (s, CH_3), 1.69 (s, C_5Me_5), 1.30 (s, CMe_3). ^{13}C{^{1}H} NMR (C_6D_6, 0.07 M Cr(acac)$_3$, 126 MHz) δ 210.6 (CO), 208.2 (CO), 99.3 (C_5Me_5), 90.5 (≡CCMe$_3$), 72.5 (≡CMe), 33.7 (CMe$_3$), 31.8 (CMe_3), 11.4 (≡CMe), 10.5 (C_5Me_5). IR (THF) 1944, 1863 cm^{-1}. HRMS (EI) Calcd (obsd) for $C_{19}H_{27}O_2Re$ 474.1571 (474.1565).

$C_5Me_5(CO)_2Re(\eta^2\text{-}CH_3CH_2C{\equiv}CCH_2CH_3)$ (2c). 3-Hexyne (3 mmol) and **1** (100 mg, 0.223 mmol) gave **2c** (0.139 mmol, 62%). ^{1}H NMR (THF-d_8, 500 MHz) δ 2.67 (q, J = 7 Hz, CH_2), 1.98 (s, C_5Me_5), 1.26 (t, J = 7 Hz, CH_3). ^{13}C{^{1}H} NMR (THF-d_8, 126 MHz) δ 209.5 (CO), 99.9 (C_5Me_5), 78.2 (C≡C), 21.7 (CH$_2$), 16.3 (CH$_3$), 10.6 (C_5Me_5). IR (THF) 1945, 1859 cm^{-1}. HRMS (EI) Calcd (obsd) for $C_{18}H_{25}O_2Re$ 460.1414 (460.1408).

$C_5Me_5(CO)_2Re(\eta^2\text{-}CH_3C{\equiv}CCH_2CH_3)$ (2d). 2-Pentyne (0.24 mmol) and **1** (49 mg, 0.109 mmol) gave **2d** (30 mg, 62%). ^{1}H NMR (C_6D_6, 298 K, 500 MHz) δ 2.55 (br, CH_2), 2.32 (t, J = 2 Hz, CH_3), 1.69 (s, C_5Me_5), 1.19 (t, J = 7 Hz, CH_3). ^{13}C{^{1}H} NMR (C_6D_6, 126 MHz) δ 99.1 (C_5Me_5), 77.4 (C≡CCH$_2$CH$_3$), 71.4 (C≡CCH$_3$), 21.2 (CH$_2$CH$_3$), 15.6 (CH$_2$$CH_3$), 11.4 (C≡$CCH_3$), 10.3 ($C_5Me_5$), CO not observed. IR (THF) 1947, 1859 cm^{-1}. HRMS (EI) Calcd (obsd) for $C_{17}H_{23}O_2Re$ 446.1257 (446.1305).

$C_5Me_5(CO)_2Re[\eta^2\text{-}CH_3C{\equiv}CCH(CH_3)_2]$ (2f). 4-Methyl-2-pentyne (3 mmol) and **1** (48 mg, 0.107 mmol) gave **2f** (25 mg, 50%). ^{1}H NMR (C_6D_6, 200 MHz) δ 2.76 (sept q, J = 7 Hz, CH), 2.32 (d, J = 2 Hz, ≡CCH$_3$), 1.69 (s, C_5Me_5), 1.28 [d, J = 7 Hz, CH(CH_3)CH$_3$], 1.26 [d, J = 7 Hz, CH(CH$_3$)CH_3]. ^{13}C{^{1}H} NMR (C_6D_6, 126 MHz) δ 99.3 (C_5Me_5), 83.8 (CHC≡), 72.0 (≡CMe), 28.6 (CH), 24.3 [CH(CH$_3$)CH$_3$], 23.5 [CH(CH$_3$)CH$_3$], 11.4 (≡CMe), 10.4 (C_5Me_5), CO not observed. IR (THF) 1945, 1859 cm^{-1}. HRMS (EI) Calcd (obsd) for $C_{18}H_{25}O_2Re$ 460.1414 (460.1451).

$C_5Me_5(CO)_2Re[\eta^2\text{-}(CH_3)_2CHC{\equiv}CCH(CH_3)_2]$ (2g). 2,5-Dimethyl-3-hexyne (0.65 mmol) and **1** (30 mg, 0.067 mmol) gave **2g** (18 mg, 55%). ^{1}H NMR (toluene-d_8, 500 MHz, 298 K) δ 2.82 (sept, J = 7 Hz, CH$_2$), 1.72 (s, C_5Me_5), 1.26 [d, J = 7 Hz, CH(CH_3)CH$_3$], 1.24 [d, J = 7 Hz, CH(CH$_3$)CH_3]. ^{13}C{^{1}H} (C_6D_6, 68 MHz, 0.07 M Cr(acac)$_3$) δ 209.6 (CO), 99.1 (C_5Me_5), 83.5 (C≡C), 28.6 (CHMe$_2$), 25.2 [CH(CH$_3$)CH$_3$], 23.8 [CH(CH$_3$)CH_3], 10.3 (C_5Me_5). IR (THF) 1942, 1858 cm^{-1}. HRMS (EI) Calcd (obsd) for $C_{20}H_{29}O_2Re$ 488.1728 (488.1697).

$C_5H_5(CO)_2Re(\eta^2\text{-}H_3CC{\equiv}CCH_3)$ (5).[24] A solution of $CH_3C{\equiv}CCH_3$ (3.3 mmol, 7 equiv) and $C_5H_5(CO)_2Re(THF)$[25] (200 mg, 0.53 mmol) in 5 mL of THF was stirred overnight. Volatiles were evaporated under vacuum and the residual solid was chromatographed on silica gel using 4:1 hexanes:CH_2Cl_2 to give **5** (120 mg, 62%) as a yellow solid. ^{1}H NMR (C_6D_6, 200 MHz) δ 5.27 (s, C_5H_5), 2.41 (s, CH_3). IR (THF) 1964, 1941, 1872 cm^{-1}.

General Procedure for Hydride Abstraction Route to η^3-Propargyl Complexes. A yellow solution of solid η^2-alkyne complex (0.033−0.37 mmol) and $Ph_3C^+PF_6^-$ (∼1 equiv) in 10 mL of CH_2Cl_2 turned yellow-brown with stirring for 60−90 min at room temperature. Most of the CH_2Cl_2 was evaporated under vacuum and 15 mL of Et_2O was condensed to give a tan precipitate. The precipitate was collected on a frit, washed three times with Et_2O/CH_2Cl_2, condensed from the filtrate back into the frozen top of the reversible frit assembly, and dried under vacuum to give η^3-propargyl rhenium complexes **3** as yellow powders. These complexes are stable under N_2 at −20 °C but decompose slowly in air at room temperature.

$C_5Me_5(CO)_2Re(\eta^3\text{-}CH_2{-}C{\equiv}CCH_3)^+PF_6^-$ (3a-PF_6). $C_5Me_5(CO)_2Re(CH_3C{\equiv}CCH_3)$ (**2a**) (160 mg, 0.371 mmol) and $Ph_3C^+PF_6^-$ (145 mg, 0.371 mmol) gave **3a-PF_6** (185 mg, 87%). ^{1}H NMR (CD_2Cl_2, 500 MHz) δ 4.38 (dq, J = 10, 3 Hz, CHH), 3.32 (dq, J = 10, 3 Hz, CHH), 2.58 (t, J = 3 Hz, ≡CCH$_3$), 2.11 (s, C_5Me_5). ^{13}C NMR (CD_2Cl_2, 126 MHz) δ 198.0 (s, CO), 195.3 (s, CO), 106.2 (s, C_5Me_5), 76.6 (s, ≡CCH$_3$), 56.7 (s, ≡CCH$_2$), 29.0 (t, J = 170 Hz, CH$_2$), 10.1 (q, J = 130 Hz, C_5Me_5), 8.2 (q, J = 134 Hz, ≡CCH$_3$). IR (Nujol) 2028 (s), 1954 (s) cm^{-1}; IR (THF) 2027 (s), 1957 (s) cm^{-1}. Anal. Calcd for $C_{16}H_{20}O_2RePF_6$: C, 33.39; H, 3.50. Found C, 33.24; H, 3.61.

$C_5Me_5(CO)_2Re[\eta^3\text{-}CH_2{-}C{\equiv}CC(CH_3)_3]^+PF_6^-$ (3b). $C_5Me_5(CO)_2Re[\eta^2\text{-}H_3CC{\equiv}CC(CH_3)_3]$ (**2b**) (16 mg, 0.033 mmol) and $Ph_3C^+PF_6^-$ (14 mg, 0.036 mmol) gave **3b** (10 mg, 49%). ^{1}H NMR (CD_2Cl_2, 300 MHz) δ 4.40 (d, J = 10 Hz, CHH), 3.40 (d, J = 10 Hz, CHH), 2.13 (s, C_5Me_5), 1.52 (s, CMe$_3$). ^{13}C{^{1}H} NMR (CD_2Cl_2, 126 MHz) δ 198.0 (CO), 196.3 (CO), 106.6 (C_5Me_5), 94.2 (≡CCMe$_3$), 60.5 (≡CCH$_2$), 34.2 (CMe$_3$), 33.0 (CMe_3), 30.0 (≡CCH$_2$), 10.7 (C_5Me_5). IR (THF) 2024, 1952 cm^{-1}. MS (LSIMS) Calcd (obsd) for $C_{19}H_{26}O_2Re^+$ 473.1 (473.1).

$C_5Me_5(CO)_2Re(\eta^2\text{-}CH_3CH{-}C{\equiv}CCH_2CH_3)^+PF_6^-$ (3c). $C_5Me_5(CO)_2Re(\eta^2\text{-}CH_3CH_2C{\equiv}CCH_2CH_3)$ (**2c**) (24 mg, 0.052 mmol) and $Ph_3C^+PF_6^-$ (21 mg, 0.054 mmol) gave **3c** (20 mg, 64%). ^{1}H NMR (CD_2Cl_2, 300 MHz) δ 4.24 (m, CH), 2.81 (qd, J = 7, 2 Hz, CH$_2$), 2.07 (s, C_5Me_5), 2.04 (d, obscured, CH$_3$), 1.56 (t, J = 7 Hz, CH$_3$). IR (THF) 2022, 1955 cm^{-1}. ^{13}C NMR (CD_2Cl_2, 126 MHz) δ 200.9 (s, CO), 195.2 (s, CO), 105.8 (s, C_5Me_5), 83.3 (s, ≡CCH$_2$), 60.8 (s, ≡CCH), 49.3 (d, J = 178 Hz, ≡CCH), 20.3 (q, J = 132 Hz, CHCH$_3$), 18.3 (t, J = 136 Hz, CH$_2$), 16.6 (q, J = 131 Hz, CH$_2$$CH_3$), 10.2 (q, J = 130 Hz, C_5Me_5). MS (LSIMS) Calcd (obsd) for $C_{18}H_{24}O_2Re^+$ 459.1 (459.1). Anal. Calcd for $C_{18}H_{24}O_2RePF_6$: C, 35.81; H, 4.00. Found: C, 35.66; H, 3.72.

$C_5Me_5(CO)_2Re(\eta^3\text{-}CH_3CH{-}C{\equiv}CCH_3)^+PF_6^-$ (*anti*-3d-PF_6) and $C_5Me_5(CO)_2Re(\eta^3\text{-}CH_2{-}C{\equiv}CCH_2CH_3)^+PF_6^-$ (3e-PF_6). $C_5Me_5(CO)_2Re(\eta^2\text{-}CH_3C{\equiv}CCH_2CH_3)$ (**2d**) (27 mg, 0.061 mmol) and $Ph_3C^+PF_6^-$ (24 mg, 0.062 mmol) gave a 2.5:1 mixture of ***anti*-3d-PF_6:3e-PF_6** (28 mg, 79% combined yield). The mixture of isomers was characterized spectroscopically. IR (THF) 2023, 1956 cm^{-1}. MS (LSIMS) Calcd (obsd) for $C_{17}H_{22}O_2Re^+$ 445 (445).

$C_5Me_5(CO)_2Re(\eta^3{-}CH_3CH{-}C{\equiv}CCH_3)^+PF_6^-$ (***anti*-3d-PF_6**): ^{1}H NMR (CD_2Cl_2, 300 MHz) δ 4.20 (m, CHMe), 2.63 (d, J = 2 Hz, H$_3$CC≡), 2.08 (s, C_5Me_5), 2.05 (d, J = 7 Hz, CHCH_3). ^{13}C{^{1}H} NMR (CD_2Cl_2, 126 MHz) δ 200.7 (CO), 195.3 (CO), 105.8 (C_5Me_5), 77.0 (≡CCH$_3$), 59.8 (≡CCH), 48.1 (CHCH$_3$), 20.1 (CHCH$_3$), 10.1 (C_5Me_5), 8.3 (≡CCH$_3$).

$C_5Me_5(CO)_2Re(\eta^3\text{-}CH_2{-}C{\equiv}CCH_2CH_3)^+PF_6^-$ (**3e-PF_6**): ^{1}H NMR (CD_2Cl_2, 300 MHz) δ 4.41 (dt, J = 10, 3 Hz, CHH), 3.34 (dt, J = 10, 3 Hz, CHH), 2.75 (br, CH_2CH$_3$), 2.10 (s, C_5Me_5), 1.54 (t, J = 7 Hz, CH$_3$). ^{13}C{^{1}H} NMR (CD_2Cl_2, 126 MHz) δ 198.1 (CO), 195.1 (CO), 106.2 (C_5Me_5), 82.9 (≡CEt), 57.8 (≡CCH$_2$), 29.9 (≡CCH$_2$), 18.2 (CH$_2$CH$_3$), 16.3 (CH$_2$$CH_3$), 10.2 ($C_5Me_5$).

$C_5Me_5(CO)_2Re[\eta^3\text{-}CH_2{-}C{\equiv}CCH(CH_3)_2]^+PF_6^-$ (3f). $C_5Me_5(CO)_2Re[\eta^2\text{-}CH_3C{\equiv}CCH(CH_3)_2]$ (**2f**) (25 mg, 0.054 mmol) and $Ph_3C^+PF_6^-$ (23 mg, 0.059 mmol) gave **3f** (12 mg, 37% yield) along with 20% of an unidentified impurity. ^{1}H NMR (CD_2Cl_2, 300 MHz, CHMe$_2$ not observed) δ 4.40 (dd, J = 10, 2 Hz, CHH), 3.35 (dd, J = 10, 2 Hz, CHH), 2.11 (s, C_5Me_5), 1.63 [d, J = 7 Hz, CH(CH_3)CH$_3$], 1.38 [d, J = 7 Hz, CH(CH$_3$)CH_3]. IR (THF) 2021, 1957 cm^{-1}. MS (LSIMS) Calcd (obsd) for $C_{18}H_{24}O_2Re^+$ 459.1 (459.3).

$C_5Me_5(CO)_2Re\{\eta^3\text{-}endo,syn\text{-}(H_3C)_2C{-}CH{-}CH[CH(CH_3)_2]\}^+PF_6^-$ (4a-PF_6) and $C_5Me_5(CO)_2Re\{\eta^3\text{-}exo,syn\text{-}(H_3C)_2C{-}CH{-}CH[CH(CH_3)_2]\}^+PF_6^-$ (4b-PF_6). Reaction of $C_5Me_5(CO)_2Re[\eta^2\text{-}(CH_3)_2CHC{\equiv}CCH(CH_3)_2]$ (**2g**) (16 mg, 0.032 mmol) and $Ph_3C^+PF_6^-$ (14 mg, 0.036 mmol) in CH_2Cl_2 (10 mL) followed by workup as described for η^3-propargyl complexes gave a 1:1 mixture of **4a-PF_6:4b-PF_6** (9 mg, 43% yield) as an off-white powder. The 1:1 mixture equilibrated over 2 days in CD_2Cl_2 solution to produce a 1.3:1 ratio of **4a-PF_6:4b-PF_6**. The mixture was characterized spectroscopically. IR (THF) 2011, 1951 cm^{-1}. MS (LSIMS) Calcd (obsd) for $C_{20}H_{30}O_2Re^+$ 489.18 (489.2). ^{13}C{^{1}H} NMR (CD_2Cl_2, 126 MHz) for a mixture of isomers: δ 203.6 (CO), 200.1 (CO), 195.44 (CO), 194.45 (CO), 107.4 (CCC), 105.6 (C_5Me_5), 104.4 (C_5Me_5), 87.9 (CCC), 76.0 (CCC), 75.9 (CCC), 72.2 (CCC), 68.5 (CCC), 32.4 (CHMe$_2$), 31.3 (CHMe$_2$), 29.6 (CH$_3$), 28.9 (CH$_3$), 27.6 (CH$_3$), 27.2 (CH$_3$), 26.6 (CH$_3$), 24.2 (CH$_3$), 23.4 (CH$_3$), 23.3 (CH$_3$), 10.6 (C_5Me_5), 10.4 (C_5Me_5).

(24) Alt, H. G.; Engelhardt, H. E. *J. Organomet. Chem.* **1988**, *342*, 235−241.

(25) Sellman, D.; Kleinschmidt, E. *Z. Naturforsch. B* **1977**, *32*, 795−801.

Endo, syn isomer **4a-PF$_6$**: ^{1}H NMR (CD_2Cl_2, 300 MHz) δ 3.92 (d, J = 10 Hz, Me_2CCH), 3.02 (t, J = 11 Hz, $CHCHCH$), 2.14 (s, C_5Me_5), 2.11 [s, $C(CH_3)CH_3$], 1.89 [s, $C(CH_3)CH_3$], 1.42 [d, J = 7 Hz, $CH(CH_3)CH_3$], 1.18 [d, J = 7 Hz, $CH(CH_3)CH_3$], $CHMe_2$ not observed.

Exo, syn isomer **4b-PF$_6$**: ^{1}H NMR (CD_2Cl_2, 300 MHz) δ 3.43 (d, J = 9 Hz, Me_2CCH), 3.16 (t, J = 10 Hz, $CHCHCH$), 2.10 (s, C_5Me_5), 2.07 [s, $C(CH_3)CH_3$], 1.69 [s, $C(CH_3)CH_3$), 1.29 [d, J = 7 Hz, $CH(CH_3)CH_3$], 1.14 [d, J = 7 Hz, $CH(CH_3)CH_3$], $CHMe_2$ not observed.

$C_5Me_5(CO)_2Re\{\eta^3$-*endo,syn*-$(H_3C)_2C-CH-CH[CH(CH_3)_2]\}^+BF_4^-$ (4a-BF$_4$) and $C_5Me_5(CO)_2Re\{\eta^3$-*exo,syn*-$(H_3C)_2C-CH-CH[CH(CH_3)_2]\}^+BF_4^-$ (4b-BF$_4$). $HBF_4\cdot Et_2O$ (5.4 μL 85%, 0.076 mmol) was added to $(C_5Me_5)(CO)_2Re[\eta^2$-$(CH_3)_2CHC\equiv CCH(CH_3)_2]$ (**2g**) (15 mg, 0.031 mmol) in CD_2Cl_2 in a resealable NMR tube. Upon mixing the yellow solution turned pale red. NMR spectra of **4a-BF$_4$** and **4b-BF$_4$** were broad due to excess HBF_4. The solution was transferred to a reversible frit assembly and most of the CD_2Cl_2 was evaporated under vacuum. A tan solid precipitated when 10 mL of Et_2O was added. The precipitate was filtered, washed three times with the Et_2O/CD_2Cl_2 solution, and dried under vacuum to give a 1:1 mixture of **4a-BF$_4$**:**4b-BF$_4$** (10 mg, 52%) as an off-white powder. The spectra of **4a-BF$_4$** and **4b-BF$_4$** were very similar to those of **4a-PF$_6$** and **4b-PF$_6$**.

General Procedure for Preparation of Propargyl Alcohol Complexes. An excess of a propargyl alcohol (0.2 mL, 5−15 equiv) was added via syringe to a solution of $C_5Me_5(CO)_2Re(THF)$ (**1**) in 1 mL of THF at −78 °C. The yellow solution turned red upon warming to room temperature. After 1 h, volatiles were evaporated under vacuum and the solid residue was chromatographed (silica gel, 2:1 hexanes:Et_2O) to give the corresponding rhenium propargyl alcohol complex as a yellow solid.

$C_5Me_5(CO)_2Re(\eta^2$-$CH_3C\equiv CCH_2OH)$ (6a). But-2-yn-1-ol (3 mmol) and **1** (198 mg, 0.45 mmol) gave **6a** (94 mg, 47%) as a yellow solid. ^{1}H NMR (C_6D_6, 300 MHz) δ 4.69 (br d, J = 10 Hz, CHH), 4.41 (br d, J = 10 Hz, CHH), 2.33 (t, J = 2 Hz, CH_3), 1.66 (s, C_5Me_5), −OH not observed. ^{13}C NMR (C_6D_6, 125 MHz) δ 209.0 (s, CO), 208.5 (s, CO), 99.7 (s, C_5Me_5), 76.5 (s, $C\equiv C$), 75.9 (s, $C\equiv C$), 59.2 (t, J = 145 Hz, CH_2), 11.4 (q, J = 127 Hz, $\equiv CCH_3$), 10.3 (q, J = 124 Hz, C_5Me_5). IR (THF): 1950 (s), 1862 (s) cm^{-1}. HRMS (EI) Calcd (obsd) for $C_{16}H_{21}O_3Re$ 448.1021 (448.1054). Anal. Calcd for $C_{16}H_{21}O_3Re$: C, 42.94; H, 4.73. Found: C, 43.05; H, 4.39.

$C_5Me_5(CO)_2Re[\eta^2$-$CH_3C\equiv CCH(CH_3)OH]$ (6d). Pent-3-yn-2-ol[26] (0.2 mL, 2 mmol) and **1** (199 mg, 0.44 mmol) gave **6d** (67 mg, 33%). ^{1}H NMR for a 1:1 mixture of diastereomers (CD_2Cl_2, 500 MHz) δ 4.88 [br q, J = 6 Hz, $CH(CH_3)OH$], 4.73 [br q, J = 6 Hz, $CH(CH_3)OH$], 2.45 (s, $H_3CC\equiv$), 2.45 (s, $H_3CC\equiv$), 2.01 (s, C_5Me_5), 1.51 [d, J= 6 Hz, $CH(CH_3)OH$], 1.43 [d, J = 6 Hz, $CH(CH_3)OH$], −OH not observed. ^{13}C NMR (CD_2Cl_2, 90.6 MHz) δ 210.3, 210.0, 208.9, 208.8 (CO), 100.5 (C_5Me_5), 82.1, 81.8 ($H_3CC\equiv C$), 76.7, 76.4 ($H_3CC\equiv C$), 65.5, 64.2 [$CH(CH_3)OH$], 24.6, 24.5 [$CH(CH_3)OH$], 11.2 ($H_3CC\equiv$), 10.6 (C_5Me_5). IR (THF) 1950 (s), 1863 (s) cm^{-1}. HRMS (EI) Calcd (obsd) for $C_{17}H_{23}O_3Re$ 460.1021 (460.1032). Anal. Calcd for $C_{17}H_{23}O_3Re$: C, 44.24; H, 5.02. Found: C, 44.48; H, 4.86.

$C_5Me_5(CO)_2Re[\eta^2$-$CH_3CH_2C\equiv CCH_2OH]$ (6e). Pent-2-yn-1-ol[27] (0.2 mL, 2 mmol) and **1** (130 mg, 0.29 mmol) gave **6e** (26 mg, 20%). ^{1}H NMR (CD_2Cl_2, 500 MHz) δ 4.74 (br d, J = 15 Hz, CH_2OH), 4.56 (br d, J = 15 Hz, CH_2OH), 2.71 (qt, J = 7, 2 Hz, CH_3CH_2), 2.00 (C_5Me_5), 1.28 (t, J = 7 Hz, CH_3CH_2). ^{13}C NMR (CD_2Cl_2, 125 MHz) δ 209.7, 209.1 (CO), 100.4 (C_5Me_5), 83.3, 76.6 (C≡C), 59.2 (t, J = 145 Hz, CH_2OH), 21.0 (t, J = 131 Hz, CH_2CH_3), 16.0 (q, J = 124 Hz, CH_2CH_3), 10.7 (C_5Me_5). IR (THF) 1950 (s), 1863 (s) cm^{-1}. HRMS (EI) Calcd (obsd) for $C_{17}H_{23}O_3Re$ 462.1177 (462.1197).

$C_5Me_5(CO)_2Re(\eta^2$-$HC\equiv CCH_2OH)$ (6h). Propargyl alcohol (3 mmol) and **1** (200 mg, 0.45 mmol) gave **6h** (128 mg, 66%). ^{1}H NMR (C_6D_6, 200 MHz) δ 4.86 (t, J = 2 Hz, ≡CH), 4.57 (br, CH_2), 1.61 (s, C_5Me_5), −OH not observed. ^{13}C NMR (C_6D_6, 125 MHz) δ 99.7 (s, C_5Me_5), 89.4 (d, ^2J = 34 Hz, $HC\equiv C$), 64.9 (d, J = 229 Hz, HC≡), 59.1 (t, J = 147 Hz, CH_2), 10.2 (q, J = 128 Hz, C_5Me_5), CO not observed. IR (THF): 1951 (s), 1867 (s) cm^{-1}. HRMS (EI) Calcd (obsd) for $C_{15}H_{19}O_3Re$ 434.0894 (434.0893). Anal. Calcd for $C_{15}H_{19}O_3Re$: C, 41.56; H, 4.42. Found: C, 40.92; H, 4.35.

$C_5Me_5(CO)_2Re[\eta^2$-$HC\equiv CC(CH_3)_2OH]$ (6i). 2-Methylbut-3-yn-2-ol (0.2 mL, 2 mmol) and **1** (70 mg, 0.16 mmol) gave **6i** (35 mg, 49%). ^{1}H NMR (CD_2Cl_2, 300 MHz) δ 5.04 (s, HC≡), 1.99 (s, C_5Me_5), 1.88 (s, OH), 1.53 [br s, $C(CH_3)_2$]. ^{13}C NMR (CD_2Cl_2, 90 MHz) δ 100.6 (C_5Me_5), 99.7 [$C(Me)_2OH$], 70.1 [$\equiv CC(Me)_2OH$], 63.4 ($HC\equiv$), 32.2 [$C(Me)_2OH$], 10.6 (C_5Me_5), CO not observed. IR (THF): 1951 (s), 1866 (s) cm^{-1}. HRMS (EI) Calcd (obsd) for $C_{17}H_{23}O_3Re$ 462.1177 (462.1209).

$C_5Me_5(CO)_2Re(\eta^3$-$CH_2-C\equiv CH)^+BF_4^-$ (3h). $HBF_4\cdot Et_2O$ (50 μL, 85%, 0.80 mmol) was added to a solution of $C_5Me_5(CO)_2Re(\eta^2$-$HC\equiv CCH_2OH)$ (**6h**) (60 mg, 23 μmol) in CH_2Cl_2 (10 mL) at −78 °C. When Et_2O (20 mL) was vacuum transferred into the solution at −78 °C, a yellow precipitate formed. Solvent was decanted from the precipitate at −78 °C. The precipitate was washed twice with 10 mL of Et_2O at −78 °C and dried under vacuum at 0 °C to give **3h** (62 mg, 89%) as an unstable yellow solid. ^{1}H NMR (acetone-d_6, 500 MHz, −43 °C) δ 6.8 (br t, HC≡), 5.0 (br d, J = 11 Hz, CHH), 4.0 (br d, J = 11 Hz, CHH), 2.15 (s, C_5Me_5); ^{13}C NMR (acetone-d_6, 126 MHz, −43 °C) δ 200.0 (CO), 194.4 (CO), 106.5 (C_5Me_5), 65.3 (dt, J = 232, 5 Hz, $HC\equiv$), 64.2 (q, J = 5 Hz, $C\equiv CCH_2$), 32.0 (t, J = 170 Hz, CH_2), 9.6 (q, J = 130 Hz, C_5Me_5). ^{1}H NMR (CD_2Cl_2, 360 MHz, −53 °C) δ 6.09 (t, J = 2.4 Hz, HC≡), 4.52 (dd, J = 11, 2.4 Hz, CHH), 3.51 (dd, J = 11, 2.4 Hz, CHH), 2.07 (s, C_5Me_5); ^{13}C {^{1}H} NMR (CD_2Cl_2, 90.7 MHz, −53 °C) δ 198.6 (CO), 191.9 (CO), 105.4 (C_5Me_5), 64.4 ($HC\equiv$), 62.7 ($\equiv CCH_2$), 32.6 (CH_2), 9.6 (C_5Me_5). IR (CD_3NO_2): 2040 (s), 1971 (s) cm^{-1}. MS (LSIMS) Calcd (obsd) for $C_{15}H_{18}O_2Re^+$ 417.0 (417.0).

General Procedure for Preparation of η^3-Propargyl Complexes by Protonation of Propargyl Alcohol Complexes. $HBF_4\cdot Et_2O$ (10 μL, 85%) was added to a yellow solution of propargyl alcohol complex in CH_2Cl_2 (10 mL) at room temperature. When Et_2O (20 mL) was syringed into the solution, a yellow precipitate formed. The reaction tube was centrifuged, solvent was decanted, and the precipitate was washed twice with 10 mL of Et_2O and dried under vacuum to give η^3-propargyl complexes as yellow powders. These complexes are stable under N_2 at −20 °C but decompose slowly in air at room temperature.

$C_5Me_5(CO)_2Re(\eta^3$-$CH_2-C\equiv CCH_3)^+BF_4^-$ (3a-BF$_4$). Addition of $HBF_4\cdot Et_2O$ (10 μL, 85%) to a yellow solution of **6a** (74 mg, 0.165 mmol) in CH_2Cl_2 (10 mL) at room temperature gave **3a-BF$_4$** (64 mg, 75%), which was isolated as a yellow solid. ^{1}H NMR (CD_2Cl_2, 500 MHz) δ 4.38 (dq, J = 10, 3 Hz, CHH), 3.32 (dq, J = 10, 3 Hz, CHH), 2.58 (t, J = 3 Hz, $\equiv CCH_3$), 2.11 (s, C_5Me_5). ^{13}C NMR (CD_2Cl_2, 126 MHz) δ 198.0 (s, CO), 195.3 (s, CO), 106.2 (s, C_5Me_5), 76.6 (s, $\equiv CCH_3$), 56.7 (s, $\equiv CCH_2$), 29.0 (t, J = 170 Hz, CH_2), 10.1 (q, J = 130 Hz, C_5Me_5), 8.2 (q, J = 134 Hz, $\equiv CCH_3$). IR (THF) 2027 (s), 1957 (s) cm^{-1}. MS (LSIMS) Calcd (obsd) for $C_{16}H_{20}O_2Re^+$ 449.2 (449.2).

$C_5Me_5(CO)_2Re(\eta^3$-$CH_3CH-C\equiv CCH_3)^+BF_4^-$ (*anti*-3d-BF$_4$). Addition of $HBF_4\cdot Et_2O$ (10 μL, 85%) to a yellow solution of **6d** (10.7 mg, 0.023 mmol) in CH_2Cl_2 (10 mL) at room temperature gave ***anti*-3d-BF$_4$** (9.8 mg, 80%), which was isolated as a yellow solid. ^{1}H NMR (CD_2Cl_2, 300 MHz) δ 4.20 (m, $CHMe$), 2.63 (d, J = 2 Hz, $H_3CC\equiv$), 2.08 (s, C_5Me_5), 2.05 (d, J = 7 Hz, $CHCH_3$). ^{13}C{^{1}H} NMR (CD_2Cl_2, 126 MHz) δ 200.7 (CO), 195.3 (CO), 105.8 (C_5Me_5), 77.0 ($\equiv CCH_3$), 59.8 ($\equiv CCH$), 48.1 ($CHCH_3$), 20.1 ($CHCH_3$), 10.1 (C_5Me_5), 8.3 ($\equiv CCH_3$). IR (THF) 2023 (s), 1956 (s) cm^{-1}.

$C_5Me_5(CO)_2Re(\eta^3$-$CH_2-C\equiv CCH_2CH_3)^+BF_4^-$ (3e-BF$_4$). Addition of $HBF_4\cdot Et_2O$ (10 μL, 85%) to a yellow solution of **6e** (20.0 mg, .043 mmol) gave **3e-BF$_4$** (19.6 mg, 85%), which was isolated as a yellow solid. ^{1}H NMR (CD_2Cl_2, 300 MHz) δ 4.41 (dt, J = 10, 3 Hz, CHH), 3.34 (dt, J = 10, 3 Hz, CHH), 2.75 (br, CH_2CH_3), 2.10 (s, C_5Me_5), 1.54 (t, J = 7 Hz, CH_3). ^{13}C{^{1}H} NMR (CD_2Cl_2, 126 MHz) δ 198.1 (CO), 195.1 (CO), 106.2 (C_5Me_5), 82.9 ($\equiv CEt$), 57.8 ($\equiv CCH_2$), 29.9 ($\equiv CCH_2$), 18.2 (CH_2CH_3), 16.3 (CH_2CH_3), 10.2 (C_5Me_5). IR (THF) 2023 (s), 1956 (s) cm^{-1}.

X-ray Crystallographic Determinations. Crystals of **3b** and **6h** were coated in epoxy and mounted on the tip of a thin glass fiber. Diffraction data were obtained with graphite-monochromated Mo Kα radiation on either a Siemens P4 diffractometer at 113 K (**3b**) or a Siemens P_{3f} diffractometer at 183 K (**6h**). Intensity data were collected in the range $3 \le 2\theta \le 45°$ using ω scans for **3b** and in the range $4 \le 2\theta \le 50°$ using θ:2θ for **6h**. Standard reflections for each data set showed no significant decrease in intensity throughout acquisition.

(26) Fleming, I.; Takaki, K.; Thomas, A. P. *J. Chem. Soc., Perkin Trans. 1* **1987**, 2269−2273.

(27) Lai, M. T. Y. *Bull. Soc. Chim. Fr.* **1933**, *4 (53)*, 682−687.

Table 4. X-ray Crystal Structure Data for $C_5Me_5(CO)_2Re[\eta^3\text{-}CH_2\text{-}C{\equiv}CC(CH_3)_3]^+PF_6^-$ (**3b**), and $C_5Me_5(CO)_2Re(\eta^2\text{-}HC{\equiv}CCH_2OH)$ (**6h**)

	3b	**6h**
empirical formula	$C_{19}H_{26}F_6O_2PRe$	$C_{15}H_{19}O_3Re$
color; habit	yellow prism	red plate
crystal system	monoclinic	tetragonal
space group	$P2_1/c$	$I4_1/a$
unit cell dimens	$a = 8.9937(8)$ Å $b = 14.2444(13)$ Å $c = 17.484(2)$ Å $\beta = 103.634(10)°$	$a = 29.196(4)$ Å $c = 7.0100(10)$ Å
volume	2176.8(3) Å^3	5975.4(14) Å^3
no. of peaks to determine cell	57	25
θ range of cell peaks	4.7 to 12.5°	12.5 to 14.0°
Z	4	16
formula wt	617.57	433.5
density (calcd)	1.884 Mg/m^3	1.927 Mg/m^3
absorption coeff	5.718 mm^{-1}	8.245 mm^{-1}
$F(000)$	1200	3328
$R(F)^a$	3.36%	3.30%
$wR(F^2)^a$	8.42%	8.61%

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

Initial positions for Re atoms were found by direct methods, and all non-hydrogen atoms were located from successive difference Fourier maps. All non-hydrogen atoms were refined anisotropically; hydrogen atoms were refined from initial idealized positions with a riding model using isotropic displacement parameters of 1.2 × isotropic equivalent of the bonded atom. In the riding model, hydrogens are fixed a set distance and geometry from the heavy atom, and "ride" the motions of the heavy atom during refinement. Crystallographic computations were performed using the SHELXTL-PLUS[28] software and the SHELXL-93[29] program on a Silicon Graphics Indigo computer.

X-ray Crystallography of $C_5Me_5(CO)_2Re[\eta^3\text{-}CH_2\text{-}C{\equiv}CC(CH_3)_3]^+PF_6^-$ (3b). Crystals of **3b** suitable for X-ray diffraction were obtained by slow evaporation of a CD_2Cl_2 solution at −20 °C. Systematic absences uniquely defined the space group as $P2_1/c$. The 3041 reflections collected produced 2828 independent reflections. Crystallographic data (Table 4) and selected bond lengths and angles (Table 1) are presented.

X-ray Crystallography of $C_5Me_5(CO)_2Re(\eta^2\text{-}HC{\equiv}CCH_2OH)$ (6h). Single crystals of **6h** suitable for X-ray analysis were obtained by slow evaporation of solvent from an ether/hexane solution. Systematic absences and statistical analyses were consistent with the space group $I4_1/a$. The 2964 reflections collected produced 2404 independent reflections. Crystallographic data (Table 4) and selected bond lengths and angles (Table 3) are presented.

Acknowledgment. Financial support from the National Science Foundation is gratefully acknowledged.

Supporting Information Available: Tables of structure determination data, atomic coordinates, positional and anisotropic thermal parameters for non-hydrogen atoms, selected interatomic distances and angles, and idealized atomic parameters for hydrogen atoms for compounds **3b** and **6h** (15 pages). See any current masthead page for ordering and Internet access instructions.

JA960375D

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

(29) Sheldrick, G. M. *J. Appl. Crystallogr.* In preparation.