Quantitative Determination of the Regioselectivity of Nucleophilic Addition to η^3-Propargyl Rhenium Complexes and Direct Observation of an Equilibrium between η^3-Propargyl Rhenium Complexes and Rhenacyclobutenes

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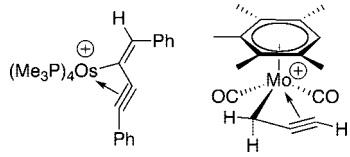
PMe_3 adds selectively to the central carbon of the η^3-propargyl complex $[C_5Me_5(CO)_2Re(\eta^3\text{-}CH_2C{\equiv}CCMe_3)][BF_4]$ (**1-*t*-Bu**) to form the metallacyclobutene $[C_5Me_5(CO)_2Re(CH_2C(PMe_3){=}CCMe_3)][BF_4]$ (**7**). The rate of rearrangement of the metallacyclobutene **7** to η^2-alkyne complex $[C_5Me_5(CO)_2Re(\eta^2\text{-}Me_3PCH_2C{\equiv}CCMe_3)][BF_4]$ (**8**) is independent of phosphine concentration, consistent with a dissociative mechanism proceeding via η^3-propargyl complex **1-*t*-Bu**. The rate of this rearrangement is 480 times slower than the rate of exchange of PMe_3 with the labeled metallacyclobutene **7-*d*$_9$**. This rate ratio provides an indirect measurement of the regioselectivity for addition of PMe_3 to the central carbon of η^3-propargyl complex **1-*t*-Bu** to give **7** compared to addition to a terminal carbon to give **8**. The addition of PPh_3 to **1-*t*-Bu** gives the metallacyclobutene $[C_5Me_5(CO)_2Re(CH_2C(PPh_3){=}CCMe_3)][BF_4]$ (**11**). Low-temperature ^{1}H NMR spectra provide evidence for an equilibrium between metallacyclobutene **11** and η^3-propargyl complex **1-*t*-Bu** ($K_{eq} \approx 44$ M^{-1} at −46 °C and $\Delta G°(0\ °C) = -1.2 \pm 0.2$ kcal mol^{-1}).

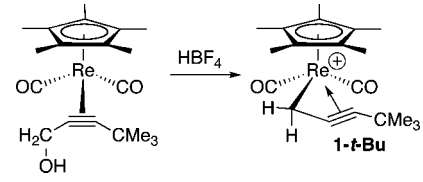
Introduction

η^3-Propargyl transition metal complexes, the triple-bond analogues of the very well studied η^3-allyl complexes, are becoming increasingly important in synthetic chemistry.[1] The first stable η^3-propargyl complex, $[(Me_3P)_4Os(\eta^3\text{-}PhC{\equiv}CC{=}CHPh)][PF_6]$, was reported by Werner in 1985,[2] and the first isolated η^3-propargyl complex not having an *exo*-double bond, $[(C_6Me_5H)Mo(CO)_2(\eta^3\text{-}CH_2C{\equiv}CH)][BF_4]$, was reported by Kryvich in 1991.[3]



We first synthesized η^3-propargyl rhenium complexes by hydride abstraction from alkyne complexes and later developed a regioselective synthesis via protonation of propargyl alcohol complexes (Scheme 1).[4] Other methods for the synthesis of isolable η^3-propargyl complexes include halide abstraction from

Scheme 1



η^1-propargyl or η^1-allenyl metal halide complexes,[5] reaction of metal halides with propargyl nucleophiles,[6] reaction of propargyl ether complexes with Lewis acids,[7] rearrangement of η^1-homopropargyl metal complexes,[8] and oxidative addition of propargyl halides or tosylates to metal complexes.[6,9]

^{1}H and ^{13}C NMR spectroscopic data and X-ray crystallographic structures suggest that η^3-propargyl complexes are best represented as a combination of η^3-propargyl and η^3-allenyl resonance structures (Figure 1).[1] Crystallographic data show that all three carbons are within bonding distance of the metal (2.2−2.5 Å), with the central carbon often nearest to the metal center. The $CR_2{=}C$ bond length is substantially longer (1.34−1.40

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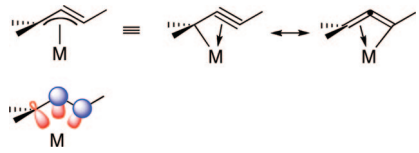
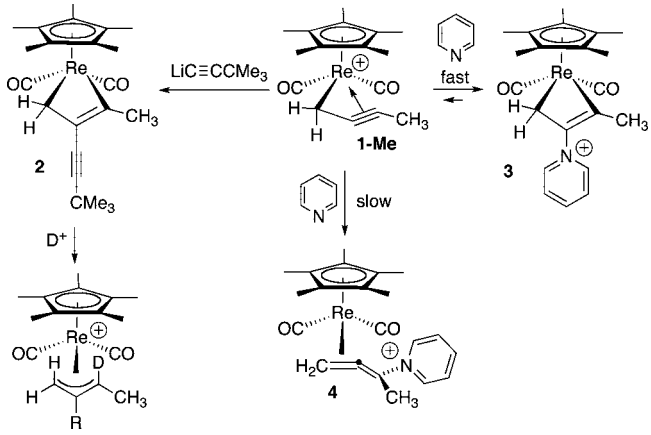


Figure 1. Resonance structures for η^3-propargyl complexes.

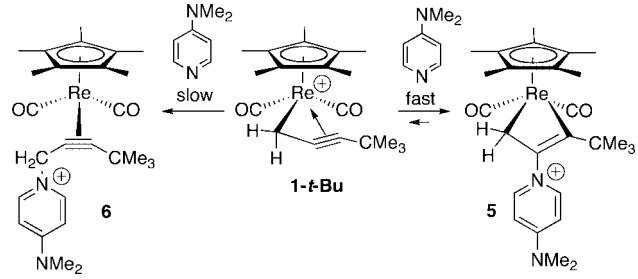
Å) than in free allenes, and the C≡CR bond length is longer than in free acetylenes. The $CR_2-C\equiv CR$ angle varies from 145° to 155°, implying substantial strain about the central carbon. This strain may be responsible for the highly reactive nature of η^3-propargyl complexes.

Scheme 2



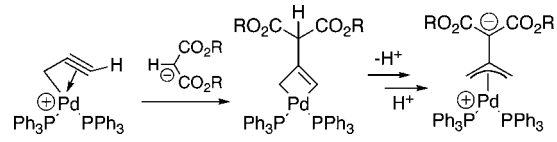
In contrast to η^3-allyl metal complexes, which are usually attacked by nucleophiles at a terminal carbon, η^3-propargyl metal complexes are selectively attacked by nucleophiles at the center carbon.[1] Nucleophiles have been observed to attack each of the three carbon centers of η^3-propargyl rhenium complexes. We found that while kinetic addition of nucleophiles occurs at the center carbon of the η^3-propargyl ligand to give rhenacyclobutene complexes, this addition is sometimes reversible and can be followed by addition at either of the other two metal-bound carbon atoms to give η^2-allene or η^2-alkyne complexes.[4a,10,11] The methyl-substituted η^3-propargyl complex $[C_5Me_5(CO)_2Re(\eta^3\text{-}CH_2C\equiv CMe)][BF_4]$ (**1-Me**) reacted irreversibly with carbon nucleophiles such as malonates and acetylides to give metallacyclobutenes (Scheme 2); protonation of the metallacyclobutenes led to η^3-allyl complexes. At low temperature, nitrogen nucleophiles added to the central propargyl carbon to produce the metastable metallacyclobutene complexes. Upon warming, the nitrogen nucleophile dissociated from the rhenacyclobutenes and then readded to the resulting η^3-propargyl complex at one of the terminal sites to give either an η^2-allene or an η^2-alkyne complex. For example, **1-Me** reacted with pyridine at −40 °C to give rhenacyclobutene **3**, which rearranged to η^2-allene complex **4** at room temperature (Scheme 2). 4-Dimethylaminopyridine added to the central carbon of the *tert*-butyl-substituted **1-*t*-Bu** below −40 °C to give the rhenacyclobutene complex **5**, which rearranged to η^2-alkyne complex **6** at room temperature; apparently, attack at the *t*-Bu-substituted carbon to give an allene complex was prevented by steric hindrance (Scheme 3).

Scheme 3



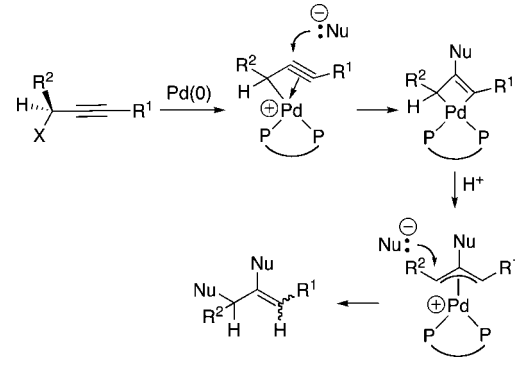
In some cases, nucleophilic additions to η^3-propargyl complexes have led to η^3-allyl complexes, consistent with initial kinetic attack at the center carbon of the η^3-propargyl ligand followed by protonation of the metallacyclobutene intermediate.[12,6] In other cases, nucleophilic additions to η^3-propargyl complexes have led to η^3-trimethylenemethane complexes, consistent with initial kinetic attack at the center carbon of the η^3-propargyl ligand followed by protonation of the metallacyclobutene intermediate and deprotonation at the atom α to the central allyl carbon (Scheme 4).[13]

Scheme 4



Tsuji pioneered the development of palladium-catalyzed reactions for addition of two nucleophiles to propargyl substrates.[14] For example, the reactions of carbon nucleophiles with propargyl carbonates produce double nucleophilic addition products where nucleophiles have added to both the central and a terminal carbon of the propargyl unit. We have proposed that these double nucleophilic additions occur by oxidative addition to produce an η^3-propargyl intermediate, which then undergoes addition of the first nucleophile to the central propargyl carbon to produce a metallacyclobutene; this is followed by protonation of the metallacyclobutene to generate an η^3-allyl complex that is attacked by a second nucleophile (Scheme 5).[10]

Scheme 5

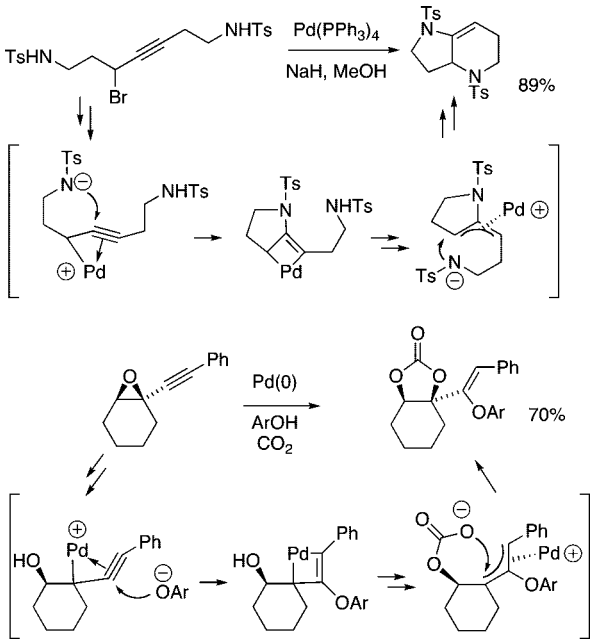


Ohno has imaginatively constructed bicyclic heterocycles by palladium-catalyzed domino cyclization of propargyl bromides.[15] Yoshida has devised a clever palladium-catalyzed three-component coupling of propargylic oxiranes, phenols, and

(10) Casey, C. P.; Nash, J. R.; Yi, C. S.; Selmeczy, A. D.; Chung, S.; Powell, D. R.; Hayashi, R. K. *J. Am. Chem. Soc.* **1998**, *120*, 722.

(11) The Pd-catalyzed reaction of propargyl halides with thiols gives mixtures of propargyl and allenyl sulfides. These reactions have been proposed to occur by attack of nucleophiles at the terminal carbons of an η^3-propargyl intermediate. However, kinetic attack at the central propargyl carbon might be reversible. Tsutsumi, K.; Yabukami, T.; Fujimoto, K.; Kawase, T.; Morimoton, T.; Kakiuchi, K. *Organometallics* **2003**, *22*, 2996.

Scheme 6



carbon dioxide.[16] Both of these processes involve double nucleophilic addition to propargyl substrates (Scheme 6).[17]

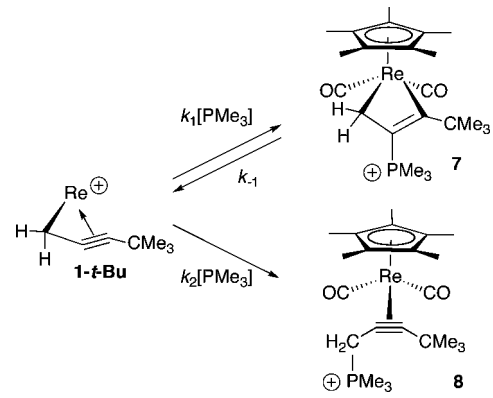
Because rhenacyclobutenes are the only observed kinetic product of nucleophilic attack on η^3-propargyl rhenium complexes, it was not possible to quantitatively measure the regioselectivity from product ratios. Here we report an indirect method for the quantitative determination of this regioselectivity. We also report the first direct observation of an equilibrium between an η^3-propargyl metal complex and a metallacyclobutene.

Results

Both the rate and the regioselectivity of the addition of nucleophiles to the central carbon of η^3-propargyl rhenium complexes are so high that it is not possible to directly measure how much faster attack at the center carbon is than attack at one of the terminal carbons. Since the rhenacyclobutene is the only observed initial product and neither an η^2-alkyne complex nor an η^2-allene complex is initially seen, estimates of >20 can be placed on the regioselectivity. In some cases, the initially formed metallacyclobutene rearranged to a thermodynamically more stable η^2-alkyne complex ($\Delta G^\circ \leq -2.3$ kcal mol^{-1}). The reaction was complete before the cold sample was inserted into the precooled NMR probe; this requires a $t_{1/2}$ of less than a minute at −50 °C and $\Delta G^\ddagger$(0.02 M ligand) ≤ 14.7 kcal mol^{-1}, $\Delta G^\ddagger$(1.0 M ligand) ≤ 12.9 kcal mol^{-1}.

Indirect Determination of Regioselectivity of Attack of Phosphines. The relative rates of nucleophilic addition to the center and terminal carbons can be measured indirectly by comparing the rates of exchange of nucleophiles with the metallacyclobutene adducts and of rearrangement of the metallacyclobutene to an η^2-alkyne complex (eqs 1−4, Scheme 7, and Figure 2). The difference between the barriers for exchange and rearrangement is also the difference between the barriers for attack at the central and terminal carbons. This method assumes a dissociative mechanism for nucleophilic exchange with the metallacyclobutene that proceeds via an η^3-propargyl intermediate.

Scheme 7



$$\text{Rate(exchange)} = k_{-1}[\mathbf{7}] \quad (1)$$

$$\text{Rate(rearrangement)} = k_{-1}[\mathbf{7}](k_2[\text{PMe}_3]/\{k_1[\text{PMe}_3] + k_2[\text{PMe}_3]\} = k_{-1}[\mathbf{7}](k_2/\{k_1 + k_2\}) \quad (2)$$

$$\text{Rate(rearrangement)}/\text{Rate(exchange)} = k_2/\{k_1 + k_2\} \quad (3)$$

$$\text{Rate(rearrangement)}/\text{Rate(exchange)} \approx k_2/k_1 \text{ when } k_1 \gg k_2 \quad (4)$$

We chose to study the exchange and rearrangement kinetics of $[C_5Me_5(CO)_2Re(CH_2C(PMe_3)=CCMe_3)][BF_4]$ (**7**) since this metallacyclobutene is relatively stable and had been fully characterized by X-ray crystallography.[10] In addition, **7** had been found to slowly rearrange at room temperature to a single product, the η^2-alkyne complex $[C_5Me_5(CO)_2Re(\eta^2$-Me$_3$-

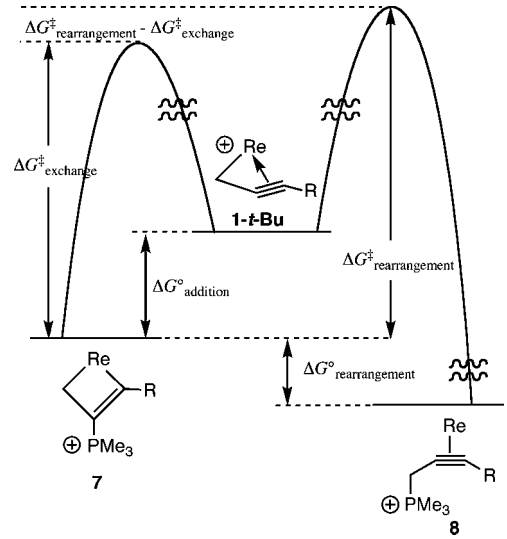


Figure 2. Free energy diagram for nucleophilic addition to η^3-propargyl complex **1-*t*-Bu**.

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(16) Yoshida, M.; Murao, T.; Sugimoto, K.; Ihara, M. *Synlett* **2007**, 575.

(17) Another interesting synthetic application that involves propargyl complexes is the palladium-catalyzed deoxygenation of propargyl formates. Radinov, R.; Hutchings, S. D. *Tetrahedron Lett.* **1999**, *40*, 8955.

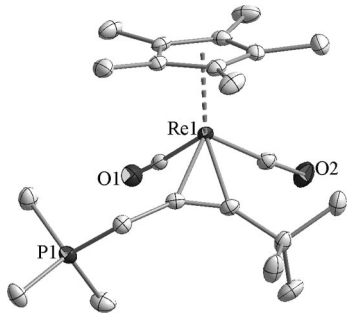
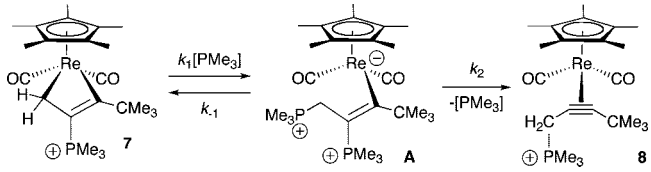


Figure 3. X-ray structure of $[C_5Me_5(CO)_2Re(\eta^2\text{-}Me_3PCH_2C{\equiv}CCMe_3)]^+$.

$PCH_2C{\equiv}CCMe_3)][BF_4]$ (**8**),[10] which was further characterized in the current work by X-ray diffraction (Figure 3). The rearrangement product, η^2-alkyne complex **8**, results from nucleophilic addition to the less crowded terminal CH_2 carbon of the intermediate η^3-propargyl complex **1-*t*-Bu** and not to the more sterically hindered *tert*-butyl-substituted carbon to form an η^2-allene isomer.

Since our method for determining relative regioselectivity depends on the assumption that rearrangement of metallacyclobutene **7** to η^2-alkyne complex **8** proceeds by phosphine dissociation to generate an η^3-propargyl intermediate, we needed to establish the rate law for the rearrangement. This was particularly necessary since associative mechanisms are conceivable. For example, phosphine attack might occur at the terminal carbon of **7** to give intermediate **A**, which could then undergo loss of phosphine to generate **8** (Scheme 8). Alkyl and vinyl $CpRe(CO)_2R^-$ anions are well-known stable species.[18] The dissociative mechanism of Scheme 7 and the associative mechanism of Scheme 8 are readily distinguished by their kinetic independence or dependence on $[PR_3]$.

Scheme 8



The rate of rearrangement of metallacyclobutene complex **7** was studied in the presence and absence of added PMe_3. Two yellow CD_3CN solutions[19] of **7** were prepared in resealable NMR tubes, and excess PMe_3 was condensed into one. The rate of rearrangement of **7** to **8** was monitored by ^1H NMR spectroscopy at 64 °C. First-order rate law fits were obtained. The rate in the absence of added PMe_3 ($k_{rearr} = (8.2 \pm 0.1) \times 10^{-4}$ s^{-1}) and in the presence of 0.29 M added PMe_3 ($k_{rearr} = (7.9 \pm 0.1) \times 10^{-4}$ s^{-1}) were very similar. The failure to observe a rate enhancement in the presence of added PMe_3 rules out an associative mechanism for the rearrangement of metallacyclobutene complex **7** to η^2-alkyne complex **8**.[20]

The deuterium-labeled metallacyclobutene $[C_5Me_5(CO)_2Re(CH_2C[P(CD_3)_3]{=}CCMe_3)][BF_4]$ (**7-*d*$_9$**) was prepared by addition of $P(CD_3)_3$ to **1-*t*-Bu**. The kinetics of the exchange of a 4.5-fold excess of $P(CH_3)_3$ with 0.1 M **7-*d*$_9$** were studied by ^1H NMR spectroscopy at 10 °C in CD_3CN by monitoring the appearance of the $P(CH_3)_3$ resonance of the exchanged metallacyclobutene **7** (Figure 4). Data analysis gave $k_{exch} = (4.9 \pm 0.5) \times 10^{-5}$ s^{-1} and $\Delta G^{\ddagger}_{10\ °C} = 22.4$ kcal·mol^{-1}.

Since exchange of phosphine with **7** is much faster than rearrangement to **8**, it was not possible to measure both rates at the same temperature. We therefore measured the rate of rearrangement of **7** to **8** by ^1H NMR spectroscopy in CD_3CN between 35 and 65 °C. A linear Eyring plot of $\ln[k/T]$ versus $1/T$ gave $\Delta H^{\ddagger} = 30.1 \pm 0.9$ kcal·mol^{-1}, $\Delta S^{\ddagger} = 16.0 \pm 0.9$ eu, and $\Delta G^{\ddagger}_{10\ °C} = 25.6$ kcal·mol^{-1}. Extrapolation of the rearrangement rate to 10 °C gave $k_{rearr} = 1.02 \times 10^{-7}$ s^{-1}.

The rate of exchange of PMe_3 with metallacyclobutene **7** is therefore 480 times faster than the rearrangement of **7** to **8** at 10 °C ($k_{exch}/k_{rearr} = [4.9 \times 10^{-7}\ s^{-1}] \div [1.0 \times 10^{-7}\ s^{-1}] = 480$). Inspection of Figure 2 reveals that this is also the rate difference between attack of PMe_3 at the center carbon and the CH_2 terminal carbon of η^3-propargyl complex **1-*t*-Bu**. This rate difference corresponds to a 3.2 kcal·mol^{-1} difference in free energy of activation ($\Delta\Delta G^{\ddagger}_{10\ °C} = 25.6 - 22.4$ kcal·mol^{-1}).

Regioselectivity of addition of $PMePh_2$ to 1-*t*-Bu was also determined indirectly by comparing the rates of rearrangement and exchange of rhenacyclobutene $[C_5Me_5(CO)_2Re(CH_2C[PMePh_2]{=}CCMe_3)][BF_4]$ (**9**). Addition of $PMePh_2$ to η^3-propargyl complex **1-*t*-Bu** at −88 °C led to complete conversion to the rhenacyclobutene **9**, which had characteristic ^1H NMR resonances at δ 0.11 (d, $J = 12.6$ Hz, C*H*H), 1.49 (d, $J = 12.2$ Hz, CH*H*), and 2.39 (d, $J_{PH} = 12.2$ Hz, PCH_3). The reaction of excess PMe_3 with PPh_2Me-substituted metallacycle **9** led to exchange and formation of the more stable PMe_3-substituted metallacycle **7**. The rate constant for exchange at −40 °C was determined by ^1H NMR spectroscopy: $k = 5.85 \times 10^{-4}$ s^{-1}, $\Delta G^{\ddagger} = 16.9$ kcal·mol^{-1}.

Upon warming to room temperature, **9** rearranged to η^2-alkyne complex $[C_5Me_5(CO)_2Re(\eta^2\text{-}Ph_2MePCH_2C{\equiv}CCMe_3)][BF_4]$ (**10**), which had characteristic ^1H NMR resonances at δ 2.45 (d, $J_{PH} = 13.1$ Hz, PCH_3), 4.15 (t, $J = 16.1$ Hz, C*H*H), and 4.72 (t, $J = 15.8$ Hz, CH*H*). The rate of rearrangement of **9** to **10** at −15 °C was measured by ^1H NMR spectroscopy: $k = 3.27 \times 10^{-5}$ s^{-1}, $\Delta G^{\ddagger}(-15\ °C) = 20.3$ kcal·mol^{-1}. The difference between this barrier for rearrangement and the barrier for exchange ($\Delta\Delta G^{\ddagger} = 20.3 - 16.9 = 3.4$ kcal·mol^{-1}) is similar to the difference in barriers for exchange and rearrangement of PMe_3-substituted metallacycle **7** and implies a regioselective preference of 960 for addition of $PMePh_2$ to the center propargyl carbon of **1-*t*-Bu**.

More Rapid Dissociation of PPh_3 than PMe_3 from Metallacyclobutenes. Previously, we had reported that the addition of PPh_3 to **1-*t*-Bu** gave the metallacyclobutene complex $[C_5Me_5(CO)_2Re(CH_2C(PPh_3){=}CCMe_3)][BF_4]$ (**11**), which subsequently rearranged to alkyne complex $[C_5Me_5(CO)_2Re(\eta^2\text{-}Ph_3PCH_2C{\equiv}CCMe_3)][BF_4]$ (**12**). In repeating this work, we monitored the reaction of **1-*t*-Bu** (0.030 M) with PPh_3 (0.063 M) in CD_2Cl_2 by ^1H NMR spectroscopy and found that metallacycle **11** was formed at −78 °C with characteristic low-frequency doublets for the metal-bound CH_2 group at δ 0.14 and 1.1 ($^2J = 12$ Hz). When the sample was warmed to −20 °C, the conversion of metallacycle **11** to alkyne complex **12** was observed by ^1H NMR spectroscopy to be 80% complete within 2 h ($\Delta G^{\ddagger} \approx 18.9(5)$ kcal·mol^{-1}). Upon warming to 25

(18) (a) Casey, C. P.; Vosejpka, P. C.; Askham, F. R. *J. Am. Chem. Soc.* **1990**, *112*, 3713. (b) Casey, C. P.; Vosejpka, P. C.; Gavney, J. A., Jr. *J. Am. Chem. Soc.* **1990**, *112*, 4083.

(19) Phosphine reactions in CD_2Cl_2 were problematic at elevated temperatures due to nucleophilic attack of PMe_3 on the solvent.

(20) The intriguing possibility of an associative mechanism for rearrangement of a metallacyclobutene was explored by studying rearrangements involving 1,2-bis(diphenylphosphino)ethane ligands, where the associative mechanism would be more likely with the possibility of intramolecular attack by a second phosphine. Even with diphos ligands, the dissociative mechanism is strongly favored. See Supporting Information.

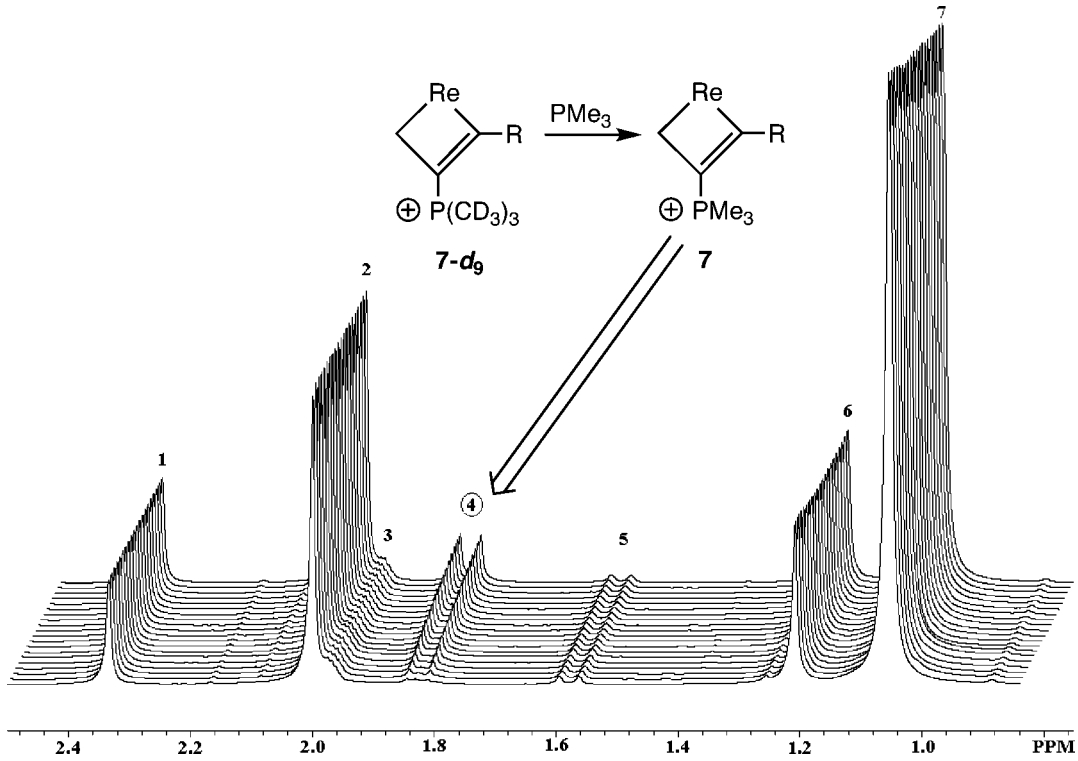
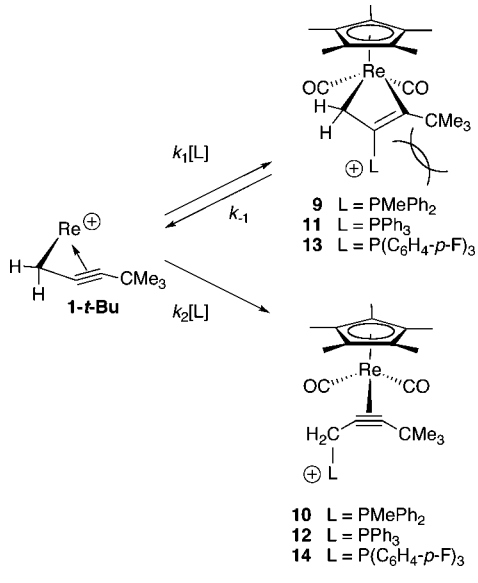


Figure 4. Elapsed time ^{1}H NMR spectra for exchange at 10 °C in CD_3CN: **7-*d*$_9$** + $P(CH_3)_3$ approaches equilibrium with **7** + $P(CD_3)_3$. Peak 4, $P(CH_3)_3$ of **7**. Other peaks: peak 2, Cp* of **7**; 5, C*H* of **7**; 6, ^{t}Bu of **7**; 7, excess $P(CH_3)_3$; 1, toluene standard; 3, CD_3CN.

Scheme 9



°C, only η^2-alkyne complex **12** was observed by ^{1}H NMR spectroscopy (Scheme 9). *Note that this rate of rearrangement conflicts with the previously reported slow rearrangement of the metallacycle **11** to η^2-alkyne complex **12** over 2 days at room temperature in CD_2Cl_2.*[10]

The much more rapid rearrangement of the PPh_3-substituted rhenacyclobutene **9** than the PMe_3-substituted rhenacyclobutene **7** ($\Delta\Delta G^{\ddagger} \approx 6.7(5)$ kcal·mol^{-1}) implies a correspondingly more rapid dissociation of phosphine from their respective rhenacyclobutenes and can be attributed in part to the greater leaving group ability of the much less nucleophilic PPh_3 group. In addition, the particularly unfavorable steric interaction between the large PPh_3 and the bulky *tert*-butyl group is relieved upon PPh_3 dissociation. The much less congested methyl-substituted metallacyclobutene $[C_5Me_5(CO)_2Re(CH_2C(PPh_3)=CCH_3)][BF_4]$ does not rearrange to either an η^2-alkyne or η^2-allene complex even upon extended heating at 50−60 °C. Only eventual decomposition is observed.

Observation of Equilibrium between η^3-Propargyl Complex 1-*t*-Bu and PPh_3-Substituted Metallacyclobutene 11. Upon close examination of the low-temperature ^{1}H NMR spectra, it became apparent that the formation of metallacyclobutene **11** did not go to completion and that an equilibrium was established with the η^3-propargyl complex **1-*t*-Bu**. After PPh_3 (0.063 M in CD_2Cl_2) was added to a yellow solution of η^3-propargyl complex **1-*t*-Bu** (0.030 M in CD_2Cl_2) at −78 °C, ^{1}H NMR spectroscopy at −88 °C showed a tiny resonance at δ 3.41 (CH*H*) characteristic of **1-*t*-Bu** in addition to intense resonances for the metallacyclobutene **11** (δ 0.14, CH*H*). Upon increasing the temperature to −66 °C, the amount of η^3-propargyl complex **1-*t*-Bu** increased and a 9.6:1 equilibrium mixture of **11**/**1-*t*-Bu** was observed (K_{eq} = [**11**]/[**1-*t*-Bu**][PPh_3] ≈ 280 M^{-1}). At −56 °C, the amount of the η^3-propargyl complex increased further, and a 4.5:1 equilibrium mixture of **11**/**1-*t*-Bu** was observed ($K_{eq} \approx 100$ M^{-1}). When the sample was recooled to −66 °C, the ratio of **11**: **1-*t*-Bu** reverted to 9.6:1. At −46 °C, the ratio of **11**:**1-*t*-Bu** dropped to 1.9:1 ($K_{eq} \approx 44$ M^{-1}). When the temperature was lowered to −66 °C, the ratio of **11**:**1-*t*-Bu** increased to 10.8:1 ($K_{eq} \approx 310$ M^{-1}). Thus, as the temperature increases, the equilibrium shifts toward η^3-propargyl complex **1-*t*-Bu** and free PPh_3 at the expense of the adduct rhenacyclobutene **11** (Figure 5).

When the sample was warmed to −34 °C, the ratio of **11**: **1-*t*-Bu** fell to 1.1:1 ($K_{eq} \approx 25$ M^{-1}) and some conversion to η^2-alkyne complex $[C_5Me_5(CO)_2Re(\eta^2\text{-}Ph_3PCH_2C{\equiv}CCMe_3)][BF_4]$ (**12**) (16% after 10 min) was seen ($\Delta G^{\ddagger} \approx 17.5(5)$ kcal·mol^{-1}).[21] At −23.5 °C, a 1:2 ratio of **11**:**1-*t*-Bu** ($K_{eq} \approx$ 11 M^{-1}) was seen along with 56% conversion to the thermodynamically stable η^2-alkyne complex **12** after 10 min ($\Delta G^{\ddagger} \approx$

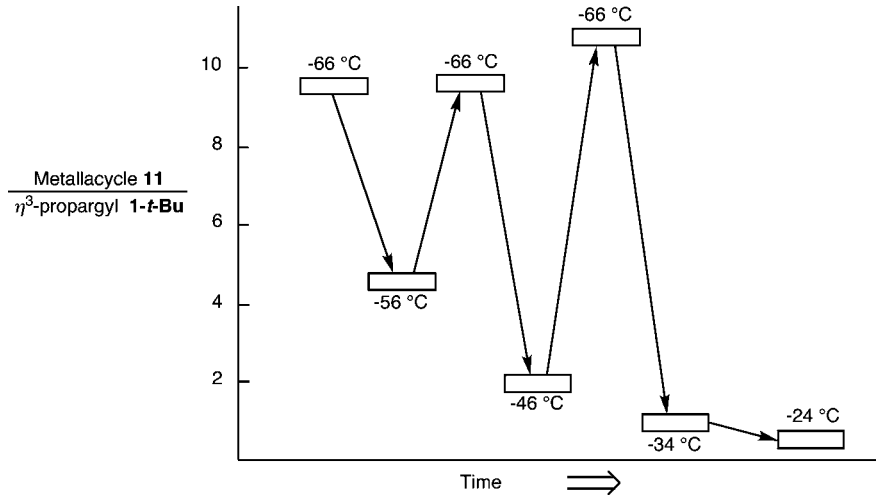


Figure 5. Ratio of rhenacyclobutene **11** to η^3-propargyl complex **1-*t*-Bu** as temperature is raised and lowered.

17.8(5) kcal mol^{-1}).[21] After 1 h at room temperature, complete conversion to **12** was seen. When this solution of η^2-alkyne complex **12** was recooled to −66 °C, no change in the NMR spectrum was seen, demonstrating that the formation of the thermodynamically stable η^2-alkyne complex is irreversible.

Additional measurements of the equilibrium between the rhenacyclobutene and the η^3-propargyl complex carried out using lower concentrations of the PPh_3 (0.042 M in CD_2Cl_2) and the same concentration of η^3-propargyl complex **1-*t*-Bu** (0.03 M in CD_2Cl_2) gave similar values for the equilibrium constants. At −66 °C, a 4.5:1 equilibrium mixture of rhenacyclobutene **11**:η^3-propargyl complex **1-*t*-Bu** was observed by ^{1}H NMR spectroscopy ($K_{eq} \approx 260$ M^{-1}). At −46 °C, a 1:1 mixture of **11/1-*t*-Bu** was seen ($K_{eq} \approx 35$ M^{-1}). A van't Hoff plot of all the equilibrium data gave $\Delta H° = -8.0 \pm 1$ kcal·mol^{-1}, $\Delta S° = -25 \pm 3$ eu, and $\Delta G°(0\ °C) = -1.2 \pm 0.2$ kcal·mol^{-1}.

Equilibrium between η^3-Propargyl Complex 1-*t*-Bu and Other Phosphine-Substituted Metallacyclobutenes. The more nucleophilic phosphine $PMePh_2$ formed the more stable metallacyclobutene **9**, and the less nucleophilic phosphine $P(C_6H_4$-*p*-F$)_3$ formed the less stable metallacyclobutene **13**.

Addition of $PMePh_2$ (0.05 M in CD_2Cl_2) to η^3-propargyl complex **1-*t*-Bu** (0.030 M in CD_2Cl_2) at −88 °C led to complete conversion to rhenacyclobutene **9**. Neither η^3-propargyl complex **1-*t*-Bu** nor the stable η^2-alkyne complex **10** was observed by ^{1}H NMR spectroscopy below −24 °C. However, upon warming to −13 °C, ^{1}H NMR spectroscopy showed small amounts of the η^3-propargyl complex **1-*t*-Bu** (8%) and of η^2-alkyne complex **10** (17% after 10 min and increasing amounts at longer times). When the temperature was raised to 8 °C, the amount of η^3-propargyl complex **1-*t*-Bu** remained relatively constant (8%) while the amount of rhenacyclobutene complex **9** decreased and the amount of η^2-alkyne complex **10** increased.

At lower than stoichiometric concentrations of $PMePh_2$ (0.011 M in CD_2Cl_2) compared to **1-*t*-Bu** (0.030 M in CD_2Cl_2), a relatively constant 0.43:1 ratio of rhenacyclobutene complex **9** to η^3-propargyl complex **1-*t*-Bu** was seen between −88 and −56 °C. Too little free $PMePh_2$ was present to be observed. When the temperature was increased to −24 °C, some dissociation of $PMePh_2$ from the metallacycle occurred and the ratio of **9**:**1-*t*-Bu** decreased to 0.32:1 ($K_{eq} \approx 80$ M^{-1}, $\Delta G(-24\ °C) \approx -2.2$ kcal·mol^{-1}).[22] When the solution was recooled to −66 °C, the ratio reverted to 0.43:1. When the solution was warmed to −2 °C, the ratio dropped to 0.2:1 ($K_{eq} \approx 50$ M^{-1}, $\Delta G°(-2\ °C) \approx -2.1$ kcal·mol^{-1}) and some rearrangement to the thermodynamically stable η^2-alkyne complex **10** was observed (6% after 5 min). Upon further increasing the temperature to 9 °C, the ratio of **9**:**1-*t*-Bu** dropped to 0.1:1 ($K_{eq} \approx 25$ M^{-1}, $\Delta G°(9\ °C) \approx -1.8$ kcal·mol^{-1}). After 15 min at 9 °C, all the $PMePh_2$ was consumed and only propargyl complex **1-*t*-Bu** and η^2-alkyne complex **10** were observed. A plot of ΔG versus temperature allowed extrapolation to $\Delta G°(0\ °C) \approx -2.0$ kcal·mol^{-1}.

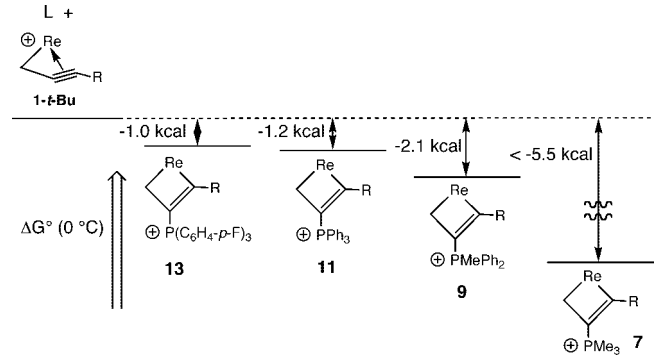


Figure 6. Thermodynamics of rhenacyclobutene formation.

Addition of the less nucleophilic phosphine $P(C_6H_4$-*p*-F$)_3$ (0.05 M in CD_2Cl_2) to η^3-propargyl complex **1-*t*-Bu** (0.030 M in CD_2Cl_2) at −80 °C led to slow conversion ($\Delta G^‡$ (metallacycle formation) ≈ 14.2(8) kcal mol^{-1})[21] to the rhenacyclobutene $[C_5Me_5(CO)_2Re(CH_2C[P(C_6H_4$-*p*-F$)_3]{=}CCMe_3)][BF_4]$ (**13**), which had characteristic ^{1}H NMR resonances at δ 0.05 (CH*H*) and 0.70 (CMe_3). After 2 h, a 1.3:1 equilibrium mixture of **13/1-*t*-Bu** was observed ($K_{eq} = [\mathbf{13}]/[\mathbf{1\text{-}t\text{-}Bu}][PAr_3] \approx 38$ M^{-1}). When the solution was warmed to −70 °C, the ratio dropped to 0.56:1 ($K_{eq} \approx 14$ M^{-1}). Upon further increasing the temperature to −60 °C, the ratio of **13**:**1-*t*-Bu** dropped to 0.2:1 ($K_{eq} \approx 4.6$ M^{-1}). Conversion to the η^2-alkyne complex $[C_5Me_5(CO)_2Re[\eta^2$-(*p*-F-$C_6H_4)_3PCH_2C{\equiv}CCMe_3][BF_4]$ (**14**) began at −30 °C and was complete at −20 °C ($\Delta G^‡ \approx 17.2(8)$ kcal·mol^{-1}).[21]

(21) These approximate $\Delta G^‡$ values are obtained from the approximate rates. If rate estimates are off by a factor of 3 at 0 °C, $\Delta G^‡$ would be off by 0.6 kcal·mol^{-1}.

(22) Because the free phosphine was difficult to observe directly, its concentration was estimated by subtracting the concentration of rhenacyclobutene complex and η^2-alkyne complex from the initial phosphine concentration. Errors in estimation are considerable, and only very approximate equilibrium constants were obtained.

Additional measurements of the equilibrium between the **13** and **1-*t*-Bu** were carried out using a higher concentration of the $P(C_6H_4$-*p*-$F)_3$ (0.10 M in CD_2Cl_2), and the same concentration of **1-*t*-Bu** (0.03 M in CD_2Cl_2) gave similar values for the equilibrium constants. [At −80 °C, 4.3:1 **13**:**1-*t*-Bu**, $K_{eq} \approx 54$ M^{-1}; at −70 °C, 1.7:1 **13**:**1-*t*-Bu**, $K_{eq} \approx 20$ M^{-1}; at −60 °C, 0.7:1 **13**:**1-*t*-Bu**, $K_{eq} \approx 7.6$ M^{-1}.] A van't Hoff plot gave $\Delta H° = -7.2 \pm 0.5$ kcal·mol^{-1}, $\Delta S° = -30$ eu ± 4, and $\Delta G°(0\ °C) = -1.0 \pm 0.2$ kcal·mol^{-1}.

The equilibrium between PMe_3-substituted metallacycle **7** and η^3-propargyl complex **1-*t*-Bu** lay too far on the side of the metallacycle to be directly observable. A limit on the equilibrium constant can be estimated from the fact that none of **1-*t*-Bu** was detectable by ^{1}H NMR spectroscopy of 0.1 M solutions of **7**, and 2% of **1-*t*-Bu** would have been readily detected. This requires $K_{eq} \geq 25\,000$ M^{-1} and $\Delta G°(0\ °C) \leq -5.5$ kcal·mol^{-1}. Figure 5 summarizes the thermodynamic information of the equilibrium between rhenacyclobutenes and η^3-propargyl complex **1-*t*-Bu**.

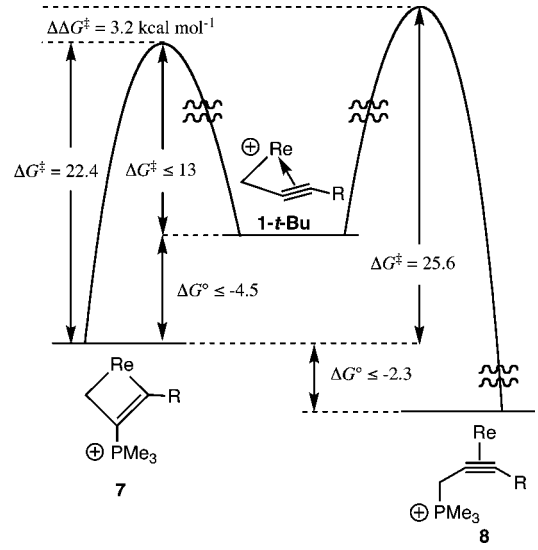


Figure 7. Free energy diagram for reaction of PMe_3 with **1-*t*-Bu**.

Discussion

Thermodynamics of Rhenacyclobutene Formation. It is surprising that the metallacyclobutene complexes and η^3-propargyl complex **1-*t*-Bu** are so similar in thermodynamic stability. For PPh_3, PPh_2Me, and $P(C_6H_4$-*p*-$F)_3$, both species were observable in solution and K_{eq} could be measured directly. For PMe_3, η^3-propargyl complex **1-*t*-Bu** was not directly observable, and a limit of $\Delta G° \leq -5.5$ kcal·mol^{-1} was placed on the stability of the metallacycle. The stability of the metallacycles follows the same order as the nucleophilicity of the phosphines. Steric effects are also important in determining the stability of the metallacycles, as shown by the fact that the metallacycle formed by addition of PPh_3 to Me-substituted η^3-propargyl complex **1-Me** is much more kinetically stable than the metallacycle **11** formed by addition of PPh_3 to *t*-Bu-substituted **1-*t*-Bu**.

Kinetics of Exchange and Rearrangement. The kinetics of exchange of phosphines with the metallacycles proceed by a kinetically first-order dissociative mechanism and were measured only for metallacycles **7** and **9**. The barrier for exchange of PMe_3 with PPh_2Me-substituted metallacycle **9** was 5.5 kcal lower than the barrier for PMe_3 exchange with deuterium-labeled metallacycle **7-*d*$_9$**. This activation energy difference parallels the thermodynamic stability of the metallacycles and the leaving group ability of the phosphines.

Crude measurements of the rates of rearrangement of all the metallacycles to η^2-alkyne complexes were made for all the metallacycles. The barriers for rearrangement also paralleled the thermodynamic stability of the metallacycles and the leaving group ability of the metallacycles [$\Delta G^‡$ for PMe_3 (25.6) > PPh_2Me (20.3) > PPh_3 (∼18) > $P(C_6H_4$-*p*-$F)_3$ (∼17)].

Regioselectivity of metallacyclobutene formation was too high to be measured directly for all of the phosphines studied. The regioselectivity of PMe_3 addition to **1-*t*-Bu** was carefully determined by an indirect method: comparison of the rate of exchange of PMe_3 with deuterium-labeled metallacycle **7-*d*$_9$** with the rate of rearrangement of metallacycle **7** to η^2-alkyne complex **8** (Figure 7). The regioselectivity for addition of PMe_3 to the central carbon of **1-*t*-Bu** was 480:1 ($\Delta\Delta G^‡ = 3.2$ kcal·mol^{-1}). Similarly, a similar regioselectivity ($\Delta\Delta G^‡ = 3.4$ kcal·mol^{-1}) for addition of PPh_2Me to the central carbon of **1-*t*-Bu** was estimated from the rate of exchange of PMe_3 with rhenacyclobutene **9** and from the rate of rearrangement of **9** to **10**.

DFT computational studies of rhenium η^3-propargyl complexes were undertaken to better understand the regioselective addition of nucleophiles to the central propargyl carbon. Discussions of nucleophilic addition to η^3-propargyl complexes usually involve comparisons with well-studied η^3-allyl complexes.

Transition metal η^3-allyl complexes usually undergo nucleophilic addition to a terminal carbon,[23] although an increasing number of cases of attack at the central carbon have been reported. The most direct evidence for attack at the central carbon of η^3-allyl complexes comes from isolation of metallacyclobutanes.[24] Formation of cyclopropanes in the reaction of nucleophiles with η^3-allyl complexes is best explained by attack at the central carbon followed by reductive elimination (Scheme 10).[25] η^3-Allyl complexes having a leaving group such as Cl or OR at the central carbon sometimes react with nucleophiles to give products in which the substituent at the central carbon is replaced by a nucleophile and another nucleophile adds to the

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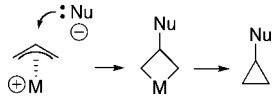
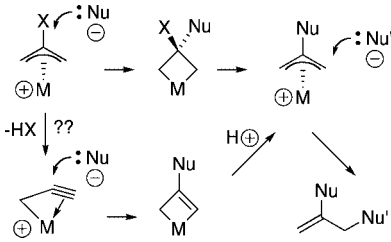
Scheme 10



Scheme 11



terminal carbon (Scheme 11).[26] These reactions have been suggested to proceed by an unusual addition of a nucleophile to the central carbon followed by elimination of the leaving group from the central carbon to give a substituted η^3-allyl complex, which is then attacked at a terminal carbon by a second nucleophile. However, an alternative mechanism involves elimination of HX from the η^3-allyl complex to produce an η^3-propargyl complex, which then undergoes "normal" addition of a nucleophile to the central carbon to produce a metallacyclobutene; protonation of the metallacyclobutene can then produce an η^3-allyl complex, which is then attacked at a terminal carbon by a second nucleophile.

Several computational studies of η^3-allyl compounds have addressed the regioselectivity issue and provided insight into the importance of ligand substitution, conformational preference, and the question of orbital control versus charge control.[27] Most studies have focused on η^3-allyl palladium and platinum complexes.[28]

Green has reported extended Hückel molecular orbital calculations (EHMO) on the neutral η^3-propargyl molybdenum complex $C_5H_5(\eta^2\text{-HC}{\equiv}\text{CH})\text{Mo}(\eta^3\text{-CH}_2\text{C}{\equiv}\text{CH})$.[29] Although the regiochemistry of nucleophilic addition was not commented upon, the EHMO results indicated a significant difference in calculated atomic charges between the center (positive) and terminal (negative) carbons, which might form the basis of a charge-controlled explanation of addition of nucleophiles to the center carbon. Wojcicki and Bursten reported[30] calculations of the model η^3-propargyl complex $[(PH_3)_2\text{Pt}(\eta^3\text{-CH}_2\text{C}{\equiv}\text{CH})]^+$ using the Fenske−Hall (FH) molecular orbital method and later DFT calculations[31] and concluded that nucleophilic addition to the central η^3-propargyl carbon was charge controlled.

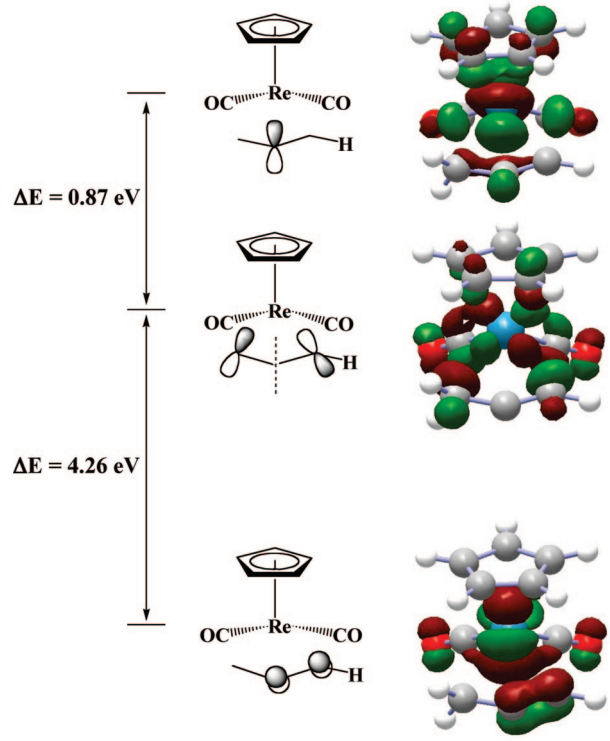


Figure 8. HOMO, LUMO, and LUMO+1 of $[C_5H_5(CO)_2\text{Re}(\eta^3\text{-CH}_2\text{C}{\equiv}\text{CH})]^+$ (**B**).

Since no analogous theoretical studies of mid-transition metal η^3-propargyl compounds were available, we carried out DFT calculations on the model complex $[C_5H_5(CO)_2\text{Re}(\eta^3\text{-CH}_2\text{C}{\equiv}\text{CH})]^+$ (**B**) using B3LYP/LANL2DZ,[32] available in the Gaussian 94[33] and Gaussian 98[34] packages. The molecular orbitals of the η^3-propargyl fragment may be described as the simple combination of π-systems for its allyl and ethylene fragments. DFT calculations gave an accurate picture of the frontier molecular orbitals (FMOs) for **B** and provided insight into the regioselectivity of nucleophilic additions. The energy diagram and the molecular orbitals of the HOMO, LUMO, and LUMO+1 of **B** are shown in Figure 8.

If kinetic addition of nucleophiles to **B** were orbital controlled, the LUMO of **B** should have a significant coefficient on the central carbon. Since the LUMO calculated for **B** has a node at the center carbon and is concentrated on the terminal carbons, the observed nucleophilic attack at the central carbon is not orbital controlled. If nucleophilic attack at the η^3-fragment were charge controlled,

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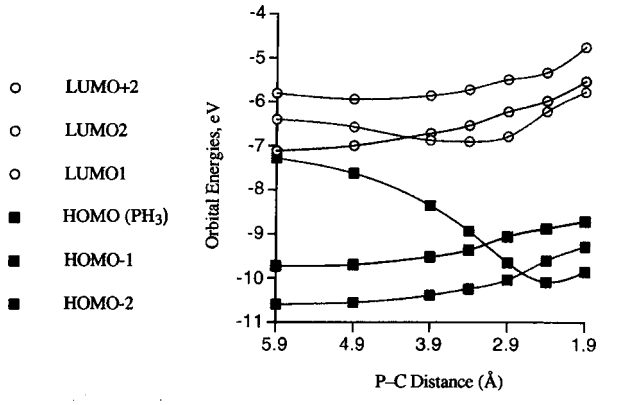

Figure 9. Walsh orbital diagram for approach of PH_3 to the center carbon of **B**.

the charge on the central carbon of the η^3-propargyl unit should be more positive than that on the terminal carbons. The natural charges computed by the natural population analysis[35]subset of the DFT calculation show a greater positive charge on the center carbon and support the hypothesis that the observed kinetic addition to the central carbon is charge controlled (Figure 8).[36]

The attack of a nucleophile at the central carbon of an η^3-propargyl complex can be envisioned as attack at LUMO+1, which has a major contribution from the central carbon. Thus, an incoming nucleophile could interact with the slightly higher energy LUMO+1 orbital to avoid steric repulsions at the C_1 and C_3 positions, resulting in a preference for central attack. A linear synchronous transit calculation (LST) was performed to approximate addition of the model nucleophile PH_3 to the central propargyl carbon of **B** to give the model metallacyclobutene complex $[C_5H_5(CO)_2Re(CH_2C(PH_3)=CH)]^+$. Along the reaction coordinate, a rapid decrease in energy of the HOMO (lone pair of PH_3) was observed as the lone pair develops a bonding interaction, and an inversion of the LUMO and LUMO+1 orbitals was observed as the nucleophile approaches (Figure 9). This implies that while charge controls the site of nucleophilic attack, the accessible energy and nodal properties of LUMO+1 allow the attack to proceed smoothly. An exclusive LUMO orbital control argument can be made for the observed η^2-alkyne and η^2-allene rearrangement products arising from nucleophilic attack at the terminal carbons.

A similar DFT study of $[(PH_3)_2Pd(\eta^3\text{-}CH_3CHC{\equiv}CH)]^+$ was performed by Delbecq, Sinou, and co-workers.[37] Similar to the results reported here for a rhenium cation, they found that the central propargylic carbon was most positive, that the LUMO had a node at the central carbon, and that nucleophilic attack at the central carbon involved interaction with LUMO+1. Their conclusion that regioselective attack at the central carbon resulted from a combination of charge control and the availability of a low-lying orbital centered on the middle propargylic carbon is similar to that reported here.

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Experimental Section

Rate of Rearrangement of 7 to 8. A CD_3CN solution of **7** (26 mg, 0.04 mmol, 0.085 M) containing toluene as an internal integration standard (10 μL, 8.5 μmol) was monitored by ^{1}H NMR spectroscopy at 64.5 °C over 1.5 h. A plot of ln [**7**] versus time was linear to over 3 half-lives ($R^2 > 0.98$) and gave $k_{rearr} = 7.25 \times 10^{-4}$ s^{-1}, $t_{1/2} = 16$ min, and $\Delta G^{\ddagger} = 24.7$ kcal·mol^{-1}.

Measurements were repeated on similarly prepared samples of **7** over the temperature range 35−55 °C, and the resulting rates of rearrangement were used in an Eyring plot of k_{obs} versus $1/T$: k_{obs}(35 °C) $= 9.2 \times 10^{-6}$ s^{-1}; k_{obs}(44 °C) $= 3.1 \times 10^{-5}$ s^{-1}; k_{obs}(54 °C) $= 1.7 \times 10^{-4}$ s^{-1} [see Figure 1-S in the Supporting Information for Eyring plot]. These data provided $\Delta H^{\ddagger} = 30.1 \pm 0.9$ kcal·mol^{-1}, $\Delta S^{\ddagger} = 16.0 \pm 0.9$ eu, and were used to calculate $\Delta G^{\ddagger}_{10\ °C} = 25.6$ kcal·mol^{-1}, $k_{rearr} = 1.02 \times 10^{-7}$ s^{-1}, $t_{1/2} \approx 78$ days.

$[C_5Me_5(CO)_2Re(CH_2C[P(CD_3)_3]{=}CCMe_3)][BF_4]$ (7-*d*$_9$). An excess of $P(CD_3)_3$ was condensed onto a frozen CH_2Cl_2 solution of **1-*t*-Bu** (28.2 mg, 0.05 mmol) at 77 K. A pale yellow-green solution was obtained upon brief mixing at room temperature. Volatile material was evaporated to give **7-*d*$_9$** in quantitative yield as an off-white flaky powder. ^{1}H NMR (CD_3CN, 360 MHz, −20 °C): δ 0.086 (d, $J = 12.2$ Hz, CH*H*), 1.01 (s, CMe_3), 1.40 (dd, $J = 12.3$, 1.1 Hz, C*H*H), 1.85 (s, C_5Me_5).

Rate of Exchange of $P(CH_3)_3$ with 7-*d*$_9$. Excess $P(CH_3)_3$ was condensed onto a frozen (77 K) CD_3CN solution of **7-*d*$_9$** (30 mg, 0.047 mmol, 0.107 M) containing toluene (10 μL, 8.5 μmol) as an internal standard for NMR integration. The sample was melted, thoroughly mixed at −78 °C, and transferred to a NMR spectrometer probe precooled to −20 °C. Integration showed that its initial concentration of $P(CH_3)_3$ was 0.55 M (5 equiv relative to **7-*d*$_9$**). The NMR probe was warmed to 10 °C (thermocouple calibration), and the appearance of the $P(CH_3)_3$ ^{1}H NMR resonance of **7** (δ 1.79) was monitored versus toluene internal standard. The reaction was monitored for 1.5 half-lives, with a late data point acquired after 3 half-lives [see Figure 2-S in the Supporting Information for kinetic plot]. Exponential fit of the concentration versus time data ($R^2 > 0.98$) gave a calculated equilibrium concentration for **7** (0.0979 M) and $k_{exch} = (4.9 \pm 0.5) \times 10^{-5}$ s^{-1}, $t_{1/2} = 3.9$ h, and $\Delta G^{\ddagger} = 22.1$ kcal·mol^{-1}.

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Supporting Information Available: General experimental information, experimental procedures, additional free energy diagrams for reactions of phosphines with **1-*t*-Bu$_3$**, information on rearrangement of diphosphine-substituted metallacyclobutenes, selected computational output for $[C_5H_5(CO)_2Re(\eta^3\text{-}CH_2C{\equiv}CH)]^+$ (**B**), X-ray crystallographic data for **8-Cl** and $\{C_5Me_5(CO)_2Re[\eta^2\text{-}(Ar_2PCH_2CH_2PPh_2)CH_2C{\equiv}CCMe_3]\}[BF_4]\cdot 2CH_2Cl_2$ (**18-CH_2Cl_2**). This material is available free of charge via the Internet at http://pubs.acs.org.

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