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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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Abstract

PMe₃ adds selectively to the central carbon of the η^3 -propargyl complex [C₅Me₅(CO)₂Re(η^3 -CH₂C≡CCMe₃)] [BF₄] (**1-*t*-Bu**) to form the metallacyclobutene [C₅Me₅(CO)₂Re(CH₂C(PMe₃)=CCMe₃)] [BF₄] (**7**). The rate of rearrangement of the metallacyclobutene **7** to η^2 -alkyne complex [C₅Me₅(CO)₂Re(η^2 -Me₃PCH₂C≡CCMe₃)] [BF₄] (**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 PMe₃ with the labeled metallacyclobutene **7-d₉**. This rate ratio provides an indirect measurement of the regioselectivity for addition of PMe₃ 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 PPh₃ to **1-*t*-Bu** gives the metallacyclobutene [C₅Me₅(CO)₂Re(CH₂C(PPh₃)=CCMe₃)] [BF₄] (**11**). Low temperature ¹H NMR spectra provide evidence for an equilibrium between metallacyclobutene **11** and η^3 -propargyl complex **1-*t*-Bu** ($K_{eq} \approx 44 \text{ M}^{-1}$ at -46 °C and $\Delta G^\circ (0^\circ\text{C}) = -1.2 \pm 0.2 \text{ kcal mol}^{-1}$).

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, [(Me₃P)₄Os(η^3 -PhC≡CC=CHPh)] [PF₆], was reported by Werner in 1985,² and the first isolated η^3 -propargyl complex not having an *exo*-double bond [(C₆Me₅H)Mo(CO)₂(η^3 -CH₂C≡CH)] [BF₄] 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 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.^{6e,9}

¹H and ¹³C 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 shows 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 CR₂=C bond length is substantially longer (1.34–1.40 Å) than in free allenes, and the C≡CR bond length is longer than in free acetylenes. The CR₂-C≡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.

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 [C₅Me₅(CO)₂Re(η^3 -CH₂C≡CMe)][BF₄] (**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 re-added 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 *t*-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).

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.^{12,6e} 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

Tsuiji 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

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 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 are 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 pre-cooled 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 (Equations 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.

1. Rate(exchange) = k_{-1} [7]
2. Rate(rearrangement) = k_{-1} [7] (k_2 [PMe₃]/{ k_1 [PMe₃] + k_2 [PMe₃]} = k_{-1} [7] (k_2 / { k_1 + k_2 })
3. Rate(rearrangement)/Rate(exchange) = k_2 / { k_1 + k_2 }
4. Rate(rearrangement)/Rate(exchange) $\approx k_2/k_1$ when $k_1 \gg k_2$

We chose to study the exchange and rearrangement kinetics of [C₅Me₅(CO)₂Re(CH₂C(PMe₃)=CCMe₃)] [BF₄] (**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 [C₅Me₅(CO)₂Re(η^2 -Me₃PCH₂C $\equiv$ CCMe₃)] [BF₄] (**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 CH₂ carbon of the intermediate η^3 -propargyl complex **1-*t*-Bu**, and not to the more sterically hindered *t*-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 $\text{CpRe}(\text{CO})_2\text{R}^-$ 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 $[\text{PR}_3]$.

The rate of rearrangement of metallacyclobutene complex **7** was studied in the presence and absence of added PMe_3 . Two yellow CD_3CN solutions¹⁹ of **7** were prepared in resealable NMR tubes and excess of 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 ($k_{\text{rearr}} = 8.2 \pm 0.1 \times 10^{-4} \text{ s}^{-1}$) and in the presence of 0.29 M added PMe_3 ($k_{\text{rearr}} = 7.9 \pm 0.1 \times 10^{-4} \text{ s}^{-1}$) 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 $[\text{C}_5\text{Me}_5(\text{CO})_2\text{Re}(\text{CH}_2\text{C}(\text{P}(\text{CD}_3)_3)=\text{CCMe}_3)][\text{BF}_4]$ (**7-d₉**) was prepared by addition of $\text{P}(\text{CD}_3)_3$ to **1-*t*-Bu**. The kinetics of the exchange of a 4.5-fold excess $\text{P}(\text{CH}_3)_3$ with 0.1 M **7-d₉** were studied by ^1H NMR spectroscopy at 10 °C in CD_3CN by monitoring the appearance of the $\text{P}(\text{CH}_3)_3$ resonance of the exchanged metallacyclobutene **7** (Figure 4). Data analysis gave $k_{\text{exch}} = 4.9 \pm 0.5 \times 10^{-5} \text{ s}^{-1}$ and $\Delta G^\ddagger_{10^\circ\text{C}} = 22.4 \text{ kcal}\cdot\text{mol}^{-1}$.

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 $\ln[k/T]$ vs. $1/T$ gave $\Delta H^\ddagger = 30.1 \pm 0.9 \text{ kcal}\cdot\text{mol}^{-1}$, $\Delta S^\ddagger = 16.0 \pm 0.9 \text{ eu}$, and $\Delta G^\ddagger_{10^\circ\text{C}} = 25.6 \text{ kcal}\cdot\text{mol}^{-1}$. Extrapolation of the rearrangement rate to 10 °C gave $k_{\text{rearr}} = 1.02 \times 10^{-7} \text{ s}^{-1}$.

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 ($k_{\text{exch}}/k_{\text{rearr}} = [4.9 \times 10^{-5} \text{ s}^{-1}]/[1.0 \times 10^{-7} \text{ s}^{-1}] = 480$). 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 $\text{kcal}\cdot\text{mol}^{-1}$ difference in free energy of activation ($\Delta\Delta G^\ddagger_{10^\circ\text{C}} = 25.6 - 22.4 \text{ kcal}\cdot\text{mol}^{-1}$).

The regioselectivity of addition of PMePh_2 to 1-*t*-Bu was also determined indirectly by comparing the rates of rearrangement and exchange of rhenacyclobutene $[\text{C}_5\text{Me}_5(\text{CO})_2\text{Re}(\text{CH}_2\text{C}(\text{PMePh}_2)=\text{CCMe}_3)][\text{BF}_4]$ (**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, $J = 12.6 \text{ Hz}$, CHH), 1.49 (d, $J = 12.2 \text{ Hz}$, CHH), and 2.39 (d, $J_{\text{PH}} = 12.2 \text{ Hz}$, 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: $k = 5.85 \times 10^{-4} \text{ s}^{-1}$, $\Delta G^\ddagger = 16.9 \text{ kcal}\cdot\text{mol}^{-1}$.

Upon warming to room temperature, **9** rearranged to η^2 -alkyne complex $[\text{C}_5\text{Me}_5(\text{CO})_2\text{Re}(\eta^2\text{-Ph}_2\text{MePCH}_2\text{C}\equiv\text{CCMe}_3)][\text{BF}_4]$ (**10**), which had characteristic ^1H NMR resonances at δ 2.45 (d, $J_{\text{PH}} = 13.1 \text{ Hz}$, PCH_3), 4.15 (t, $J = 16.1 \text{ Hz}$, CHH), and 4.72 (t, $J = 15.8 \text{ Hz}$, CHH). The rate of rearrangement of **9** to **10** at -15 °C was measured by ^1H NMR spectroscopy: $k = 3.27 \times 10^{-5} \text{ s}^{-1}$, $\Delta G^\ddagger (-15^\circ\text{C}) = 20.3 \text{ kcal}\cdot\text{mol}^{-1}$. The difference between this barrier for rearrangement and the barrier for exchange ($\Delta\Delta G^\ddagger = 20.3 - 16.9 = 3.4 \text{ kcal}\cdot\text{mol}^{-1}$) 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 PMePh₂ to the center propargyl carbon of **1-*t*-Bu**.

More Rapid Dissociation of PPh₃ than PMe₃ from Metallacyclobutenes

Previously, we had reported that the addition of PPh₃ to **1-*t*-Bu** gave the metallacyclobutene complex [C₅Me₅(CO)₂Re(CH₂C(PPh₃)=CCMe₃)] [BF₄] (**11**), which subsequently rearranged to alkyne complex [C₅Me₅(CO)₂Re(η^2 -Ph₃PCH₂C $\equiv$ CCMe₃)] [BF₄] (**12**). In repeating this work, we monitored the reaction of **1-*t*-Bu** (0.030 M) with PPh₃ (0.063 M) in CD₂Cl₂ by ¹H NMR spectroscopy, and found that metallacycle **11** was formed at -78 °C with characteristic low frequency doublets for the metal-bound CH₂ 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 °C, only η^2 -alkyne complex **12** was observed by ¹H 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 CD₂Cl₂.*¹⁰

The much more rapid rearrangement of the PPh₃-substituted rhenacyclobutene **9** than the PMe₃-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 PPh₃ group. In addition, the particularly unfavorable steric interaction between the large PPh₃ and the bulky *t*-butyl group is relieved upon PPh₃ dissociation. The much less congested methyl-substituted metallacyclobutene [C₅Me₅(CO)₂Re(CH₂C(PPh₃)=CCH₃)] [BF₄] 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 PPh₃ Substituted Metallacyclobutene **11**

Upon close examination of the low temperature ¹H 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 PPh₃ (0.063 M in CD₂Cl₂) was added to a yellow solution of η^3 -propargyl complex **1-*t*-Bu** (0.030 M in CD₂Cl₂) at -78 °C, ¹H NMR spectroscopy at -88 °C showed a tiny resonance at δ 3.41 (CHH) characteristic of **1-*t*-Bu** in addition to intense resonances for the metallacyclobutene **11** (δ 0.14, CHH). 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 ($K_{eq} = [\mathbf{11}]/[\mathbf{1-*t*-Bu}][\text{PPh}_3] \approx 280 \text{ M}^{-1}$). 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 ($K_{eq} \approx 100 \text{ M}^{-1}$). When the sample was re-cooled 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 ($K_{eq} \approx 44 \text{ M}^{-1}$). When the temperature was lowered to -66 °C, the ratio of **11**: **1-*t*-Bu** increased to 10.8:1 ($K_{eq} \approx 310 \text{ M}^{-1}$). Thus, as the temperature increases, the equilibrium shifts towards η^3 -propargyl complex **1-*t*-Bu** and free PPh₃ 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 ($K_{eq} \approx 25 \text{ M}^{-1}$) and some conversion to η^2 -alkyne complex [C₅Me₅(CO)₂Re(η^2 -Ph₃PCH₂C $\equiv$ CCMe₃)] [BF₄] (**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** ($K_{eq} \approx 11 \text{ M}^{-1}$) was seen along with 56% conversion to the thermodynamically stable η^2 -alkyne complex **12** after 10 min ($\Delta G^\ddagger \approx 17.8(5)$ 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 re-cooled to $-66\text{ }^{\circ}\text{C}$, 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 $-66\text{ }^{\circ}\text{C}$, a 4.5:1 equilibrium mixture of rhenacyclobutene **11**: η^3 -propargyl complex **1-*t*-Bu** was observed by ^1H NMR spectroscopy ($K_{\text{eq}} \approx 260\text{ M}^{-1}$). At $-46\text{ }^{\circ}\text{C}$, a 1:1 mixture of **11**: **1-*t*-Bu** was seen ($K_{\text{eq}} \approx 35\text{ M}^{-1}$). A van't Hoff plot of all the equilibrium data gave $\Delta H^{\circ} = -8.0 \pm 1\text{ kcal mol}^{-1}$, $\Delta S^{\circ} = -25 \pm 3\text{ eu}$, and $\Delta G^{\circ}(0\text{ }^{\circ}\text{C}) = -1.2 \pm 0.2\text{ kcal mol}^{-1}$.

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 $\text{P}(\text{C}_6\text{H}_4\text{-}p\text{-F})_3$ 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 $-88\text{ }^{\circ}\text{C}$ led to complete conversion to rhenacyclobutene **9**. Neither η^3 -propargyl complex **1-*t*-Bu** nor the stable η^2 -alkyne complex **10** were observed by ^1H NMR spectroscopy below $-24\text{ }^{\circ}\text{C}$. However, upon warming to $-13\text{ }^{\circ}\text{C}$, ^1H 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 $8\text{ }^{\circ}\text{C}$, 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**: η^3 -propargyl complex **1-*t*-Bu** was seen between -88 to $-56\text{ }^{\circ}\text{C}$. Too little free PMePh_2 was present to be observed. When the temperature was increased to $-24\text{ }^{\circ}\text{C}$, some dissociation of PMePh_2 from the metallacycle occurred and the ratio of **9**: **1-*t*-Bu** decreased to 0.32:1 ($K_{\text{eq}} \approx 80\text{ M}^{-1}$, $\Delta G(-24\text{ }^{\circ}\text{C}) \approx -2.2\text{ kcal mol}^{-1}$).²² When the solution was re-cooled to $-66\text{ }^{\circ}\text{C}$, the ratio reverted to 0.43:1. When the solution was warmed to $-2\text{ }^{\circ}\text{C}$, the ratio dropped to 0.2:1 ($K_{\text{eq}} \approx 50\text{ M}^{-1}$, $\Delta G^{\circ}(-2\text{ }^{\circ}\text{C}) \approx -2.1\text{ kcal mol}^{-1}$) and some rearrangement to the thermodynamically stable η^2 -alkyne complex **10** was observed (6 % after 5 min). Upon further increasing the temperature to $9\text{ }^{\circ}\text{C}$, the ratio of **9**: **1-*t*-Bu** dropped to 0.1:1 ($K_{\text{eq}} \approx 25\text{ M}^{-1}$, $\Delta G^{\circ}(9\text{ }^{\circ}\text{C}) \approx -1.8\text{ kcal mol}^{-1}$). After 15 min at $9\text{ }^{\circ}\text{C}$, 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 vs. temperature allowed extrapolation to $\Delta G^{\circ}(0\text{ }^{\circ}\text{C}) \approx -2.0\text{ kcal mol}^{-1}$.

Addition of the less nucleophilic phosphine $\text{P}(\text{C}_6\text{H}_4\text{-}p\text{-F})_3$ (0.05 M in CD_2Cl_2) to η^3 -propargyl complex **1-*t*-Bu** (0.030 M in CD_2Cl_2) at $-80\text{ }^{\circ}\text{C}$ led to slow conversion ($\Delta G^{\ddagger}$ (metallacycle formation) $\approx 14.2(8)\text{ kcal mol}^{-1}$)²¹ to the rhenacyclobutene $[\text{C}_5\text{Me}_5(\text{CO})_2\text{Re}(\text{CH}_2\text{C}[\text{P}(\text{C}_6\text{H}_4\text{-}p\text{-F})_3]=\text{CCMe}_3)][\text{BF}_4]$ (**13**), which had characteristic ^1H NMR resonances at δ 0.05 (CHH) and 0.70 (CMe₃). After 2 h, a 1.3:1 equilibrium mixture of **13**: **1-*t*-Bu** was observed ($K_{\text{eq}} = [\text{13}]/[\text{1-*t*-Bu}][\text{PAr}_3] \approx 38\text{ M}^{-1}$). When the solution was warmed to $-70\text{ }^{\circ}\text{C}$, the ratio dropped to 0.56:1 ($K_{\text{eq}} \approx 14\text{ M}^{-1}$). Upon further increasing the temperature to $-60\text{ }^{\circ}\text{C}$, the ratio of **13**: **1-*t*-Bu** dropped to 0.2:1 ($K_{\text{eq}} \approx 4.6\text{ M}^{-1}$). Conversion to the η^2 -alkyne complex $[\text{C}_5\text{Me}_5(\text{CO})_2\text{Re}[\eta^2\text{-(}p\text{-F-C}_6\text{H}_4)_3\text{PCH}_2\text{C}\equiv\text{CCMe}_3]][\text{BF}_4]$ (**14**) began at $-30\text{ }^{\circ}\text{C}$ and was complete at $-20\text{ }^{\circ}\text{C}$ ($\Delta G^{\ddagger} \approx 17.2(8)\text{ kcal mol}^{-1}$)²¹.

Additional measurements of the equilibrium between the **13** and **1-*t*-Bu** were carried out using higher concentration of the $\text{P}(\text{C}_6\text{H}_4\text{-}p\text{-F})_3$ (0.10 M in CD_2Cl_2) and the same concentration of

1-*t*-Bu (0.03 M in CD₂Cl₂) gave similar values for the equilibrium constants. [At -80 °C, 4.3:1 **13: 1-*t*-Bu**, $K_{eq} \approx 54 \text{ M}^{-1}$; at -70 °C, 1.7:1 **13: 1-*t*-Bu**, $K_{eq} \approx 20 \text{ M}^{-1}$; at -60 °C, 0.7:1 **13: 1-*t*-Bu**, $K_{eq} \approx 7.6 \text{ M}^{-1}$.] A van't Hoff plot gave $\Delta H^\circ = -7.2 \pm 0.5 \text{ kcal mol}^{-1}$, $\Delta S^\circ = -30 \text{ eu} \pm 4$, and $\Delta G^\circ (0^\circ \text{C}) = -1.0 \pm 0.2 \text{ kcal mol}^{-1}$.

The equilibrium between PMe₃ 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 ¹H NMR spectroscopy of 0.1 M solutions of **7**, and 2% of **1-*t*-Bu** would have been readily detected. This requires $K_{eq} \geq 25,000 \text{ M}^{-1}$ and $\Delta G^\circ (0^\circ \text{C}) \leq -5.5 \text{ kcal mol}^{-1}$. Figure 5 summarizes the thermodynamic information of the equilibrium between rhenacyclobutenes and η^3 -propargyl complex **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 PPh₃, PPh₂Me, and P(C₆H₄-*p*-F)₃, both species were observable in solution and K_{eq} could be measured directly. For PMe₃, η^3 -propargyl complex **1-*t*-Bu** was not directly observable and a limit of $\Delta G^\circ \leq -5.5 \text{ kcal mol}^{-1}$ 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 PPh₃ to Me-substituted η^3 -propargyl complex **1-Me** is much more kinetically stable than the metallacycle **11** formed by addition of PPh₃ to *t*-Bu-substituted **1-*t*-Bu**.

Kinetics of Exchange and Rearrangement

The kinetics of exchange of phosphines with the metallacycles proceeds by a kinetically first-order dissociative mechanism and were measured only for metallacycles **7** and **9**. The barrier for exchange of PMe₃ with PPh₂Me-substituted metallacycle **9** was 5.5 kcal lower than the barrier for PMe₃ exchange with deuterium labeled metallacycle **7-d₉**. 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 [$\Delta G^\ddagger$ for PMe₃ (25.6) > PPh₂Me (20.3) > PPh₃ (~18) > P(C₆H₄-*p*-F)₃ (~17)].

Regioselectivity of Metallacyclobutene Formation was too high to be measured directly for all of the phosphines studied. The regioselectivity of PMe₃ addition to **1-*t*-Bu** was carefully determined by an indirect method: comparison of the rate of exchange of PMe₃ with deuterium labeled metallacycle **7-d₉** with the rate of rearrangement of metallacycle **7** to η^2 -alkyne complex **8** (Figure 6). The regioselectivity for addition of PMe₃ to the central carbon of **1-*t*-Bu** was 480:1 ($\Delta\Delta G^\ddagger = 3.2 \text{ kcal mol}^{-1}$). Similarly, a similar regioselectivity ($\Delta\Delta G^\ddagger = 3.4 \text{ kcal mol}^{-1}$) for addition of PPh₂Me to the central carbon of **1-*t*-Bu** was estimated from the rate of exchange of PMe₃ 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 metallacyclobutenes.²⁴ Formation of cyclopropanes in the reaction of nucleophiles with η^3 -allyl complexes is best explained by attack at central carbon followed by reductive elimination (Scheme 10).²⁵ Reaction of 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 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 involving 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 vs. 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 $C_5H_5(\eta^2-HC\equiv CH)Mo(\eta^3-CH_2C\equiv CH)$.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 reported³⁰ calculations of the model η^3 -propargyl complex $[(PH_3)_2Pt(\eta^3-CH_2C\equiv CH)]^+$ 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.

Since no analogous theoretical studies of mid-transition metal η^3 -propargyl compounds were available, we carried out DFT calculations on the model complex $[C_5H_5(CO)_2Re(\eta^3-CH_2C\equiv CH)]^+$ (**B**) using B3LYP/LANL2DZ³² 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 (FMO's) 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 7.

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, 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 7).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 C₁ and C₃ positions, resulting in a preference for central attack. A Linear Synchronous Transit calculation (LST) was performed to approximate addition of the model nucleophile PH₃ to the central propargyl carbon of **B** to give the model metallacyclobutene complex [C₅H₅(CO)₂Re(CH₂C(PH₃)=CH)]⁺. Along the reaction coordinate, a rapid decrease in energy of the HOMO (lone pair of PH₃) 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 8). This implies that while charge controls the site of nucleophilic attack, the accessible energy and nodal properties of LUMO+1 allows 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 [(PH₃)₂Pd(η^3 -CH₃CHC≡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 middle propargylic carbon is similar to that reported here.

Experimental

Rate of Rearrangement of **7** to **8**

A CD₃CN solution of **7** (26 mg, 0.04 mmol, 0.085 M) containing toluene as an internal integration standard (10 μ l, 8.5 μ mol) was monitored by ¹H NMR spectroscopy at 64.5 °C over 1.5 h. A plot of ln [**7**] vs. time was linear to over 3 half-lives ($R^2 > 0.98$) and gave $k_{\text{rearr}} = 7.25 \times 10^{-4} \text{ s}^{-1}$, $t_{1/2} = 16 \text{ min}$, and $\Delta G^\ddagger = 24.7 \text{ kcal}\cdot\text{mol}^{-1}$.

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} vs 1/ T : $k_{\text{obs}}(35 \text{ °C}) = 9.2 \times 10^{-6} \text{ s}^{-1}$; $k_{\text{obs}}(44 \text{ °C}) = 3.1 \times 10^{-5} \text{ s}^{-1}$; $k_{\text{obs}}(54 \text{ °C}) = 1.7 \times 10^{-4} \text{ s}^{-1}$ [See Figure 1-S in Supporting Information for Eyring plot]. These data provided $\Delta H^\ddagger = 30.1 \pm 0.9 \text{ kcal}\cdot\text{mol}^{-1}$, $\Delta S^\ddagger = 16.0 \pm 0.9 \text{ eu.}$, and were used to calculate $\Delta G^\ddagger_{10 \text{ °C}} = 25.6 \text{ kcal}\cdot\text{mol}^{-1}$, and $k_{\text{rearr}} = 1.02 \times 10^{-7} \text{ s}^{-1}$, $t_{1/2} \sim 78 \text{ days}$.

[C₅Me₅(CO)₂Re(CH₂C[P(CD₃)₃]=CCMe₃)] [BF₄] (**7-d₉**)

An excess of P(CD₃)₃ was condensed onto to frozen CH₂Cl₂ 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-d₉** in quantitative yield as an off-white flaky powder. ¹H NMR (CD₃CN, 360 MHz, –20 °C) δ 0.086 (d, $J = 12.2 \text{ Hz}$, CHH), 1.01 (s, CMe₃), 1.40 (dd, $J = 12.3, 1.1 \text{ Hz}$, CHH), 1.85 (s, C₅Me₅).

Rate of Exchange of P(CH₃)₃ with **7-d₉**

Excess P(CH₃)₃ was condensed onto a frozen (77 K) CD₃CN solution of **7-d₉** (30 mg, 0.047 mmol, 0.107 M) containing toluene (10 μ l, 8.5 μ mol) as an internal standard for NMR integration. The sample was melted, thoroughly mixed at –78 °C, and transferred to NMR spectrometer probe pre-cooled to –20 °C. Integration showed that its initial concentration of P(CH₃)₃ was 0.55 M (5 equiv relative to **7-d₉**). The NMR probe was warmed to 10 °C (thermocouple calibration) and the appearance of the P(CH₃)₃ ¹H NMR resonance of **7** (δ 1.79) was monitored vs. 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 Supporting Information for

kinetic plot]. Exponential fit of the concentration vs. time data ($R^2 > 0.98$) gave a calculated equilibrium concentration for **7** (0.0979 M) and $k_{\text{exch}} = 4.9 \pm 0.5 \times 10^{-5} \text{ s}^{-1}$, $t_{1/2} = 3.9 \text{ hr}$, and $\Delta G^\ddagger = 22.1 \text{ kcal}\cdot\text{mol}^{-1}$.

Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

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21. These approximate $\Delta G^\ddagger$ values are obtained from the approximate rates. If rate estimates are off by a factor of 3 at 0 °C, $\Delta G^\ddagger$ would be off by 0.6 kcal mol⁻¹.
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Figure 1.
Resonance Structures for η^3 -Propargyl Complexes.

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

Figure 3.
X-Ray Structure of $[\text{C}_5\text{Me}_5(\text{CO})_2\text{Re}(\eta^2\text{-Me}_3\text{PCH}_2\text{C}\equiv\text{CCMe}_3)]^+$.

Figure 4.

Elapsed time ^1H NMR spectra for exchange at 10 °C in CD_3CN : **7-d₉** + $\text{P}(\text{CH}_3)_3$ approaches equilibrium with **7** + $\text{P}(\text{CD}_3)_3$. Peak 4, $\text{P}(\text{CH}_3)_3$ of **7**. Other peaks: peak 2, Cp^* of **7**; 5, CH of **7**; 6, $t\text{Bu}$ of **7**; 7, excess $\text{P}(\text{CH}_3)_3$; 1, toluene standard; 3, CD_3CN .

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

Figure 6.
Free Energy Diagram for Reaction of PMe_3 with **1-t-Bu**.

Natural Charges: $CH_2(-0.473)-C(+0.065)-CH(-0.222)$

Figure 7. HOMO, LUMO, and LUMO+1 of $[C_5H_5(CO)_2Re(\eta^3-CH_2C\equiv CH)]^+$ (B).

Figure 8.
Walsh orbital diagram for approach of PH₃ to center carbon of **B**.

Scheme 1.

Scheme 2.

Scheme 3.

Scheme 4.

Scheme 5.

Scheme 6.

Scheme 7.

Scheme 8.

Scheme 9.

Scheme 10.

Scheme 11.