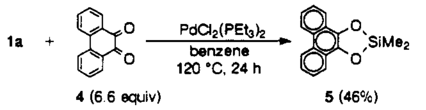
(eq 3). This may suggest silylene species are involved in the polymerization of *p*-quinones, similar to the polymerization of stable germylenes with quinones.[8] However, the silylene mechanism cannot be applied to cyclic disilanes. Further studies are awaited to propose the mechanism.



(3)

Since aromatic rings and Si–O bonds are thermally stable, the polymers obtained herein are expected to possess high heat resistance. In fact, thermogravimetric analyses (10 °C/min raising rate, 50 mL/min He stream) showed that the temperatures at 5% and 10% weight loss (T_5 and T_{10}) are 400 and 485 °C for **3c**, 380 and 480 °C for **3d** (soluble part), 250 and 400 °C for **3e**, and 390 and 410 °C for **3f**, respectively.

Supplementary Material Available: Physical, spectral, and analytical data of **3a–f** and **5** (2 pages). Ordering information is given on any current masthead page.

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Nucleophilic Attack at the Central Carbon of a Cationic (η^3-Propargyl)rhenium Complex

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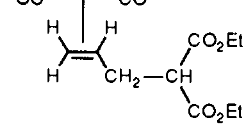
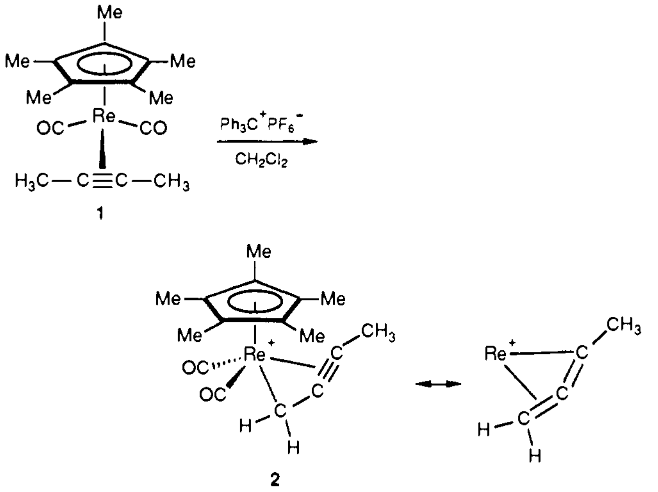
We recently reported an efficient synthesis of the cationic (η^3-allyl)rhenium complex $C_5H_5(CO)_2Re(\eta^3\text{-}CH_2CHCH_2)^+PF_6^-$ by hydride abstraction from the rhenium–propene complex $C_5H_5(CO)_2Re(CH_2{=}CHCH_3)$ with $Ph_3C^+PF_6^-$. The resulting cationic (η^3-allyl)rhenium complex reacted with carbon nucleophiles to produce elaborated rhenium–alkene complexes.[1] We have begun to explore the extension of this hydride abstraction process to rhenium–alkyne complexes. Here we report the synthesis of a cationic (η^3-propargyl)rhenium complex by hydride abstraction from a rhenium–alkyne complex and its reactions with nucleophiles at the central carbon of the propargyl unit to produce metallacyclobutene complexes.



The reaction of $C_5Me_5(CO)_2Re(THF)^2$ with a 5-fold excess of 2-butyne in THF at room temperature for 12 h gave an 85% yield of $C_5Me_5(CO)_2Re(CH_3C{\equiv}CCH_3)$ (**1**),[3] which was isolated as a yellow solid after column chromatography (silica gel, 3:1 hexane/Et_2O).



Hydride abstraction from the rhenium-2-butyne complex **1** produced the η^3-propargyl complex $C_5Me_5(CO)_2Re(\eta^3\text{-}CH_2C{\equiv}CCH_3)^+PF_6^-$ (**2**). Reaction of $Ph_3C^+PF_6^-$ (145 mg, 0.371 mmol) with **1** (160 mg, 0.371 mmol) in 10 mL of CH_2Cl_2 at room temperature for 1 h produced a dark brown solution. The solution was concentrated to ~5 mL, and diethyl ether was added. The resulting precipitate was filtered and washed with diethyl ether (3 × 10 mL) to give the pure cationic (η^3-propargyl)rhenium complex $C_5Me_5(CO)_2Re(\eta^3\text{-}CH_2C{\equiv}CCH_3)^+PF_6^-$ (**2**) (185 mg, 87%) as a pale brown solid.[4] The ^1H NMR spectrum of **2** in CD_2Cl_2 exhibited a downfield-shifted Cp* signal at δ 2.11, a methyl resonance at δ 2.58 (t, J = 2.7 Hz), and two doublets of quartets at δ 4.38 and 3.32, which were assigned to the inequivalent propargyl hydrogens coupled to each other (J_{gem} = 10.1 Hz) and to the methyl group (^5J = 2.7 Hz). In the coupled ^{13}C NMR spectrum of **2**, two singlets at δ 76.6 and 56.7 were assigned to the quarternary propargyl carbons and a triplet (J = 170.0 Hz) at δ 29.0 was assigned to the terminal propargyl CH_2. The propargyl carbon chemical shifts of **2** were similar to those previously reported for η^3-propargyl complexes.[5] In the IR spectrum of **2**, two strong CO bands were observed at 1974 and 1904 cm⁻¹.

η^3-Propargyl complexes are rare. Werner[5] reported the first η^3-propargyl complex, $(Me_3P)_4Os(\eta^3\text{-}PhC{\equiv}CC{=}CHPh)^+PF_6^-$. Related Ru,[6,7] W,[8] and Fe[9] complexes which also have a ═CHR group attached to the propargyl terminus have been reported. The

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[3] See supplementary material for full characterization data.

[4] For $C_5Me_5(CO)_2Re(\eta^3\text{-}CH_2C{\equiv}CCH_3)^+PF_6^-$ (**2**): ^1H NMR (CD_2Cl_2, 500 MHz) δ 4.38 (dq, J = 10.1, 2.7 Hz, ReC*H*H), 3.32 (dq, J = 10.1, 2.7 Hz, ReCH*H*), 2.58 (t, J = 2.7 Hz, ≡CCH_3), 2.11 (s, C_5Me_5); ^{13}C NMR (CD_2Cl_2, 126 MHz) δ 198.0 and 195.3 (s, CO's), 106.2 (s, C_5Me_5), 76.6 (s, ≡CCH_3), 56.7 (s, $C{\equiv}CCH_3$), 29.0 (t, J = 170.0 Hz, CH_2), 10.1 (q, J = 129.7 Hz, C_5Me_5), 8.2 (q, J = 134.1 Hz, ≡CCH_3); IR (Nujol) 2028 (s), 1954 (s), 838 (s), 722 (w) cm⁻¹; IR (THF) 1974 (s), 1904 (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.

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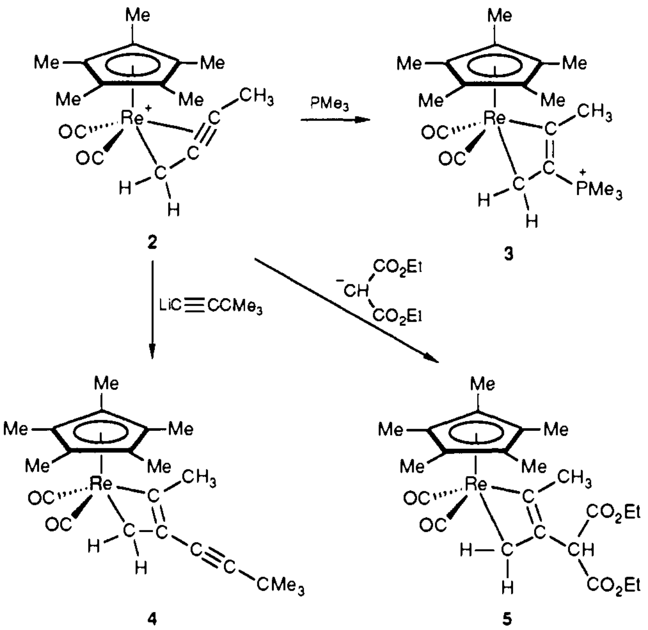
first unsubstituted η^3-propargyl complex, $C_6Me_6(CO)_2Mo(\eta^3\text{-}CH_2C{\equiv}CH)^+BF_4^-$, was prepared by Krivykh[10] by photolysis of $C_6Me_6Mo(CO)_3$ and propargyl alcohol in the presence of HBF_4. The preparation of (η^3-propargyl)rhenium complex **2** constitutes the first synthesis of an η^3-propargyl complex by hydride abstraction from an alkyne complex. The structure and bonding of η^3-propargyl complexes are often discussed in terms of η^3-propargyl and η^3-allenyl resonance structures. The large J_{CH} = 170 Hz coupling of the propargyl CH_2 unit of **2** is indicative of the importance of the η^3-allenyl resonance structure.

The cationic (η^3-propargyl)rhenium complex $C_5Me_5(CO)_2Re(\eta^3\text{-}CH_2C{\equiv}CCH_3)^+PF_6^-$ (**2**) reacted with a variety of soft nucleophiles to produce stable rhenacyclobutene complexes. Exclusive addition of nucleophiles to the central carbon of the η^3-propargyl complex **2** was observed. For example, when **2** (50 mg, 0.087 mmol) was treated with excess PMe_3 (10 equiv) in CH_2Cl_2, a white precipitate formed gradually over 30 min at room temperature. Solvent was evaporated, and the resulting solid was washed several times with diethyl ether to give the white phosphine-substituted rhenacyclobutene complex $[C_5Me_5(CO)_2\overline{ReCH_2C(PMe_3){=}C}CH_3]^+PF_6^-$ (**3**) (41 mg, 72%).[11]



The structure of rhenacyclobutene complex **3** was established spectroscopically. The α-CH_2 group of metallacyclobutene complexes gives rise to high-field resonances in the ^1H and ^{13}C NMR spectra;[12] for example, the α-CH_2 group of *mer*-$(PMe_3)_3\overline{Ir(Br)CH_2C(Ar){=}C}(Ar)$ gives rise to resonances at δ 1.16 in the ^1H NMR and δ −18.0 in the ^{13}C NMR spectra.[12d] In the ^1H NMR spectrum of **3**, resonances at δ 0.3 (dq, J_{gem} = 11.5 Hz, ^5J = 2.3 Hz) and δ 1.45 (dq, J_{gem} = 11.5 Hz, ^5J = 2.3 Hz) were assigned to the inequivalent protons of the α-CH_2 unit of the metallacyclobutene. In the ^{13}C NMR spectrum of **3**, an upfield triplet at δ −31.7 (t, J_{CH} = 145.0 Hz) was assigned to the α-CH_2 carbon of the metallacyclobutene and a doublet at δ 128.0 (t, J_{CP} = 33.2 Hz) was assigned to the central carbon of the metallacyclobutene ring of **3**.

Nucleophilic addition to the central propargyl carbon of $C_5Me_5(CO)_2Re(\eta^3\text{-}CH_2C{\equiv}CCH_3)^+PF_6^-$ (**2**) was also observed with $LiC{\equiv}CCMe_3$ and $NaCH(CO_2Et)_2$. Reaction of **2** (50 mg, 0.087 mmol) with $LiC{\equiv}CC(CH_3)_3$ (8 mg, 0.087 mmol) produced the neutral rhenacyclobutene complex $C_5Me_5(CO)_2\overline{ReCH_2C(C{\equiv}CCMe_3){=}C}CH_3$ (**4**)[3] as an orange-red liquid (29 mg, 47% yield). Similarly, the reaction of **2** (30 mg, 0.052 mmol) with $NaCH(CO_2Et)_2$ (10 mg, 0.052 mmol) gave the malonate-substituted rhenacyclobutene complex $(C_5Me_5(CO)_2\overline{ReCH_2C[CH(CO_2Et)_2]{=}C}CH_3$ (**5**)[3] as an orange red liquid in 55% yield. These three rhenacyclobutene complexes are stable at room temperature and show no tendency to ring-open to vinyl carbene complexes.

While nucleophiles normally add to a terminal carbon of η^3-allyl complexes, nucleophilic addition to the central carbon of η^3-allyl complexes to produce metallacyclobutanes has also been observed.[13] The attack of nucleophiles at the central carbon of η^3-propargyl complex **2** to generate metallacyclobutenes observed here may turn out to be the normal mode of reaction of η^3-propargyl complexes. Attack at the central carbon may relieve some strain in the η^3-propargyl complexes. Clearly, the reactivity pattern of η^3-propargyl complexes with nucleophiles needs to be further investigated. Some of the eventual products obtained from nucleophilic attack on $C_6Me_6(CO)_2Mo(\eta^3\text{-}CH_2C{\equiv}CH)^+BF_4^-$ can be explained by initial nucleophilic attack on the central carbon of the η^3-propargyl group.[10] Similarly, the palladium-catalyzed reactions of propargyl esters with organic nucleophiles can be explained in terms of nucleophilic attack at the central carbon of propargyl metal complexes.[14]

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

Supplementary Material Available: Characterization data for compounds **1**, **4**, and **5** (1 page). Ordering information is given on any current masthead page.

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(11) For $C_5Me_5(CO)_2\overline{ReCH_2C(PMe_3){=}C}CH_3{}^+PF_6^-$ (**3**): ^1H NMR (acetone-d_6, 200 MHz) δ 2.36 (q, J_{HH} = J_{PH} = 2.3 Hz, CCH_3), 2.05 (s, C_5Me_5), 1.95 (d, J_{PH} = 13.9 Hz, PMe_3), 1.45 (dqd, J = 11.5, 2.3 Hz, J_{PH} = 0.7 Hz, ReC*H*H), 0.3 (dq, J = 11.5, 2.3 Hz, ReCH*H*); ^{13}C NMR (acetone-d_6, 126 MHz) δ 213.5 (s, CO), 207.0 (s, CO), 157.7 (s, $={C}CH_3$), 128.0 (d, J_{PC} = 33.2 Hz, $={C}PMe_3$), 103.3 (s, C_5Me_5), 24.8 (q, J = 130.3 Hz, $=CCH_3$), 9.9 (q, J = 128.6 Hz, C_5Me_5), 9.2 (qd, J_{CH} = 132.7 Hz, J_{PC} = 53.0 Hz, PMe_3), −31.7 (t, J = 145.0 Hz, $ReCH_2$); $^{31}P\{^1H\}$ NMR (acetone-d_6, 202.5 MHz) δ 3.3 (s, PMe_3); IR (acetone) 1991 (s), 1915 (m) cm^{-1}. Anal. Calcd for $C_{19}H_{29}O_2ReP_2F_6$: C, 35.02; H, 4.49; P, 9.51. Found: C, 35.31; H, 4.36; P, 10.36.

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