

Synthesis and reactions of rhenium enyne, and vinylalkenylidene complexes *

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Abstract

Reaction of $\text{Cp}^*\text{Re}(\text{CO})_2(\text{THF})$ with $\text{HC}\equiv\text{CC}(\text{CH}_3)=\text{CH}_2$ produced the conjugated enyne complex $\text{Cp}^*(\text{CO})_2\text{Re}[\eta^2\text{-HC}\equiv\text{CC}(\text{CH}_3)=\text{CH}_2]$ (**1**). Attempted preparation of an η^3 -propargyl complex by protonation of **1** with HBF_4 failed. Thermolysis of **1** led to the corresponding alkenylidene complex $\text{Cp}^*(\text{CO})_2\text{Re}=\text{C}=\text{CHC}(\text{CH}_3)=\text{CH}_2$ (**2**), which reacted with HBF_4 to give the cationic alkylidyne complex $[\text{Cp}^*(\text{CO})_2\text{Re}\equiv\text{CCH}=\text{C}(\text{CH}_3)_2][\text{BF}_4^-]$ (**3**). Nucleophiles including $\text{NaCH}(\text{CO}_2\text{C}_2\text{H}_5)_2$, PMe_3 , and NaBH_4 attack regioselectively at the γ -carbon of the alkylidyne ligand of **3**. Both the conjugated enyne complex **1** and vinylalkenylidene complex **2** underwent reaction with dimethyl acetylenedicarboxylate (DMAD), eventually producing dimethyl 4-methylphthalate (**9**).

Key words: Vinylalkenylidene; Rhenium; Alkylidyne

1. Introduction

We recently reported the synthesis of a cationic η^3 -propargylrhenium complex by hydride abstraction from a rhenium-alkyne complex and studied its reactions with nucleophiles [1]. As a possible alternate route to η^3 -propargyl complexes, we initiated a study of the synthesis and protonation of conjugated enyne complexes. The analogous protonation of conjugated diene metal complexes is known to produce η^3 -allyl complexes [2]. Here we report the synthesis and structural characterization of the enyne complex $\text{Cp}^*(\text{CO})_2\text{Re}[\eta^2\text{-HC}\equiv\text{CC}(\text{CH}_3)=\text{CH}_2]$ (**1**) and unsuccessful attempts to prepare an η^3 -propargyl complex by protonation of **1**. In addition we present interesting chemistry of **1** and the related alkenylidene complex $\text{Cp}^*(\text{CO})_2\text{Re}=\text{C}=\text{CHC}(\text{CH}_3)=\text{CH}_2$ (**2**). Protonation of **2** gave the cationic carbyne complex $[\text{Cp}^*(\text{CO})_2\text{Re}\equiv\text{CCH}=\text{C}(\text{CH}_3)_2]^+[\text{BF}_4]^-$ (**3**), which underwent nucleophilic attack to produce substituted alkenylidene complexes. The unusual reactions of both **1** and **2** with dimethyl

acetylenedicarboxylate (DMAD) to eventually produce dimethyl 4-methylphthalate (**9**) are also reported.

2. Results

2.1. Synthesis and characterization of $\text{Cp}^*(\text{CO})_2\text{Re}[\eta^2\text{-HC}\equiv\text{CC}(\text{CH}_3)=\text{CH}_2]$ (**1**)

When a THF solution of the conjugated enyne, $\text{HC}\equiv\text{CC}(\text{CH}_3)=\text{CH}_2$, and $\text{Cp}^*\text{Re}(\text{CO})_2(\text{THF})$ was warmed slowly from -78°C to room temperature over several hours, a 21% yield of the yellow rhenium-alkyne complex, $\text{Cp}^*(\text{CO})_2\text{Re}[\eta^2\text{-HC}\equiv\text{CC}(\text{CH}_3)=\text{CH}_2]$ (**1**), was obtained (Scheme 1). The structure of **1** was determined by spectroscopy and confirmed by X-ray crystallography. In the ^1H NMR spectrum, the two vinyl hydrogens of the non-coordinated isopropenyl group appeared as finely split multiplets at δ 5.58 and 5.35 while the proton on the coordinated acetylene appeared as a sharper singlet at δ 5.50. The acetylenic proton was shifted to high frequency compared with non-coordinated acetylenic protons which normally appear at δ 1.8 to 2.0; this shift can be understood in terms of the metallacyclopentadiene resonance structure **1b**. Complexation of the triple bond was readily distinguished from complexation of the double bond which would have led to vinyl resonances shifted to lower

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* Dedicated to Professor Helmut Werner on the occasion of his 60th birthday and in recognition of his outstanding contributions to organometallic chemistry.

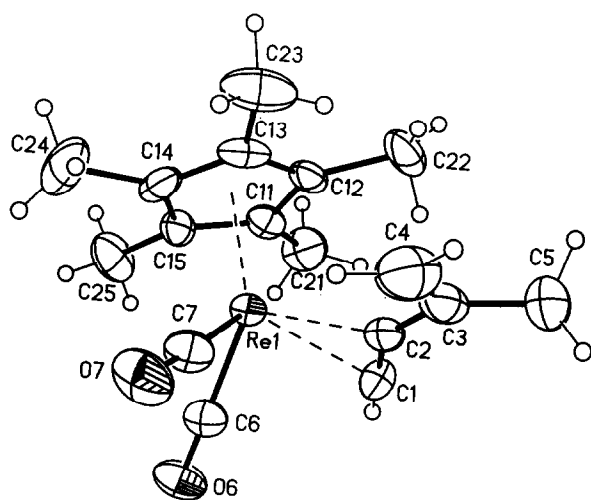


Fig. 1. X-Ray structure of $\text{Cp}^*(\text{CO})_2\text{Re}[\eta^2\text{-HC}\equiv\text{C}(\text{CH}_3)=\text{CH}_2]$ (**1**).

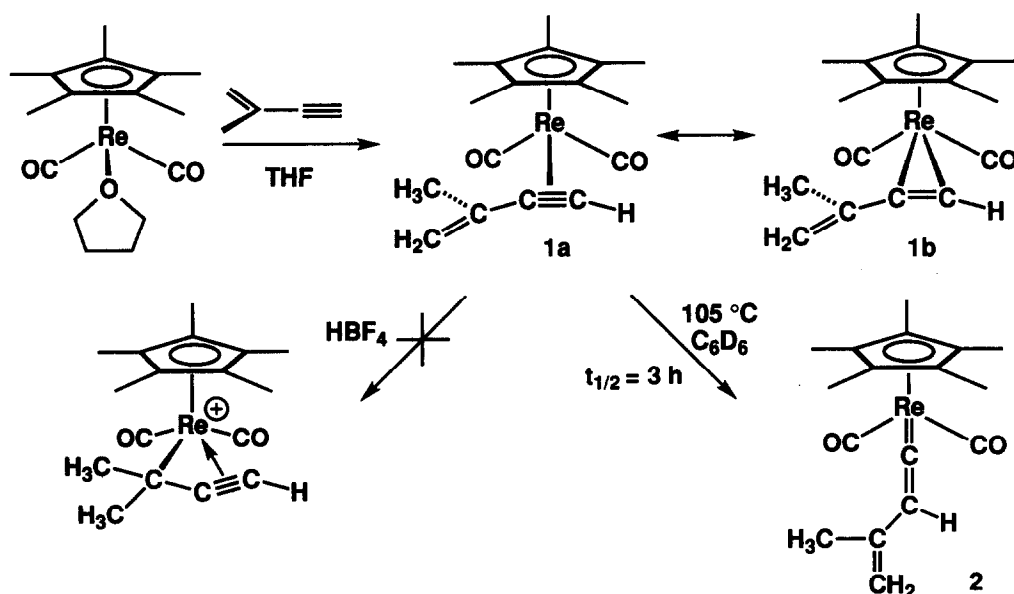
TABLE 1. Selected bond lengths (Å) and bond angles (°) for $\text{Cp}^*(\text{CO})_2\text{Re}[\eta^2\text{-HC}\equiv\text{C}(\text{CH}_3)=\text{CH}_2]$ (**1**)

Bond lengths			
Re(1)–C(1)	2.198(9)	C(2)–C(3)	1.411(12)
Re(1)–C(2)	2.192(8)	C(3)–C(4)	1.335(19)
Re(1)–C(6)	1.903(8)	C(3)–C(5)	1.478(17)
Re(1)–C(7)	1.865(9)	C(6)–O(6)	1.135(10)
C(1)–C(2)	1.244(13)	C(7)–O(7)	1.172(12)
Bond angles			
C(1)–Re(1)–C(2)	32.9(3)	C(1)–C(2)–C(3)	147.5(10)
C(1)–Re(1)–C(6)	82.5(3)	C(4)–C(3)–C(2)	121.7(10)
C(2)–Re(1)–C(7)	89.6(4)	C(5)–C(3)–C(2)	116.4(10)
C(6)–Re(1)–C(7)	84.2(4)	C(4)–C(3)–C(5)	122.0(10)
Re(1)–C(1)–C(2)	73.3(6)	Re(1)–C(6)–O(6)	178.6(8)
Re(1)–C(2)–C(1)	73.8(5)	Re(1)–C(7)–O(7)	175.9(8)
Re(1)–C(2)–C(3)	138.6(7)		

frequency. The presence of only a single CO resonance at δ 209 in the ^{13}C NMR spectrum of **1** is consistent with rapid rotation of the coordinated alkyne. Earlier, we found that rotation of complexed ethylene in $\text{Cp}(\text{CO})_2\text{Re}(\text{CH}_2=\text{CH}_2)$ was rapid at room temperature with a barrier to rotation of only 8.3 kcal mol $^{-1}$ [3].

The X-ray crystal structure of **1** (Figure 1 and Table 1) will be discussed in terms of two limiting resonance descriptions of the alkyne complex as a three-legged piano stool **1a** and as a four-legged piano stool metallacyclopentene **1b**. The OC–Re–CO angle of 84.2(4)° is

intermediate between the 90° angle anticipated for **1a** and the 70° angle anticipated for the four-legged piano stool geometry of **1b**. The coordinated alkyne is approximately parallel to the plane of the Cp* ligand. [The angle between the (Cp* centroid, Re, alkyne midpoint) plane and the (alkyne-rhenium) plane is 98.4°.] This is similar to the four-legged piano stool geometry of $\text{CpM}(\text{CO})_2\text{R}_2$ complexes and is consistent with an important resonance contribution from metallacyclopentene **1b**. The alkyne carbon-carbon bond is lengthened to 1.244(13) Å and the alkyne substituent is bent away from the metal center [$\text{C}\equiv\text{C}-\text{C}$, 147.5(10)°] consistent with a significant contribution from **1b**. The alkyne is bound symmetrically to Re with Re–C dis-



Scheme 1.

tances of 2.192(8) Å and 2.198(9) Å. The isopropenyl group is twisted 27.7(8)° from coplanarity with the Re-alkyne plane.

The reaction of **1** with acids was investigated as a possible route to an η^3 -propargyl complex by protonation of the vinyl group. However, attempted protonation of **1** with either $\text{HBF}_4 \cdot \text{Et}_2\text{O}$ or $\text{CF}_3\text{SO}_3\text{H}$ gave no immediate reaction and exposure of **1** to the acidic media for longer times (> 12 h) led to decomposition.

2.2. Thermal rearrangement of alkyne complex **1** to alkenylidene complex **2**

When a benzene solution of alkyne complex **1** was heated at 105°C, clean rearrangement to the alkenylidene complex $\text{Cp}^*(\text{CO})_2\text{Re}=\text{C}=\text{CHC}(\text{CH}_3)=\text{CH}_2$ (**2**) was observed. When the reaction was followed by ^1H NMR spectroscopy, no intermediates were observed and the time for half reaction was 3 h. Photolysis of **1** in benzene also yielded a small amount of **2** but the photolytic conversion was accompanied by severe decomposition.

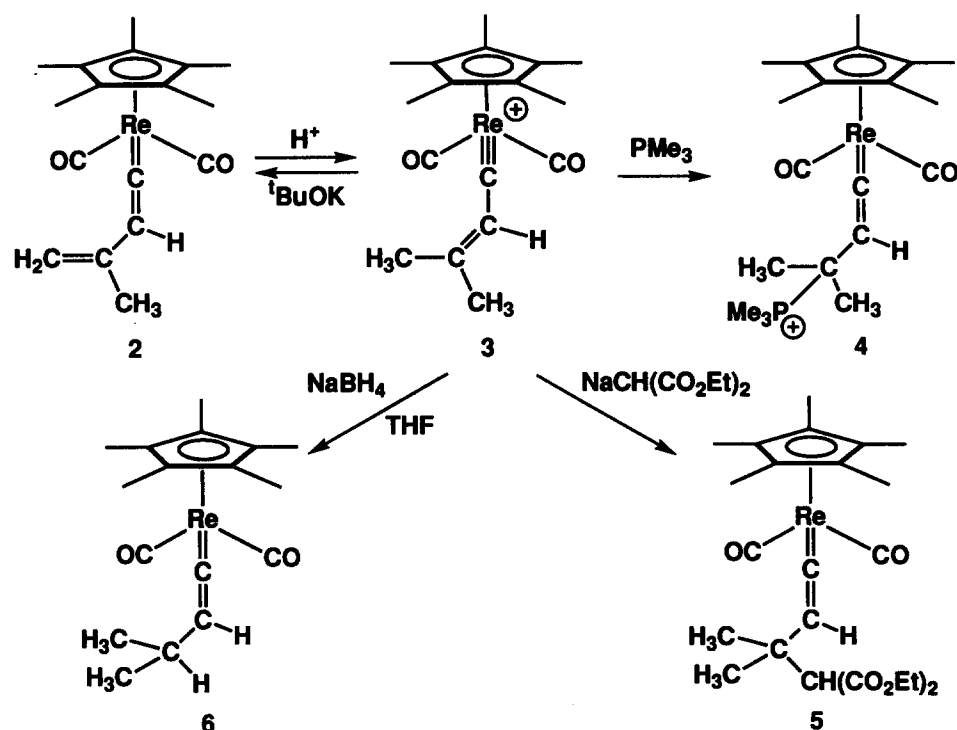
The structure of **2** was established by spectroscopy. In the ^{13}C NMR spectrum, a high frequency resonance at δ 332.1 was assigned to the alkenylidene carbon of **2**. Cationic alkenylidene complexes with similar alkenylidene carbon resonances shifted to high frequency include $[\text{CpRu}(\text{C}=\text{CH}_2)(\text{PMe}_2\text{Ph})_2][\text{BF}_4]$ (δ

346.2) [4] and $[\text{CpRe}(\text{C}=\text{CHCMe}_3)(\text{NO})(\text{PPh}_3)_2][\text{BF}_4]$ (δ 328.7) [5]. In the ^1H NMR spectrum of **2**, finely split multiplets at δ 4.63 and 4.26 are assigned to the isopropenyl group and a sharp singlet at δ 4.39 is assigned to the alkenylidene proton.

Spectral comparisons indicate that the alkenylidene ligand of **2** is a substantially better π -acceptor ligand than the alkyne ligand of **1**. In the IR spectra, greater electron donation to the alkenylidene ligand shifts ν_{CO} to higher energy for **2** (1979, 1908 cm^{-1}) compared to **1** (1956, 1873 cm^{-1}). The Cp^* resonances of **2** are shifted to higher frequency relative to those of **1** in both the ^1H NMR (δ 1.74 for **2**, δ 1.66 for **1**) and ^{13}C NMR spectra (δ 102.6 for **2**, δ 99.7 for **1**), consistent with a more electron poor Re center in **2**. The low frequency ^1H NMR shift of the isopropenyl vinyl hydrogens of **2** (δ 4.63 and 4.26) compared to **1** (δ 5.58 and 5.35) is also consistent with greater electron donation to the alkenylidene ligand of **2** [6].

2.3. Protonation of alkenylidene complex **2** to produce the cationic carbyne complex, $[\text{Cp}^*(\text{CO})_2\text{Re}\equiv\text{CCH}=\text{C}(\text{CH}_3)_2][\text{BF}_4]$ (**3**)

Protonation of the Re-vinylalkenylidene complex **2** with $\text{HBF}_4 \cdot \text{Et}_2\text{O}$ occurred exclusively at the δ -carbon to produce the cationic Re-carbyne complex $[\text{Cp}^*(\text{CO})_2\text{Re}\equiv\text{CCH}=\text{C}(\text{CH}_3)_2][\text{BF}_4]$ (**3**), which was isolated



Scheme 2.

as an unstable brown solid in 40% yield (Scheme 2). Since solutions of **3** decomposed rapidly and solid **3** decomposed within several days in a glove box, **3** was used in subsequent reactions without purification. The structure of **3** was determined spectroscopically. In the ^{13}C NMR spectrum of **3**, the carbyne carbon appeared at characteristically high frequency (δ 315.0). The carbonyl stretching frequencies of the cationic complex **3** were shifted to higher energy (2066 and 2012 cm^{-1}) than the neutral precursor **2** (1979 and 1908 cm^{-1}). The observation of two equal intensity CH_3 resonances in the ^1H NMR spectrum of **3** at δ 2.24 and 2.03 established that protonation occurred at the vinyl δ -carbon of **2**.

When a THF solution of the cationic carbyne complex **3** was treated with KOCMe_3 , clean deprotonation occurred to regenerate **2**.

2.4. Reaction of nucleophiles with the vinyl carbyne complex **3**

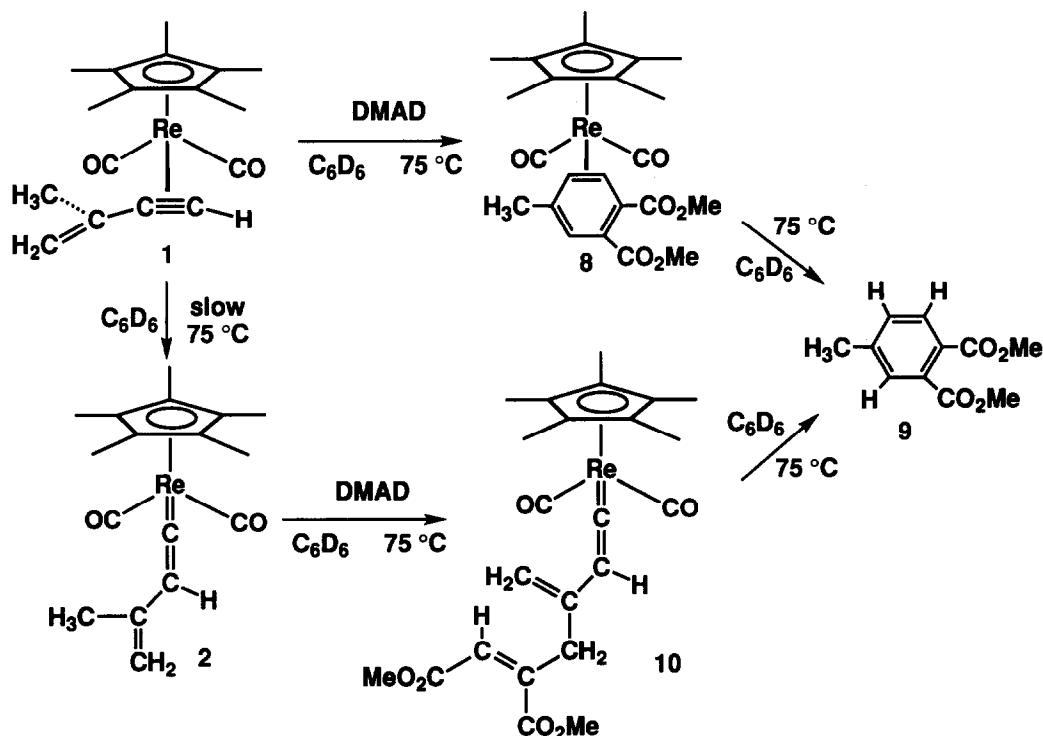
Nucleophilic addition of PMe_3 , $\text{NaCH}(\text{CO}_2\text{Et})_2$, and NaBH_4 occurred exclusively at the terminal γ -vinyl carbon of the cationic vinyl carbyne complex **3** to give substituted alkenylidene complexes (Scheme 2). In all cases, attack at the γ -carbon was established by ^1H NMR spectroscopy which showed an alkenylidene singlet at high frequency and a resonance for a gem-di-

methyl group. If nucleophilic attack had occurred at the carbyne carbon, the product would have contained an isopropenyl group.

Reaction of PMe_3 with carbyne complex **3** gave a 60% yield of the alkenylidene complex $[\text{Cp}^*(\text{CO})_2\text{Re}=\text{C}=\text{CHC}(\text{CH}_3)_2(\text{PMe}_3)][\text{BF}_4]$ (**4**). In the ^{13}C NMR spectrum of **4**, the alkenylidene carbon appeared at characteristically high frequency at δ 318.5. In the ^1H NMR spectrum, a doublet at δ 2.96 ($^3J_{\text{PH}} = 4.2$ Hz) was assigned to the alkenylidene proton coupled to phosphorus, and a six proton doublet at δ 1.35 ($^3J_{\text{PH}} = 17.1$ Hz) was assigned to the gem-dimethyl group coupled to phosphorus.

Similarly, addition of $\text{NaCH}(\text{CO}_2\text{Et})_2$ occurred at the γ -carbon of vinyl carbyne complex **3** to produce the alkenylidene complex $\text{Cp}^*(\text{CO})_2\text{Re}=\text{C}=\text{CHC}(\text{CH}_3)_2\text{CH}(\text{CO}_2\text{Et})_2$ (**5**) in 50% yield. In the ^1H NMR spectrum, a singlet at δ 4.01 was assigned to the alkenylidene proton, and a six proton singlet at δ 1.58 was assigned to the gem-dimethyl group. The diastereotopic methylene protons of the two OCH_2CH_3 groups of the malonate adduct did not have different chemical shifts and gave rise to a single quartet.

Reaction of NaBH_4 with **3** led to hydride addition at the γ -carbon to give the isopropyl substituted alkenylidene complex $\text{Cp}^*(\text{CO})_2\text{Re}=\text{C}=\text{CHCH}(\text{CH}_3)_2$ (**6**) in only 40% yield. In the ^1H NMR spectrum, a



Scheme 3.

doublet at δ 3.45 ($J = 7$ Hz) was assigned to the alkenylidene proton and a six proton doublet at δ 1.09 was assigned to the *gem*-dimethyl group. A major contaminant was $\text{Cp}^*(\text{CO})_2\text{Re}[\mu\text{-C}=\text{CHCH}(\text{CH}_3)_2]\text{Re}(\text{CO})_2\text{Cp}^*$ [7a]. A pure sample of **6** was obtained in 80% isolated yield by thermolysis of the alkyne complex $\text{Cp}^*(\text{CO})_2\text{Re}[\eta^2\text{-HC}\equiv\text{CCH}(\text{CH}_3)_2]$ (**7**).

2.5. Formation of dimethyl 4-methylphthalate from reaction of either **1** or **2** with DMAD

When the Re-enyne complex **1** was heated with dimethyl acetylenedicarboxylate (DMAD) at 75°C , a slow reaction occurred over 50 h to eventually give dimethyl 4-methylphthalate (**9**) in 60% yield. **9** was unambiguously identified by ^1H and ^{13}C NMR spectroscopy and by mass spectrometry [8].

To further investigate this intriguing process, the course of the reaction of **1** with DMAD was followed by ^1H NMR. After 15 h at 75°C , 20% of an intermediate along with 20% **9** were observed. The intermediate was isolated by column chromatography and shown to be the η^2 -dimethyl 4-methylphthalate complex $\text{Cp}^*(\text{CO})_2\text{Re}[\eta^2(5,6)\text{-C}_6\text{H}_3(4\text{-CH}_3)(1,2\text{-CO}_2\text{CH}_3)_2]$ (**8**). Further heating of the solution (> 25 h) eventually released free **9** from **8** (Scheme 3).

The structure of **8** was established spectroscopically. ^1H NMR resonances at δ 5.13 and 5.04 weakly coupled to one another ($J = 2$ Hz) were attributed to protons on the aromatic carbons η^2 -coordinated to Re. The low frequency position and weak coupling of these protons is characteristic of η^2 -coordination [9]. A broad resonance at δ 8.06 was assigned to the remaining aromatic hydrogen. Since only two of the three aromatic resonances were shifted to lower frequency, η^6 -coordination was discounted. ^{13}C NMR and DEPT135 spectra also supported the η^2 -coordination of the aromatic compound. The aromatic resonances shifted to lower frequency (δ 68.0 and 64.9) were assigned to the η^2 -coordinated carbons. The presence of a coordinated aromatic species and of two carbonyl groups was further supported by the observation of the molecular ion in high resolution mass spectrometry.

Reaction of Re alkenylidene complex **2** with DMAD at 75°C also produced dimethyl 4-methylphthalate (**9**) in 60% yield (Scheme 3). The reaction of **2** with DMAD was somewhat faster than the reaction of **1** with DMAD and was complete within 10 h. When the course of the reaction was followed by ^1H NMR and ^{13}C NMR spectroscopy, the intermediate $\text{Cp}^*(\text{CO})_2\text{Re}=\text{C}=\text{CHC}(\text{CH}_3)=\text{CH}_2$ (**10**) resulting from an ene reaction was observed. The maximum amount of **10** observed was 20% of the reaction mixture. Because **10** was unstable to chromatography, it was characterized only by spectroscopy. In the ^{13}C

NMR spectrum of **10**, a characteristic high frequency resonance at δ 332 was assigned to the alkenylidene carbon. In the ^1H NMR spectrum, a high frequency resonance at δ 6.03 with weak allylic coupling (t , $J < 1$ Hz) was assigned to the vinylic proton of the unsaturated ester. Two multiplets at δ 4.71 and 4.25 were assigned to the protons of $\text{C}=\text{CH}_2$ and a singlet at δ 4.14 was assigned to the alkenylidene proton. Resonances at δ 1.87 in ^1H NMR and at δ 39.2 in ^{13}C NMR spectra were assigned to the doubly allylic methylene group.

3. Discussion

The reaction of $\text{Cp}^*\text{Re}(\text{CO})_2(\text{THF})$ with $\text{HC}\equiv\text{CC}(\text{CH}_3)=\text{CH}_2$ yielded alkyne coordinated $\text{Cp}^*\text{Re}(\text{CO})_2(\text{HC}\equiv\text{CC}(\text{CH}_3)=\text{CH}_2)$ (**1**) rather than an alkene coordinated product. We had anticipated this result since alkynes generally form more stable complexes than alkenes. For example, the coordinated ethylene in $(\text{Ph}_3\text{P})_2\text{Pt}(\text{C}_2\text{H}_4)$ was completely replaced by a variety of alkynes at room temperature within 1 h [7b,10].

Two possible protonation products of **1** were considered. Protonation at the coordinated terminal alkyne carbon would result in an η^3 -allyl complex, while protonation at the uncoordinated alkene would give an η^3 -propargyl complex. However, $\text{HBF}_4 \cdot \text{Et}_2\text{O}$ failed to protonate **1** at short times and decomposition occurred at longer times.

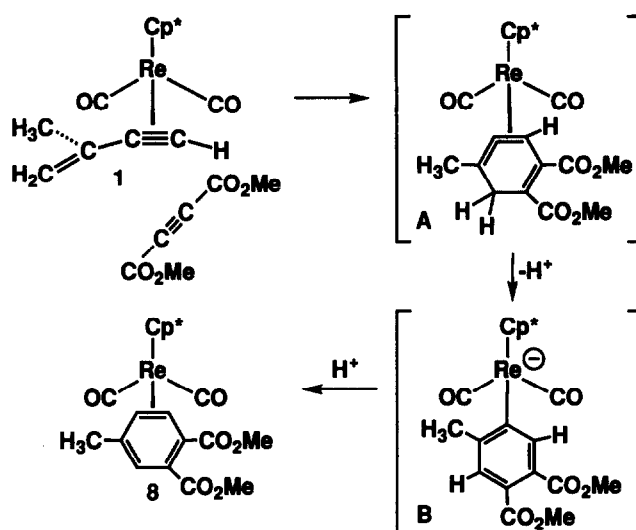
We also sought to investigate the protonation of an η^4 -coordinated enyne. η^4 -Coordinated conjugated enyne complexes are rare and their chemistry has not been extensively explored [11]. In attempting to photolytically dissociate CO from $\text{Cp}^*\text{Re}(\text{CO})_2(\text{HC}\equiv\text{CC}(\text{CH}_3)=\text{CH}_2)$ (**1**) to prepare the desired η^4 -coordinated product, we instead found that **1** was converted to the dicarbonyl alkenylidene complex $\text{Cp}^*(\text{CO})_2\text{Re}=\text{C}=\text{CHC}(\text{CH}_3)=\text{CH}_2$ (**2**) in 25% yield.

A cleaner and faster ($t_{1/2} = 3$ h) conversion of **1** to **2** was achieved by thermolysis at 105°C . The closest analogy of the conversion of **1** to **2** is the rearrangement of the rhodium enyne complex $(\text{P}^i\text{Pr}_3)_2\text{ClRh}(\text{HC}\equiv\text{CC}(\text{CH}_3)=\text{CH}_2)$ (**11**) to the alkenylidene complex $(\text{P}^i\text{Pr}_3)_2\text{ClRh}=\text{C}=\text{CHC}(\text{CH}_3)=\text{CH}_2$ (**12**) reported by Werner [12]. Bruce and Swincer have reviewed the synthesis and reactions of alkenylidene complexes [13]. Recent syntheses of alkenylidene complexes from alkyne complexes include Selegue's $[\text{Cp}(\text{PMe}_2\text{Ph})_2\text{Ru}=\text{C}=\text{CH}_2][\text{BF}_4]$ [4], Fryzuk's $[\text{N}(\text{SiMe}_2\text{CH}_2\text{PPh}_2)_2]\text{Ir}=\text{C}=\text{CH}_2$ [14], and Gladysz' $[\text{Cp}(\text{NO})(\text{PPh}_3)\text{Re}=\text{C}=\text{CH}^t\text{Bu}][\text{BF}_4]$ [5].

The vinylalkenylidene complex **2** underwent regioselective protonation at the δ -carbon of the vinylalkenylidene unit, yielding the cationic Re carbyne complex **3**. Werner observed similar regioselectivity in the conver-

sion of **12** to the rhodium carbyne complex $[(P^iPr_3)_2-CIRh\equiv CCH=C(CH_3)_2][BF_4]$ [12]. The reaction of the cationic carbyne complex **3** with a variety of nucleophiles led to regioselective nucleophilic attack at the γ -carbon of the vinyl carbyne ligand. Geoffroy recently reported that $Cp(PPh_3)(CO)Mn\equiv C(Me)=CPh_2^+$ reacted with nucleophiles at both the α - and γ -carbons of the vinyl substituted alkylidyne ligand [15]. Steric effects are probably responsible for attack at the remote vinyl carbon of **3** in preference over direct attack at the carbyne carbon adjacent to the crowded metal center.

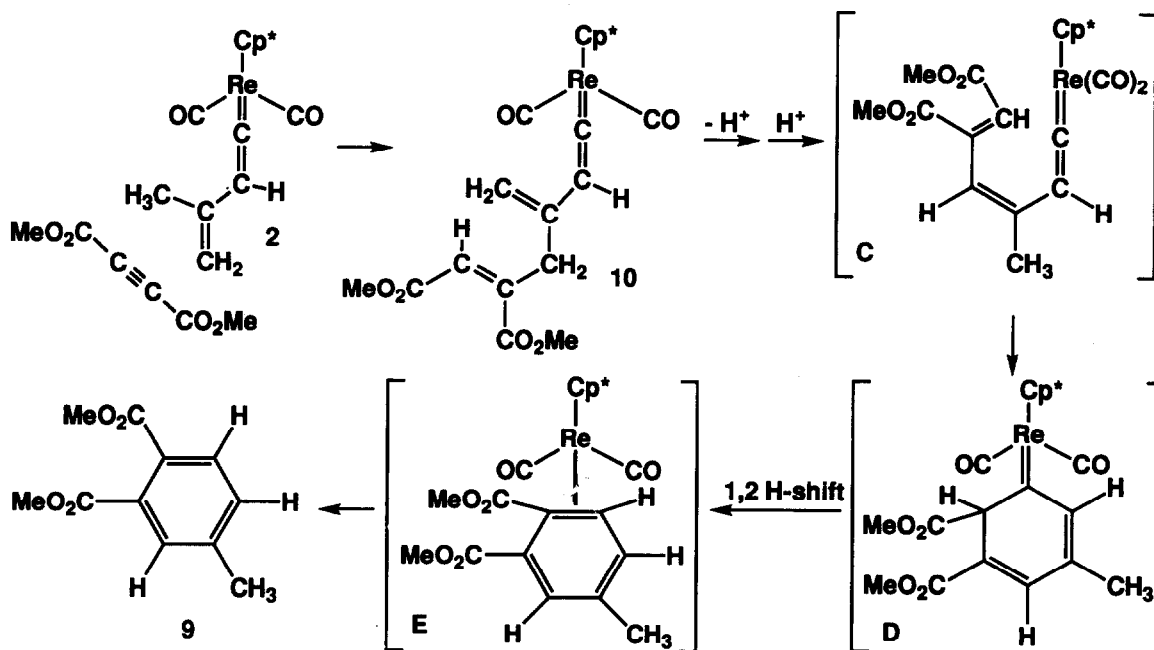
The conversion of enyne complex **1** to η^2 -arene complex **8** is very unusual. While η^2 -arene complexes including $[Cp^*Re(CO)_2]_2(\mu-\eta^2,\eta^2-C_6H_6)$ [9a] and $Cp^*(PMe_3)Rh(\eta^2-C_6H_4Me_2)$ [9c] are well known, such complexes are normally formed by photolytic substitution of a CO ligand or by reductive elimination from an aryl metal hydride. A highly speculative mechanism which efficiently accounts for the formation of **8** is shown in Scheme 4. We suggest that Diels–Alder addition of DMAD to the complexed enyne ligand to **1** could produce cycloallene complex **A**. Complexation of the enyne may aid the Diels–Alder reaction by bending the alkyne (the $C_1-C_2-C_3$ angle is 147°) and might also stabilize the cycloallene intermediate **A**. Related cycloallene complexes include $[Cp(CO)(PPh_3)Fe-(C_7H_{10})][PF_6]$ [16]. Deprotonation of **A** could then generate the Re aryl anion **B** and reprotonation at Re



Scheme 4.

followed by reductive elimination would produce the observed η^2 -arene complex **8**.

The reaction of **2** with DMAD began with a normal ene reaction to produce **10**. Our speculations on the mechanism of the unusual transformation of **10** to **9** are summarized in Scheme 5. We suggest that **10** is first converted to **C** by deprotonation of the methylene group to give an anion conjugated with the ester functionality, followed by reprotonation at the more remote



Scheme 5.

site. Electrocyclic ring closure of the hexatriene unit of **C** generates cyclic carbene complex **D**, which can then undergo a 1,2-hydrogen shift to give η^2 -arene complex **E**. η^2 -Arene intermediate **E** is more substituted than the isolated η^2 -arene complex **8** and readily dissociates from rhenium to give free dimethyl 4-methylphthalate (**9**).

In related chemistry, Selegue reported that attempted generation of $\text{Cp}(\text{PPh}_3)_2\text{Ru}=\text{C}=\text{C}=\text{CMe}_2^+$ (**F**) led to the formation of a dimer containing a six membered carbocycle [17]; it is possible that this dimerization is initiated by an ene reaction between **F** and the vinyl alkenylidene complex $\text{Cp}(\text{PPh}_3)_2\text{Ru}=\text{C}=\text{CHCMe}=\text{CH}_2^+$.

Both reactions of **1** and **2** with DMAD produce **9** but are mechanistically distinct. The conversion of **1** to **2** was much slower than the reaction of **1** with DMAD; consequently, **2** cannot be an intermediate in the reaction of **1** with DMAD. The reaction of **2** with DMAD was much faster than the reaction of **1** with DMAD; therefore, **1** cannot be an intermediate in the reaction of **2** with DMAD. Different intermediates were seen in the reactions of **1** and **2** with DMAD. η^2 -arene complex **8** was observed as an intermediate only in the reaction of **1** with DMAD. **10** was observed only in the reaction of **2** with DMAD.

4. Experimental details

4.1. General methods

^1H NMR spectra were obtained on Bruker WP200, WP270, or AM500 spectrometers. $^{13}\text{C}\{^1\text{H}\}$ and $^{31}\text{P}\{^1\text{H}\}$ NMR spectra were obtained on a Bruker AM500 spectrometer (126 MHz and 203 MHz, respectively). DEPT135 and/or DEPT90 spectra were obtained to identify the number of hydrogens on a carbon. Infrared spectra were measured on a Mattson Polaris (FT) spectrometer. Mass spectra were determined on a Kratos MS-80.

Benzene, C_6D_6 , Et_2O , hexane, and THF were distilled from purple solutions of sodium benzophenone ketyl immediately prior to use. CH_2Cl_2 , CD_2Cl_2 , CHCl_3 , and CDCl_3 were dried over P_2O_5 and distilled prior to use. Air-sensitive materials were manipulated by standard Schlenk techniques or in an inert atmosphere glove box.

4.2. $\text{Cp}^*(\text{CO})_2\text{Re}[\eta^2\text{-HC}\equiv\text{CC}(\text{CH}_3)=\text{CH}_2]$ (**1**)

When the bath surrounding a flask containing a solution of $\text{HC}\equiv\text{CC}(\text{CH}_3)=\text{CH}_2$ (0.5 mL, 5.3 mmol) and $\text{Cp}^*\text{Re}(\text{CO})_2(\text{THF})$ (250 mg, 0.55 mmol) [18] in 30 mL THF was allowed to warm slowly from -78°C to room temperature, the yellow solution slowly became browned. After 24 h, the IR spectrum showed complete disappearance of $\text{Cp}^*\text{Re}(\text{CO})_2(\text{THF})$. Solvent was

TABLE 2. Crystal structure data for $\text{Cp}^*(\text{CO})_2\text{Re}[\eta^2\text{-HC}\equiv\text{CC}(\text{CH}_3)=\text{CH}_2]$ (**1**)

Empirical formula	$\text{C}_{17}\text{H}_{21}\text{O}_2\text{Re}$
Color; Habit	Orange transparent blocks
Crystal size (mm)	$0.2 \times 0.2 \times 0.3$
Crystal system	Monoclinic
Space group	$P2_1/n$
Unit cell dimensions	
$a =$	$7.5973(8) \text{ \AA}$
$b =$	$15.227(2) \text{ \AA}$
$c =$	$13.9344(11) \text{ \AA}$
$\beta =$	$90.239(10)^\circ$
Volume	$1611.9(3) \text{ \AA}^3$
Peaks to determine cell	25
2θ range of cell peaks	22.0 to 25.0°
Z	4
Formula weight	443.5
Density (calc.)	1.828 g cm^{-3}
Absorption coefficient	7.639 mm^{-1}
$F(000)$	856
$R(F)$ (%)	3.54
$R_w(F)$ (%)	4.41

evaporated and the residue was separated by column chromatography (silica gel, 3:1 hexane: Et_2O). A yellow-orange band after the leading $\text{Cp}^*\text{Re}(\text{CO})_3$ band was recrystallized by slow evaporation of its Et_2O solution at -20°C to give **1** (53 mg, 21%) as a yellow-orange solid. ^1H NMR (C_6D_6 , 200 MHz): δ 5.58 (m, $\text{C}=\text{CHH}$), 5.50 (s, $\text{HC}\equiv\text{C}$), 5.35 (m, $\text{C}=\text{CHH}$), 2.11 (m, CH_3), 1.66 (s, Cp^*). ^{13}C NMR (C_6D_6 , 126 MHz): δ 209 (CO), 133.1 ($\text{C}=\text{CH}_2$), 120.4 ($\text{C}=\text{CH}_2$), 99.7 (Cp^*C), 91.5 ($\text{HC}\equiv\text{C}$), 75.2 ($\text{HC}\equiv\text{C}$), 25.3 (CH_3), 10.3 (Cp^*CH_3). IR (THF): 1956 (s), 1873 (s) cm^{-1} . HRMS calcd for $\text{C}_{17}\text{H}_{21}\text{O}_2\text{Re}$ m/e 444.1101, found m/e 444.1112. Anal. Calcd for $\text{C}_{17}\text{H}_{21}\text{O}_2\text{Re}$: C, 46.00; H, 4.77. Found C, 46.22; H, 4.68.

4.3. X-ray crystal structure of $\text{Cp}^*(\text{CO})_2\text{Re}[\eta^2\text{-HC}\equiv\text{CC}(\text{CH}_3)=\text{CH}_2]$ (**1**)

Suitable crystals of **1** were grown by slow evaporation of a hexane- Et_2O solution of **1** at -20°C . An orange block-shaped crystal was mounted on the tip of a thin glass fiber and X-ray data were collected on a Siemens P4 diffractometer and the structure was solved by direct methods (Table 2). Although the crystal showed significant decay during data collection, no special problems occurred during the solution and refinement of the structure. Four molecules of **1** crystallized in a monoclinic unit cell with space group symmetry $P2_1/n$; $a = 7.5973(8) \text{ \AA}$, $b = 15.227(2) \text{ \AA}$, $c = 13.9344(11) \text{ \AA}$, $\beta = 90.239(10)^\circ$, $V = 1611.9(3) \text{ \AA}^3$, $T = 295 \text{ K}$. A total of 3796 data were collected to $2\theta < 50^\circ$ ($\lambda = 0.71073 \text{ \AA}$) which yielded 2340 observed [$F > 4\sigma(F)$] independent ($R_{\text{int}} = 0.0432$) data. In full matrix least-squares refinements using SHELXTL PLUS/1990,

all non-hydrogen atoms were refined independently with anisotropic thermal parameters. All hydrogen atoms were fixed at idealized positions. An empirical absorption correction was applied to the data and the final difference map disclosed no unusual features. Refinement converged to $R(F) = 0.0354$, $wR(F) = 0.0441$, and $S = 1.44$, using weights of $w^{-1} = \sigma^2(F) + 0.0003 \cdot F^2$. Tables giving full crystallographic details for **1** are available upon request from the authors.

4.4. $\text{Cp}^*(\text{CO})_2\text{Re}=\text{C}=\text{CHC}(\text{CH}_3)=\text{CH}_2$ (**2**)

A solution of **1** (20 mg, 45 μmol) in 2 mL benzene in an NMR tube sealed under vacuum was heated at 105°C for 24 h. Clean conversion (> 99%) of **1** to **2** was observed by ^1H NMR spectroscopy. Evaporation of solvent gave $\text{Cp}^*(\text{CO})_2\text{Re}=\text{C}=\text{CHC}(\text{CH}_3)=\text{CH}_2$ (**2**) as a thick red oil, which was shown by ^1H NMR spectroscopy to be > 95% pure. Attempted purification by silica gel chromatography or by low temperature crystallization led to decomposition. ^1H NMR (C_6D_6 , 200 MHz): δ 4.63 (m, $\text{C}=\text{CHH}$), 4.39 (s, $=\text{C}=\text{CH}$), 4.26 (m, $\text{C}=\text{CHH}$), 1.95 (m, CH_3), 1.74 (s, Cp^*). ^{13}C NMR (C_6D_6 , 126 MHz): δ 332.1 ($\text{Re}=\text{C}$), 203 (CO), 133.6 ($=\text{C}(\text{CH}_3)$), 121.4 ($=\text{CH}$), 106.8 ($=\text{CH}_2$), 102.6 (C_5Me_5), 21.3 (CH_3), 10.5 (Cp^*CH_3). IR (THF): 1979 (s), 1908 (s) cm^{-1} . HRMS calcd for $\text{C}_{17}\text{H}_{21}\text{O}_2\text{Re}$ m/e 444.1101, found m/e 444.1106.

4.5. $[\text{Cp}^*(\text{CO})_2\text{Re}=\text{CCH}=\text{C}(\text{CH}_3)_2][\text{BF}_4]$ (**3**)

When $\text{HBF}_4 \cdot \text{Et}_2\text{O}$ (5 μL) was added to a clear red solution of alkenylidene complex **2** (10 mg, 23 μmol) in benzene (2 mL), the solution became brown and cloudy. Addition of Et_2O (5 mL) induced solidification. The resulting brown precipitate was filtered through a glasswool plug and washed with Et_2O to give $[\text{Cp}^*(\text{CO})_2\text{Re}=\text{CCH}=\text{C}(\text{CH}_3)_2][\text{BF}_4]$ (**3**) (5 mg, 40%) as a brown solid. Because **3** was unstable, it was used without further purification for subsequent reactions. ^1H NMR (CD_2Cl_2 , 200 MHz): δ 5.57 (m, $\text{CH}=\text{CMe}_2$), 2.33 (s, Cp^*), 2.24 (d, $J = 3$ Hz, $\text{HC}=\text{C}(\text{CH}_3)(\text{CH}_3)$), 2.03 (d, $J = 2$ Hz, $\text{HC}=\text{C}(\text{CH}_3)(\text{CH}_3)$). ^{13}C NMR (CD_2Cl_2 , 126 MHz): δ 315 ($\text{Re}=\text{C}$), 191 (CO), 182 ($\text{C}=\text{CMe}_2$), 136 ($\text{CH}=\text{CMe}_2$), 107 (C_5Me_5), 27.8 (both $\text{C}=\text{C}(\text{CH}_3)_2$), 10.9 (Cp^*CH_3). IR (CH_2Cl_2): 2066 (s), 2012 (s) cm^{-1} .

4.6. $[\text{Cp}^*(\text{CO})_2\text{Re}=\text{C}=\text{CHC}(\text{CH}_3)_2(\text{PMe}_3)][\text{BF}_4]$ (**4**)

A solution of $[\text{Cp}^*(\text{CO})_2\text{Re}=\text{CCH}=\text{C}(\text{CH}_3)_2][\text{BF}_4]$ (**3**) (10 mg, 19 μmol) and excess PMe_3 in CH_2Cl_2 was slowly warmed from -78°C to room temperature. Solvent was evaporated and hexane was added to induce precipitation. The resulting orange precipitate was filtered through a glasswool plug and washed with hexane to give **4** (7 mg, 60%). ^1H NMR (CD_2Cl_2 , 500 MHz): δ 2.96 (d, $J_{\text{PH}} = 4.2$ Hz, $\text{C}=\text{CH}$), 2.15 (s, Cp^*),

1.82 (d, $J_{\text{PH}} = 13.1$ Hz, $\text{P}(\text{CH}_3)_3$), 1.35 (d, $J_{\text{PH}} = 17.1$ Hz, $\text{C}(\text{CH}_3)_2\text{PMe}_3$). ^{13}C NMR (CD_2Cl_2 , 126 MHz): δ 318.5 ($\text{Re}=\text{C}$), 201.9 (CO), 113.3 ($\text{C}=\text{CH}$), 104.0 (Cp^*C), 29.5 (d, $J_{\text{PC}} = 54.0$ Hz, $(\text{C}(\text{CH}_3)_2\text{PMe}_3)$), 23.0 ($(\text{C}(\text{CH}_3)_2\text{PMe}_3)$), 10.9 (Cp^*CH_3), 5.46 (d, $J_{\text{PC}} = 51.8$ Hz). ^{31}P NMR (CD_2Cl_2 , 203 MHz): δ 39.1. MS calcd for $\text{C}_{20}\text{H}_{31}\text{O}_2\text{RePBF}_4 - \text{BF}_4$ m/e 520.63, found m/e 521. Anal. Calcd for $\text{C}_{20}\text{H}_{31}\text{O}_2\text{RePBF}_4$: C, 39.55; H, 5.14. Found C, 39.47; H, 5.01.

4.7. $\text{Cp}^*(\text{CO})_2\text{Re}=\text{C}=\text{CHC}(\text{CH}_3)_2\text{CH}(\text{CO}_2\text{Et})_2$ (**5**)

Solid $\text{NaCH}(\text{CO}_2\text{Et})_2$ (5 mg, 27 μmol) was added to a THF solution of $[\text{Cp}^*(\text{CO})_2\text{Re}=\text{CCH}=\text{C}(\text{CH}_3)_2][\text{BF}_4]$ (10 mg, 18 μmol). After 0.5 h, solvent was evaporated, and the resulting red-brown residue was column chromatographed through a short silica gel plug (1:1 hexane:benzene, and then Et_2O). The major red-brown band eluted with Et_2O gave **5** (6 mg, 50%) as a thick red oil. ^1H NMR (C_6D_6 , 200 MHz): δ 4.02 (q, OCH_2CH_3 's), 4.01 (s, $\text{C}=\text{CH}$), 3.54 (s, $\text{HC}(\text{CO}_2\text{Et})_2$), 1.80 (s, Cp^*), 1.58 (s, $\text{C}(\text{CH}_3)_2$), 0.98 (t, OCH_2CH_3 's). IR (THF): 1975 (s), 1902 (s), 1751 (w), 1734 (m), 1653 (m) cm^{-1} . HRMS calcd for $\text{C}_{24}\text{H}_{33}\text{O}_6\text{Re}$ m/e 604.1838, found m/e 604.1852.

4.8. $\text{Cp}^*(\text{CO})_2\text{Re}=\text{C}=\text{CHCH}(\text{CH}_3)_2$ (**6**)

Excess NaBH_4 (4 mg, 106 μmol) was added to a THF solution of $[\text{Cp}^*(\text{CO})_2\text{Re}=\text{C}=\text{CH}=\text{C}(\text{CH}_3)_2][\text{BF}_4]$ (10 mg, 18 μmol). The solution was stirred overnight and the solvent was evaporated. The residue was dissolved in benzene, passed through the Celite plug, and the solvent was evaporated to yield **6** (6 mg, 40%) as a red solid. **6** obtained by this method was only ~60% pure as shown by the Cp^* region of the ^1H NMR spectrum. One of the major impurities was the dimeric complex $\text{Cp}^*(\text{CO})_2\text{Re}[\mu-\text{C}=\text{CHCH}(\text{CH}_3)_2]\text{Re}(\text{CO})_2\text{Cp}^*$ [**7b**].

A pure sample of **6** was prepared by thermolysis of the alkyne complex, $\text{Cp}^*(\text{CO})_2\text{Re}[\text{HC}\equiv\text{CCH}(\text{CH}_3)_2]$ (**7**). Reaction of $\text{HC}\equiv\text{CCH}(\text{CH}_3)_2$ (0.15 mL) with $\text{Cp}^*\text{Re}(\text{CO})_2(\text{THF})$ (51 mg, 0.11 mmol) in 15 mL THF gave **7** (15 mg, 30%) which was isolated by column chromatography (3:1 hexane: Et_2O). ^1H NMR (C_6D_6): δ 4.67 (d, $^4J = 1.8$ Hz, $\text{HC}\equiv$), 2.86 (dm, $J = 6.9$ Hz, $^4J = 1.8$ Hz, CHMe_2), 1.27 (d, $J = 6.9$ Hz, $\text{CH}(\text{CH}_3)_2$), 1.65 (s, Cp^*). IR (Et_2O): 1954 (s), 1873 (s) cm^{-1} . HRMS calcd for $\text{C}_{17}\text{H}_{23}\text{O}_2\text{Re}$ m/e 446.1257, found m/e 446.1257.

Thermolysis of a benzene solution of **7** at 105°C led to clean conversion to **6**, which was isolated by column chromatography (12 mg, 80%). ^1H NMR (C_6D_6 , 200 MHz): δ 3.45 (d, $J = 7$ Hz, $\text{C}=\text{CH}$), 2.62 (m, $J = 7$ Hz, $\text{CH}(\text{CH}_3)_2$), 1.81 (s, Cp^*), 1.09 (d, $J = 6.7$ Hz, $\text{CH}(\text{CH}_3)_2$). IR (hexane): 1982 (s), 1913 (s) cm^{-1} . HRMS calcd for $\text{C}_{17}\text{H}_{23}\text{O}_2\text{Re}$ m/e 446.1257, found

m/e 446.1261. Anal. Calcd for $C_{17}H_{23}O_2Re$: C, 45.83; H, 5.20. Found C, 45.49; H, 5.07.

4.9. $Cp^*(CO)_2Re[\eta^2(5,6)-C_6H_3(4-CH_3)(1,2-CO_2CH_3)_2]$ (**8**)

When a solution of **1** (5 mg, 11 μ mol) and dimethyl acetylenedicarboxylate (2.3 μ L, 18 μ mol) in C_6D_6 (0.3 mL) was heated at 75°C, 1H NMR spectroscopy showed the buildup of **8** to a maximum of 20% after 15 h along with 20% **9**. Chromatography through a short silica gel plug gave a yellow band eluted with 1:1 hexane:benzene containing **9**, followed by an orange band eluted with 1:1 hexane:Et₂O from which **8** (1 mg, 20%) was isolated as an orange solid and shown to be ~70% pure by 1H NMR. 1H NMR (C_6D_6 , 200 MHz): δ 8.06 (br s, $CMeCHCCO_2Me$); 5.13 (m, $\eta^2-CH=CHCMe$); 5.04 (d, $J = 2$ Hz, $\eta^2-CH=CHCMe$); 3.77, 3.46 (s, CO_2CH_3 's); 2.15 (m, CCH_3), 1.57 (s, Cp^*). ^{13}C NMR (C_6D_6 , 126 MHz): δ 207.0 (CO); 169.8, 165.4 (CO_2Me 's); 150.0 (CCH_3); 148.1 (CH); 127.4 (CCO_2Me 's); 102.6 (Cp^*C); 68.0, 64.9 ($\eta^2-CH=CH$); 51.5, 51.1 (CO_2CH_3 's); 25.1 (CCH_3); 9.6 (Cp^*CH_3). HRMS calcd for $C_{23}H_{27}O_6Re$ m/e 586.1368, found m/e 586.1355.

4.10. $Cp^*(CO)_2Re=C=CHC(=CH_2)CH_2C(CO_2CH_3)=CH(CO_2CH_3)$ (**10**)

When a solution of **2** (4 mg, 9 μ mol) and dimethyl acetylenedicarboxylate (2.3 μ L, 18 μ mol) in C_6D_6 (0.3 mL) was heated at 75°C, 1H NMR spectroscopy showed the buildup of **10** to a maximum of 20% after 3 h. Because **10** was unstable to silica gel chromatography, it was characterized by spectroscopy of a solution also containing the final product **9**. 1H NMR (C_6D_6 , 200 MHz): δ 6.03 (t, $J \leq 1$ Hz, $CH(CO_2Me)$); 4.71, 4.25 (m, $C=CH_2$); 4.14 (s, $C=CH$); 3.54, 3.32 (s, $C(CO_2CH_3)=CH(CO_2CH_3)$); 1.87 (br s, CH_2); 1.81 (s, Cp^*). ^{13}C NMR (C_6D_6 , 126 MHz): δ 332 (Re=C), 203 (CO 's), 176 (CO_2Me 's), 134 ($C=CH_2$), 133 ($MeO_2CC=$), 127 ($=CHCO_2Me$), 120 ($=CH$), 109 ($=CH_2$), 103 (Cp^*C), 52.0, 51.2 (CO_2CH_3 's), 39.2 (CH_2 , negative peak in DEPT135 spectrum), 10.7 (Cp^*CH_3). HRMS $M^+ - 2(CO)$ calcd for $C_{21}H_{27}O_4Re$ m/e 530.1470, found m/e 530.1433.

4.11. Dimethyl 4-methylphthalate (**9**)

When a solution of **1** (20 mg, 45 μ mol) and dimethyl acetylenedicarboxylate (11 μ L, 89 μ mol) in 2 mL benzene was heated at 70°C for 50 h, dimethyl 4-methylphthalate (**9**) was formed. The second yellow band obtained from chromatography through a short silica gel plug (1:1 hexane:benzene) gave **9** as an oil (6 mg, 60%), contaminated by a yellow impurity.

9 was also prepared by heating a solution of **2** (15 mg, 34 μ mol) and DMAD (10 μ L, 81 μ mol) in benzene for 10 h followed by purification by column chromatography (1:1 hexane:benzene) (4 mg, 60%). 1H NMR (C_6D_6 , 200 MHz): δ 7.55 (d, $J = 9$ Hz, $CHCHMe$), 7.32 (m, $CMeCHCCO_2Me$), 6.73 (dm, $J = 9$ Hz, $CHCHMe$); 3.57, 3.51 (s, CO_2CH_3 's); 1.83 (br s, CCH_3). $^{13}C\{^1H\}$ NMR (C_6D_6 , 126 MHz): δ 168.3 (CO_2Me 's); 141.7 (CCH_3); 131.2, 129.6, 129.4 (CH 's, confirmed by DEPT135); 128.6 (CCO_2Me 's); 52.1, 51.0 (OCH_3 's); 20.9 (CCH_3). HRMS calcd for $C_{11}H_{12}O_4$ m/e 208.0736, found m/e 208.0745. The 1H NMR of **9** in CCl_4 was the same as reported [8].

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