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Synthesis and Reactions of Dirhenium Alkenylidene and Alkylidyne Complexes

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Abstract: Reaction of $Cp^*(CO)_2Re{=}Re(CO)_2Cp^*$ with the enyne $HC{\equiv}CC(CH_3){=}CH_2$ gave $Cp^*(CO)_2Re\{\mu\text{-}\eta^1,\eta^3\text{-}CH{=}C[C(CH_3){=}CH_2]CO\}Re(CO)Cp^*$ (**1**), in which an α,β-unsaturated carbonyl unit bridges the Re–Re bond. Thermal rearrangement of **1** led to the isopropenyl-substituted μ-alkenylidene complex $Cp^*(CO)_2Re[\mu\text{-}C{=}CHC(CH_3){=}CH_2]Re(CO)_2Cp^*$ (**2**). Protonation of the conjugated μ-alkenylidene complex **2** occurred exclusively at the remote δ-carbon to produce the cationic μ-alkylidyne dirhenium complex $\{Cp^*(CO)_2Re[\mu\text{-}CCH{=}C(CH_3)_2]Re(CO)_2Cp^*\}(BF_4)$ (**3**). Nucleophilic addition to **3** occurred selectively at the γ-carbon to give addition products including $Cp^*(CO)_2Re[\mu\text{-}C{=}CHC(CH_3)_2CH(CO_2Et)_2]Re(CO)_2Cp^*$ (**6**) and $Cp^*(CO)_2Re[\mu\text{-}C{=}CHC(CH_3)_3]Re(CO)_2Cp^*$ (**7**). μ-Alkenylidene complex **3** underwent an unusually facile ene reaction with dimethyl acetylenedicarboxylate (DMAD) to produce $Cp^*(CO)_2Re[\mu\text{-}C{=}CHC({=}CH_2)CH_2C(CO_2Me){=}CH(CO_2Me)]Re(CO)_2Cp^*$ (**8**).

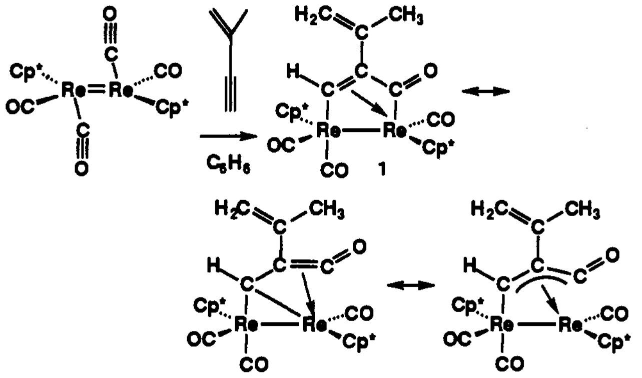
Introduction

We recently reported the synthesis of $Cp^*(CO)_2Re{=}Re(CO)_2Cp^*$, which is a highly unusual formal dimer of a 16-electron metal fragment.[1] This metal-metal double-bonded compound is thermally stable to over 100 °C, but is also kinetically very reactive toward H_2 and CO at −78 °C. Here we report the reaction of $Cp^*(CO)_2Re{=}Re(CO)_2Cp^*$ with the enyne $HC{\equiv}CC(CH_3){=}CH_2$, which produces the dimetallacyclopentenone $Cp^*(CO)_2Re\{\mu\text{-}\eta^1,\eta^3\text{-}CH{=}C[C(CH_3){=}CH_2]CO\}Re(CO)Cp^*$ (**1**). This compound serves as an entry point into the synthesis of a variety of dirhenium complexes including μ-alkenylidene and μ-alkylidyne complexes that can be used in new carbon–carbon bond-forming reactions.

Results and Discussion

Alkyne Addition to $Cp^*(CO)_2Re{=}Re(CO)_2Cp^*$. Addition of the conjugated enyne, 2-methyl-1-buten-3-yne, to a benzene solution of $Cp^*(CO)_2Re{=}Re(CO)_2Cp^*$ gave an 81% yield of the 1:1 adduct $Cp^*(CO)_2Re\{\mu\text{-}\eta^1,\eta^3\text{-}CH{=}C[C(CH_3){=}CH_2]CO\}Re(CO)Cp^*$ (**1**). The formation of **1** involves a formal addition of the alkyne triple bond across the Re–Re–carbonyl carbon unit of $Cp^*(CO)_2Re{=}Re(CO)_2Cp^*$. The ^1H NMR spectrum of **1** shows two inequivalent Cp* resonances at δ 1.80 and 1.68, a characteristic resonance at δ 8.27 for the β-hydrogen of the complexed enone, and resonances for the isopropenyl side chain. The reactions of alkynes with $Cp^*(CO)_2Re{=}Re(CO)_2Cp^*$ will be discussed in detail elsewhere.[2]

The structure of **1** was definitively established by a single-crystal X-ray structure determination (Figure 1, Table 1). The similar bond distances between the carbons of the bridging ligand (C(1)–C(2) 1.39(3) Å, C(2)–C(3) 1.41(4) Å) suggest that the structure of **1** can be understood as a resonance hybrid of dimetallacyclopentenone, complexed ketene, and η^1,η^3-allyl formulations as depicted below. Several diiron[3] and iron-platinum[4] compounds with similar dimetallacyclopentenone units have been described.



Rearrangement of 1 to a Bridging Alkenylidene Dirhenium Complex. When adduct **1** was heated at 70 °C for 24 h, a 1:2 mixture of $Cp^*Re(CO)_3$ and the μ-alkenylidene dirhenium complex $Cp^*(CO)_2Re[\mu\text{-}C{=}CHC(CH_3){=}CH_2]Re(CO)_2Cp^*$ (**2**) was formed. At 60 °C, little reaction occurred, and at 80 °C, more $Cp^*Re(CO)_3$ was formed. Pure **2** was isolated in 50% yield by column chromatography. The structure of **2** was established spectroscopically and confirmed by a single-crystal X-ray structure determination. The μ-C=CH resonance appeared as a broad multiplet at δ 6.89 in the ^1H NMR spectrum, and the bridging vinylidene carbon appeared at δ 241.2 in the ^{13}C NMR spectrum of **2**. The shifts of these resonances to higher frequency are characteristic of μ-alkenylidene complexes.[5]

2 is the first dirhenium μ-alkenylidene complex to be characterized by X-ray crystallography. The μ-alkenylidene ligand of **2** is severely distorted to avoid interaction with the bulky Cp* groups (Figure 2, Table 2). The alkenylidene ligand bends away from the Cp* group cis to the isopropenyl substituent: the Re-

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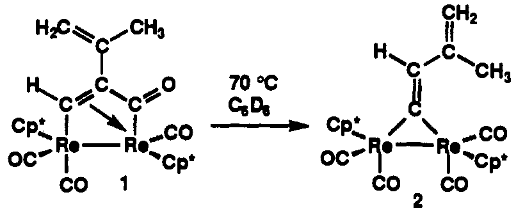
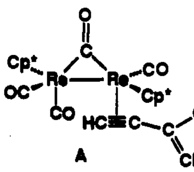


(1)-μ-C=C angle is 116(2)°, while the Re(2)-μ-C=C angle is 152(2)°. The β-alkenylidene carbon is thrust toward Re(1) by this distortion and is bent away from the Cp* ligand on Re(2): the β-alkenylidene carbon lies 0.29 Å out of the Re–Re–(μ-C) plane. The μ-C=C–C angle (127.3°) is within the normal range of C=C–C angles. The extreme distortion of the Re–(μ-C)=C angle indicates that this type of distortion is unusually easy to achieve. We plan to explore this notion with molecular orbital calculations.

When the course of this unusual isomerization was followed by ^{1}H NMR spectroscopy, an intermediate was detected at early times. In addition to resonances of **1** and **2**, an intermediate was observed which had two Cp* resonances at δ 1.85 and 1.67 and resonances due to the vinyl hydrogens (δ 5.08 and 4.71) and methyl group (δ 1.61) of an isopropenyl group. The resonance due to the remaining hydrogen was not observed. After 2.5 h at 70 °C, the ratio of **1**:intermediate:**2** was 50:25:25, and after 4 h, the ratio was approximately 30:20:50.

The overall rearrangement of **1** to **2** requires CO deinsertion, a 1,2-hydrogen shift, and Re–C bond formation (not necessarily in that order). While the structure of the intermediate observed in this transformation remains a mystery, **A**, **B**, and **C** must be considered as possible structures since we have observed similar complexes in reactions of **1** with other alkynes.[2] It is not obvious why any of these structures might lie along the reaction pathway from **1** to **2**.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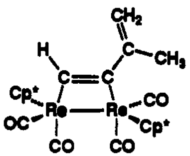
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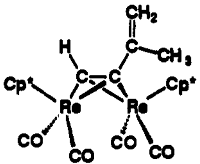
C

Protonation of 2 Produces a Cationic μ-Alkylidyne Dirhenium Complex. Selective protonation of **2** with HBF$_4$·Et$_2$O occurred exclusively at the remote δ-carbon of the μ-alkenylidene ligand to give a 90% yield of the green cationic μ-alkylidyne dirhenium complex {Cp*(CO)$_2$Re[μ-CCH=C(CH$_3$)$_2$]Re(CO)$_2$Cp*}(BF$_4$) (**3**) (Scheme 1). No product from protonation at the β-carbon was observed. In the ^{13}C NMR spectrum of **3**, the μ-carbyne carbon appeared at characteristically high frequency at δ 371.3; μ-carbyne carbon resonances of dimetal μ-alkylidyne compounds are seen in the range δ 350–526.[6] In the ^{1}H NMR spectrum, the two vinyl methyl groups appeared at δ 1.90 and 1.82 and the vinyl hydrogen adjacent to the electron deficient bridging carbon appeared at high frequency at δ 7.58.

When **2** was treated with excess CF$_3$CO$_2$D in CD$_2$Cl$_2$, deuteration occurred selectively at the δ 1.80 methyl group. No incorporation of deuterium at the β-carbon was observed. This demonstrates that protonation of **2** at the δ-carbon is under kinetic control.

The selective protonation of **2** at the remote δ-site is readily understood since it produces a cationic alkylidyne complex stabilized by conjugation with the vinyl substituent. Both the protonation of μ-alkenylidene complexes to μ-alkylidyne complexes[7] and the remote protonation of vinyl-substituted alkenylidene complexes are precedented.[8]

The Cp* ligands of **3** gave rise to a single resonance at δ 2.03, indicative of rapid rotation of the vinyl group of the μ-vinylcarbyne ligand. Earlier we reported that cationic diiron μ-vinylcarbyne complexes have unusually low barriers to vinyl rotation because

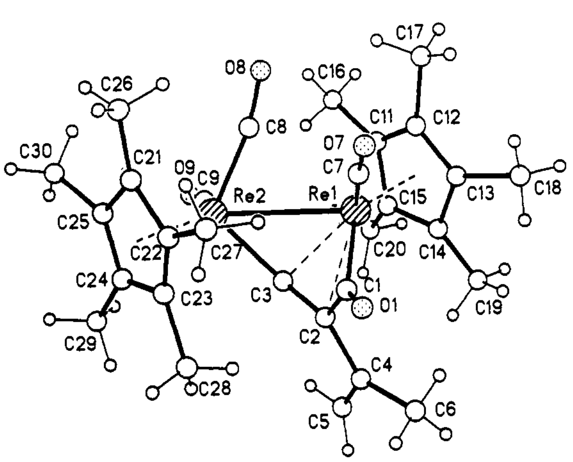

Figure 1. X-ray crystal structure of Cp*(CO)$_2$Re{μ-η^1,η^3-CH=C[C(CH$_3$)=CH$_2$]CO}Re(CO)Cp* (**1**).

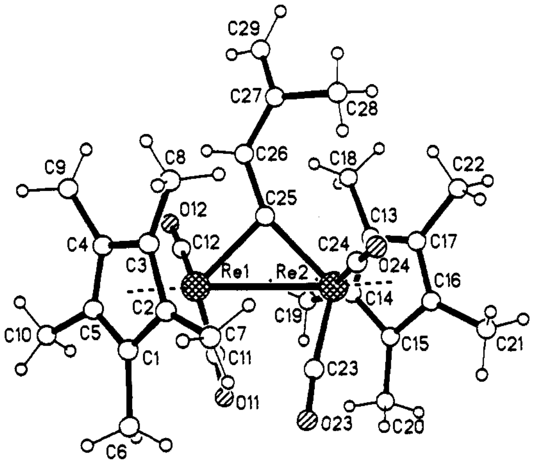

Figure 2. X-ray crystal structure of Cp*(CO)$_2$Re[μ-C=CHC(CH$_3$)=CH$_2$]Re(CO)$_2$Cp* (**2**).

Table 1. Selected Bond Lengths (Å) and Bond Angles (deg) for Cp*(CO)$_2$Re{μ-η^1,η^3-CH=C[C(CH$_3$)=CH$_2$]CO}Re(CO)Cp* (**1**)

Re(1)–Re(2)	2.928(1)	Re(1)–C(3)	2.18(2)	C(1)–O(1)	1.20(3)
Re(1)–C(1)	2.09(2)	Re(2)–C(3)	2.06(2)	C(2)–C(3)	1.41(4)
Re(1)–C(2)	2.25(2)	C(1)–C(2)	1.39(3)	C(2)–C(4)	1.58(4)

Re(1)–C(1)–C(2)	78(2)	C(2)–C(1)–O(1)	139(3)
C(1)–C(2)–C(3)	118(2)	Re(1)–C(1)–O(1)	142(2)
C(2)–C(3)–Re(2)	126(2)	C(1)–C(2)–C(4)	120(3)
C(3)–Re(2)–Re(1)	48.0(4)	C(3)–C(2)–C(4)	121(2)
Re(2)–Re(1)–C(1)	83.3(5)	C(2)–C(3)–Re(1)	74(1)
Re(1)–C(3)–Re(2)	87.3(6)	C(3)–C(2)–Re(1)	69(1)

Table 2. Selected Bond Lengths (Å) and Bond Angles (deg) for Cp*(CO)$_2$Re[μ-C=CHC(CH$_3$)=CH$_2$]Re(CO)$_2$Cp* (**2**)

Re(1)–Re(2)	2.917(1)	C(25)–C(26)	1.42(3)	C(27)–C(28)	1.51(4)
Re(1)–C(25)	2.10(2)	C(26)–C(27)	1.40(3)	C(27)–C(29)	1.31(5)
Re(2)–C(25)	2.07(2)				

C(25)–Re(1)–Re(2)	45.2(4)	C(27)–C(26)–C(25)	127(3)
C(25)–Re(2)–Re(1)	45.9(5)	C(26)–C(27)–C(28)	123(3)
Re(1)–C(25)–Re(2)	88.9(6)	C(26)–C(27)–C(29)	118(3)
C(26)–C(25)–Re(2)	152(2)	C(28)–C(27)–C(29)	117(3)
C(26)–C(25)–Re(1)	116(2)		

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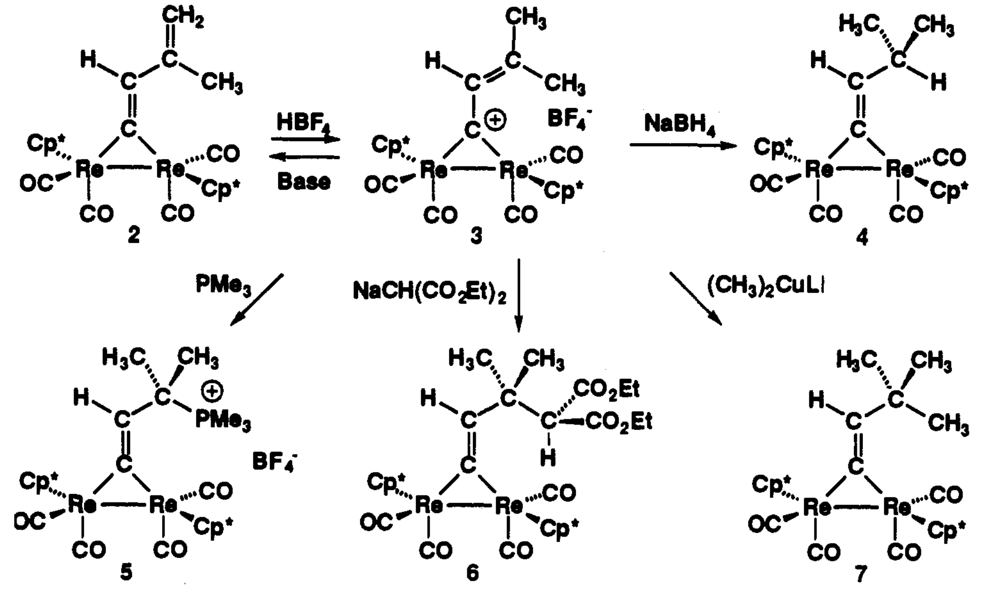
[6] (a) Carr, N.; Fernandez, J. R.; Stone, F. G. A. *Organometallics* **1991**, *10*, 2718–2725. (b) Casey, C. P.; Meszaros, M. W.; Fagan, P. J.; Bly, R. K.; Marder, S. R.; Austin, E. A. *J. Am. Chem. Soc.* **1986**, *108*, 4043–4053. (c) Casey, C. P.; Meszaros, M. W.; Fagan, P. J.; Bly, R. K.; Colborn, R. E. *J. Am. Chem. Soc.* **1986**, *108*, 4053–4059.

Scheme 1



conjugation is maintained throughout rotation; Fenske–Hall molecular orbital calculations showed that the bridging carbyne carbon has orthogonal p-orbitals which can accept electron density from the vinyl unit throughout rotation.[9]

Treatment of μ-alkylidyne complex **3** with $KOCMe_3$, CH_3Li, or CH_3MgBr all led to deprotonation and reisolation of μ-alkenylidene complex **2** in high yield.

Nucleophilic Additions to the Cationic μ-Alkylidyne Complex 3. Nucleophilic additon of hydride and of PMe_3 occurred cleanly at the remote γ-carbon of the cationic μ-alkylidyne complex **3** (Scheme 1). Reaction of $NaBH_4$ with **3** gave a 67% isolated yield of isopropyl-substituted μ-alkenylidene complex $Cp^*(CO)_2Re[\mu\text{-}C{=}CHCH(CH_3)_2]Re(CO)_2Cp^*$ (**4**), which was fully characterized by spectroscopy and elemental analysis. In the ^{13}C NMR spectrum of **4**, the bridging μ-$C{=}C$ carbon appeared at characteristically high frequency at δ 240; the six μ-alkenylidene complexes reported here (**2**, **4**–**8**) had μ-$C{=}C$ resonances in the range δ 228–243. Reaction of PMe_3 with **3** gave a 74% isolated yield of the addition product $\{Cp^*(CO)_2Re[\mu\text{-}C{=}CHC(CH_3)_2PMe_3]Re(CO)_2Cp^*\}(BF_4)$ (**5**). Fast atom bombardment mass spectrometry of **5** showed prominent peaks for the $(M^- - BF_4)^+$ and $(M - BF_4 - PMe_3)^+$ ions. In the ^1H NMR spectrum of **5**, the μ-alkenylidene proton appeared as a doublet at δ 5.70 coupled to ^{31}P (J = 11 Hz) and the diastereotopic gem dimethyl group appeared as two ^{31}P coupled doublets at δ 1.68 and 1.51.

Reaction of **3** with $NaCH(CO_2Et)_2$ and with $(CH_3)_2CuLi$ gave mixtures of products resulting from nucleophilic addition to the γ-carbon of the vinylcarbyne ligand of **3** and from deprotonation of the δ-carbon to give isopropenyl-substituted μ-alkenylidene complex $Cp^*(CO)_2Re[\mu\text{-}C{=}CHC(CH_3){=}CH_2]Re(CO)_2Cp^*$ (**2**) (Scheme 1). Addition of $NaCH(CO_2Et)_2$ to **3** gave a 0.75:1 mixture of γ-addition product $Cp^*(CO)_2Re[\mu\text{-}C{=}CHC(CH_3)_2CH(CO_2Et)_2]Re(CO)_2Cp^*$ (**6**) and δ-deprotonation product **2**. Chromatography allowed isolation of **6** as a yellow oil in 35% yield. In the ^1H NMR spectrum of **6**, separate resonances were observed for the diastereotopic gem dimethyl group and for the diastereotopic methylene and methyl groups of the diethyl esters. Addition of $(CH_3)_2CuLi$ to **3** gave a 1.2:1 mixture of *tert*-butyl-substituted μ-alkenylidene complex $Cp^*(CO)_2Re[\mu\text{-}C{=}CHC(CH_3)_3]Re(CO)_2Cp^*$ (**7**) and deprotonation product **2**, which could not be separated by chromatography. The structure of **7** relies upon spectroscopic observations on the mixture of **2** and **7**. In the ^1H NMR spectrum, a singlet at δ 6.24 was assigned to the μ-$C{=}CH$ group of **7** and an intense singlet at δ 1.41 was assigned to the CMe_3 group of **7**.

Selective attack of nucleophiles at the γ-carbon of cationic vinyl-substituted μ-alkylidyne complexes has been observed previously for reactions of Fe_2 complexes.[10] The preference for γ-attack over α-attack at the bridging carbon of **3** may be the result of greater steric crowding at the bridging carbon flanked by bulky Cp* ligands on Re. Alternatively, it may reflect the greater stability of the conjugated product of γ-attack. Most of the nucleophiles studied showed competition between γ-attack to produce the corresponding adducts and deprotonation to regenerate **2**. It should be noted that the softer carbon nucleophiles $NaCH(CO_2Et)_2$ and $(CH_3)_2CuLi$ gave mainly products from γ-nucleophilic attack, while the harder carbon nucleophiles CH_3MgBr and CH_3Li gave the deprotonation product exclusively.[11]

Ene Reaction of 2 with DMAD. To explore the possibility of Diels–Alder reactions involving the diene component of alkenylidene complex **2**, the reaction of the dienophile dimethyl acetylenedicarboxylate (DMAD) with **2** was investigated. However, an ene reaction of DMAD with the isopropenyl group of **2** was observed instead. Reaction of **2** with DMAD required heating at 70 °C for 5 h and led to the formation of the ene product $Cp^*(CO)_2Re[\mu\text{-}C{=}CHC({=}CH_2)CH_2C(CO_2Me){=}CH(CO_2Me)]Re(CO)_2Cp^*$ (**8**) in 42% NMR yield (mesitylene internal standard).

Because **8** was unstable to chromatography, it was characterized only by solution spectroscopy. The presence of a μ-alkenylidene group was established by the observation of a high-frequency ^{13}C NMR resonance at 243.4 for the μ-$C{=}CH$ unit and of a multiplet in the ^1H NMR at δ 6.66 for the μ-$C{=}CH$ group. The ^1H NMR spectrum also had resonances for inequivalent methyl esters at δ 3.65 and 3.35, for a $C{=}CH_2$ group at δ 5.74 and 4.75, and for a vinyl proton on the ester-substituted double bond at δ 6.08. The most compelling evidence for the ene reaction product **8** was the absence of a C-methyl resonance and the observation of a CH_2

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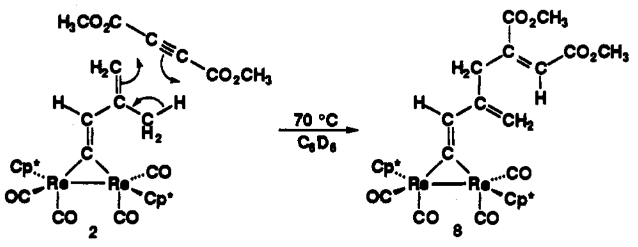
[11] Cationic μ-alkylidyne diiron complexes are readily deprotonated by base to yield alkenylidene complexes. (a) Casey, C. P.; Fagan, P. J. *J. Am. Chem. Soc.* **1982**, *104*, 4950–4951. (b) Kao, S. C.; Lu, P. P. Y.; Pettit, R. *Organometallics* **1982**, *1*, 911–918.

group in the ^{13}C NMR spectrum at δ 44.1 (negative resonance in DEPT135 experiment).



In this ene reaction, DMAD acts as an electrophile, attacking the isopropenyl group of **2**. The unusually mild conditions for an ene reaction are a reflection of the great electron donor ability of the dirhenium fragment. The less electrophilic enophile, $HC{\equiv}CCO_2CH_3$, failed to react with **2** at 75 °C. The failure of **2** to undergo a Diels–Alder reaction with DMAD may be a result of steric problems.

Experimental Section

General Methods. ^{1}H NMR spectra were obtained on a Bruker WP200, WP270, or AM500 spectrometer. ^{13}C{^{1}H} (126 MHz) and ^{31}P{^{1}H} (203 MHz) NMR spectra were obtained on a Bruker AM500 spectrometer. DEPT135 and/or DEPT90 spectra were obtained to determine 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. Elemental analyses were performed by Desert Analytics-Organic microanalysis (Tucson, AZ).

Hexane, C_6H_6, C_6D_6, Et_2O, 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 glovebox.

Cp*(CO)$_2$Re{μ-η^1,η^3-CH=C[C(CH$_3$)=CH$_2$]CO}Re(CO)Cp* (1). When $HC{\equiv}CC(CH_3){=}CH_2$ (0.05 mL, 0.526 mmol) was condensed into a frozen green solution of $Cp^*(CO)_2Re{=}Re(CO)_2Cp^*$ (25 mg, 0.033 mmol) in benzene (1.5 mL) at −78 °C and the solution was warmed to room temperature, an immediate color change to orange-red was observed. After stirring for 1 h, solvent and excess alkyne were evaporated under vacuum, and the residue was chromatographed (silica gel, 75:25 hexane:Et_2O). The second orange-red band was collected and recrystallized from CH_2Cl_2–Et_2O to give **1** (22 mg, 81%) as an orange-red solid. ^{1}H NMR (C_6D_6, 200 MHz): δ 8.27 (s, HC=C), 5.65 (m, *H*HC=C), 5.35 (q, *H*HC=C), 1.87 (m, C=CCH$_3$), 1.80 (s, Cp*), 1.68 (s, Cp*). ^{13}C NMR (C_6D_6, 126 MHz): δ 211.7, 208.4, 208.2 (CO's), 141.0 (H$_2$C=*C*), 117.5 (H$_2$*C*=C), 115.2 (H*C*=C), 98.2 (both Cp*C's), 53.1 (HC=*C*), 23.4 (CH$_3$), 10.7, 9.6 (Cp* CH$_3$'s). IR (CH_2Cl_2): 1950 (s), 1902 (s), 1851 (w), 1685 (w) cm^{-1}. HRMS calcd for $C_{29}H_{36}O_4Re_2$ *m/e* 822.1738, found *m/e* 822.1756. Anal. Calcd for $C_{29}H_{36}O_4Re_2$: C, 42.43; H, 4.42. Found: C, 42.69; H, 4.33.

Cp*(CO)$_2$Re[μ-C=CHC(CH$_3$)=CH$_2$]Re(CO)$_2$Cp* (2). A red degassed solution of **1** (10 mg, 0.012 mmol) in C_6D_6 (1.5 mL) was heated at 70 °C in a sealed NMR tube. After 24 h, the only products observed by ^{1}H NMR were **2** and Cp*Re(CO)$_3$ (2:1). Solvent was evaporated, and the residue was chromatographed (silica gel, hexane, then 50:50 hexane:Et_2O, then Et_2O). The second dark yellow band eluted with Et_2O was collected and dried under vacuum to give **2** (5 mg, 50%) as a yellow-orange solid. ^{1}H NMR (C_6D_6, 200 MHz): δ 6.89 (br m, μ-C=CH), 5.49, 4.82 (m, H$_2$C=C), 2.12 (br dd, C=CCH$_3$), 1.84, 1.77 (s, Cp*'s). ^{13}C NMR (C_6D_6, 126 MHz): δ 241.2 (μ-*C*=C), 209.1, 207.7 (CO's), 145.8 (*C*=CH$_2$), 142.2 (μ-C=*C*H), 108.5 (C=*C*H$_2$), 100.7, 99.9 (Cp* C's), 24.5 (C=C*C*H$_3$), 10.4, 10.1 (Cp* CH$_3$'s). IR (THF): 1957 (m), 1921 (s), 1886 (s), 1860 (w) cm^{-1}. HRMS calcd for $C_{29}H_{36}O_4Re_2$ *m/e* 822.1738, found *m/e* 822.1882. Anal. Calcd for $C_{29}H_{36}O_4Re_2$: C, 42.43; H, 4.42. Found: C, 42.67; H, 4.41.

X-ray Crystal Structures of 1 and 2. Suitable crystals of **1** were grown by layering hexane over a CH_2Cl_2 solution of **1** at −18 °C. Suitable crystals of **2** were grown by slow evaporation of a diethyl ether solution of **2** at −18 °C. X-ray data were collected on a Siemens P4 diffractometer, and the structures were solved by direct methods (Table 3). In full-matrix least-squares refinements using SHELXL-93, all non-hydrogen atoms were refined independently with anisotropic thermal parameters.

Table 3. Crystal Structure Data for **1** and **2**

	1	**2**
empirical formula	$C_{29}H_{36}O_4Re_2$	$C_{29}H_{36}O_4Re_2$
crystal size (mm)	0.50 × 0.20 × 0.10	0.15 × 0.10 × 0.10
crystal system	orthorhombic	triclinic
space group	*Iba*2	$P\bar{1}$
unit cell dimensions (Å, deg)	$a = 18.737(4)$	$a = 9.051(2)$
	$b = 31.532(6)$	$b = 9.395(2)$
	$c = 9.389(2)$	$c = 17.060(2)$
	$\alpha = \beta = \gamma = 90$	$\alpha = 81.117(13)$
		$\beta = 82.27(2)$
		$\gamma = 76.79(2)$
volume (Å^3)	5547.5(1)	1387.9(5)
θ range of cell peaks (deg)	2.17–25.00	2.25–22.50
Z	8	2
formula weight	820.98	820.98
density (calc) (g cm^{-3})	1.966	1.965
absorption coefficient (mm^{-1})	8.752	8.745
F(000)	3136	784
R(*F*) (%)	4.57	5.59
wR(*F*) (%)	11.50	13.91

{Cp*(CO)$_2$Re[μ-CCH=C(CH$_3$)$_2$]Re(CO)$_2$Cp*}(BF$_4$) (3). Addition of $HBF_4{\cdot}Et_2O$ (5 μL) to a dark yellow solution of **2** (12 mg, 0.015 mmol) in benzene (2 mL) led immediately to formation of a green solution and a dark green precipitate. Et_2O was added to give additional green precipitate, which was collected by filtration and recrystallized from CH_2Cl_2–Et_2O to give **3** (12 mg, 90%). ^{1}H NMR (CD_2Cl_2, 200 MHz): δ 7.58 (s, CH), 2.03 (s, Cp*'s), 1.90 (s, CH$_3$), 1.82 (s, CH$_3$). ^{13}C NMR (CD_2Cl_2, 126 MHz): δ 371.3 (μ-*C*), 202.7, 197.2 (CO's), 155.5 (H*C*=C), 150.3 (C=*C*Me$_2$), 105.1 (Cp* C's), 29.8, 22.6 (CH$_3$'s), 10.2 (Cp* CH$_3$'s). Anal. Calcd for $C_{29}H_{37}O_4Re_2BF_4$: C, 38.33; H, 4.10. Found: C, 37.07; H, 3.96.

Cp*(CO)$_2$Re[μ-C=CHCH(CH$_3$)$_2$]Re(CO)$_2$Cp* (4). When excess solid $NaBH_4$ (5 mg, 0.13 mmol) was added to a green solution of **3** (6 mg, 0.007 mmol) in THF (1.5 mL), the solution became yellow immediately. After 5 h, solvent was evaporated and the residue was dissolved in hexane and chromatographed (silica gel, 4:1 hexane:Et_2O) to give **4** (4 mg, 67%) as a yellow solid. ^{1}H NMR (C_6D_6, 200 MHz): δ 5.85 (d, J = 8.8 Hz, μ-C=CH), 1.88, 1.78 (s, Cp*'s), 1.64 (d, J = 12.8 Hz, HC(C*H$_3$*)$_2$), *H*C(CH$_3$)$_2$ was presumably obscured by Cp* or isopropyl resonances. IR (THF): 1953 (m), 1921 (s), 1883 (s), 1861 (w) cm^{-1}. HRMS calcd for $C_{29}H_{38}O_4Re_2$ *m/e* 824.1893, found *m/e* 824.1861. Anal. Calcd for $C_{29}H_{38}O_4Re_2$: C, 42.32; H, 4.65. Found: C, 42.55; H, 4.59.

{Cp*(CO)$_2$Re[μ-C=CHC(CH$_3$)$_2$PMe$_3$]Re(CO)$_2$Cp*}(BF$_4$) (5). When an excess of PMe$_3$ (0.1 mL) was vacuum transferred into a green solution of **3** (5 mg, 0.006 mmol) in CH_2Cl_2 (2 mL) at −78 °C, the solution became dark yellow. After 3 h at room temperature, solvent and excess PMe$_3$ were evaporated. The residue was dissolved in benzene. The solution was filtered through glass wool and evaporated to give **5** (4 mg, 74%) as a yellow solid. ^{1}H NMR (CD_2Cl_2, 500 MHz): δ 5.70 (d, J_{PH} = 11 Hz, μ-C=CH), 2.02, 1.91 (s, Cp*'s), 1.91 (d, J_{PH} = 12.9 Hz, P(CH$_3$)$_3$), 1.68 (d, J_{PH} = 19.1 Hz, HC(C*H$_3$*)(CH$_3$)PMe$_3$), 1.51 (d, J_{PH} = 18.4 Hz, HC(CH$_3$)(C*H$_3$*)PMe$_3$). ^{13}C NMR (CD_2Cl_2, 126 MHz): δ 233.1 (μ-*C*=CH), 206.8, 204.2 (CO's), 132.6 (μ-C=*C*H), 101.0, 100.6 (Cp* C's), 30.0, 26.6 (C(*C*H$_3$)$_2$PMe$_3$'s), 20.7 (d, J_{PC} = 43 Hz, *C*Me$_2$PMe$_3$), 11.0, 10.5 (Cp* CH$_3$'s), 5.8 (d, J_{PC} = 52 Hz, P(CH$_3$)$_3$). ^{31}P NMR (CD_2Cl_2 203 MHz): δ 38.82. FAB-MS: *m/e* 897 (M$^-$ − BF$_4$)$^+$, 821 (M − BF$_4$ − PMe$_3$)$^+$. Anal. Calcd for $C_{32}H_{46}O_4Re_2PBF_4$: C, 39.02; H, 4.71. Found: C, 38.30; H, 4.69.

Cp*(CO)$_2$Re[μ-C=CHC(CH$_3$)$_2$CH(CO$_2$Et)$_2$]Re(CO)$_2$Cp* (6). When excess solid NaCH(CO$_2$Et)$_2$ (5 mg, 0.027 mmol) was added to a green solution of **3** (10 mg, 0.011 mmol) in THF (2 mL), the solution became dark yellow immediately. After 3 h, solvent was evaporated and the residue was dissolved in benzene and chromtographed (silica gel, hexane, then 50:50 hexane:Et_2O, then Et_2O). The second yellow band eluted with Et_2O after the leading yellow band containing Cp*(CO)$_2$Re[μ-C=CHC(CH$_3$)=CH$_2$]Re(CO)$_2$Cp* (**2**) was collected to give **5** as a viscous yellow solid (4 mg, 35%). ^{1}H NMR (C_6D_6, 200 MHz): δ 6.66 (s, μ-C=CH), 4.30–3.95 (two dq, diastereotopic CO$_2$C*H$_2$*CH$_3$), 4.08 (s, *H*C(CO$_2$Et)$_2$, 1.88, 1.78 (s, Cp*'s), 1.15–0.95 (two t, diastereotopic CO$_2$CH$_2$C*H$_3$*), 1.15–0.95 (two s, diastereotopic C(C*H$_3$*)$_2$, partially obscured by ethyl ester resonances). ^{13}C NMR (C_6D_6, 126 MHz): δ 228.0 (μ-*C*=CH), 209.5, 208.9, 208.0, 207.3 (CO's), 168.6, 168.3 (diastereotopic *C*O$_2$Et); 147.9 (μ-C=*C*H); 100.3, 100.0 (Cp* C's); 70.9, 63.1 (diastereotopic $\mathrm{CO_2}\mathit{C}\mathrm{H_2CH_3}$'s); 34.4 ($\mathit{C}\mathrm{H(CO_2Et)_2}$); 27.2, 22.7 (diastereotopic $\mathrm{C(}\mathit{C}\mathrm{H_3)_2}$'s); 14.4, 14.2 (diastereotopic $\mathrm{CO_2CH_2}\mathit{C}\mathrm{H_3}$'s); 10.9, 10.2 (Cp* $\mathrm{CH_3}$'s). IR (THF): 1955 (m), 1920 (s), 1890 (s), 1865 (w), 1757 (m), 1741 (m) cm^{-1}. FAB-MS: *m/e* 982 ($\mathrm{MH^+}$).

Cp*(CO)$_2$Re[μ-C=CHC(CH$_3$)$_3$]Re(CO)$_2$Cp* (7). When excess $\mathrm{(CH_3)_2CuLi}$ in $\mathrm{Et_2O}$ was added to a green solution of **3** (10 mg, 0.011 mmol) in $\mathrm{CH_2Cl_2}$ (2 mL), the solution became dark yellow immediately. Solvent was evaporated under vacuum. The residue was dissolved in benzene and filtered through a silica gel plug. The second yellow band was collected and dried under vacuum to give a 1.2:1 mixture of **7**:**2** (60% total yield). Resonances in the mixture assigned to **7**: ^{1}H NMR ($\mathrm{C_6D_6}$, 200 MHz) δ 6.24 (s, C=CH); 1.86, 1.77 (s, Cp*'s); 1.41 (s, $\mathrm{C(CH_3)_3}$). ^{13}C NMR ($\mathrm{C_6D_6}$, 126 MHz): δ 232.0 (μ-*C*=CH); 209.0, 207.4 (CO's); 151.3 (μ-C=*C*H); 100.1, 99.8 (Cp* C's); 32.3 ($\mathrm{C(}\mathit{C}\mathrm{H_3)_3}$); 25.9 ($\mathit{C}\mathrm{(CH_3)_3}$); 10.9, 10.3 (Cp* $\mathrm{CH_3}$'s). HRMS calcd for $\mathrm{C_{30}H_{40}O_4Re_2}$ *m/e* 838.2050, found *m/e* 838.2059.

Cp*(CO)$_2$Re[μ-C=CHC(=CH$_2$)CH$_2$C(CO$_2$Me)=CH(CO$_2$Me)]Re(CO)$_2$Cp* (8). A solution of **2** (10 mg, 0.012 mmol) and dimethyl acetylenedicarboxylate (4 μL, 0.032 mmol) in $\mathrm{C_6D_6}$ (0.35 mL) was heated at 70 °C for 5 h in a sealed NMR tube. Since attempted purification of the product led to decomposition, **8** was characterized only by solution spectroscopy. ^{1}H NMR ($\mathrm{C_6D_6}$, 200 MHz): δ 6.66 (br m, μ-C=CH); 6.08 (br t, $J \approx 1$ Hz, C=CHCO$_2$Me); 5.74, 4.75 (m, C=CH$_2$); 3.65, 3.35 (s, $\mathrm{CO_2CH_3}$'s); 1.8 (br s, CH$_2$); 1.81, 1.79 (s, Cp*'s). ^{13}C NMR ($\mathrm{C_6D_6}$, 126 MHz): δ 243.4 (μ-*C*=C); 209, 208, 207 (CO's); 152.3, 150.0 ($\mathit{C}\mathrm{O_2CH_3}$'s); 144.0, 140.9 ($\mathit{C}\mathrm{(CO_2Me)}$=$\mathit{C}\mathrm{HCO_2Me}$); 138.9, 121.9 (CH's); 109.6 (C=*C*H$_2$); 100.9, 99.8 (Cp* C's); 51.9, 51.3 ($\mathrm{CO_2}\mathit{C}\mathrm{H_3}$'s); 44.1 (CH$_2$); 10.3, 10.1 (Cp* $\mathrm{CH_3}$'s). IR (hexane): 1962 (m), 1927 (s), 1895 (s), 1869 (w), 1735 (m, C(=O)OMe), 1614 (w, C=C) cm^{-1}. HRMS calcd for $\mathrm{C_{35}H_{42}O_8Re_2}$ *m/e* 964.2003, found *m/e* 964.2008.

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Supplementary Material Available: ORTEP diagrams, tables of structure determination data, positional and anisotropic thermal parameters for non-hydrogen atoms, selected interatomic distances and angles, and idealized atomic parameters for hydrogen atoms (22 pages); tables of observed and calculated structure factor amplitudes for compounds **1** and **2** (16 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.