Reaction of $Cp^*(CO)_2Re{=}Re(CO)_2Cp^*$ with Dimethyl Acetylenedicarboxylate Produces a 3,4-Dimetallacyclobutene Which Undergoes Photochemical Isomerization to a 2,4-Dimetallabicyclo[1.1.0]butane

Charles P. Casey,* Ronald S. Cariño, Randy K. Hayashi, and Kurt D. Schladetzky

Contribution from the Department of Chemistry, University of Wisconsin,
Madison, Wisconsin 53706

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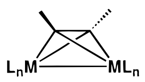
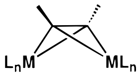
Abstract: The reaction of $Cp^*(CO)_2Re{=}Re(CO)_2Cp^*$ (**1**) with dimethyl acetylenedicarboxylate (DMAD) produced the 3,4-dimetallacyclobutene $Cp^*(CO)_2Re(\mu\text{-}\eta^1,\eta^1\text{-}CH_3O_2CC{=}CCO_2CH_3)Re(CO)_2Cp^*$ (**2**). Photochemical rearrangement of **2** produced $Cp^*(CO)_2Re(\mu\text{-}\eta^2,\eta^2\text{-}CH_3O_2CC{\equiv}CCO_2CH_3)Re(CO)_2Cp^*$ (**3**), in which both $Cp^*(CO)_2Re$ units are coordinated to the alkyne. Upon heating at 72 °C, **3** was converted ($t_{1/2} \approx 120$ min) to a 78:22 equilibrium mixture of **2**:**3**. Photolysis of **3** in a Rayonet photoreactor (maximum emission 300 nm) resulted in CO loss and formation of $Cp^*(CO)Re(\mu\text{-}\eta^2,\eta^2\text{-}CH_3O_2CC{\equiv}CCO_2CH_3)(\mu\text{-}CO)Re(CO)Cp^*$ (**4**). Compounds **2**, **3**, and **4** were characterized by X-ray crystallography: **2**, orthorhombic, *Pcba*, $a = 14.480(3)$ Å, $b = 16.246(3)$ Å, $c = 26.027(3)$ Å, $Z = 8$, $D_c = 1.946$ Mg/m^3; **3**, monoclinic, *C*2/*c*, $a = 12.854(2)$ Å, $b = 14.729(3)$ Å, $c = 16.650(3)$ Å, $\beta = 108.188(12)°$, $Z = 4$, $D_c = 1.989$ Mg/m^3; **4**, trigonal, *P*3(2), $a = 16.277(2)$ Å, $b = 16.277(2)$ Å, $c = 9.408(3)$ Å, $\alpha = 90°$, $\beta = 90°$, $\gamma = 120°$, $Z = 3$, $D_c = 2.005$ Mg/m^3.

Introduction

There is a surprisingly large variety of bimetallic complexes derived from reactions with alkynes[1] including dimetallatetrahedranes (**A**) such as $Co_2(CO)_6(PhC{\equiv}CPh)$,[2] 2,4-dimetallabicyclobutanes (**B**) such as $(R_3P)Pd(\mu\text{-}PhC{\equiv}CPh)Pd(PhC{\equiv}CPh)$,[3] and 3,4-dimetallacyclobutenes (**C**) such as $Os_2(CO)_8(\mu\text{-}RC{=}CR)$.[4] In addition, rearrangement of the alkyne fragment can lead to μ-alkenylidene complexes (**D**) such as $Cp^*(CO)_2Re[\mu\text{-}C{=}CHC(CH_3){=}CH_2]Re(CO)_2Cp^*$ [5] and CO insertion can lead to dimetallacyclopentenone complexes (**E**) such as $(CO)_2Ru(\mu\text{-}CH{=}CHCO)(\mu\text{-}dppm)_2Ru(CO)_2$,[6] μ-η^1,η^3-dimetallacyclopentenone complexes (**F**) such as $Cp(CO)Ru(\mu\text{-}\eta^1,\eta^3\text{-}CPh{=}CPhCO)(\mu\text{-}CO)RuCp$,[7] and μ-η^2,η^2-dimetallacyclopentenone complexes (**G**) such as $Cp(CO)Rh(\mu\text{-}\eta^2,\eta^2\text{-}PhC{=}CPhCO)Rh(CO)Cp$.[8]



A



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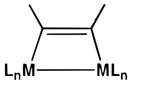

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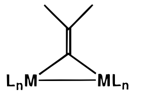

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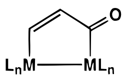

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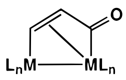

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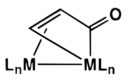

G

We recently reported the very reactive Re═Re doubled-bonded complex $Cp^*(CO)_2Re{=}Re(CO)_2Cp^*$ (**1**), which is a rare example of a dimer of 16-electron d^6 fragments.[9] **1** is extremely reactive toward nucleophiles and forms 1:1 adducts $Cp^*(CO)_2Re(\mu\text{-}CO)Re(CO)(L)Cp^*$ upon reaction with a variety of nucleophiles including L = CO, PMe_3, $CH_2{=}CH_2$, and CH_3CN.[10] We have begun to explore the reactions of **1** with alkynes and are uncovering a rich and varied chemistry. The reaction of **1** with 2-methyl-1-buten-3-yne gave $Cp^*(CO)_2Re\{\mu\text{-}\eta^1,\eta^3\text{-}CH{=}C[C(CH_3){=}CH_2]CO\}Re(CO)Cp^*$, a μ-η^1,η^3-dimetallacyclopentenone complex of type **F**.[5] Upon heating, this complex rearranged to $Cp^*(CO)_2Re[\mu\text{-}C{=}CHC(CH_3){=}CH_2]Re(CO)_2Cp^*$, a μ-alkenylidene complex of type **D**.[5] The reaction of 2-butyne with **1** at low temperature initially produced a 1:1 adduct $Cp^*(CO)_2Re(\mu\text{-}CO)Re(CO)(MeC{\equiv}CMe)Cp^*$; upon being warmed to −20 °C, this adduct rearranged to $Cp^*(CO)_2Re(\mu\text{-}\eta^1,\eta^3\text{-}CMe{=}CMeCO)Re(CO)Cp^*$, a μ-η^1,η^3-dimetallacyclopentenone complex of type **F**.[10] Upon further warming of the adduct to room temperature, fragmentation occurred to produce $Cp^*Re(CO)_3$ and $Cp^*Re(CO)(MeC{\equiv}CMe)$ which has a 4-electron donor alkyne ligand. This cleavage to monometallic complexes may occur by reversal to $Cp^*(CO)_2Re(\mu\text{-}CO)Re(CO)(MeC{\equiv}CMe)Cp^*$ followed by fragmentation (Scheme 1).

Here we report three new types of dirhenium complexes obtained from the reaction of $Cp^*(CO)_2Re{=}Re(CO)_2Cp^*$ (**1**) with the electron-deficient alkyne dimethyl acetylenedicarboxylate (DMAD). Reaction of **1** with DMAD occurs rapidly at −78 °C to give $Cp^*(CO)_2Re(\mu\text{-}\eta^1,\eta^1\text{-}CH_3O_2CC{=}CCO_2CH_3)Re(CO)_2Cp^*$ (**2**), a 3,4-dimetallacyclobutene complex of type **C**. Upon exposure to fluorescent light, **2** rearranges to $Cp^*(CO)_2Re(\mu\text{-}\eta^2,\eta^2\text{-}CH_3O_2CC{\equiv}CCO_2CH_3)Re(CO)_2Cp^*$ (**3**), a 2,4-dimetallabicyclobutane complex of type **B**. Further photolysis of **3** at shorter wavelength leads to loss of CO and formation of

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⊗ Abstract published in *Advance ACS Abstracts,* February 1, 1996.

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(4) Burke, M. R.; Takats, J. *J. Organomet. Chem.* **1986**, *302*, C25.

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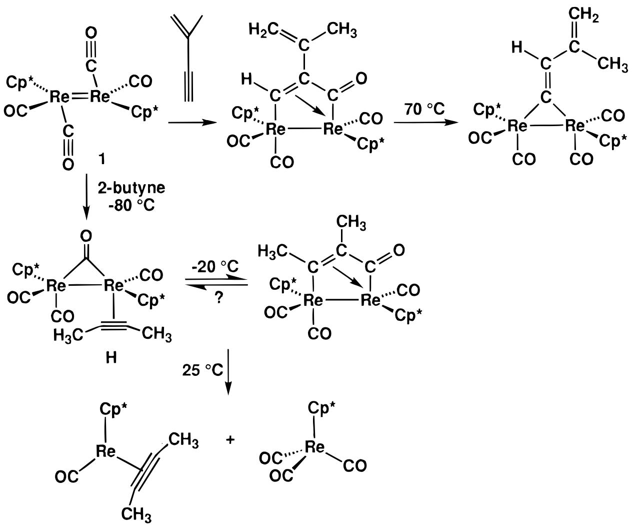
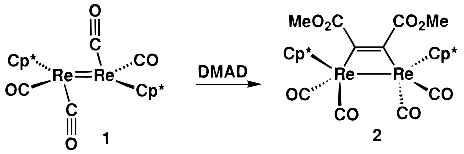
Scheme 1



$Cp^*(CO)Re(\mu\text{-}\eta^2,\eta^2\text{-}CH_3O_2CC{\equiv}CCO_2CH_3)(\mu\text{-}CO)Re(CO)Cp^*$ (**4**), a dimetallatetrahedrane structure of type **A**.

Results

$Cp^*(CO)_2Re(\mu\text{-}\eta^1,\eta^1\text{-}CH_3O_2CC{=}CCO_2CH_3)Re(CO)_2Cp^*$ (2). Reaction of a dark green solution of $Cp^*(CO)_2Re{=}Re(CO)_2Cp^*$ (**1**) with dimethyl acetylenedicarboxylate (DMAD) in THF in the dark led to the immediate formation of a red-orange solution from which the 3,4-dimetallacyclobutene, $Cp^*(CO)_2Re(\mu\text{-}\eta^1,\eta^1\text{-}CH_3O_2CC{=}CCO_2CH_3)Re(CO)_2Cp^*$ (**2**), was isolated in 62% yield as a yellow-orange powder. ^{1}H NMR spectroscopy using C_6Me_6 as an internal standard showed that the reaction occurred very cleanly in 93% yield. The ^{1}H NMR spectrum of **2** in C_6D_6 consisted of a single Cp* resonance at δ 1.83 and a single methoxy signal at δ 3.63, requiring a highly symmetric structure. Infrared spectroscopy showed only terminal CO and ester carbonyl stretches at 1970 (m), 1941 (vs), 1899 (s), 1873 (m), and 1707 (m) cm^{-1}.



X-ray crystallography established that **2** was a slightly puckered dimetallacyclobutene (Figure 1, Table 1). The C(1)−Re−(1)−Re(2)−C(2) dihedral angle is 6.1°, and the maximum deviation of a ring atom from the mean plane of the dimetallacyclobutene is 0.089 Å for C(1). The framework of **2** is similar to that of the known $Cp(CO)_2Re(\mu\text{-}CO)Re(CO)_2Cp$[11] with the DMAD unit in place of the μ-CO ligand. The Re−Re bond distance of **2** [3.0927(8) Å] is slightly longer than the Re−Re single bond of $Cp(CO)_2Re(\mu\text{-}CO)Re(CO)_2Cp$ [2.957(1) Å]. The C(1)−C(2) double bond distance of 1.27(2) Å is within the 1.27−1.34 Å range seen for dimetallacyclobutenes.[1] The combination of a long M−M bond and a short C=C bond in **2** gives rise to a relatively narrow angle at the metal (65° at Re, normally 66−72°) and to a relatively wide angle at the carbon (115° at C(1) and C(2), normally 108−112°).[12] The C(1)−C(2)−C(4) and C(2)−C(1)−C(3) angles are 125(2)° and 124(2)° consistent with sp^2 hybridization of the dimetallacyclobutene carbons. The Cp* ligands are on opposite faces of the dimetallacyclobutene (the Cp*−Re−Re−Cp* dihedral angle is 158°). A pseudoaxial CO ligand (OC−Re−Re−CO dihedral angle of 147°) and a pseudoequatorial CO ligand (OC−Re−Re−CO dihedral angle of 65°) are attached to each Re center. Each Re center has a four-legged piano stool geometry.

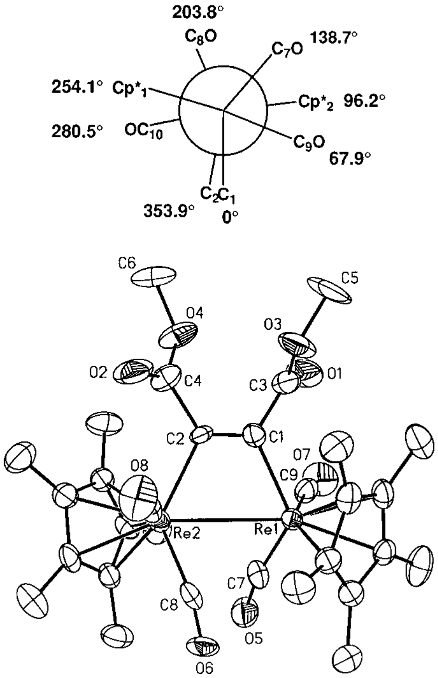
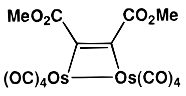


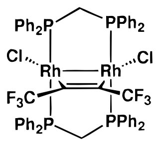
Figure 1. Newman projection and ORTEP drawing of $Cp^*(CO)_2Re(\mu\text{-}\eta^1,\eta^1\text{-}CH_3O_2CC{=}CCO_2CH_3)Re(CO)_2Cp^*$ (**2**) with atomic numbering scheme. Ellipsoids are drawn at the 35% probability level, and hydrogens are omitted for clarity.

Table 1. Selected Bond Lengths (Å) and Bond Angles (deg) for $Cp^*(CO)_2Re(\mu\text{-}\eta^1,\eta^2\text{-}CH_3O_2CC{=}CCO_2CH_3)Re(CO)_2Cp^*$ (**2**)

Re(1)−Re(2)	3.0927(8)	Re(1)−C(7)	1.86(2)
Re(1)−C(1)	2.13(2)	Re(1)−C(9)	1.90(2)
Re(2)−C(2)	2.15(2)	Re(2)−C(8)	1.91(2)
C(1)−C(2)	1.27(2)	Re(2)−C(10)	1.86(2)
Re(2)−Re(1)−C(1)	65.0(4)	Re(1)−Re(2)−C(8)	71.3(4)
Re(1)−Re(2)−C(2)	64.3(3)	Re(1)−Re(2)−C(10)	105.0(5)
Re(1)−C(1)−C(2)	115(1)	Re(2)−Re(1)−C(7)	72.5(5)
Re(2)−C(2)−C(1)	115(1)	Re(2)−Re(1)−C(9)	113.4(5)
C(1)−C(2)−C(4)	125(2)		
C(2)−C(1)−C(3)	124(2)		

X-ray crystal structures of W, Mo, Fe, Ru, Rh, Ir, Pt, Pd, and Os[14] dimetallacyclobutenes have been reported. Dimetallacyclobutenes in which the two metal atoms are also bridged by short diphosphine chains are especially common.[13]





Since we had observed both dimetallacyclopentenone[5] and alkyne complexes[12] in the reactions of other alkynes with **1**, we looked for the possible intervention of intermediate **J** or **K** in the reaction of **1** with DMAD. However, when the reaction of DMAD (18 mM) with **1** at −78 °C in toluene-d_8 was followed by ^{1}H NMR spectroscopy, complete conversion of **1** to **2** was seen in less than 3 min and no intermediates were detected ($t_{1/2} \leq 25$ s; $k_2 \geq 1.5$ M^{-1} s^{-1}; $\Delta G^\ddagger \leq 11$ kcal mol^{-1}).

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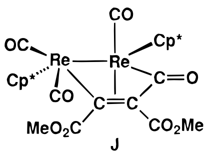
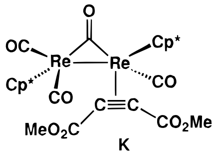
[11] Foust, A. S.; Hoyano, J. K.; Graham, W. A. G. *J. Organomet. Chem.* **1971**, *32*, C65.



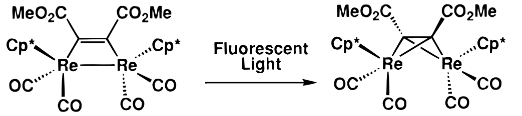
J



K

The rates of reaction of **1** with DMAD and with CO were compared in a competition experiment in which **1** (0.17 mM) was added to a toluene−THF solution of DMAD (10 mM) under 0.1 atm CO (0.6 mM)[14a−c] at −78 °C. The ratio of **2**:Cp*(CO)$_2$Re(μ-CO)Re(CO)$_2$Cp* formed was estimated to be 1:20 by IR spectroscopy.[15] The reaction of **1** with DMAD is therefore ~300 times slower than with CO. The reaction of **1** with CO (1 atm, 6 mM) gives an instantaneous color change at −78 °C; this suggests an approximate $t_{1/2} \le 0.1$ s, $k_2 \ge 1 \times 10^3$ M^{-1} s^{-1}, and an activation barrier of $\Delta G^\ddagger \le 8.5$ kcal mol^{-1}. This allows us to make a very crude estimate of the rate constant ($k_2 \ge 3$ M^{-1} s^{-1}) and activation barrier ($\Delta G^\ddagger \le 11$ kcal mol^{-1}) for the second-order reaction between **1** and DMAD.

Cp*(CO)$_2$Re(μ-η^2,η^2-CH$_3$O$_2$CC≡CCO$_2$CH$_3$)Re(CO)$_2$Cp* (3). When a red-orange solution of **2** in C$_6$D$_6$ was left in a sealed NMR tube on a desktop under fluorescent light for 2 days, the color of the solution lightened to orange. ^{1}H NMR spectroscopy showed that clean isomerization to the 2,4-dimetallabicyclo[1.1.0]butane Cp*(CO)$_2$Re(μ-η^2,η^2-CH$_3$O$_2$CC≡CCO$_2$CH$_3$)Re(CO)$_2$Cp* (**3**) had occurred in 94% NMR yield. The ^{1}H NMR spectrum of **3** in C$_6$D$_6$ showed a single Cp* resonance at δ 1.69 and a single methoxy resonance at δ 3.68, consistent with a highly symmetric structure. The IR spectrum in THF showed four terminal CO stretches at 1995 (vs), 1963 (s), 1905 (s), and 1884 (m) cm^{-1} and one ester carbonyl stretch at 1704 (m) cm^{-1}. The UV−vis spectrum of **3** showed only end absorption between 300 and 500 nm (Figure 2). The UV−vis spectrum of **2** had maxima at 326 and 440 nm consistent with the bleaching of the solution in the conversion of **2** to **3**.



2 3

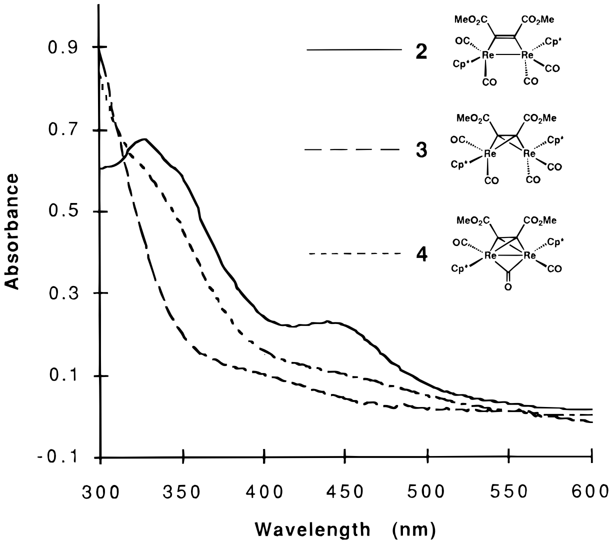


Figure 2. UV-visible spectra of 0.12 mM solutions of **2**, **3**, and **4** in C$_6$H$_6$.

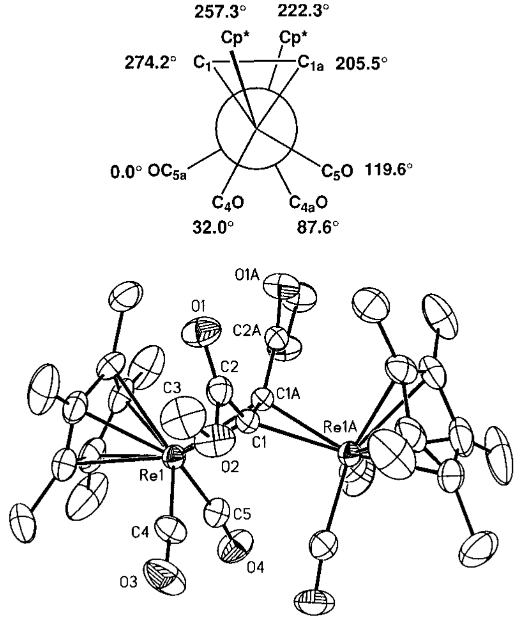


Figure 3. Newman projection and ORTEP drawings of Cp*(CO)$_2$Re(μ-η^2,η^2-CH$_3$O$_2$CC≡CCO$_2$CH$_3$)Re(CO)$_2$Cp* (**3**) with atomic numbering scheme. Ellipsoids are drawn at the 35% probability level, and hydrogens are omitted for clarity.

Table 2. Selected Bond Lengths (Å) and Bond Angles (deg) for Cp*(CO)$_2$Re(μ^2-η^2,η^2-CH$_3$O$_2$CC≡CCO$_2$CH$_3$)Re(CO)$_2$Cp* (**3**)

Re(1)−C(1)	2.255(7)	Re(1)−C(4)	1.895(8)
Re(1)−C(1A)	2.213(7)	Re(1)−C(5)	1.896(8)
C(1)−C(1A)	1.36(1)	Re(1)····Re(2)	3.766
Re(1)−C(1)−C(1A)	70.6(5)	Re(1)−C(1)−Re(1A)	115.1(3)
Re(1)−C(1A)−C(1)	74.0(5)	C(1)−C(1A)−C(2A)	136.9(4)
C(1)−Re(1)−C(1A)	35.3(3)	Re(1)−alkyne centroid−Re(1A)	126

The structure of **3** was shown to be a 2,4-dimetallabicyclo[1.1.0]butane by X-ray crystallography (Figure 3, Table 2). This structural type can also be viewed as an alkyne with metals complexed to two different π-bonds. The Re−Re distance (3.766 Å) is much longer than a Re−Re single bond (typically 2.8−3.0 Å).[14,16] The molecule sits on a crystallographic 2-fold axis with the Cp* rings syn to the methyl ester units. This places the carbonyl groups on the two rhenium centers in close

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[14] (a) Field, L. R.; Wilhelm, E.; Battino, R. *J. Chem. Thermodyn.* **1974**, *6*, 237. Mole fraction solubility data of CO in toluene at 283−313 K was extrapolated to 195 K assuming a linear relationship of ln[CO] and 1/*T*. (b) Nudelman, N. S.; Doctorovich, F. *J. Chem. Soc., Perkin Trans. 2* **1994**, 1233. Solubility of CO in THF at room temperature was calculated to be 0.011 M at 25 °C under 1 atm CO. (c) Krauss, W.; Gestrich, W. *Chem.-Tech. (Heidelberg)* **1977**, *6*, 513. The temperature dependence of the solubility of CO in THF was assumed to similar to that of 1,4-dioxane. We estimated [CO] to be 0.6 ± 0.3 mM in 1:1 toluene:THF at 195 K under 0.1 atm CO.

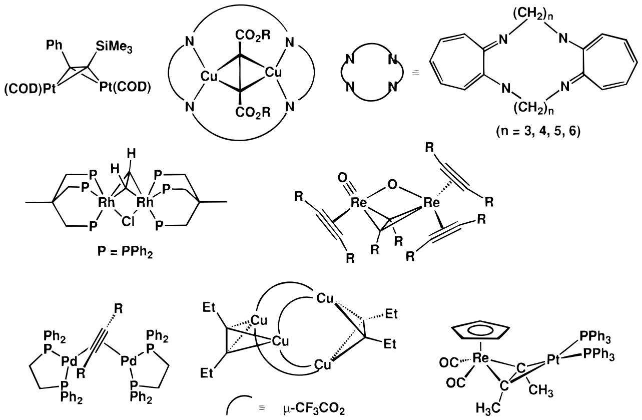
[15] Assumes similar extinction coefficients for carbonyl stretches.

[16] 3.014 Å for Re$_2$(CO)$_{10}$: Churchill, M. R.; Amoh, K. N.; Wasserman, H. J. *Inorg. Chem.* **1981**, *20*, 1609.

proximity to one another; the shortest distance between oxygens on carbonyl groups (3.0 Å) is near van der Walls contact of 2.8 Å. Apparently the molecule has made two adjustments to minimize this interaction between CO's. First, the Re(1)−(alkyne centroid)−Re(1A) angle is 126°, which is toward the high end of the range for 2,4-dimetallabicyclo[1.1.0]butanes [from 96.9° for diplatinum systems like (COD)Pt(μ-η^2,η^2-PhC≡CTMS)Pt(COD)[17] to 136° for a tropocoronand dicopper alkyne complex[18]]. Second, a view down the Re−Re vector shows that the Cp*Re(CO)$_2$ units have been twisted in opposite directions to avoid eclipsing CO's; the C(1)−Re(1)−Re(1A)−C(2A) dihedral angle is 32° (Figure 3).

The photorearrangement of **2** to **3** took place cleanly in the presence of either diethyl acetylenedicarboxylate or CO, consistent with an intramolecular mechanism. When the photolysis of **2** in THF-d_8 at −72 °C was followed by ^{1}H NMR spectroscopy, no intermediates were detected in the conversion of **2** to **3**.

Some examples of 2,4-dimetallabicyclo[1.1.0]butanes with additional bridging atoms[19] and without additional bridging atoms[19,20] which have been characterized by X-ray crystallography are shown below. Several examples of spectroscopically characterized μ-η^2,η^2-bound alkyne complexes are also shown.[20] Our research group has prepared the heterobimetallic 2,4-dimetallabicyclo[1.1.0]butane CpRe(CO)$_2$(μ-η^2,η^2-CH$_3$-C≡C-CH$_3$)Pt(PPh$_3$)$_2$.[21]



Cp*(CO)Re(μ-η^2,η^2-CH$_3$O$_2$CC≡CCO$_2$CH$_3$)(μ-CO)Re(CO)-Cp* (4). When a dilute benzene solution of the 2,4-dimetallabicyclo[1.1.0]butane **3** was photolyzed in a sealed NMR tube for 2 h in a Rayonet photoreactor (maximum emission 300 nm), photoextrusion of CO occurred and the dimetallatetrahedrane Cp*(CO)Re(μ-η^2,η^2-CH$_3$O$_2$CC≡CCO$_2$-CH$_3$)(μ-CO)Re(CO)Cp* (**4**) was formed in >83% NMR yield as determined using C$_6$Me$_6$ as an internal standard. **4** was isolated as a dark orange solid in 65% yield from a larger scale photolysis.

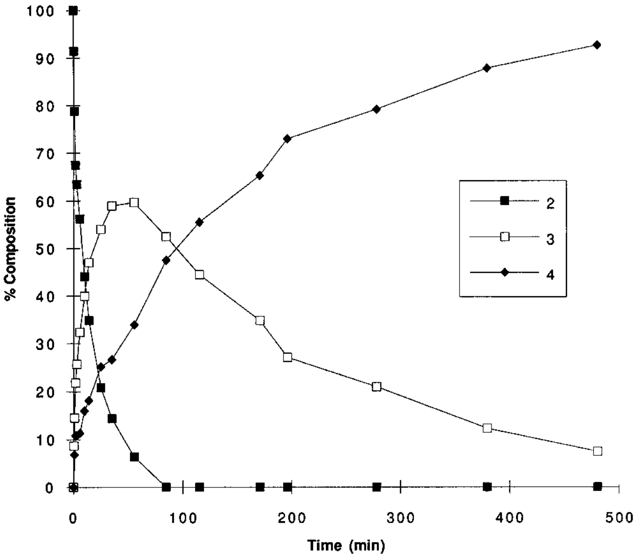
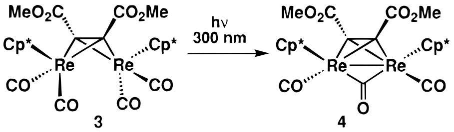


Figure 4. Relative amounts of **2**, **3**, and **4** as a function of time during photolysis of **2** (62 mM solution in C$_6$D$_6$).



Photolysis of 3,4-dimetallacyclobutene **2** in a Rayonet photoreactor (maximum emission 300 nm) also led to the formation of dimetallatetrahedrane **4** via the intermediate formation of **3**. The course of the photolysis was followed by ^{1}H NMR spectroscopy using C$_6$Me$_6$ as an internal standard for integrations. (Figure 4). The maximum concentration of **3** was 60% of total material (at 65 min). This is consistent with a reaction sequence **2** → **3** → **4**, in which conversion of **2** to **3** is ~3.3 times faster than the conversion of **3** to **4**.[22] After 85 min, complete conversion of starting material **2** had occurred. After 8 h, complete conversion to **4** had occurred in 94% yield.

The ^{1}H NMR spectrum of **4** consists of one Cp* signal (δ 1.87) and one methoxy signal (δ 3.58) and demands a highly symmetric structure. IR spectroscopy shows two terminal carbonyl stretches at 1963 and 1927 cm^{-1} and a bridging carbonyl stretch at 1703 cm^{-1}; the ester carbonyl stretch is presumably obscured by the bridging carbonyl stretch. The UV−vis spectrum of **4** in C$_6$H$_6$ shows only end absorption between 300 and 600 nm (Figure 2).

The structure of **4** (Figure 5, Table 3) was shown to be a dimetallatetrahedrane complex by X-ray crystallography. **4** has approximate C_2 symmetry. The Cp* centroids, the terminal CO's, and the rhenium atoms are approximately coplanar with the Cp* ligands trans to one another. The C−C and Re−Re bonds in the dimetallatetrahedrane are approximately orthogonal to one another. The Re(1)−(alkyne centroid)−Re(2) angle is 88°. The C(1)−C(2) distance [1.34(2) Å] is similar to that observed in other dimetallatetrahedranes (1.27−1.36 Å).[1] The Re(1)−Re(2) distance of 2.810(1) Å is similar to other rhenium−rhenium single-bonded complexes with a bridging carbonyl.[13] Dimetallatetrahedrane structures are quite common;[1]

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(17) Boag, N. M.; Green, M.; Howard, J. A. K.; Stone, F. G. A.; Wadepohl, H. *J. Chem. Soc., Dalton Trans.* **1981**, 862. Boag, N. M.; Green, M.; Howard, J. A. K.; Spencer, J. L.; Stansfield, R. F. D.; Stone, F. G. A.; Thomas, M. D. O.; Vicente, J.; Woodward, P. *J. Chem. Soc., Chem. Commun.* **1977**, 930. Boag, N. M.; Green, M.; Howard, J. A. K.; Spencer, J. L.; Stansfield, R. F. D.; Thomas, M. D. O.; Stone, F. G. A.; Woodward, P. *J. Chem. Soc., Dalton Trans.* **1980**, 2182.

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(20) Krause, J.; Bonrath, W.; Pörschke, K. R. *Organometallics* **1992**, *11*, 1158. Reger, D. L.; Huff, M. F. *Organometallics* **1992**, *11*, 69.

(21) Casey, C. P.; Wang, Y.; Tanke, R. S.; Hazin, P. N.; Rutter, E. W., Jr. *New. J. Chem.* **1994**, *18*, 43.

(22) Frost, A. A.; Pearson, R. G. *Kinetics and Mechanism*; Wiley & Sons, Inc.: New York, 1961; p 168.

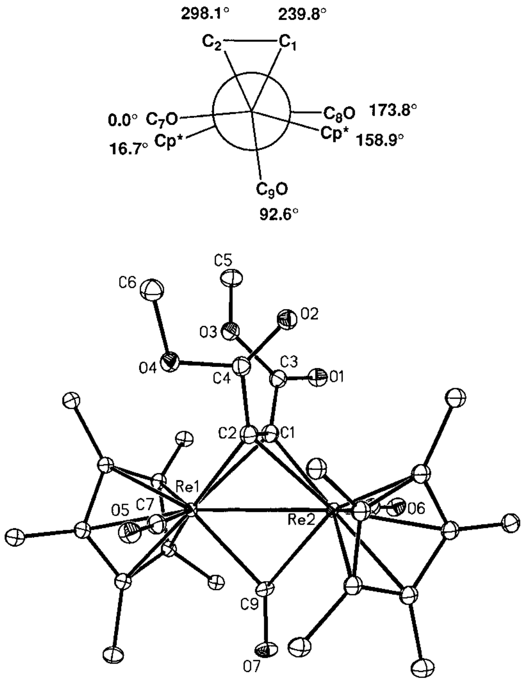

Figure 5. Newman projection and ORTEP drawing of Cp*(CO)Re(μ^2-η^2,η^2-$CH_3O_2CC{\equiv}CCO_2CH_3$)($\mu$-CO)Re(CO)Cp* (**4**) with atomic numbering scheme. Ellipsoids are drawn at the 35% probability level, and hydrogens are omitted for clarity.

Table 3. Selected Bond Lengths (Å) and Bond Angles (deg) for Cp*(CO)Re(μ-η^2,η^2-$CH_3O_2CC{\equiv}CCO_2CH_3$)($\mu$-CO)Re(CO)Cp* (**4**)

Re(1)−Re(2)	2.810(1)	Re(1)−C(7)	1.93(2)
Re(1)−C(1)	2.14(2)	Re(2)−C(8)	1.91(2)
Re(1)−C(2)	2.10(2)	Re(1)−C(9)	2.10(2)
Re(2)−C(1)	2.15(2)	Re(2)−C(9)	2.08(2)
Re(2)−C(2)	2.15(2)		
C(1)−C(2)	1.34(2)		
Re(1)−C(1)−C(2)	70(1)	C(1)−C(2)−C(4)	125(2)
Re(1)−C(2)−C(1)	73(2)	C(2)−C(1)−C(3)	131(2)
Re(2)−C(1)−C(2)	72(1)	Re(1)−C(9)−Re(2)	84.5(7)
Re(2)−C(2)−C(1)	72(1)	Re(1)−Re(2)−C(9)	48.0(5)
C(1)−Re(1)−C(2)	36.8(6)	Re(2)−Re(1)−C(9)	47.6(5)
C(1)−Re(2)−C(2)	36.3(6)	Re(1)−Re(2)−C(8)	100.5(6)
Re(1)−alkyne centroid−Re(2)	88	Re(2)−Re(1)−C(7)	90.2(6)

two classic examples are (CO)$_3$Co(μ-η^2,η^2-PhC≡CPh)Co(CO)$_3$[2] and CpNi(μ-η^2,η^2-PhC≡CPh)NiCp.[23]

Thermal Equilibration of 2 and 3. Interconversion of **2** and **3** occurred upon heating at 72 °C in the dark and was accompanied by significant decomposition of the mixture. An approximate equilibrium ratio of 78 ± 3:22 ± 3 **2**:**3** was approached starting from either **2** or **3**. The time for half-equilibration was 30−60 min.

A 0.01 M solution of **3** in C_6D_6 containing C_6Me_6 as an internal NMR standard was heated at 72 °C in a constant temperature bath, and the amounts of **2** (δ 1.83) and **3** (δ 1.69) were monitored by ^{1}H NMR spectroscopy. After 30 min, the amount of **3** in excess over equilibrium had dropped to about half (20% **2**, 70% **3**, 10% decomposition); the ratio of **2**:**3** was 22:78. After 5 h, the amount of **2** had risen to 59% of the initial material, 23% **3** remained, and about 18% decomposition had occurred; the ratio of **2**:**3** was 72:28 (Figure 6).

Similarly, when a 0.01 M solution of **2** was heated at 72 °C for 6 h, the concentration of **3** rose to 10% and the amount of **2** dropped to 46%, and 44% decomposition occurred; the ratio of **2**:**3** was 82:18. After 60 min, the amount of **3** in excess over equilibrium had dropped to about half (77% **2**, 11% **3**, 12% decomposition); the ratio of **2**:**3** was 87:13 (Figure 6).

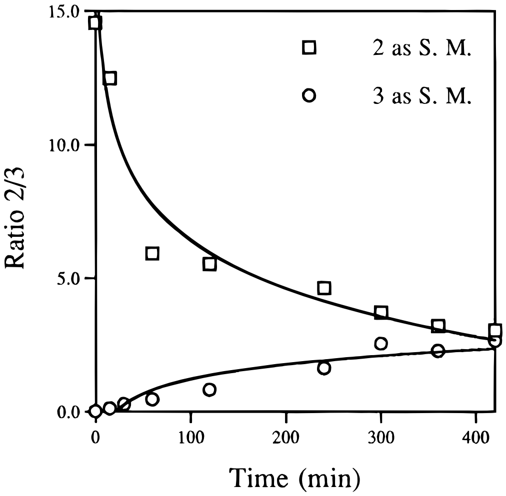

Figure 6. Thermal equilibration of **2**:**3** at 72 °C starting from a 0.01 mM solution of either **2** or **3** in C_6D_6 containing C_6Me_6 as an internal standard.

No reaction between either CO, H_2, or diethyl acetylenedicarboxylate and the equilibrating mixture of **2** and **3** was observed at 80 °C.

Discussion

The 2 + 2 suprafacial cycloaddition of two ethylenes to form cyclobutane is a symmetry forbidden reaction according to Woodward−Hoffmann rules.[24] For the microscopic reverse of this reaction, the observation that ring opening of *cis*-1,2-dideuterocyclobutane to give deuterated ethylenes is a non-stereospecific process provided evidence for the intervention of a 1,4-tetramethylene diradical intermediate.[25] While simple molecular orbital arguments also suggest that M=M + C=C cycloadditions are also symmetry forbidden, participation of metal d orbitals in the reaction might lead to allowed reactions.

In fact, there are numerous reactions that involve the net cycloaddition of a C=C[26] or C≡C[27] bond to a M=M bond. Norton's recent elegant studies showing that the exchange of *trans*-1,2-dideuterioethylene with (CO)$_4$Os(μ-*trans*-CHDCHD)-Os(CO)$_4$ proceeded with retention of stereochemistry ruled out a 1,4 diradical intermediate for cycloreversion of this dimetallacyclobutane.[28] On the basis of recent kinetic studies,[29] Norton has proposed a mechanism for exchange of alkenes with diosmacyclobutanes that avoids a (CO)$_4$Os=Os(CO)$_4$ intermediate by involving an initial equilibrium with an intermediate in which the alkene slips to one metal as CO bridges the metal centers (Scheme 2). The slipped alkene intermediate was directly observed in the reaction of photochemically generated

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[23] Mills, O. S.; Shaw, B. W. *J. Organomet. Chem.* **1968**, *11*, 595.

[24] Trinquier, G.; Hoffmann, R. *Organometallics* **1984**, *3*, 370. Woodward, R. B.; Hoffmann, R. *The Conservation of Orbital Symmetry*; Verlag Chemie: Weinheim/Bergstr., 1970.

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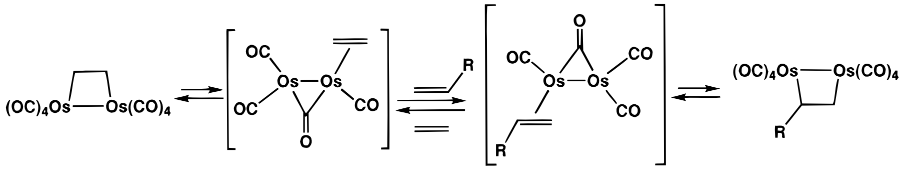
[29] (a) Norton, J. R. *Abstracts of Papers*; 209th National Meeting of the American Chemical Society, Anaheim, CA, April 1995; American Chemical Society: Washington, DC, 1995; INOR 301. (b) Ramage, D. L.; Wiser, D. C.; Norton, J. R. *J. Am. Chem. Soc.*, submitted for publication. (c) Bender, B. R.; Ramage, D. L.; Norton, J. R.; Wiser, D. C.; Rappé, A. K. *J. Am. Chem. Soc.*, submitted for publication.

Scheme 2[a]



[a] For clarity, only in-plane CO's are shown for slipped alkene intermediates.

$(CO)_4Os{=}Os(CO)_4$ with ethylene at low temperature in both solution[28] and inert-gas matrices[30] and its rearrangement to the dimetallacyclobutane has been observed in solution.[28]

We have found that many nucleophiles including CO, PMe_3, $CH_2{=}CH_2$, and CH_3CN[10] all add rapidly to one Re center of $Cp^*(CO)_2Re{=}Re(CO)_2Cp^*$ (**1**) to give adducts with a bridging CO. Recently, we found that 2-butyne also reacts with (**1**) at low temperature to give a complex in which the alkyne has coordinated to one rhenium of a bridging carbonyl complex (Scheme 1).[10] While this complex does not lead to the formation of a dimetallacyclobutene, it suggests a reactivity pattern for reactions of **1** with alkynes.

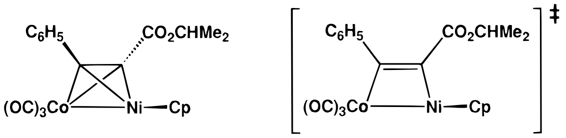
The reaction of DMAD with **1** proceeded very rapidly at −78 °C to give the dimetallacyclobutene **2**. Our very approximate estimates of the rate constant and activation barrier for the second-order reaction between **1** and DMAD are $k_2 \geq 3$ M^{-1} s^{-1} and $\Delta G^\ddagger \leq 11$ kcal mol^{-1}. Our attempts to detect a possible DMAD adduct **J** at low temperature were unsuccessful; only direct formation of **2** was seen. Nevertheless, on the basis of the analogy with the reaction of **1** with 2-butyne, we suggest that an unseen intermediate alkyne complex may precede formation of dimetallacyclobutene **2**. The intervention of such an intermediate in this net cycloaddition of an alkyne to a M=M bond would circumvent problems with a symmetry forbidden direct cycloaddition pathway.

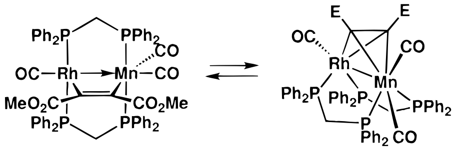
The observation that **2** has a bridging DMAD ligand and terminal CO's whereas the 2-butyne adduct **H** has a bridging CO ligand and a terminal alkyne ligand requires comment. In both complexes the better electron acceptor ligand is placed in the bridging site to more effectively remove electron density from the electron-rich rhenium centers. There are numerous examples of dimetallacyclobutenes with electron-withdrawing CF_3 or CO_2R substituents.[1]

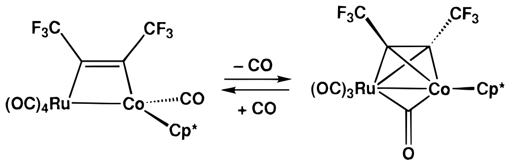
Under fluorescent lighting, the dimetallacyclobutene complex **2** rearranged to bicyclobutane complex **3**. This is the first case in which both isomers have been observed. The thermal interconversion of **2** and **3** is remarkable since Hoffmann has suggested that such processes should have high activation barriers.[1] Apparently, our system has a combination of steric and electronic factors which allow us not only to interconvert the dimetallacyclobutene and bicyclobutane isomers but also to isolate and completely characterize them.

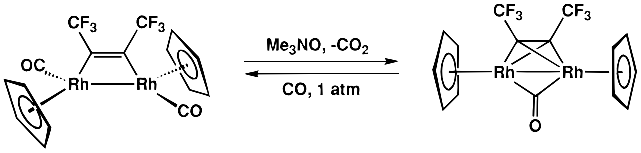
The interconversion of a dimetallatetrahedrane complex via a dimetallacyclobutene transition state has been suggested by McGlinchey[31] to explain the coalescence of the diastereotopic methyl groups of the chiral complex $CpNi(\mu\text{-}PhC{\equiv}CO_2CHMe_2)Co(CO)_3$. The equilibration of a Rh−Mn heterodimetallacyclobutene with an isomeric dimetallatetrahedrane has been reported by Cowie.[32]

The overall photochemical conversion of dimetallacyclobutene **2** to dimetallatetrahedrane **4** involving loss of CO and proceeding via the intermediate dimetallabicyclobutane complex **3** is similar to processes observed previously. For example, the dimetallacyclobutene complex $(CO)_4Ru(\mu\text{-}CF_3C{=}CCF_3)Co(CO)C_5Me_5$[33] lost CO under a nitrogen purge to give a dimetallatetrahedrane complex which was converted back to the starting dimetallacyclobutene under 1 atm CO. Similarly, the dimetallacyclobutene $Cp(CO)Rh(\mu\text{-}CF_3C{=}CCF_3)Rh(CO)Cp$ was converted to a dimetallatetrahedrane on treatment with Me_3NO and treatment with CO regenerated the dimetallacyclobutene.[34] When we placed the dimetallatetrahedrane complex **4** under 1 atm of CO, we failed to see regeneration of either dimetallacyclobutene **2** or dimetallabicyclobutane **3**.









Experimental Section

General Methods. ^1H NMR spectra were obtained on a Bruker WP200, AC300, or AM500 spectrometer. $^{13}C\{^1H\}$ spectra were obtained on a Bruker AM500 spectrometer (126 MHz). Infrared spectra were measured on a Mattson Polaris (FT) or a Mattson Genesis (FT) spectrometer. UV−vis spectra were taken on an HP 8452A diode array spectrophotometer. High-resolution mass spectroscopy were performed on a Kratos MS-80.

Toluene-d_8, THF-d_8, THF, C_6D_6, ether, and pentane were distilled from purple solutions of sodium benzophenone ketyl immediately prior to use. CH_2Cl_2 was distilled from CaH_2. CD_2Cl_2 was 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.

$Cp^*(CO)_2Re(\mu\text{-}\eta^1,\eta^1\text{-}MeO_2CC{=}CCO_2Me)Re(CO)_2Cp^*$ (2). Because **2** rearranges under fluorescent light, all operations were performed in the dark. Addition of dimethyl acetylenedicarboxylate (DMAD, 16.6 μL, 135 μmol) to a dark green THF solution (6 mL) of $Cp^*(CO)_2Re{=}Re(CO)_2Cp^*$ (**1**) (102 mg, 135 μmol) in a glovebox produced a red-orange solution. The solution was transferred to a flask attached to a reversible frit apparatus, and solvent was evaporated on a vacuum

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[30] Haynes, A.; Poliakoff, M.; Turner, J. J.; Bender, B. R.; Norton, J. R. *J. Organomet. Chem.* **1990**, *383*, 497.

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line to give a brown residue. Pentane (20 mL) was condensed into the flask, and the resulting yellow-orange solution was filtered through the reversible frit to remove a small amount of brown solid. The solid was washed with petane distilled from the lower flask until the washings were clear. The filtrate was evaporated to give **2** (75 mg, 62%) as a yellow-orange powder which was >95% pure by ^{1}H NMR. Analytically pure **2** was obtained by recrystallization from THF. Crystals suitable for X-ray diffraction were grown by slow diffusion of hexane (3 mL) into a concentrated solution of **2** in THF (85 mg in 1 mL). ^{1}H NMR (200 MHz, C_6D_6): δ 3.63 (s, OCH_3), 1.83 (s, Cp*). $^{13}C\{^1H\}$ NMR (126 MHz, THF, −50 °C): δ 215.0, 209.7 (CO); 169.8 (CO_2); 101.3 ($\mathit{C}CO_2$); 101.1 (C_5Me_5); 50.9 (OCH_3), 10.2 ($Cp^*\mathit{C}H_3$). IR (THF): 1970 (m), 1941 (vs), 1899 (s), 1873 (m), 1707 (m) cm^{-1}. UV−vis: λ_{max} 326 nm ($\epsilon = 5700\ M^{-1}\ cm^{-1}$), 440 nm ($\epsilon = 1900\ M^{-1}\ cm^{-1}$). HRMS calcd (found) for $C_{30}H_{36}O_8Re_2$: *m/z* 898.153 (898.150). Anal. Calcd for $C_{30}H_{36}O_8Re_2$: C, 40.17; H, 4.05. Found: C, 39.80; H, 3.98.

$Cp^*(CO)_2Re(\mu\text{-}\eta^2,\eta^2\text{-}MeO_2CC{\equiv}CCO_2Me)Re(CO)_2Cp^*$ (3). When 1.5 mL of a toluene solution of **2** prepared from DMAD (7.4 μL, 60.0 μmol) and **1** (45 mg, 59.6 μmol) was exposed to fluorescent lighting for 2 days, the solution turned from red-orange to light orange. Toluene was evaporated, and the resulting light orange solid was dissolved in 1 mL of THF. Slow evaporation of THF gave orange crystalline **3** (35 mg, 65%). Crystals suitable for X-ray diffraction were obtained by slow evaporation of a concentrated solution of **3** in THF (25 mg in 500 μL). ^{1}H NMR (200 MHz, C_6D_6): δ 3.68 (s, OCH_3), 1.69 (s, Cp*). $^{13}C\{^1H\}$ NMR [126 MHz, C_6D_6, 0.07 M $Cr(acac)_3$]: δ 207.9 (CO), 166.0 (CO_2), 99.7 (C_5Me_5), 51.2 (OCH_3), 9.6 ($Cp^*\mathit{C}H_3$), alkyne carbons not observed. IR (THF): 1995 (vs), 1963 (s), 1905 (s), 1884 (m), 1704 (m) cm^{-1}. UV−vis: end absorption only 326 nm ($\epsilon = 3500\ M^{-1}\ cm^{-1}$), 440 nm ($\epsilon = 400\ M^{-1}\ cm^{-1}$). HRMS calcd (found) for $C_{30}H_{36}O_8Re_2$: *m/z* 898.153 (898.150). Anal. Calcd for $C_{30}H_{36}O_8Re_2$: C, 40.17; H, 4.05. Found: C, 39.65; H, 3.54.

$Cp^*(CO)Re(\mu\text{-}\eta^2,\eta^2\text{-}CH_3O_2CC{\equiv}CCO_2CH_3)(\mu\text{-}CO)Re(CO)Cp^*$ (4). An orange solution of **3** (16 mg, 17.8 μmol) in C_6H_6 (6 mL) was photolyzed under a nitrogen atmosphere in a Rayonet photoreactor equipped with RPR 3000A bulbs with maximum emission at 300 nm. The reaction was followed by infrared spectroscopy (disappearance of the 1994 cm^{-1} band of **3** and appearance of the 1963 cm^{-1} band of **4**). After 8 h, solvent was evaporated to give **4** (10 mg, 65%) as a red-orange solid. Crystals suitable for X-ray diffraction were obtained by slow evaporation of a saturated THF solution of **4** (27 mg in 360 μL). ^{1}H NMR (200 MHz, C_6D_6): δ 3.57 (s, OCH_3), 1.87 (s, Cp*). $^{13}C\{^1H\}$ NMR (126 MHz, C_6D_6): δ 212.0 (CO), 168.8 (CO_2), 99.5 (C_5Me_5), 52.0 (OMe), 9.3 ($Cp^*\mathit{C}H_3$), μ-CO and alkyne carbons not observed. IR (THF): 1963 (m), 1927 (vs), 1703 (s) cm^{-1}. UV−vis: end absorption only 326 nm ($\epsilon = 5100\ M^{-1}\ cm^{-1}$), 440 nm ($\epsilon = 440\ M^{-1}\ cm^{-1}$). HRMS calcd (found) for $C_{29}H_{36}O_7Re_2$: *m/z* 870.158 (870.155).

X-ray Crystallographic Determination and Refinement. Intensity data were obtained with graphite monochromated Mo Kα radiation on Siemens P4 diffractometers at room temperature (**2** and **3**) or at −160 °C (**4**). Crystallographic computations were carried out with SHELXTL PLUS[35] and SHELXL-93.[36] Empirical ψ-scan absorption corrections were applied.[36] Initial positions of Re atoms were obtained by automatic Patterson interpretation. Other non-hydrogen atoms were obtained from successive Fourier difference maps coupled with isotropic least-squares refinement. All non-hydrogen atoms were refined anisotropically. Idealized positions were used for hydrogen atoms. Tables of data collection parameters, least-squares refinement parameters, positional and thermal parameters, interatomic distances, bond angles, and idealized hydrogen atom positional parameters are available as supporting information. Selected bond lengths and angles are listed in Tables 1−3.

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Supporting Information Available: 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 for compounds **2**, **3**, and **4** (19 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, can be ordered from the ACS, and can be downloaded from the Internet; see any current masthead page for ordering information and Internet access instructions.

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[35] Siemens Analytical X-Ray Instruments.

[36] Sheldrick, G. R. Manuscript in preparation.