Dimetalated Olefins Formed by the Insertion of an Alkyne into an Re—Re Bond. The Reaction of $EtO_2CC{\equiv}CCO_2Et$ with $Re_2(CO)_9(NCMe)$

Richard D. Adams* and Linfeng Chen

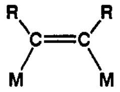
Department of Chemistry and Biochemistry, University of South Carolina,
Columbia, South Carolina 29208

Received December 14, 1993[⊗]

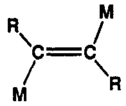
The complex $Re(CO)_4[\mu\text{-}(Z)\text{-}(EtO_2C)C{=}C(CO_2Et)]Re(CO)_5$, **2**, obtained from the reaction of $Re_2(CO)_9(NCMe)$, **1**, with $EtO_2CC{\equiv}CCO_2Et$ was analyzed by single crystal X-ray diffraction analysis and was found to be a *Z*-dimetalated olefin complex formed by the insertion of the alkyne into the rhenium—rhenium bond. One of the carboxylate groups is coordinated to one of the rhenium atoms through the ketonic oxygen atom to form a four membered metallacyclic ring. The absence of crossover in a reaction of a mixture of fully ^{13}CO labeled **1** and unlabeled **1** indicates that the insertion of the alkyne into the metal—metal bond occurs by an intramolecular mechanism. When irradiated (UV–vis), compound **2** was isomerized to the complex $Re(CO)_4[\mu\text{-}(E)\text{-}(EtO_2C)C{=}C(CO_2Et)]Re(CO)_5$, **3**, and the ketonic oxygen atom of the carboxylate group became coordinated to the other rhenium atom to form a five membered metallacyclic ring. Decarbonylation of **3** by irradiation yielded the new complex $Re(CO)_4[\mu\text{-}(E)\text{-}(EtO_2C)C{=}C(CO_2Et)]Re(CO)_4$, **4**, by coordination of the oxygen atom of the second carboxylate group. Compound **2** was found to add CO at 700 psi/25 °C by opening the Re—O bond of the metallacycle to form the simple *Z*-dimetalated olefin complex $Re(CO)_5[\mu\text{-}(Z)\text{-}(EtO_2CC{=}C(CO_2Et)]Re(CO)_5$, **5**, in 93% yield. Compound **2** reacts with a mixture of HCl/CO (gas) by cleaving off one of the rhenium groupings as $Re(CO)_5Cl$ and forming the new complex $[(E)\text{-}(EtO_2C)HC{=}C(CO_2Et)]Re(CO)_5$, **6**, in 97% yield. Crystal data: (for **2**) space group = $P2_1/c$, a = 10.292(2) Å, b = 11.731(2) Å, c = 18.704(4) Å, β = 100.14(2)°, Z = 4, 2133 reflections, R = 0.025; (for **3**) space group = $Fdd2$, a = 24.498(3) Å, b = 35.102(5) Å, c = 10.681(1) Å, Z = 16, 1843 reflections, R = 0.027; (for **4**) space group = $P\bar{1}$, a = 7.838(3) Å, b = 9.830(3) Å, c = 7.047(2) Å, α = 106.93(2)°, β = 94.84(3)°, γ = 84.28(3), Z = 2, 1927 reflections, R = 0.037; (for **5**) space group = $Pbca$, a = 14.275(2) Å, b = 33.00(1) Å, c = 10.114(2) Å, Z = 8, 2124 reflections, R = 0.036; (for **6**) space group = $P2_1/c$, a = 9.637(1) Å, b = 8.340(1) Å, c = 20.821(2) Å, β = 102.10(1)°, Z = 4, 1686 reflections, R = 0.021.

Introduction

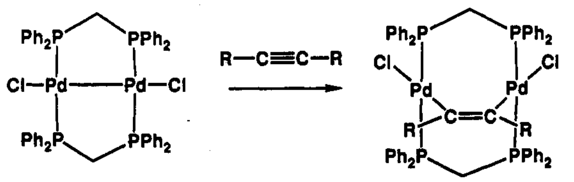
There have been reports of dimetalated olefins in both of the anticipated structural geometries: the *cis* or *Z* type **A**,[1] and *trans* or *E* type **B**.[2] *Z*-dimetalated olefins are generally prepared by the addition of alkynes to dinuclear metal complexes by insertion into a metal–metal bond. Most examples of these reactions involve dinuclear metal complexes doubly bridged by phosphine chelates with metals in d^8 configurations, e.g. eq 1. Most *E*-dimetalated olefins have been prepared through reactions of mononuclear metal complexes with alkynes. Thus, the *E* geometry at the olefin is readily established by the approach of the metals from opposite sides of the alkyne. Theoretical treatments have indicated that the $Z \rightleftarrows E$ transformation in dimetalated olefins should have a high energy barrier, thus the formation of *E*-dimetalated olefins from the *Z*-isomers should be difficult.[3]



A



B



(1)

Interestingly, we have recently observed that the reaction of $HC{\equiv}CCO_2Me$ with $Re_2(CO)_9(NCMe)$, **1**, leads to displacement of the NCMe ligand and insertion of the alkyne into the unsupported metal—metal bond to yield the dimetalated olefin complex $Re(CO)_4[\mu\text{-}(E)\text{-}HC{=}C(CO_2Me)]Re(CO)_5$ having the *E* stereochemistry, eq 2.[4] The structure of the complex $Re(CO)_4[\mu\text{-}(E)\text{-}HC{=}C(CO_2Me)]Re(CO)_5$ was established crystallographically, and

---

[⊗] Abstract published in *Advance ACS Abstracts*, March 1, 1994.

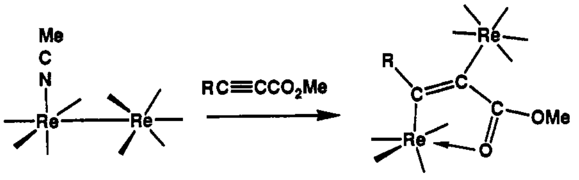
(1) (a) Mague, J. T. *Polyhedron* **1992,** *11,* 677. (b) Cowie, M.; Vasapollo, G.; Sutherland, B. R.; Ennett, J. P. *Inorg. Chem.* **1986,** *25,* 2648. (c) Mague, J. T. *Inorg. Chem.* **1983,** *22,* 45. (d) Lee, C.-L.; Hunt, C. T.; Balch, A. L. *Inorg. Chem.* **1981,** *20,* 2498. (e) Shaw, B. L.; Higgins, S. J. *J. Chem. Soc., Dalton Trans.* **1988,** 457. (f) Higgins, S. J.; Shaw, B. L. *J. Chem. Soc., Chem. Comm.* **1986,** 1629. (g) Balch, A. L.; Lee, C. L.; Lindsay, C. H.; Olmstead, M. M. *J. Organomet. Chem.* **1979,** *177,* C22. (h) Johnson, K. A.; Gladfelter, W. L. *Organometallics* **1992,** *11,* 2534.

(2) (a) Griffith, W. P.; Wilkinson, G. *J. Chem. Soc.* **1959,** 1629. (b) Breimair, J.; Steimann, Wagner, B.; Beck, W. *Chem. Ber.* **1990,** *123,* 7. (c) Lemke, F. R.; Szalda, D. J.; Bullock, R. M. *J. Am. Chem. Soc.* **1991,** *113,* 8466. (d) Grande, K.; Kunin, A. J.; Stuhl, L. S.; Foxman, B. M. *Inorg. Chem.* **1983,** *22,* 1791. (e) Kimball, M. E.; Martella, J. P.; Kaska, W. C. *Inorg. Chem.* **1967,** *6,* 414. (f) Kimball, M. E.; Martella, J. P.; Kaska, W. C. *Inorg. Chem.* **1967,** *6,* 414.

(3) Hoffman, D. M.; Hoffmann, R. *Organometallics* **1982,** *1,* 1299.

(4) Adams, R. D.; Chen, L.; Wu, W. *Organometallics* **1993,** *12,* 1257.

0276-7333/94/2313-1264$04.50/0



(2)

evidence strongly indicated that the product was formed by an *intramolecular* reaction.

We have now completed an X-ray crystallographic analysis of the product $Re(CO)_4[\mu$-(*Z*)-$(EtO_2C)C{=}C(CO_2Et)]Re(CO)_5$, **2**, obtained from the reaction of **1** with $EtO_2CC{\equiv}CCO_2Et$. The structure of **2** provides new information about the nature of the insertion of the alkynes into the metal—metal bond of **1**. We have also studied the thermal and photo transformations of **2** and its reaction with CO. The results of this study are reported here.

Experimental Section

Unless specified otherwise, all reactions were carried out under an atmosphere of nitrogen. Hexane and heptane solvents were freshly distilled over sodium before use. CH_2Cl_2 was stored over 4-Å molecular sieves. $EtO_2CC{\equiv}CCO_2Et$ was purchased from Aldrich Chemical Co. and used without further purification. CO was dehydrated by passing through a copper tube coil in a EtOH/liquid nitrogen slush bath (−116 °C). For the labeling studies CO enriched to 99% ^{13}C was obtained from Dr. Istvan Horvath of Exxon Research & Engineering Co., Annandale, NJ. UV irradiations were performed by using an externally positioned Gates (Long Island, NY) 360-W high pressure mercury lamp on solutions in Pyrex glassware. TLC separations were performed in air by using silica gel (60 Å, F_{254}) or cellulose (K2F) on plates (Whatman, 0.25 mm). IR spectra were recorded on a Nicolet 5DXB FT-IR spectrophotometer. ^1H NMR spectra were taken at 300 MHz on a Brüker AM-300 spectrometer. Elemental analyses were performed by Desert Analytics, Tucson, AZ. Mass spectra were run on a VG Model 70SQ mass spectrometer using electron impact ionization. $Re_2(CO)_9(MeCN)$,[5] **1**, and $Re_2(^{13}CO)_9(MeCN)$,[4] **1*** (99% enriched), and $Re(CO)_4[\mu$-(*Z*)-$(EtO_2C)C{=}C(CO_2Et)]Re(CO)_5$,[4] **2**, were prepared by previously reported methods.

Crossover Reaction. A 2.0-mg amount (0.0038 mmol) of $Re_2(^{12}CO)_9(MeCN)$ and a 2.0-mg amount (0.0038 mmol) of $Re_2(^{13}CO)_9(MeCN)$ were dissolved in 25 mL of hexane. To this solution was added a 1.8-μL amount (0.011 mmol) of $EtO_2CC{\equiv}CCO_2Et$. The solution was heated to reflux for 1.5 h and then cooled to room temperature. The solvent was removed by evaporation at room temperature. In order to remove a minor coproduct $Re_2(CO)_7[C(CO_2Et)C(CO_2Et)C(CO_2Et)C(CO_2Et)]$, which has daughter ions in its mass spectrum that overlap the parent ions of **2**, the residue was transferred to K2F cellulose TLC plates and separated by eluting the $Re_2(CO)_7[C(CO_2Et)C(CO_2Et)C(CO_2Et)C(CO_2Et)]$ with hexane solvent. Compound **2** which has poor solubility in hexane remains in the baseline of the plate and was subsequently removed from the cellulose with CH_2Cl_2. This material was analyzed by mass spectrometry. The mass spectrum showed ions with the natural abundance isotope distributions for dirhenium centered at *m/e* 794 (for $Re(^{12}CO)_5[\mu$-(*Z*)-$(EtO_2C)C{=}C(CO_2Et)]Re(^{12}CO)_4$, **2**) and a second cluster of ions centered at *m/e* 803 (for $Re(^{13}CO)_5[\mu$-(*Z*)-$(EtO_2C)C{=}C(CO_2Et)]Re(^{13}CO)_4$, **2***). Most importantly, the isotope patterns from the two parent ions did not overlap and virtually no intensity was observed at the *m/e* values of 798 and 799, which would have been prominantly displayed if the crossover products $Re(^{13}CO)_5[\mu$-(*Z*)-$(EtO_2C)C{=}C(CO_2Et)]Re(CO)_4$ and $Re(CO)_5[\mu$-(*Z*)-$(EtO_2C)C{=}C(CO_2Et)]Re(^{13}CO)_4$ had been present.

Photolysis of 2. A 10.0-mg amount (0.013 mmol) of **2** was dissolved in 80 mL of hexane. The solution was irradiated (UV) at 25 °C for 10 min. The solvent was evaporated in vacuum at room temperature and the residue was separated by silica gel TLC using a hexane/CH_2Cl_2, 2/1, solvent mixture to yield 3.1 mg of orange $Re(CO)_4[\mu$-(*E*)-$(EtO_2C)C{=}C(CO_2Et)]Re(CO)_4$, **4** (32%), and 4.3 mg of colorless $Re(CO)_4[\mu$-(*E*)-$(EtO_2C)C{=}C(CO_2Et)]Re(CO)_5$, **3** (43%). IR ($\nu_{CO}$ in hexane, cm^{-1}) for **3**: 2137 (w), 2096 (w), 2068 (w), 2029 (s), 2019 (s), 1995 (s), 1986 (s), 1942 (s), 1701 (w, br), 1536 (w, br). IR (ν_{CO} in hexane, cm^{-1}) for **4**: 2090 (m), 1997 (s), 1986 (s), 1948 (s), 1535 (w, br). ^1H NMR (δ in $CDCl_3$, ppm) for **3**: 4.38 (q, $^3J_{H-H}$ = 7.2 Hz, 2H, CH_2), 4.23 (q, $^3J_{H-H}$ = 7.2 Hz, 2H, CH_2), 1.40 (t, $^3J_{H-H}$ = 7.2 Hz, 3H, CH_3), 1.33 (t, $^3J_{H-H}$ = 7.2 Hz, 3H, CH_3). ^1H NMR (δ in $CDCl_3$, ppm) for **4**: 4.42 (q, $^3J_{H-H}$ = 7.2 Hz, 4H, CH_2), 1.44 (t, $^3J_{H-H}$ = 7.2 Hz, 6H, CH_3). The mass spectrum for **3** showed a parent ion at *m/e* 796 (for ^{187}Re) and ions corresponding to the loss of 1 − 7CO ligands. The mass spectrum for **4** showed a parent ion at *m/e* 768 (for ^{187}Re) and ions corresponding to the loss of 1 − 5CO ligands. Anal. Calcd (found) for **4**: C, 25.07 (25.99); H, 1.32 (1.16).

Decarbonylation of 3. A solution of 10.0-mg (0.013 mmol) of **3** in 30 mL of hexane was irradiated (UV) at 25 °C for 30 min. The solution turned from colorless to orange. After the solvent was removed by evaporation, the residue was separated with silica gel TLC using a hexane/CH_2Cl_2, 1/1, solvent mixture to yield 5.4 mg (62%) of **4** and 1.7 mg of unreacted starting material.

Pyrolysis of 2. A 50.0-mg amount (0.063 mmol) of **2** was dissolved in 80 mL of heptane. The solution was heated to reflux for 5 h. After cooling, the solvent was evaporated in vacuum. The residue was separated with silica gel TLC using a hexane/CH_2Cl_2, 1/1, solvent mixture to yield 5.3 mg of **4** in 11% yield.

Carbonylation of 2. A 50.0-mg amount (0.063 mmol) of **2** was dissolved in 5 mL of CH_2Cl_2, and the solution was placed in a Parr high-pressure reaction vessel. The vessel was pressurized to 700 psi with CO and stirred at 25 °C for 12 h. After venting, the solvent was removed and the residue was dissolved in a minimum amount of a hexane/CH_2Cl_2, 1/1, solvent mixture and cooled to −14 °C. $Re(CO)_5[\mu$-(*Z*)-$(EtO_2C)C{=}C(CO_2Et)]Re(CO)_5$, **5** (48.2 mg, 93%), precipitated as colorless crystals. IR (ν_{CO} in hexane, cm^{-1}) for **5**: 2140 (vw), 2129 (w), 2067 (w), 2043 (s), 2030 (m), 2005 (m), 1994 (w), 1984 (s), 1692 (w, br). ^1H NMR (δ in $CDCl_3$, ppm) for **5**: 4.06 (q, $^3J_{H-H}$ = 7.2 Hz, 4H, CH_2), 1.26 (t, $^3J_{H-H}$ = 7.2 Hz, 6H, CH_3). Anal. Calcd (found) for **5**: C, 26.28 (26.38); H, 1.23 (1.17).

Decarbonylation of 5. A 15.0-mg amount (0.018 mmol) of **5** was dissolved in 40-mL of hexane. The solution was heated to reflux for 10 min. An IR spectrum indicated that compound **5** was completely converted into **2**. After cooling to room temperature, the solution was evaporated to dryness. The residue was redissolved in a minimum amount of a hexane/CH_2Cl_2, 1/1, solvent mixture and cooled to −3 °C to give 13.4 mg of crystalline **2** in 92% yield.

Conversion of 2 to $Re(CO)_5[C(CO_2Et)C{=}C(H)CO_2Et]$, 6. (a) On Silica Gel. A 20.0-mg amount (0.025 mmol) of **2** was dissolved in a minimum amount of CH_2Cl_2, and the solution was applied to a silica gel TLC plate. After 10 min, the material was eluted with CH_2Cl_2 and collected. Pure colorless $Re(CO)_5[C(CO_2Et)C{=}C(H)CO_2Et]$, **6** (8.9 mg, 99%), was obtained after removal of the solvent. IR (ν_{CO} in hexane, cm^{-1}) for **6**: 2142 (w), 2072 (w), 2037 (s), 2030 (s, sh), 1727 (w, br), 1713 (w, br). ^1H NMR (δ in $CDCl_3$, ppm) for **6**: 6.19 (s, 1H, CH), 4.28 (q, $^3J_{H-H}$ = 7.2 Hz, 2H, CH_2), 4.11 (q, $^3J_{H-H}$ = 7.2 Hz, 2H, CH_2), 1.32 (t, $^3J_{H-H}$ = 7.2 Hz, 3H, CH_3), 1.25 (t, $^3J_{H-H}$ = 7.2 Hz, 3H, CH_3). Anal. Calcd (found) for **6**: C, 31.39 (32.07); H, 2.23 (2.40).

(b) Reaction of 2 with HCl. A 10.0-mg amount (0.013 mmol) of **2** was dissolved in 30-mL of hexane. CO was saturated with HCl gas by purging it through a 36% HCl aqueous solution. This gaseous mixture was dried by passing through a 5-in. column of P_2O_5. The dried HCl/CO mixture was then purged through the solution of **2** at 25 °C. After 3 h, the IR spectrum showed that **2** was converted completely to a mixture of **6** and $Re(CO)_5Cl$. The products were separated by TLC on silica gel using a hexane/

---

[5] Koelle, U. *J. Organomet. Chem.* **1978**, *155*, 53.

Table 1. Crystallographic Data for Compounds 2–6

	2	3	4	5	6
empirical formula	$Re_2O_{13}C_{17}H_{10}$	$Re_2O_{13}C_{17}H_{10}$	$ReO_6C_8H_5$	$Re_2O_{14}C_{18}H_{10}$	$ReO_9C_{13}H_{11}$
fw	794.67	794.67	383.33	822.68	497.43
cryst syst	monoclinic	orthorhombic	triclinic	orthorhombic	monoclinic
lattice params					
a (Å)	10.292(2)	24.498(3)	7.838(3)	14.275(2)	9.637(1)
b (Å)	11.731(2)	35.102(5)	9.830(3)	33.00(1)	8.340(1)
c (Å)	18.704(4)	10.681(1)	7.047(2)	10.114(2)	20.821(2)
α (deg)	90.0	90.0	106.93(2)	90.0	90.0
β (deg)	100.14(2)	90.0	94.84(3)	90.0	102.10(1)
γ (deg)	90.0	90.0	84.28(3)	90.0	90.0
V (Å^3)	2223(1)	9185(3)	516.0(6)	4764(4)	1636.1(4)
space group	$P2_1/c$ (No. 14)	$Fdd2$ (No. 43)	$P\bar{1}$ (No. 2)	$Pbca$ (No. 61)	$P2_1/c$ (No. 14)
Z	4	16	2	8	4
D_{calc} (g/cm^3)	2.37	2.30	2.47	2.29	2.02
μ(Mo Kα) (cm^{-1})	110.9	107.4	119.4	103.6	75.7
temp (°C)	20	20	20	20	20
$2\theta_{max}$ (deg)	43.0	50.0	52.0	45.0	43.0
no. of obs reflns ($I > 3\sigma(I)$)	2133	1843	1927	2124	1686
no. of variables	289	288	136	307	212
residuals: R, R_w	0.025, 0.026	0.027, 0.028	0.037, 0.048	0.036, 0.038	0.021, 0.025
goodness of fit (GOF)	1.59	1.51	2.19	1.87	1.74
max shift on final cycle	0.04	0.03	0.00	0.01	0.00
largest peak in final diff map (e/Å^3)	0.79	0.54	2.06	1.20	0.65
abs corr	empirical	empirical	empirical	DIFABS	empirical

CH_2Cl_2, 1/1, solvent mixture to yield 3.7 mg of Re(CO)$_5$Cl[6] and 4.4 mg of 6 in 97% yield.

Crystallographic Analysis. Crystals of 2 suitable for X-ray diffraction analysis were grown by slow evaporation of solvent from a solution in a hexane/CH_2Cl_2 1/1 solvent mixture at 25 °C. Crystals of compound 3 were grown by slow evaporation of solvent from a solution in a hexane/CH_2Cl_2/MeOH 2/1/1 solvent mixture at 25 °C. Crystals of compounds 4 and 5 were grown from solutions in hexane/CH_2Cl_2 1/1 solvent mixtures by slow evaporation of the solvent at −3 °C. Crystals of compound 6 were grown by slow evaporation of solvent from a solution in a hexane/CH_2Cl_2 1/1 solvent mixture at 25 °C. All crystals that were used in diffraction intensity measurements were mounted in thin-walled glass capillaries. Diffraction measurements were made on a Rigaku AFC6S fully automated four-circle diffractometer by using graphite-monochromated Mo Kα radiation. All unit cells were determined and refined from 15 randomly selected reflections obtained by using the AFC6 automatic search, center, index, and least-squares routines. All data processing was performed on a Digital Equipment Corp. VAXstation 3520 computer by using the TEXSAN structure solving program library (version 5.0) obtained from the Molecular Structure Corp., The Woodlands, TX. Neutral atom scattering factors were calculated by the standard procedures.[7a] Anomalous dispersion corrections were applied to all non-hydrogen atoms.[7b] Full-matrix least-squares refinements minimized the function: $\sum_{hkl} w(|F_o| - |F_c|)^2$, where $w = 1/\sigma(F_o)^2$, $\sigma(F_o) = \sigma(F_o^2)/2F_o$, and $\sigma(F_o^2) = [\sigma(I_{raw})^2 + (0.02I_{net})^2]^{1/2}/Lp$. Each structure was solved by a combination of direct methods (MITHRIL) and difference Fourier analyses. Crystal data and results of the analyses are listed in Table 1.

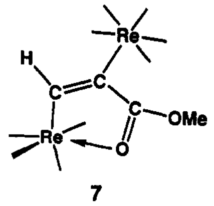
Compound 2 crystallized in the monoclinic crystal system. The space group $P2_1/c$ was identified uniquely from the patterns of systematic absences observed in the data. All non-hydrogen atoms were refined anisotropically. The positions of the hydrogen atoms were calculated by assuming an idealized geometry with C–H = 0.95 Å. They were not refined.

Compounds 3 and 5 crystallized in the orthorhomic crystal system. Their space groups $Fdd2$ and $Pbca$, respectively, were identified uniquely from the patterns of systematic absences observed in the data. All non-hydrogen atoms were refined anisotropically. The positions of the hydrogen atoms for both analyses were calculated by assuming an idealized geometry with C–H = 0.95 Å. The positions of the hydrogen atoms were not refined in either case.

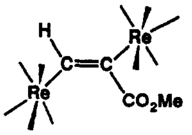
Compound 4 crystallized in the triclinic crystal system. The space group $P\bar{1}$ was assumed and confirmed by the successful solution and refinement of the structure. The crystal contains only one centrosymmetric molecular unit in the unit cell. All non-hydrogen atoms were refined with anisotropic thermal parameters. The positions of the hydrogen atoms were calculated by assuming idealized geometries but were not refined.

Compound 6 crystallized in the monoclinic crystal system. The space group $P2_1/c$ was identified uniquely from the patterns of systematic absences observed in the data. All non-hydrogen atoms were refined anisotropically. The hydrogen atom H(2) was located and refined using an isotropic thermal parameter. All hydrogen atom positions on the ethyl groups were calculated by assuming idealized geometries. They were not refined.

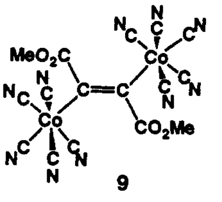
Results



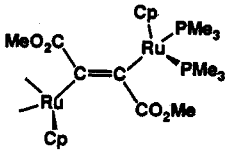
7



8



9



10

The reaction of $Re_2(CO)_9(NCMe)$, 1, with the carboxylate substituted alkynes $RC{\equiv}CCO_2R'$ (R = H, R′ = Me; R = Me, R′ = Me; R = CO_2Et, R′ = Et) at 68 °C was reported previously.[4] Due to its strong spectral similarities to the structurally characterized compound Re(CO)$_4$[μ-(E)-HC=C(CO_2Me)]Re(CO)$_5$, 7, it was assumed that the product Re(CO)$_4$[μ-(Z)-(EtO_2C)C=C(CO_2Et)]Re(CO)$_5$, 2, obtained from the reaction of $EtO_2CC{\equiv}CCO_2Et$

---

[6] Colton, R.; Knapp, J. E. *Aust. J. Chem.* **1972**, *25*, 9.

[7] (a) *International Tables for X-ray Crystallography*; Kynoch Press: Birmingham, England, 1975; Vol. IV, Table 2.2B; pp 99–101. (b) *Ibid.*, Table 2.3.1, pp 149–150.

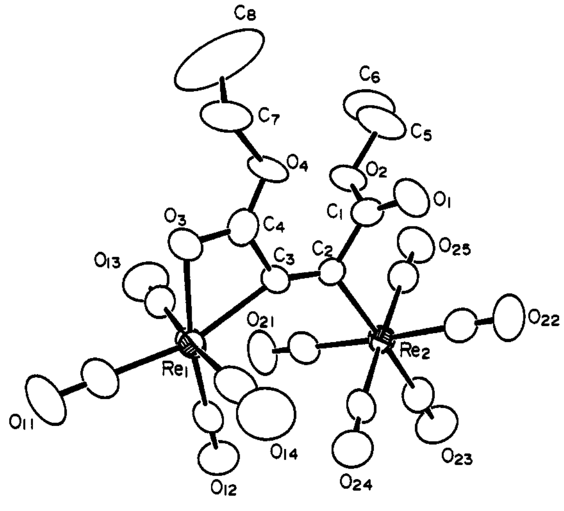


Figure 1. ORTEP diagram of $Re(CO)_4[\mu\text{-}(Z)\text{-}(EtO_2C)\text{-}C{=}C(CO_2Et)]Re(CO)_5$, **2**, showing 50% probability thermal ellipsoids. Selected intramolecular bond distances (Å) and angles (deg) are as follows: Re(1)–C(3) = 2.193(8), Re(2)–C(2) = 2.228(8), C(1)–C(2) = 1.49(1), C(2)–C(3) = 1.34(1), C(3)–C(4) = 1.46(1), Re(1)–O(3) = 2.214(6), C(1)–O(1) = 1.20(1), C(4)–O(3) = 1.27(1), Re(1)–C(3)–C(2) = 146.8(7), Re(1)–C(3)–C(4) = 90.3(6), Re(2)–C(2)–C(3) = 127.4(7), Re(2)–C(2)–C(1) = 111.0(5), C(1)–C(2)–C(3) = 121.5(8), C(2)–C(3)–C(4) = 122.8(9), C(3)–Re(1)–O(3) = 62.1(3).

Table 2. Positional Parameters and *B*(eq) for 2

atom	*x*	*y*	*z*	*B*(eq)[a] (Å^2)
Re(1)	0.71960(04)	0.20387(03)	0.002809(18)	3.14(2)
Re(2)	0.84194(04)	0.14191(03)	0.246716(18)	2.76(2)
O(1)	1.1159(07)	0.3324(06)	0.2186(04)	4.7(4)
O(2)	1.1633(06)	0.1570(06)	0.1846(03)	4.0(3)
O(3)	0.8969(06)	0.2872(06)	–0.0254(03)	3.9(3)
O(4)	1.0867(07)	0.3128(07)	0.0537(03)	5.3(4)
O(11)	0.5388(08)	0.2050(08)	–0.1476(04)	7.5(5)
O(12)	0.5043(08)	0.0837(06)	0.0670(04)	5.2(4)
O(13)	0.8415(09)	–0.0337(07)	–0.0232(04)	6.5(5)
O(14)	0.6164(09)	0.4373(07)	0.0496(05)	6.8(5)
O(21)	0.7588(08)	–0.0620(06)	0.1388(04)	5.4(4)
O(22)	0.9317(08)	0.3590(07)	0.3403(04)	5.7(4)
O(23)	0.6973(08)	0.0331(07)	0.3623(04)	6.1(4)
O(24)	0.5935(08)	0.2867(07)	0.1835(04)	5.2(4)
C(25)	1.0075(12)	0.0594(08)	0.2923(05)	3.7(5)
O(25)	1.1000(08)	0.0144(07)	0.3195(04)	5.4(4)
C(1)	1.0814(10)	0.2436(09)	0.1899(05)	3.0(4)
C(2)	0.9430(09)	0.2105(07)	0.1599(04)	2.6(4)
C(3)	0.8906(09)	0.2275(07)	0.0897(04)	2.7(4)
C(4)	0.9651(11)	0.2777(08)	0.0377(05)	3.5(5)
C(5)	1.3021(11)	0.1771(11)	0.2159(07)	6.5(7)
C(6)	1.3681(12)	0.0657(13)	0.2264(07)	7.4(8)
C(7)	1.1472(13)	0.3617(14)	–0.0052(06)	7.6(8)
C(8)	1.267(03)	0.3069(14)	–0.0088(12)	14(1)
C(11)	0.6051(11)	0.2041(09)	–0.0927(06)	4.8(5)
C(12)	0.5844(11)	0.1297(09)	0.0422(05)	3.6(5)
C(13)	0.7983(11)	0.0516(10)	–0.0149(05)	4.2(5)
C(14)	0.6555(11)	0.3535(10)	0.0309(06)	4.3(5)
C(21)	0.7894(10)	0.0084(09)	0.1787(05)	3.6(5)
C(22)	0.9002(11)	0.2794(09)	0.3069(05)	3.8(5)
C(23)	0.7500(11)	0.0746(09)	0.3209(05)	4.2(5)
C(24)	0.6842(11)	0.2308(09)	0.2044(05)	3.4(5)

[a] $B_{eq} = 8\pi^2/3\sum_{i=1}^{3}\sum_{j=1}^{3}U_{ij}a_i^*a_j^*\vec{a}_i\vec{a}_j$; see: Fischer, R. X.; Tillmanns, E. *Acta Crystallogr.* **1988**, *C44*, 775.

with 1 had an analogous structure. However, our X-ray crystallographic analysis of 2 now shows that it is quite different. An ORTEP diagram of the molecular structure of 2 is shown in Figure 1. Final atomic positional parameters are listed in Table 2. Compound 2 is indeed a dimetalated olefin complex, but it does not have the *E* stereochemistry. Instead, it has a *Z* stereochemistry of the metal groupings and one of the oxygen atoms, O(3), of one of the ester groupings is coordinated to one of the metal atoms, Re(1), to form a four membered metallacyclic ring, Re(1)—O(3) = 2.214(6) Å. The C—O bond distance of the coordinated carbonyl grouping C(4)—O(3) = 1.27(1) Å is similar to that found in 7, 1.26–1.27(2) Å, and significantly longer than the uncoordinated one, vs C(1)–O(1) = 1.20(1) Å. There may be significant strain in some of the angles in the four membered metallacyclic ring Re(1)—C(3)—C(4)—O(3). The C(3)—C(4)—O(3) angle is large 113(1)° due to the double bond character of the C(4)–O(3) bond, and the O(3)—Re(1)—C(3) angle is thus very small, 62.1(3)°. The olefin bond distance C(2)—C(3) = 1.34(1) Å is similar to that found in 7, 1.37(2) and 1.41(2) for two independent molecules, $Re(CO)_5[\mu\text{-}(E)\text{-}HC{=}C(CO_2Me)]Re(CO)_5$, **8**, 1.29(2) Å,[4] $(NC)_5Co[\mu\text{-}(E)\text{-}(MeO_2C)C{=}C(CO_2Me)]Co(CN)_5$, **9**, 1.333(5) Å,[2d] and $CpRu(CO)_2[\mu\text{-}(E)\text{-}(MeO_2C)C{=}C(CO_2Me)]RuCp(PMe_3)_2$, **10**, 1.320(5) Å,[2b] and all are typical of a normal olefin distance. The metal—carbon bond distances in 2, Re(1)—C(3) = 2.193(8) Å and Re(2)—C(2) = 2.228(8) Å, are also similar to those found in 7, Re—C = 2.17(2)–2.22(2) Å,[4] but the angle Re(1)—C(3)—C(2) = 146.8(7)° is unusually large. This is probably a consequence of the formation of the four membered ring, since the Re(2)—C(2)—C(3) angle is 20° smaller at 127.4(7)°, and this value is similar to the corresponding angles found in 7, 125(1)° [128(1)°], 8, 129(1) and 134(1)°, 9, 132.2(2)°, and 10, 130.5(2) and 127.2(2)°.

To try to obtain some information about the mechanism of the formation of 2, a test for crossover was made by performing the synthesis of 2 by using a mixture of 1 and $Re_2(^{13}CO)_9(NCMe)$, **1***, containing 99% enriched ^{13}CO. A mass spectroscopic analysis of the product 2 obtained from this reaction revealed the formation of only 2 and fully ^{13}C-labeled 2, indicating the complete absence of crossover.

When a solution of 2 was irradiated (UV) at 25 °C for 10 min, two new products $Re(CO)_4[\mu\text{-}(E)\text{-}(EtO_2C)\text{-}C{=}C(CO_2Et)]Re(CO)_5$, **3** (43% yield), and $Re(CO)_4[\mu\text{-}(E)\text{-}(EtO_2C)C{=}C(CO_2Et)]Re(CO)_4$, **4** (32% yield), were formed. Thermal decarbonylation of 2 at 97 °C for 5 h produced only compound 4 in a low yield (11%). Both products were characterized by single crystal X-ray diffraction analyses. An ORTEP drawing of the molecular structure of 3 is shown in Figure 2. Final atomic positional parameters are listed in Table 3. Compound 3 is an *E*-dimetalated olefin complex; in fact, it is the one that 2 was originally formulated to be.[4] In 3 the other carboxylate group is coordinated to Re(1) to form a five membered metallacyclic ring, Re(1)—O(1) = 2.17(2) Å. The C—O bond distance of the coordinated carboxylate group is again longer than that of the uncoordinated one, C(1)—O(1) = 1.25(2) Å vs C(4)—O(3) = 1.20(2) Å. The Re—C distances, Re(1)—C(3) = 2.17(1) Å and Re(2)—C(2) = 2.25(1) Å, and the olefin distance C(2)—C(3) = 1.32(2) Å are similar to those found in compounds 2, 7, or 8. The C(3)—Re(1)—O(1) angle in the five membered ring at 72.9(4)° is 10° larger than that found in the four membered ring in 2. The angle Re(2)—C(2)—C(3) = 130(1)° is similar to those found in compounds 2, 7, or 8.

An ORTEP drawing of the molecular structure of 4 is shown in Figure 3. Final atomic positional parameters are listed in Table 4. Compound 4 is also an *E*-dimetalated olefin complex. It is very similar to 3, but it has one less carbonyl ligand and as a result the second carboxylate

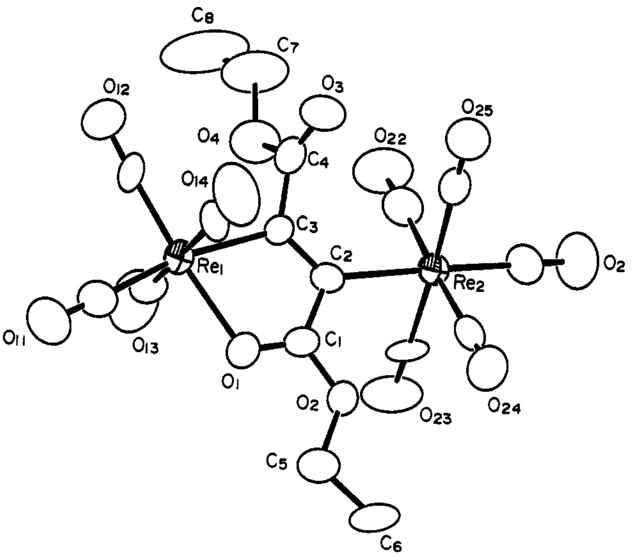


Figure 2. ORTEP diagram of $Re(CO)_4[\mu\text{-}(E)\text{-}(EtO_2C)\text{-}C{=}C(CO_2Et)]Re(CO)_5$, **3**, showing 50% probability thermal ellipsoids. Selected intramolecular bond distances (Å) and angles (deg) are as follows: Re(1)–C(3) = 2.17(1), Re(2)–C(2) = 2.25(1), C(1)–C(2) = 1.44(2), C(2)–C(3) = 1.32(2), C(3)–C(4) = 1.51(2), Re(1)–O(1) = 2.17(2), C(1)–O(1) = 1.25(2), C(4)–O(3) = 1.20(2), Re(1)–C(3)–C(2) = 120(1), Re(1)–C(3)–C(4) = 118(1), Re(2)–C(2)–C(3) = 130(1), Re(2)–C(2)–C(1) = 122(1), C(1)–C(2)–C(3) = 108(1), C(2)–C(3)–C(4) = 122(1), C(3)–Re(1)–O(1) = 72.9(4).

Table 3. Positional Parameters and *B*(eq) for 3

atom	*x*	*y*	*z*	*B*(eq)[a] (Å^2)
Re(1)	0.29427(02)	0.126982(18)	0.4849	3.48(2)
Re(2)	0.32361(02)	0.040572(16)	0.08606(07)	3.38(2)
O(1)	0.2792(04)	0.1458(03)	0.2945(09)	3.9(4)
O(2)	0.2854(04)	0.1311(02)	0.0926(09)	3.9(4)
O(3)	0.2988(05)	0.0150(03)	0.4340(12)	6.3(7)
O(4)	0.3784(05)	0.0438(04)	0.4701(13)	6.6(7)
O(11)	0.2619(07)	0.2018(04)	0.6151(14)	8.4(9)
O(12)	0.3238(05)	0.0919(04)	0.7366(13)	6.7(7)
O(13)	0.4168(05)	0.1518(05)	0.4545(13)	9(1)
O(14)	0.1788(05)	0.0901(04)	0.5156(15)	7.7(8)
O(21)	0.3482(06)	–0.01690(04)	–0.1283(14)	8.7(9)
O(22)	0.4242(06)	0.0072(04)	0.2303(16)	9(1)
O(23)	0.4009(04)	0.1026(04)	–0.0247(14)	7.0(7)
O(24)	0.2220(05)	0.0728(03)	–0.0612(11)	5.6(6)
O(25)	0.2470(06)	–0.0202(04)	0.2111(12)	7.7(8)
C(1)	0.2896(06)	0.1210(04)	0.2143(14)	3.8(7)
C(2)	0.3083(05)	0.0830(04)	0.2399(15)	3.1(6)
C(3)	0.3122(05)	0.0792(04)	0.3630(12)	3.0(6)
C(4)	0.3282(07)	0.0419(05)	0.4228(15)	4.6(8)
C(5)	0.2690(08)	0.1694(05)	0.0608(17)	5(1)
C(6)	0.2691(11)	0.1719(06)	–0.0797(18)	7(1)
C(7)	0.3968(12)	0.0123(08)	0.542(03)	11(2)
C(8)	0.4288(18)	0.0184(11)	0.627(05)	19(4)
C(11)	0.2731(08)	0.1746(05)	0.5645(16)	5(1)
C(12)	0.3118(07)	0.1060(05)	0.6417(14)	4.5(8)
C(13)	0.3732(08)	0.1442(04)	0.4656(15)	4.9(8)
C(14)	0.2203(07)	0.1054(04)	0.5017(16)	4.3(7)
C(21)	0.3391(09)	0.0047(05)	–0.0511(17)	6(1)
C(22)	0.3864(08)	0.0189(05)	0.1760(18)	5.3(9)
C(23)	0.3732(07)	0.0806(04)	0.0126(14)	4.3(7)
C(24)	0.2574(06)	0.0609(04)	–0.0109(16)	3.7(6)
C(25)	0.2731(07)	0.0022(05)	0.1674(13)	4.5(8)

[a] $B_{eq} = 8\pi^2/3\sum_{i=1}^{3}\sum_{j=1}^{3}U_{ij}a_i^*a_j^*\vec{a}_i\vec{a}_j$; see: Fischer, R. X.; Tillmanns, E. *Acta Crystallogr.* **1988**, *C44*, 775.

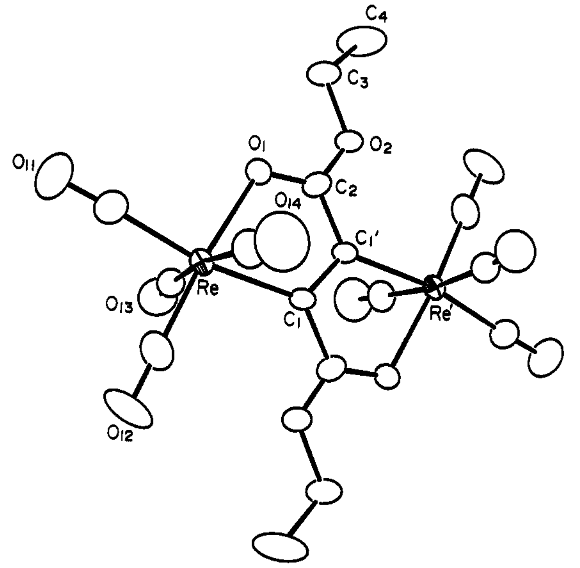


Figure 3. ORTEP diagram of $Re(CO)_4[\mu\text{-}(E)\text{-}(EtO_2C)\text{-}C{=}C(CO_2Et)]Re(CO)_4$, **4**, showing 50% probability thermal ellipsoids. Selected intramolecular bond distances (Å) and angles (deg) are as follows: Re(1)–C(1) = 2.160(8), C(1)–C(1′) = 1.37(1), C(1′)–C(2) = 1.47(1), Re–O(1) = 2.203(6), C(2)–O(1) = 1.26(1), C(2)–O(2) = 1.24(1), Re–C(1)–C(1′) = 118.0(7), C(1)–C(1′)–C(2) = 111.7(8), C(1)–Re(1)–O(1) = 74.0(2).

Table 4. Positional Parameters and *B*(eq) for 4

atom	*x*	*y*	*z*	*B*(eq)[a] (Å^2)
Re	0.22937(03)	0.15438(03)	–0.04192(04)	1.86(1)
O(1)	0.2599(07)	–0.0785(06)	–0.1736(09)	2.3(2)
O(2)	0.1463(07)	–0.2781(06)	–0.2125(08)	2.4(2)
O(11)	0.5719(10)	0.2138(09)	–0.1836(13)	4.7(3)
O(12)	0.1546(12)	0.4733(07)	0.1546(13)	5.1(4)
O(13)	0.3824(10)	0.1291(10)	0.3713(10)	4.3(3)
O(14)	0.0129(13)	0.1854(13)	–0.4224(14)	5.8(4)
C(1)	0.0063(09)	0.0721(08)	0.0320(11)	1.8(2)
C(2)	0.1416(10)	–0.1469(09)	–0.1453(11)	2.2(3)
C(3)	0.2903(12)	–0.3570(10)	–0.3284(14)	3.2(3)
C(4)	0.2847(20)	–0.5101(11)	–0.351(02)	5.9(6)
C(11)	0.4451(12)	0.1882(10)	–0.1347(14)	2.9(3)
C(12)	0.1834(13)	0.3522(10)	0.0786(15)	3.2(4)
C(13)	0.3340(11)	0.1364(10)	0.2193(14)	2.9(3)
C(14)	0.0936(13)	0.1743(11)	–0.2866(15)	3.3(4)

[a] $B_{eq} = 8\pi^2/3\sum_{i=1}^{3}\sum_{j=1}^{3}U_{ij}a_i^*a_j^*\vec{a}_i\vec{a}_j$; see: Fischer, R. X.; Tillmanns, E. *Acta Crystallogr.* **1988**, *C44*, 775.

group has become coordinated to the second metal atom to form a second five membered metallacyclic ring, Re—O(1) = 2.203(6) Å. Crystallographically, the molecule contains a center of symmetry; thus the two metallacyclic rings lie in a common plane. The Re—C distance, Re—C(1) = 2.160(8) Å, is similar to those in compounds **2**, **3**, **7**, or **8**. The olefin C—C distance, C(1)—C(1′) = 1.37(1) Å, is slightly longer than those in **2**, **3**, and **8**, but similar to that found in **7**. The Re—C(1)—C(1′) angle is an interior angle of the five membered metallacyclic ring and is much smaller at 118.0(7)° than the exocyclic angles observed previously; however, it is similar to the endocyclic angles M—C=C, 120(1) and 116(1)° [118(1)°] observed in **3** and **7**, respectively. As expected, compound **3** is a precursor to **4**. When a solution of **3** in hexane solvent was irradiated (UV) at 25 °C for 30 min, compound **4** was obtained in 62% yield.

When **2** was treated with CO at 700 psi at 25 °C for 12 h, the new CO adduct $Re(CO)_5[\mu\text{-}(Z)\text{-}(EtO_2C)C{=}C(CO_2Et)]Re(CO)_5$, **5**, was obtained in 93% yield. The molecular structure of **5** was also established by X-ray crystallographic analysis. An ORTEP drawing of the molecular structure of **5** is shown in Figure 4. Final atomic positional parameters are listed in Table 5. Compound **5** is also a simple *Z*-dimetalated olefin complex. It is very similar to

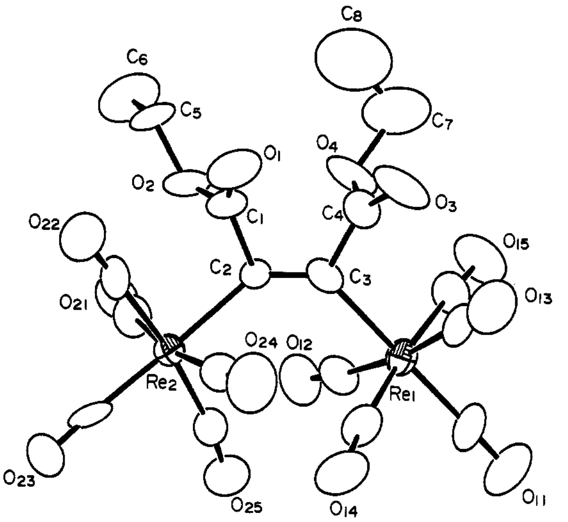


Figure 4. ORTEP diagram of $Re(CO)_5$[*trans*-μ-(EtO_2C)-C=C(CO_2Et)]$Re(CO)_5$), **5**, showing 50% probability thermal ellipsoids. Selected intramolecular bond distances (Å) and angles (deg) are as follows: Re(1)–C(3) = 2.24(1), Re(2)–C(2) = 2.23(1), C(1)–C(2) = 1.49(2), C(2)–C(3) = 1.36(2), C(3)–C(4) = 1.48(2), Re(1)–C(3)–C(2) = 135(1), Re(1)–C(3)–C(4) = 108(1), Re(2)–C(2)–C(3) = 137(1), Re(2)–C(2)–C(1) = 108(1), C(1)–C(2)–C(3) = 114(1), C(2)–C(3)–C(4) = 117(1).

Table 5. Positional Parameters and *B*(eq) for 5

atom	*x*	*y*	*z*	*B*(eq)[a] (Å^2)
Re(1)	0.28722(04)	0.087524(19)	0.19450(05)	3.17(3)
Re(2)	0.46655(04)	0.098012(19)	−0.18100(05)	2.86(3)
O(1)	0.2371(08)	0.1502(04)	−0.2775(12)	7.1(8)
O(2)	0.3510(08)	0.1901(04)	−0.2061(12)	5.9(7)
O(3)	0.1147(07)	0.1346(04)	−0.0101(13)	6.4(8)
O(4)	0.2067(07)	0.1852(04)	0.0411(13)	6.1(7)
O(11)	0.2985(10)	0.0417(04)	0.4642(12)	7.6(8)
O(12)	0.4711(09)	0.1368(04)	0.2290(11)	5.8(7)
O(13)	0.0930(09)	0.0495(05)	0.1154(12)	7.1(8)
O(14)	0.3791(10)	0.0107(04)	0.0798(13)	7.1(8)
O(15)	0.1894(09)	0.1578(04)	0.3510(12)	7.0(8)
O(21)	0.5564(08)	0.1817(04)	−0.1165(12)	5.8(7)
O(22)	0.4096(08)	0.1254(04)	−0.4677(11)	5.9(7)
O(23)	0.6430(09)	0.0563(04)	−0.3052(12)	6.8(8)
O(24)	0.3366(09)	0.0227(04)	−0.2173(13)	6.8(8)
O(25)	0.5574(08)	0.0672(04)	0.0779(11)	5.8(7)
C(1)	0.2991(12)	0.1549(05)	−0.2054(16)	4.1(9)
C(2)	0.3350(09)	0.1261(05)	−0.1043(12)	2.8(7)
C(3)	0.2787(09)	0.1216(05)	0.0029(13)	3.2(7)
C(4)	0.1922(11)	0.1466(05)	0.0060(14)	3.6(9)
C(5)	0.3244(14)	0.2197(07)	−0.308(02)	9(1)
C(6)	0.3704(17)	0.2581(08)	−0.270(04)	15(2)
C(7)	0.1173(17)	0.2111(07)	0.065(02)	8(1)
C(8)	0.107(02)	0.2312(11)	−0.050(03)	15(3)
C(11)	0.2938(14)	0.0593(05)	0.3655(16)	5(1)
C(12)	0.4053(12)	0.1174(06)	0.2225(14)	4.2(9)
C(13)	0.1641(12)	0.0639(06)	0.1456(14)	4(1)
C(14)	0.3432(12)	0.0405(05)	0.1137(15)	4.0(9)
C(15)	0.2242(11)	0.1330(05)	0.2912(14)	3.9(8)
C(21)	0.5261(12)	0.1508(05)	−0.1467(16)	5(1)
C(22)	0.4288(11)	0.1154(05)	−0.3632(14)	3.4(8)
C(23)	0.5795(14)	0.0733(05)	−0.2586(16)	4(1)
C(24)	0.3851(11)	0.0489(05)	−0.2072(15)	3.6(8)
C(25)	0.5176(11)	0.0792(05)	−0.0128(14)	3.4(8)

[a] $B_{eq} = 8\pi^2/3\sum_{i=1}^{3}\sum_{j=1}^{3}U_{ij}a_i{}^*a_j{}^*\vec{a}_i\vec{a}_j$; see: Fischer, R. X.; Tillmanns, E. *Acta Crystallogr.* **1988**, *C44*, 775.

2, but it has one more carbonyl ligand. The CO addition occurred by the cleavage of the Re—O bond in the metallacyclic ring of **2** and the addition of the new CO ligand at that site. As a result, compound **5** contains two $Re(CO)_5$ groupings in the *Z* configuration. The olefin C—C bond distance, C(2)—C(3) = 1.36(2) Å is again similar to those found in **2**, **3**, **4**, and **7–10**. The Re—C distances Re(1)—C(3) = 2.24(1) Å and Re(2)—C(2) = 2.23(1) Å are similar to those of the other dimetalated olefin complexes of rhenium that we have studied, but the Re—C=C angles, Re(1)—C(3)—C(2) = 135(1)° and Re(2)—C(2)—C(3) = 137(1)° are the largest except for the one angle in **2** that is exterior to the four membered ring. This is probably due to steric repulsions between the two $Re(CO)_5$ groups. There is also a slight deviation of the Re—C=C—Re grouping from planarity. For example, the dihedral angle between the planes Re(1)—C(4)—C(3) and Re(2)—C(2)—C(1) is 9.1°. Both carboxylate groups are twisted 75–80° from the Re—C=C—Re plane. These twists probably also relieve some of the steric crowding. Similar twisting of the carboxylate groups was also observed in compounds **9** and **10**. When heated to 68 °C, compound **5** is readily converted back to **2** in 92% yield in 10 min.

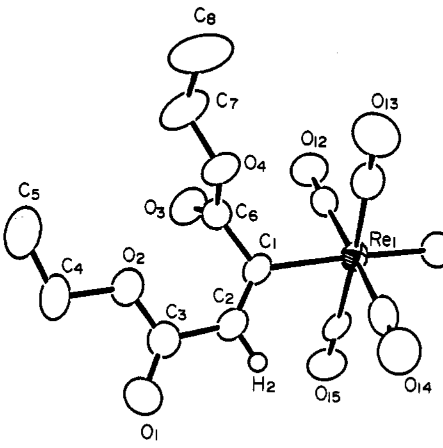


Figure 5. ORTEP diagram of [(*E*)-(EtO_2C)HC=C(CO_2Et)]-$Re(CO)_5$, **6** showing 50% probability thermal ellipsoids. Selected intramolecular bond distances (Å) and angles (deg) are as follows: Re(1)–C(1) = 2.207(6), C(1)–C(2) = 1.334(9), C(2)–C(3) = 1.474(9), C(1)–C(6) = 1.484(8), C(3)–O(1) = 1.207(8), C(6)–O(3) = 1.201(7), Re(1)–C(1)–C(2) = 124.7(4), Re(1)–C(1)–C(6) = 115.5(4), C(1)–C(2)–C(3) = 129.2(6).

Compound **2** is unstable to interaction with silica gel supports and attempts to isolate **2** by TLC on silica gel led to its transformation in excellent yield (99%) to the compound [(*E*)-(EtO_2C)HC=C(CO_2Et)]$Re(CO)_5$, **6**. Compound **6** can also be prepared in excellent yield (97%) by treatment of **5** with HCl under a CO atmosphere. In the latter reaction the coproduct $Re(CO)_5Cl$ is also formed. Compound **6** was characterized crystallographically. An ORTEP drawing of the molecular structure of **6** is shown in Figure 5. Final atomic positional parameters are listed in Table 6. This complex has only one rhenium atom. It contains five linear terminal carbonyl ligands and a σ-bonded 1,2-di-CO_2Et substituted vinyl ligand. This molecule is very similar to **5** except that it contains a hydrogen atom on the olefin site C(2) instead of a Re-$(CO)_5$ group. The Re—C distance, Re(1)—C(1) = 2.207(6) Å, is shorter than those in **5** and the Re—C=C angle is over 10° smaller, Re(1)—C(1)—C(2) = 124.7(4)°. Both factors can be attributed to a reduction of the steric effects that exist in **5**. Also, unlike **5** the plane of one of the carboxylate groups, O(1)—C(3)—O(2), is coplanar to the Re—C=C plane. The other carboxylate group remains perpendicular to the Re—C=C plane. The carbon—carbon double bond, C(1)—C(2) = 1.334(9) Å, is slightly shorter than that in **5**, but this is not statistically significant based on the size of the errors. The alkenyl hydrogen atom on C(2) was located and refined crystallographically.

Table 6. Positional Parameters and *B*(eq) for 6

atom	*x*	*y*	*z*	*B*(eq)[a] (Å^2)
Re(1)	0.22566(03)	0.26841(03)	1.004293(12)	2.79(1)
O(1)	0.5289(06)	−0.2389(06)	1.1313(03)	6.0(3)
O(2)	0.3868(05)	−0.1255(05)	1.1900(02)	4.6(2)
O(3)	0.0868(05)	−0.0217(06)	1.1205(02)	4.5(2)
O(4)	0.2070(05)	0.1821(05)	1.1740(02)	4.4(2)
O(11)	0.1486(06)	0.5116(07)	0.8889(03)	6.8(3)
O(12)	−0.0962(06)	0.2173(05)	1.0051(03)	4.8(2)
O(13)	0.2248(07)	0.5330(06)	1.1103(03)	6.7(3)
O(14)	0.5533(06)	0.3232(06)	1.0214(03)	5.6(3)
O(15)	0.2384(05)	−0.0160(06)	0.9068(02)	4.8(2)
C(1)	0.2841(06)	0.0862(07)	1.0821(03)	2.6(3)
C(2)	0.3950(07)	−0.0125(07)	1.0881(03)	3.3(3)
C(3)	0.4433(07)	−0.1377(08)	1.1377(03)	3.8(3)
C(4)	0.4281(09)	−0.2442(09)	1.2417(04)	5.8(4)
C(5)	0.3579(14)	−0.2097(13)	1.2937(05)	10.8(7)
C(6)	0.1849(07)	0.0701(07)	1.1275(03)	3.1(3)
C(7)	0.1089(11)	0.1822(11)	1.2182(04)	7.3(5)
C(8)	0.1233(12)	0.3205(13)	1.2573(05)	9.3(6)
C(11)	0.1783(08)	0.4244(08)	0.9324(03)	4.1(3)
C(12)	0.0205(09)	0.2308(07)	1.0032(03)	3.3(3)
C(13)	0.2252(07)	0.4372(08)	1.0717(03)	4.0(3)
C(14)	0.4351(09)	0.3050(07)	1.0138(03)	3.9(3)
C(15)	0.2315(06)	0.0875(08)	0.9413(03)	3.0(3)

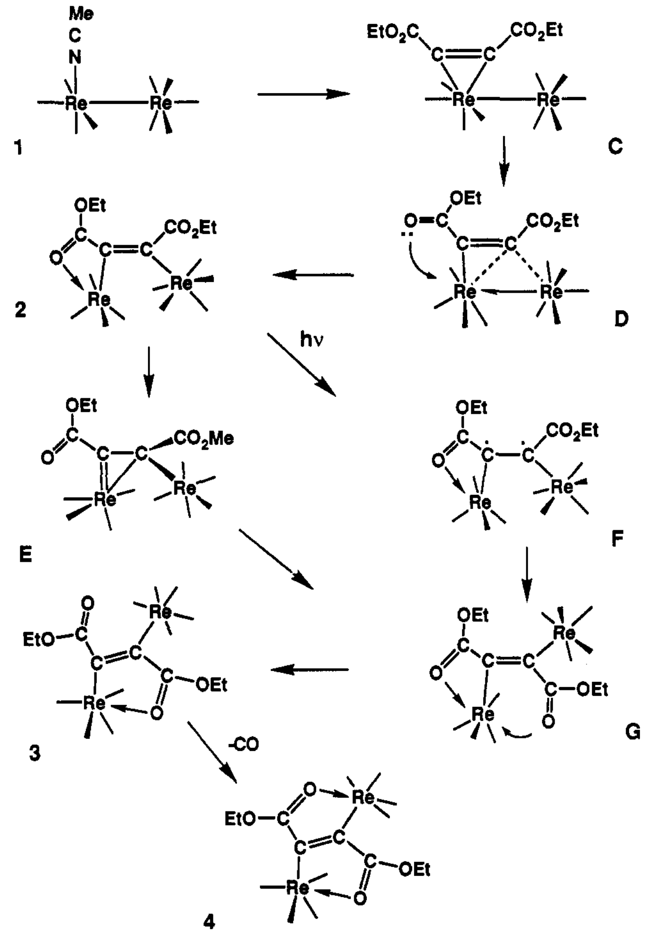
[a] $B_{eq} = 8\pi^2/3\sum_{i=1}^{3}\sum_{j=1}^{3}U_{ij}a_i{}^*a_j{}^*\bar{a}_i\bar{a}_j$; see: Fischer, R. X.; Tillmanns, E. *Acta Crystallogr.* **1988**, *C44*, 775.

It also exhibits a characteristically deshielded NMR shift at δ = 6.19 ppm.

Discussion

In accord with our previously proposed mechanism,[4] the structural characterization of 2 shows that the insertion of the alkyne $EtO_2CC{\equiv}CCO_2Et$ into the rhenium—rhenium bond of 1 occurs in a *cis* fashion to yield a dimetalated olefin having the metal substituents in a *Z* structural geometry. The mechanism as it applies for this dicarboxylate substituted alkyne is shown in Scheme 1. In the first step the alkyne simply displaces the NCMe ligand to form a species such as **C**, which has not yet been observed, in which the alkyne is simply π-bonded to one metal atom. As the alkyne ligand begins to form a bonding interaction with the second metal atom, the metal—metal bond begins to develop a heteropolar character, species **D**. At some stage in the course of this transformation, the ketonic oxygen atom of one of the carboxylate groups is added to the first metal atom to form the four membered metallacyclic ring and induce the cleavage of the metal—metal bond to yield 2. A species similar to 2 might also be traversed in the course of the insertion of $HC{\equiv}CCO_2Me$ into the Re—Re bond of 1,[4] but that species cannot be stabilized by interaction with the CO_2Me group since the carbon containing that group must be bonded to the $Re(CO)_5$ grouping. The absence of the formation of crossover products in the reaction of labeled and unlabeled 1 with $EtO_2CC{\equiv}CCO_2Et$ is consistent with an intramolecular mechanism such as this. In the reaction of 1 with $HC{\equiv}CCO_2Me$, the *E* species 7 was formed in good yield under mild thermal conditions (68 °C). The formation of 7 was proposed to occur via an η^2-alkenyl intermediate such as **E** shown in Scheme 1. In contrast, the thermal transformation of 2 to 3 occurs in a poor yield even at 97 °C. We think this is reasonable, because the formation of **E** would require cleavage of the Re—O bond, which would not have to occur in the transformation to 7, and is thus energetically more difficult. We have, however, been able to convert 2 to 3 in a good yield, but this was achieved photolytically. The irradiation could promote the transformation via **E** by facilitating the cleavage of the Re—O bond in 2, but the irradiation might change the form of the transition state completely; for example, excitation of one of the π-electrons in the C—C double bond could lead to a diradical intermediate such as **F**. In the latter case there is no need to cleave the Re—O bond, and rotation about C—C could occur easily. Also, other mechanisms that might involve fragmentation and recombination of metal containing groupings cannot be ruled out at this time. Once a species with the *E* geometry such as **G** is formed, the formation of 3 is assured since the five membered metallacyclic ring will be much more stable than a strained four membered metallacyclic ring. Finally, the decarbonylation of 3 to 4 is a simple process of CO loss followed by the formation of a second five membered metallacyclic ring by using the second carboxylate group of the alkyne. The *cis* insertion of alkynes into metal—metal bonds may resemble the *cis* insertion of alkynes into metal—carbon and metal—hydrogen bonds.[8]

Scheme 1

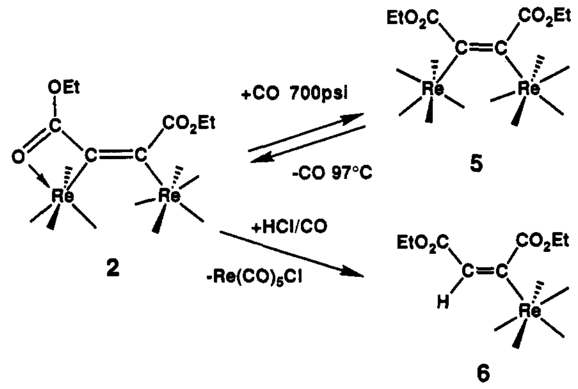


The reactions of 2 with CO and an HCl/CO mixture were investigated also. These results are summarized in Scheme 2. As expected, the reaction of 2 with CO leads to an opening of the four membered metallacyclic ring by cleavage of the Re–O bond and the addition of CO to the rhenium atom to form 5. This process is readily reversed by heating 5 to 97 °C. The reaction of 2 with HCl in the

---

(8) (a) Maitlis, P. M. *Acc. Chem. Res.* **1976**, *9*, 93. (b) Murray, T. F.; Norton, J. R. *J. Am. Chem. Soc.* **1979**, *101*, 4107. (c) Taylor, P.; Orchin, M. *J. Organomet. Chem.* **1971**, *26*, 389. (d) Zargarian, D.; Alper, H. *Organometallics* **1991**, *10*, 2914. (e) van der Zeijden, A. A. H.; Bosche, H. W.; Berke, H. *Organometallics* **1992**, *11*, 563. (f) Bianchini, C.; Meli, A.; Peruzzini, M.; Vizza, F. *Organometallics* **1990**, *9*, 1146. (g) de Vaal, P.; Dedieu, A. *J. Organomet. Chem.*, in press.

Scheme 2



presence of CO resulted in the cleavage of one of the rhenium groupings from the complex and the formation of **6** and Re(CO)$_5$Cl. Compound **6** is also obtained in high yield by addition of **2** to silica gel, but in this case the cleaved metal containing grouping could not be identified or recovered.

Acknowledgment. This research was supported by the Office of Basic Energy Science of U.S. Department of Energy.

Supplementary Material Available: The mass spectrum of **2** obtained from the reaction of a mixture of $Re_2(^{12}CO)_9(MeCN)$ and $Re_2(^{13}CO)_9(MeCN)$ with $EtO_2CC{\equiv}CCO_2Et$ and tables of interatomic distances, intramolecular bond angles, hydrogen atom positional parameters, and anisotropic thermal parameters for the structural analyses of each of compounds **2**–**6** (22 pages). Ordering information is given on any current masthead page.

OM9308452