Organic Reactions upon Dimetalated Olefins. Insertion Reactions at Both Ends of the Alkyne in the Dirhenium Complex $Re(CO)_4[\textit{trans}\text{-}\mu\text{-}HC{=}C(CO_2Me)]Re(CO)_4(NCMe)$

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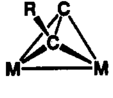
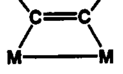
The reaction of $(OC)_4Re[\textit{trans}\text{-}\mu\text{-}HC{=}C(CO_2Me)Re(CO)_4(MeCN)$, **1**, with CS_2 yielded the new complex $(OC)_4Re[(E)\text{-}HC{=}C(CO_2Me)CS_2]Re(CO)_4$, **2**, in 78% yield by displacement of the NCMe ligand and the addition and insertion of a CS_2 molecule into one of the Re—C bonds in **1**. The CS_2 grouping is chelated to the rhenium atom through the sulfur atoms. Reaction of **2** with pyridine *N*-oxide yielded two new compounds $(OC)_4Re[OC(H)C(CO_2Me)C(S)S]Re(CO)_4$, **3a**, in 97% yield and an isomer $Re_2(CO)_8[\mu\text{-}SC(S)C(CO_2Me)C(H)O]$, **4a**, in 3% yield. The related sulfur derivatives $(OC)_4Re[SC(H)C(CO_2Me)CS_2]Re(CO)_4$, **3b**, 50% yield, and $Re_2(CO)_8[\mu\text{-}SC(S)C(CO_2Me)C(H)S]$, **4b**, 6% yield, were obtained from the reaction of **2** with ethylene sulfide at 25 °C for 3 h. Compounds **3a,b** will isomerize to **4a,b** in quantitative yields. Compounds **3a,b** were formed by the insertion of the heteroatom O or S into the Re—C bond in **2**. The isomers **4a,b** were formed by release of the coordinated carboxylate group in **3a,b** and the formation of a bridging coordination between the rhenium atoms by one of the sulfur atoms of the CS_2 grouping. Two products $(OC)_4Re[C_3H_2(CO_2Me)(CO_2Et)C(S)S]Re(CO)_4$, **5**, 5%, and $Re_2(CO)_8[SC(S)C(CHCHCO_2Et)C(OMe)O]$, **6**, 52%, were obtained from the reaction of **2** with ethyl diazoacetate. Compound **6** was also obtained from **5** in 28% yield by heating to 90 °C. Compounds **2**, **3b**, **4a**, **5**, and **6** were characterized by single crystal X-ray diffraction analyses. Crystal data: (for **2**) space group $C2/c$, $a = 18.651(3)$ Å, $b = 11.513(3)$ Å, $c = 17.952(2)$ Å, $\beta = 97.54(1)°$, $Z = 8$, 2320 reflections, $R = 0.028$; (for **3b**) space group = $P\bar{1}$, $a = 12.363(2)$ Å, $b = 13.880(3)$ Å, $c = 5.973(1)$ Å, $\alpha = 93.09(2)°$, $\beta = 101.06(1)°$, $\gamma = 77.81(1)°$, $Z = 2126$ reflections, $R = 0.020$; (for **4a**) space group = $P\bar{1}$, $a = 10.784(2)$ Å, $b = 12.337(2)$ Å, $c = 7.2712(9)$ Å, $\alpha = 95.30(1)°$, $\beta = 92.55(1)°$, $\gamma = 97.52(1)°$, $Z = 2$, 1906 reflections, $R = 0.023$; (for **5**) space group = $P\bar{1}$, $a = 13.184(2)$ Å, $b = 15.658(2)$ Å, $c = 6.5470(8)$ Å, $\alpha = 100.26(1)°$, $\beta = 101.31(1)°$, $\gamma = 65.16(1)°$, $Z = 2$, 2253 reflections, $R = 0.020$; (for **6**) space group = $Pbca$, $a = 14.800(3)$ Å, $b = 12.312(3)$ Å, $c = 26.308(4)$ Å, $Z = 8$, 2070 reflections, $R = 0.031$.

Introduction

Modifications of the reactivity of alkynes through complexation to metals have played a major role in the development of their organic chemistry.[1,2] Alkynes have been shown to coordinate to dimetal groups in two fundamentally different ways. The most common mode involves the use of the π orbitals, **A**, in which the alkyne is coordinated perpendicular to the metal–metal bond. The second type involves σ-type bonds to the metal atoms, **B**–**D**. In the absence of a metal–metal bond the structures **C** and **D** are frequently called dimetalated olefins.[3]



A



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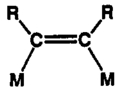
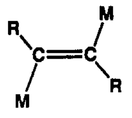


C



D

Although insertions of small molecules into metal–carbon σ bonds are an important and well studied class of reactions,[4] there have been very few reports of the functionalization of dimetalated olefins by this reaction.[5–7]

We have recently prepared the *trans*-dimetalated olefin complex $Re(CO)_4[\textit{trans}\text{-}\mu\text{-}HC{=}C(CO_2Me)]Re(CO)_5$, **E**, and converted it into the more reactive acetonitrile derivative $Re(CO)_4[\textit{trans}\text{-}\mu\text{-}HC{=}C(CO_2Me)]Re(CO)_4(NCMe)$, **1**, by treatment with Me_3NO in acetonitrile.[6a] We have shown that compound **1** reacts with alkynes[6a] and aryl isothiocyanates[6b] by displacement of the acetonitrile ligand and addition and insertion of the alkyne or

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[2] (a) Palyi, G.; Vardi, G.; Markó, L. *Stereochemistry of Organometallic and Inorganic Compounds*; Bernal, I., Ed.; Elsevier: Amsterdam, 1986; Vol. I, p 358. (b) Dickson, R. S. *Polyhedron* **1991**, *10*, 1995. (c) Adams, R. D.; Daran, J. C.; Jeannin, Y. *J. Cluster Sci.* **1992**, *3*, 1. (d) Sappa, E.; Tiripicchio, A.; Braunstein, P. *Chem. Rev.* **1983**, *83*, 203.

[3] Hoffman, D. M.; Hoffmann, R. *Organometallics* **1982**, *1*, 1299.

[4] See ref 1b, Chapter 6.

[5] (a) Lemke, F. R.; Szalda, D. J.; Bullock, R. M. *Organometallics* **1992**, *11*, 876. (b) Lemke, F. R.; Bullock, R. M. *Organometallics* **1992**, *11*, 4261. (c) Lemke, F. R.; Szalda, D. J.; Bullock, R. M. *J. Am. Chem. Soc.* **1991**, *113*, 8466.

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[7] Adams, R. D.; Chen, L.; Wu, W. *Organometallics* **1993**, *12*, 3812.

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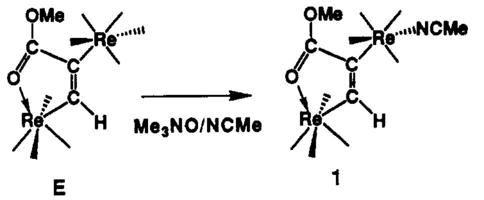

(1)

aryl isothiocyanate into the carboxylated substituted metal–carbon bond.

In this study we have investigated the reactions of 1 with a series of reagents: (1) CS_2 and (2) pyridine *N*-oxide, ethylene sulfide, or ethyl diazoacetate. In the first step, the CS_2 is inserted into the carboxylated substituted Re—C bond to yield the product $Re(CO)_4[(E)\text{-}HC{=}C(CO_2Me)CS_2]Re(CO)_4$, 2. In the second step an O or S atom is inserted into the hydrogen substituted metal—carbon bond. For comparison, the reaction of 2 with ethyl diazoacetate was also investigated. A preliminary report of this work has been published.[8]

Experimental Section

All reactions were carried out under an atmosphere of nitrogen. Hexane and heptane were freshly distilled over sodium before use. CH_2Cl_2 was freshly distilled from CaH_2. Me_3NO was dried by sublimation from $Me_3NO{\cdot}2H_2O$. CS_2, pyridine *N*-oxide (C_5H_5NO), ethylene sulfide, and ethyl diazoacetate (N_2CHCO_2Et) were purchased from Aldrich and were used without further purification. TLC separations were performed in air by using silica gel (60 Å, F_{254}) on plates (Whatman, 0.25 mm). IR spectra were recorded on a Nicolet 5DXB FT-IR spectrophotometer. ^{1}H NMR spectra were taken at 300 MHz on a Brüker AM-300 spectrometer. Mass spectra were run on a VG Model 70SQ mass spectrometer using electron impact ionization. Elemental analyses were performed by Desert Analytics, Tucson, AZ. ($OC_4Re[\textit{trans}\text{-}\mu\text{-}HC{=}C(CO_2Me)Re(CO)_4(MeCN)$, 1, was prepared by the previously reported procedure.[6a]

Preparation of $(OC)_4Re[(E)\text{-}HC{=}C(CO_2Me)CS_2]Re(CO)_4$, 2. A 100.0-mg amount (0.139 mmol) of 1 and a 100.0-μL amount (1.660 mmol) of CS_2 were dissolved in 200 mL of CH_2Cl_2. The solution was heated to reflux for 4 h. After cooling, the solvent was evaporated under vacuum, and the residue was separated by TLC using a hexane/CH_2Cl_2 2/1 solvent mixture to give 82.8 mg of orange $(OC)_4Re[(E)\text{-}HC{=}C(CO_2Me)CS_2]Re(CO)_4$, 2, in 78% yield. IR ($\nu_{CO}$ in hexane, cm^{-1}) for 2: 2098 (w), 2008 (s), 1995 (m), 1959 (s), 1582 (w). ^{1}H NMR (δ in $CDCl_3$, ppm) for 2: 11.65 (s, 1H, C*H*), 4.09 (s, 3H, O*Me*). The mass spectrum for 2 showed parent ion at *m/e* = 758 (for ^{187}Re) and ions corresponding to the loss of eight carbonyl ligands. Anal. Calcd (found) for 2 ($Re_2S_2O_{10}C_{13}H_4$): C, 20.64 (20.44); H, 0.53 (0.44).

Reaction of 2 with C_5H_5NO. A 20.0-mg (0.026 mmol) amount of 2 was dissolved in 30 mL of CH_2Cl_2 and was allowed to react with a 3.0-mg (0.032 mmol) amount of C_5H_5NO at 25 °C for 20 min. The solvent was evaporated at 25 °C, and the residue was separated by TLC using a hexane/CH_2Cl_2 1/1 solvent mixture to give 19.8 mg of yellow $(OC)_4Re[OC(H)C(CO_2Me)C(S)S]Re(CO)_4$, 3a, 97% yield, and 0.6 mg of yellow $Re_2(CO)_8[\mu\text{-}SC(S)C(CO_2Me)C(H)O]$, 4a, in 3% yield. IR ($\nu_{CO}$ in hexane, cm^{-1}) for 3a: 2120 (w), 2101 (w), 2018 (s), 2002 (s), 1991 (s), 1958 (s), 1605 (m). ^{1}H NMR (δ in $CDCl_3$, ppm) for 3a: 9.64 (s, 1H, C*H*), 3.92 (s, 3H, O*Me*). Anal. Calcd (found) for 3a ($Re_2S_2O_{11}C_{13}H_4$): C, 20.21 (20.90); H, 0.52 (0.82). The mass spectrum of 3a showed a parent ion at *m/e* = 774 (for ^{187}Re) and ions corresponding to the loss of six carbonyl ligands. IR (ν_{CO} in hexane, cm^{-1}) for 4a: 2118 (w), 2103 (w), 2025 (s), 2010 (s), 2002 (s), 1997 (s), 1938 (m), 1959 (s), 1726 (w), 1708 (w), 1552 (w), 1525 (w). ^{1}H NMR (δ in $CDCl_3$, ppm) for 4a: 8.92 (s, 1H, C*H*), 3.77 (s, 3H, O*Me*). Anal. Calcd (found) for 4a ($Re_2S_2O_{11}C_{13}H_4$): C, 20.21 (20.14); H, 0.52 (0.54).

Reaction of 2 with Me_3NO. A solution containing a 50.0-mg (0.066-mmol) amount of 2 dissolved in 50 mL of CH_2Cl_2 was cooled to −77 °C in a EtOH/dry ice slush bath. A 4.9-mg (0.066-mmol) amount of Me_3NO in 5 mL of CH_2Cl_2 was added to the above solution during a period of 5 min, while the temperature of the slush bath was maintained at −77 °C. The bath was then allowed to warm slowly to 25 °C over a period of 40 min. The solvent was removed, and the residue was separated by TLC using a hexane/CH_2Cl_2 2/1 solvent mixture to give the following compounds in order of elution: 25.7 mg of starting material; 11.6 mg of yellow $(OC)_4Re[OC(H)C(CO_2Me)C(S)S]Re(CO)_4$, 3a, in 23% yield; 0.5 mg of yellow $Re_2(CO)_8[\mu\text{-}SC(S)C(CO_2Me)C(H)O]$, 4a, in 1% yield.

Transformations between 3a and 4a. A 5.0-mg amount of 3a was dissolved in 0.8 mL of $CDCl_3$ and placed in a 5-mm NMR tube at 25 °C. The conversion to 4a was monitored by ^{1}H NMR spectroscopy. After 5 days the ratio of 3a/4a was 1/30. A 3.0-mg amount of 4a was dissolved in 0.8 mL of $CDCl_3$ in a 5-mm NMR tube. After 5 days, there was no evidence for the formation of 3a.

Reaction of 2 with C_2H_4S. A 20.0-mg amount (0.026 mmol) of 2 and a 20.0-μL amount (0.336 mmol) of C_2H_4S were dissolved in 20 mL of hexane and stirred at 25 °C for 3 h. The solvent was then removed at 25 °C, and the residue was separated by TLC using a hexane/CH_2Cl_2 2/1 solvent mixture to give the following compounds in order of elution: 2.0 mg of starting material; 10.2 mg of orange $(OC)_4Re[SC(H)C(CO_2Me)CS_2]Re(CO)_4$, 3b, in 50% yield; 1.3 mg of red $Re_2(CO)_8[\mu\text{-}SC(S)C(CO_2Me)C(H)S]$, 4b, in 6% yield. IR ($\nu_{CO}$ in hexane, cm^{-1}) for 3b: 2114 (w), 2101 (w), 2019 (s), 2004 (s), 1993 (m), 1963 (s), 1958 (m), 1585 (w). ^{1}H NMR (δ in C_6D_6, ppm) for 3b: 1017 (s, 1H, C*H*), 2.82 (s, 3H, O*Me*). Anal. Calcd (found) for 3b ($Re_2S_3O_{10}C_{13}H_4$): C, 19.80 (19.98); H, 0.51 (0.67). IR (ν_{CO} in hexane, cm^{-1}) for 4b: 2115 (w), 2101 (w), 2024 (s), 2013 (s), 1999 (m), 1977 (w), 1963 (s), 1728 (w), 1718 (w). ^{1}H NMR (δ in C_6D_6, ppm) for 4b: 9.23 (s, 1H, C*H*), 3.29 (s, 3H, O*Me*). Mass spectrum for 4b showed the parent ion at *m/e* = 790 (for ^{187}Re) and ions corresponding to the loss of eight carbonyl ligands.

Conversion of 3b into 4b. A 4.0-mg amount of 3b was dissolved in 1.0 mL of C_6D_6 and placed in a 5-mm NMR tube. The conversion of 3b to 4b was performed at 53 °C and followed by ^{1}H NMR spectroscopy. After 42 h, 3b was converted completely into 4b. Note: The isomerizations of 3a to 4a and 3b to 4b appear to occur faster during the process of chromatography. Thus, to obtain the best yields of 3a and 3b, the separation should be performed as quickly as possible.

Reaction of 2 with Ethyl Diazoacetate. A 10.0-mg amount (0.013 mmol) of 2 and a 1.5-μL amount (0.013 mmol) of ethyl diazoacetate were dissolved in 20 mL of hexane. The solution was stirred at 25 °C for 12 h. The solvent was then evaporated at 25 °C, and the residue was separated by TLC using a hexane/CH_2Cl_2 2/1 solvent mixture to give the following compounds in order of elution: 1.4 mg of unreacted starting material; 0.5 mg of pale yellow $(OC)_4Re[C_3H_2(CO_2Me)(CO_2Et)C(S)S]Re(CO)_4$, 5, 5% yield; 5.7 mg of bright yellow $Re_2(CO)_8[SC(S)C(CHCHCO_2Et)C(OMe)O]$, 6, 52% yield. IR spectra (ν_{CO} in hexane, cm^{-1}) for 5: 2108 (w), 2198 (m), 2013 (s), 1999 (m), 1991 (s, br), 1963 (s), 1948 (s), 1728 (w, br), 1623 (w, br). ^{1}H NMR (δ in $CDCl_3$, ppm) for 5: 4.18 (dq, $^2J_{H\text{-}H}$ = 10.2 Hz, $^3J_{H\text{-}H}$ = 7.2 Hz, 1H, CH*H*), 4.11 (dq, $^2J_{H\text{-}H}$ = 10.2 Hz, $^3J_{H\text{-}H}$ = 7.2 Hz, 1H, C*H*H), 4.03 (s, 3H, OC*H*$_3$), 3.99 (d, $^3J_{H\text{-}H}$ = 12.0 Hz, 1H, C*H*), 2.58 (d, $^3J_{H\text{-}H}$ = 12.0 Hz, 1H, C*H*), 1.30 (t, $^3J_{H\text{-}H}$ = 7.2 Hz, 3H, C*H*$_3$). Anal. Calcd (found) for 5: C, 24.23 (24.43); H, 1.20 (1.11). IR spectra (ν_{CO} in hexane, cm^{-1}) for 6: 2118 (w), 2102 (m), 2024 (s), 2008 (s), 1994 (s), 1969 (s), 1957 (s), 1723 (w, br), 1715 (w, br), 1620 (w, br), 1565 (w, br). ^{1}H NMR (δ in $CDCl_3$, ppm) for 6: 7.75 (d, $^3J_{H\text{-}H}$ = 16.0 Hz, 1H, C*H*), 6.43 (d, $^3J_{H\text{-}H}$ = 16.0 Hz, 1H, C*H*), 4.19 (q, $^3J_{H\text{-}H}$ = 7.1 Hz, 2H, C*H*$_2$), 3.88 (s, 3H, O*Me*), 1.28 (t, $^3J_{H\text{-}H}$ = 7.1 Hz, 3H, C*H*$_3$). Anal. Calcd (found) for 6: C, 24.23 (23.97); H, 1.20 (1.21).

Conversion of 5 to 6. A 10.0-mg amount (0.012 mmol) of 5

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[8] Adams, R. D.; Chen, L.; Wu, W. *Angew. Chem., Int. Ed. Engl.*, in press.

Table 1. Crystal Data for Compounds 2–6

	2	3b	4a	5	6
formula	$Re_2S_2O_{10}C_{13}H_4$	$Re_2S_3O_{10}C_{13}H_4$	$Re_2S_2O_{11}C_{13}H_4$	$Re_2S_2O_{12}C_{17}H_{10}$	$Re_2S_2O_{12}C_{17}H_{10}$
fw	756.70	788.76	772.70	842.79	842.79
cryst syst	monoclinic	triclinic	triclinic	triclinic	orthorhombic
lattice params					
a (Å)	18.651(3)	12.363(2)	10.784(2)	13.184(2)	14.800(3)
b (Å)	11.513(3)	13.880(3)	12.337(2)	15.658(2)	12.312(3)
c (Å)	17.952(2)	5.973(1)	7.2712(9)	6.5470(8)	26.308(4)
α (deg)		93.09(2)	95.30(1)	100.26(1)	
β (deg)	97.54(1)	101.06(1)	92.55(1)	101.31(1)	
γ (deg)		77.81(1)	97.52(1)	65.16(1)	
V (Å^3)	3821(1)	983.1(6)	953.4(4)	1195.7(6)	4794(2)
space group	$C2/c$ (No. 15)	$P\bar{1}$ (No. 2)	$P\bar{1}$ (No. 2)	$P\bar{1}$ (No. 2)	$Pbca$ (No. 61)
Z value	8	2	2	2	8
ρ_{calc} (g/cm^3)	2.63	2.66	2.69	2.34	2.34
μ(Mo Kα) (cm^{-1})	130.89	128.24	131.23	104.76	104.52
temp (°C)	20	20	20	20	20
$2\theta_{max}$ (deg)	46.0	45.0	43.0	44.0	45.0
no. obs reflns ($I>3\sigma$)	2320	2126	1906	2253	2070
residuals: R; R_w	0.028; 0.032	0.020; 0.022	0.023; 0.028	0.020; 0.022	0.031; 0.029

was dissolved in 30 mL of heptane and then heated to 90 °C for 1 h. After cooling to 25 °C, the solvent was evaporated to dryness under vacuum, and the residue was separated by TLC using a hexane/CH_2Cl_2 1/1 solvent mixture to give 1.1 mg of unreacted starting material and 2.8 mg of **6** in 28% yield.

Crystallographic Analyses. Orange crystals of **2** were obtained by slow evaporation of solvent from a 2/1 hexane/CH_2Cl_2 solvent mixture at 25 °C. Orange crystals of **3b** were obtained by slow evaporation of the solvent from a 2/1 hexane/CH_2Cl_2 solvent mixture at −14 °C. Crystals of **4a**, **5**, and **6** were grown from solutions in hexane/CH_2Cl_2 2/1 solvent mixtures by slow evaporation of the solvent at −3 °C. All crystals used for diffraction measurements were mounted in thin-walled glass capillaries. Diffraction measurements were made on a Rigaku AFC6S automatic diffractometer by using graphite-monochromated Mo Kα radiation. Unit cells were determined from 15 randomly selected reflections obtained by using the AFC6 automatic search, center, index, and least-squares routines. Crystal data, data collection parameters, and results of the analyses are listed in Table 1. 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.[9a] Anomalous dispersion corrections were applied to all non-hydrogen atoms.[9b] Full matrix least-squares refinements minimized the function $\sum_{hkl}w(|F_o| - |F_c|)^2$, where $w = 1/\sigma(F)^2$, $\sigma(F) = \sigma(F_o^2)/2F_o$, and $\sigma(F_o^2) = [\sigma(I_{raw})^2 + (0.02I_{net})^2]^{1/2}/Lp$. Lorentz-polarization ($Lp$) and empirical absorption corrections were applied in each analysis. All structures were solved by a combination of direct methods and difference Fourier syntheses. For each structure the scattering contributions of calculated hydrogen atoms were added to the structure factor calculations, but their positions were not refined.

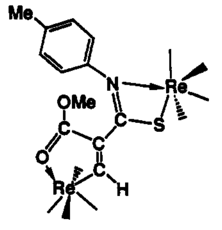
Compound **2** crystallized in the monoclinic crystal system. The patterns of systematic absences observed during the collection of the intensity data were consistent with either of the space groups $C2/c$ or Cc. The centrosymmetric space group $C2/c$ was selected initially and was confirmed by the successful solution and refinement of the structure. All non-hydrogen atoms were refined using anisotropic thermal parameters. The alkenyl hydrogen atom H(3) was located and refined using an isotropic thermal parameter. The positions of the hydrogen atoms on the methyl group were calculated by assuming an idealized geometry.

Compounds **3b**, **4a**, and **5** crystallized in the triclinic crystal system. The centrosymmetric space group $P\bar{1}$ was assumed and confirmed by the successful solution and refinement of the structures. For **3b** all non-hydrogen atoms were refined using anisotropic thermal parameters and all hydrogen atoms were refined using isotropic thermal parameters. For **4a** all non-hydrogen atoms were refined with anisotropic thermal parameters. The alkenyl hydrogen atom H(3) was located and refined in the analysis using an isotropic thermal parameter. The positions of the hydrogen atoms on the methyl group were calculated by assuming an idealized geometry. For **5** all non-hydrogen atoms were refined with anisotropic thermal parameters. The cyclopropyl hydrogen atoms H(3) and H(6) were located and refined in the analysis using isotropic thermal parameters. The positions of the hydrogen atoms on the methyl and ethyl groups were calculated by assuming idealized geometries.

Compound **6** crystallized in the orthorhombic crystal system. The patterns of systematic absences observed during the collection of the intensity data identified the space group uniquely as $Pbca$. All non-hydrogen atoms were refined with anisotropic thermal parameters. Both alkenyl hydrogen atoms H(3) and H(6) were located and refined on their positional parameters using fixed isotropic thermal parameters. The positions of the hydrogen atoms on the methyl and ethyl groups were calculated by assuming idealized geometries.

Results

Compound **1** reacts with CS_2 in CH_2Cl_2 at reflux to form the new compound **2** in 78% yield. Compound **2** was characterized by IR, ^1H NMR, and single crystal X-ray diffraction analyses. An ORTEP diagram of its molecular structure is shown in Figure 1. A listing of the final atomic positional parameters is given in Table 2. The molecule contains two rhenium tetracarbonyl groupings that are linked by the HC=C(CO_2Me)CS_2 ligand that was formed by the insertion of a CS_2 molecule into the carboxylate substituted metal—carbon bond of **1**. This molecule is very similar to the compounds Re(CO)$_4$[(E)-HC=C(CO_2Me)C=N(tolyl)S]Re(CO)$_4$, **7**,[6b] and (OC)$_4$Re[μ-C(H)=C(CO_2Me)C(H)=C(CO_2Me)]Re(CO)$_5$, **8**,[6a] formed by the



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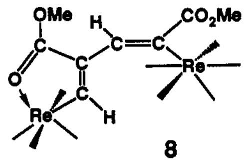

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(9) (a) *International Tables for X-ray Crystallography*; Kynoch Press: Birmingham, England, 1975; Vol. IV, Table 2.2B, pp 99–101. (b) *Ibid.*, Table 2.3.1, pp 149–150.

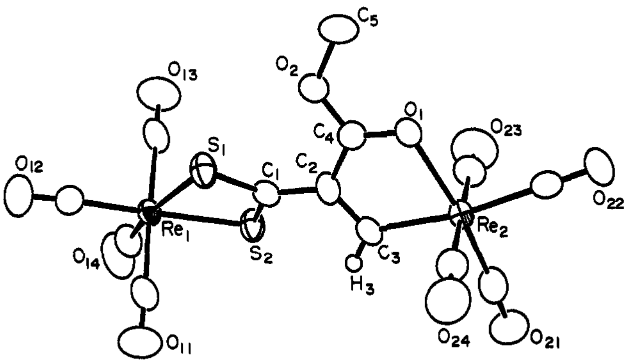

Figure 1. ORTEP diagram of Re(CO)$_4$[(*E*)-HC=C(CO$_2$Me)-CS$_2$]Re(CO)$_4$, **2**, showing 50% probability thermal ellipsoids. Selected interatomic distances (Å) are Re(1)–S(1) = 2.496(2), Re(1)–S(2) = 2.495(2), Re(2)–C(3) = 2.125(9), Re(2)–O(1) = 2.201(5), C(1)–C(2) = 1.47(1), C(2)–C(3) = 1.35(1), C(1)–S(1) = 1.686(8), C(1)–S(2) = 1.696(9), C(2)–C(4) = 1.45(1).

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

atom	*x*	*y*	*z*	*B*(eq) (Å^2)
Re(1)	0.484685(19)	0.23097(03)	0.088823(17)	2.56(2)
Re(2)	0.667358(20)	0.28567(03)	−0.246749(17)	2.76(2)
S(1)	0.55977(14)	0.10836(20)	0.01442(12)	3.4(1)
S(2)	0.53820(14)	0.35081(20)	−0.00569(12)	3.5(1)
O(1)	0.7125(03)	0.1601(05)	−0.1607(03)	3.0(3)
O(2)	0.7038(03)	0.0912(06)	−0.0459(03)	3.8(3)
O(11)	0.3457(05)	0.1969(10)	−0.0260(04)	8.0(5)
O(12)	0.4222(04)	0.0453(07)	0.1849(04)	5.5(4)
O(13)	0.6246(05)	0.2618(09)	0.2018(05)	7.5(5)
O(14)	0.4112(05)	0.4273(07)	0.1649(04)	6.6(5)
O(21)	0.5872(04)	0.4707(07)	−0.3473(04)	5.9(4)
O(22)	0.7813(04)	0.2453(07)	−0.3569(04)	5.1(4)
O(23)	0.7671(05)	0.4785(08)	−0.1660(05)	7.3(5)
O(24)	0.5637(05)	0.1026(07)	−0.3325(04)	6.0(4)
C(1)	0.5771(05)	0.2283(07)	−0.0341(04)	2.6(4)
C(2)	0.6184(05)	0.2304(07)	−0.0986(04)	2.9(4)
C(3)	0.6010(05)	0.2984(08)	−0.1594(05)	3.0(4)
C(4)	0.6812(05)	0.1577(07)	−0.1036(04)	3.0(4)
C(5)	0.7680(06)	0.0223(10)	−0.0497(05)	5.2(6)
C(11)	0.3972(06)	0.2069(10)	0.0144(05)	4.4(5)
C(12)	0.4472(05)	0.1152(09)	0.1505(05)	3.4(4)
C(13)	0.5747(06)	0.2521(09)	0.1607(05)	4.1(5)
C(14)	0.4377(06)	0.3536(09)	0.1364(05)	3.9(4)
C(21)	0.6186(06)	0.3999(09)	−0.3102(05)	4.1(5)
C(22)	0.7398(05)	0.2603(08)	−0.3157(05)	3.6(4)
C(23)	0.7314(06)	0.4087(09)	−0.1945(05)	4.1(5)
C(24)	0.6024(05)	0.1672(09)	−0.2994(05)	3.8(4)

reactions of **1** with (tolyl)N=C=S and HC≡CCO$_2$Me, respectively. Compound **2** contains a $\overline{\mathrm{ReCH{=}CC{=}O}}$ ring formed by the coordination of the ketonic oxygen atom of the carboxylate group to the rhenium atom, Re(2). Compounds **1**, **7**, and **8** also have similar $\overline{\mathrm{ReCH{=}CC{=}O}}$ rings. The C(2)—C(3) bond is double, 1.35(1) Å, while the C—C bond to the CS$_2$ group is single C(1)—C(2) = 1.47(1) Å. The CS$_2$ grouping is chelated to the second rhenium atom and both sulfur atoms are bonded equally to the rhenium and carbon atoms, Re(1)—S(1) = 2.496(2) Å, Re(1)—S(2) = 2.495(2) Å, C(1)—S(1) = 1.686(8) Å, and C(1)—S(2) = 1.696(9) Å. Similar Re—S and C—S distances were found for the dithioformato ligand in the complex Re(CO)$_2$(PPh$_3$)$_2$(S$_2$CH).[10] The alkenyl hydrogen atom H(3) exhibits a deshielded resonance, δ = 11.65 ppm, similar to that found in compounds **1**, **7**, and **8**.

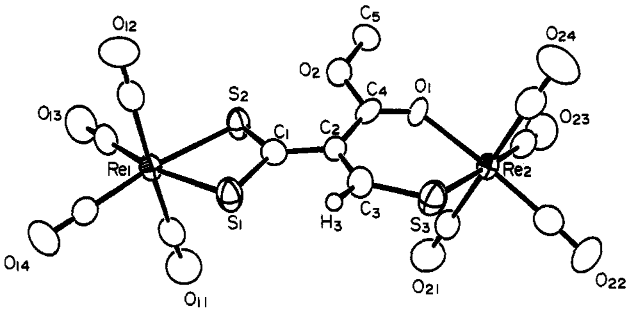

Figure 2. ORTEP diagram of Re(CO)$_4$[SC(H)C(CO$_2$Me)-CS$_2$]Re(CO)$_4$, **3b**, showing 50% probability thermal ellipsoids. Selected intramolecular bond distances (Å) and angles (deg) are Re(1)–S(1) = 2.495(2), Re(1)–S(2) = 2.481(2), Re(2)–S(3) = 2.452(2), Re(2)–O(1) = 2.163(5), C(1)–C(2) = 1.46(1), C(2)–C(3) = 1.38(1), C(2)–C(4) = 1.47(1), C(1)–S(1) = 1.713(7), C(1)–S(2) = 1.702(7), C(3)–S(3) = 1.676(8), C(1)–C(2)–C(3) = 117.1(6), C(1)–C(2)–C(4) = 122.1(6), C(2)–C(3)–S(3) = 133.8(6), C(3)–C(2)–C(4) = 120.8(6).

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

atom	*x*	*y*	*z*	*B*(eq) (Å^2)
Re(1)	0.29838(03)	0.22233(02)	0.79955(05)	2.62(2)
Re(2)	0.24294(03)	−0.33183(02)	0.39322(05)	2.80(2)
S(1)	0.32237(19)	0.09698(15)	0.4880(04)	3.7(1)
S(2)	0.20496(18)	0.08455(15)	0.8425(03)	3.4(1)
S(3)	0.29268(19)	−0.20789(15)	0.1760(04)	3.8(1)
O(1)	0.1491(04)	−0.2068(03)	0.5540(09)	3.0(3)
O(2)	0.0837(04)	−0.0647(04)	0.7069(09)	3.6(3)
O(11)	0.5199(06)	0.1046(05)	1.0944(13)	6.4(4)
O(12)	0.0718(05)	0.3311(05)	0.5097(11)	5.3(4)
O(13)	0.2406(06)	0.3531(05)	1.2079(10)	5.3(4)
O(14)	0.4264(05)	0.3715(04)	0.6635(10)	4.6(3)
O(21)	0.4546(06)	−0.3202(05)	0.7683(12)	6.1(4)
O(22)	0.3835(05)	−0.4960(05)	0.1433(12)	5.9(4)
O(23)	0.1795(06)	−0.4803(05)	0.6850(12)	5.7(4)
O(24)	0.0300(06)	−0.3499(06)	0.0287(11)	6.5(4)
C(1)	0.2470(06)	0.0287(05)	0.6039(12)	2.9(4)
C(2)	0.2285(06)	−0.0661(05)	0.5061(12)	2.4(3)
C(3)	0.2787(07)	−0.1008(05)	0.3219(13)	3.0(4)
C(4)	0.1550(06)	−0.1206(05)	0.5896(12)	2.8(4)
C(5)	0.0079(08)	−0.1116(07)	0.799(02)	4.3(5)
C(11)	0.4396(08)	0.1473(06)	0.9891(16)	4.2(5)
C(12)	0.1544(07)	0.2925(06)	0.6104(14)	3.3(4)
C(13)	0.2621(07)	0.3045(06)	1.0574(14)	3.4(4)
C(14)	0.3799(06)	0.3166(06)	0.7141(14)	3.3(4)
C(21)	0.3782(07)	−0.3220(06)	0.6311(14)	3.5(4)
C(22)	0.3299(07)	−0.4355(06)	0.2403(15)	4.0(5)
C(23)	0.2031(07)	−0.4268(06)	0.5764(15)	3.7(4)
C(24)	0.1070(08)	−0.3414(06)	0.1604(15)	4.0(5)

Compound **2** reacts with the heteroatom donors pyridine *N*-oxide, Me$_3$NO, and ethylene sulfide at 25 °C by transfer and insertion of the heteroatom, O or S, into the metal—carbon bond of the alkenyl group to yield the compounds **3a,b**, respectively. The 97% yield of **3a** obtained from pyridine *N*-oxide is significantly better than that from Me$_3$NO, 23%. Compounds **3a,b** were characterized by IR and ^{1}H NMR spectroscopy and by mass spectrometry. Compound **3b** was also characterized crystallographically. An ORTEP diagram of the molecular structure of **3b** is shown in Figure 2, and a listing of the final atomic positional parameters is given in Table 3. This complex is very similar to that of **2** except that a sulfur atom has been inserted between the rhenium atom Re(2) and alkenyl carbon C(3), Re(2)–S(3) = 2.452(2) Å, C(3)–S(3) = 1.676(8) Å. The carbon–sulfur distance is significantly shorter than that of carbon–sulfur single bonds which are about 1.80 Å. It is even shorter than the carbon–sulfur bonds involving the CS$_2$ grouping in this molecule, C(1)–S(1) = 1.713(7), C(1)–S(2) = 1.702(7), and in **2** for which substantial multiple bonding character can be anticipated. Thus, we feel that there is considerable

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[10] Albano, W. G.; Bellon, P. L.; Ciani, G. *J. Organomet. Chem.* 1971, *31*, 75.

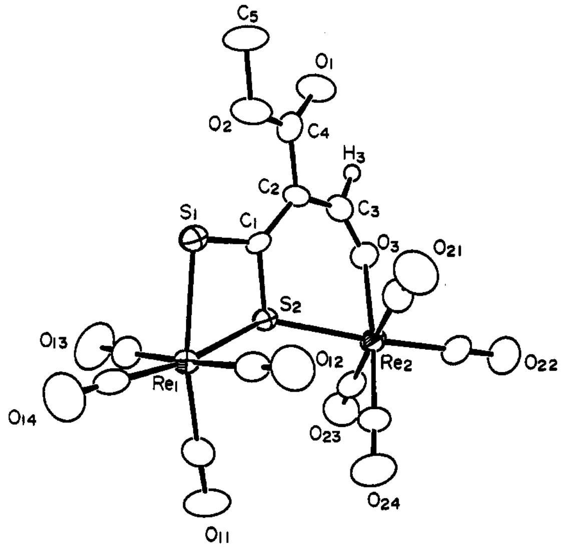


Figure 3. ORTEP diagram of $Re_2(CO)_8[\mu\text{-}SC(S)C(CO_2Me)C(H)O]$, **4a**, showing 50% probability thermal ellipsoids. Selected intramolecular bond distances (Å) and angles (deg) are Re(1)–S(1) = 2.502(3), Re(1)–S(2) = 2.474(2), Re(2)–S(2) = 2.456(2), Re(2)–O(3) = 2.165(7), C(1)–C(2) = 1.41(1), C(2)–C(3) = 1.42(1), C(2)–C(4) = 1.48(1), C(1)–S(1) = 1.705(9), C(1)–S(2) = 1.76(1), C(3)–O(3) = 1.25(1), C(1)–C(2)–C(3) = 122.1(9), C(1)–C(2)–C(4) = 124.5(8), C(3)–C(2)–C(4) = 112.7(8), Re(1)–S(2)–Re(2) = 127.0(1).

multiple bonding character between atoms C(3) and S(3). The $HC{=}C(CO_2Me)CS_2$ grouping is very similar to that found in **2**, although the C(2)—C(3) bond is slightly longer, 1.38(1) Å. As expected, the alkenyl hydrogen atom H(3) both in **3a** and **3b** exhibits a strongly deshielded resonance, δ = 9.64 and 10.17 ppm, respectively.

Very small amounts of isomers **4a**,**b** were also obtained in the syntheses of **3a**,**b**. Compounds **4a**,**b** are actually the more stable isomeric forms of the molecules and both **3a** and **3b** will convert to **4a**,**b** in essentially quantitative yields. The rate of isomerization is, of course, accelerated by mild heating. Compound **4a** was characterized crystallographically, and an ORTEP diagram of its molecular structure is shown in Figure 3. A listing of the final atomic positional parameters is given in Table 4. In this complex the carboxylate group is not coordinated to any metal atom. Instead, one of the sulfur atoms, S(2), of the CS_2 grouping has adopted a bridging position between the two metal atoms, Re(1)–S(2) = 2.474(2) Å and Re(2)–S(2) = 2.456(2) Å. The associated carbon–sulfur bond to the bridging sulfur atom, C(1)–S(2) = 1.76(1) Å is much longer and much closer to the single bond value than the other, C(1)–S(1) = 1.705(9) Å. The added heteroatom in **4a** is oxygen and the C–O distance is very short, C(3)–O(3) = 1.25(1) Å, and typical of a C–O double bond. The adjacent carbon–carbon bond is much longer than that in **2**, C(2)–C(3) = 1.42(1) Å, but should still have considerable double bond character on this basis. Accordingly, it is believed that there is considerable delocalization across the entire C(2)–C(3)–O(3) triatomic unit. The alkenyl hydrogen resonances in both **4a** and **4b** are strongly deshielded, δ = 8.92 and 9.23 ppm, respectively.

Two very interesting isomeric products were obtained from the reaction of compound **2** with ethyl diazoacetate, $N_2C(H)CO_2Et$, at 25 °C. Both products were characterized crystallographically and were identified as $(OC)_4Re[C_3H_2(CO_2Me)(CO_2Et)C(S)S]Re(CO)_4$, **5**, and $Re_2(CO)_8[SC(S)C(CHCHCO_2Et)C(OMe)O]$, **6**. Compound **6** is by far the major product, 52% vs 5% yield, and also the more stable isomer since compound **5** is converted to **6** when heated to 90 °C. Although the yield of **5** to **6** is low, 28%, the reverse reaction does not occur. An ORTEP diagram of the molecular structure of **5** is shown in Figure 4. A listing of the final atomic positional parameters is given in Table 5. Compound **5** is very similar to **2** except that a $C(H)CO_2Et$ grouping derived from $N_2C(H)CO_2Et$ has been added across the C–C double bond. This has resulted in the formation of a substituted cyclopropane ring involving the atoms C(2), C(3), and C(6). The rhenium–carbon single bond is significantly longer than

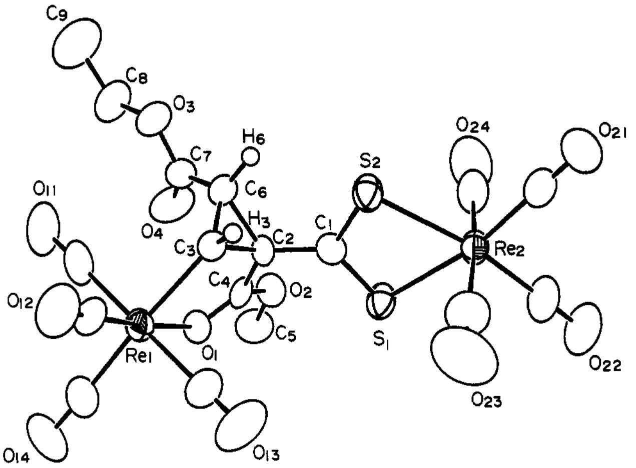


Figure 4. ORTEP diagram of $(OC)_4Re[C_3H_2(CO_2Me)(CO_2Et)C(S)S]Re(CO)_4$, **5**, showing 50% probability thermal ellipsoids. Selected interatomic distances (Å) and angles (deg) are Re(2)–S(1) = 2.500(2), Re(2)–S(2) = 2.494(2), Re(1)–C(3) = 2.189(7), Re(1)–O(1) = 2.206(5), C(1)–C(2) = 1.460(9), C(2)–C(3) = 1.542(9), C(2)–C(6) = 1.534(9), C(2)–C(4) = 1.498(9), C(1)–S(1) = 1.691(7), C(1)–S(2) = 1.691(7), C(3)–C(6) = 1.49(1), C(1)–C(2)–C(3) = 120.7(5), C(1)–C(2)–C(6) = 119.5(6), C(1)–C(2)–C(4) = 118.3(5), C(3)–C(2)–C(4) = 110.4(5), Re(1)–C(3)–C(2) = 112.0(4), Re(1)–C(3)–C(6) = 128.3(5), C(2)–C(3)–C(6) = 60.8(4), C(2)–C(6)–C(3) = 61.3(4), C(3)–C(2)–C(4) = 110.4(5), C(3)–C(2)–C(6) = 58.0(4).

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

atom	*x*	*y*	*z*	*B*(eq) (Å^2)
Re(1)	0.44533(03)	0.23118(03)	1.00171(05)	2.16(2)
Re(2)	0.08054(03)	0.30798(03)	1.19038(05)	2.46(2)
S(1)	0.3837(02)	0.0579(02)	1.1483(04)	2.9(1)
S(2)	0.2154(02)	0.1933(02)	1.0199(03)	2.3(1)
O(1)	0.0451(07)	−0.1245(07)	1.3842(12)	4.9(4)
O(2)	0.2511(07)	−0.0884(06)	1.3768(11)	4.4(4)
O(3)	−0.0277(05)	0.1466(06)	1.1794(09)	2.9(3)
O(11)	0.4409(08)	0.4441(07)	0.8138(11)	5.0(4)
O(12)	0.4756(08)	0.3514(08)	1.4006(12)	5.5(4)
O(13)	0.4155(09)	0.0937(08)	0.6140(12)	6.2(5)
O(14)	0.7326(07)	0.2418(07)	1.0091(12)	5.4(4)
O(21)	0.2035(08)	0.2824(08)	1.5780(12)	5.2(4)
O(22)	−0.1200(07)	0.4267(07)	1.3793(13)	5.5(4)
O(23)	−0.0258(08)	0.3618(08)	0.8084(12)	5.2(4)
O(24)	0.2581(07)	0.5215(07)	1.1984(14)	6.0(5)
C(1)	0.2327(08)	0.0846(07)	1.1553(12)	2.1(4)
C(2)	0.1299(08)	0.0294(08)	1.2369(13)	2.4(4)
C(3)	0.0075(09)	0.0581(09)	1.2176(13)	2.8(4)
C(4)	0.1344(09)	−0.0694(08)	1.3361(14)	2.9(4)
C(5)	0.2637(11)	−0.1774(11)	1.4864(19)	5.4(6)
C(11)	0.4471(09)	0.3661(10)	0.8854(13)	3.0(4)
C(12)	0.4642(09)	0.3100(09)	1.2564(16)	3.1(5)
C(13)	0.4257(09)	0.1447(10)	0.7534(17)	3.5(5)
C(14)	0.6255(11)	0.2350(08)	1.0051(13)	2.9(5)
C(21)	0.1580(09)	0.2856(09)	1.4375(17)	3.4(5)
C(22)	−0.0468(10)	0.3829(09)	1.3107(16)	3.5(5)
C(23)	0.0097(09)	0.3393(09)	0.9441(18)	3.5(5)
C(24)	0.1886(09)	0.4418(09)	1.1949(16)	3.5(5)

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

atom	*x*	*y*	*z*	*B*(eq) (Å^2)
Re(1)	0.42595(02)	0.31228(02)	0.97768(04)	3.27(2)
Re(2)	0.17470(02)	0.036703(19)	0.28247(04)	3.26(2)
S(1)	0.15453(17)	0.14342(13)	0.6185(03)	4.0(1)
S(2)	0.25058(17)	0.15808(14)	0.2814(03)	4.1(1)
O(1)	0.2507(04)	0.3396(03)	1.0058(07)	3.4(3)
O(2)	0.0858(04)	0.3399(03)	0.8434(07)	3.6(3)
O(3)	0.2173(04)	0.5017(03)	0.4588(08)	4.5(3)
O(4)	0.1470(05)	0.4897(04)	0.7277(09)	6.1(4)
O(11)	0.3763(05)	0.5199(05)	0.9197(11)	7.5(5)
O(12)	0.6636(05)	0.2612(04)	0.8845(10)	6.0(4)
O(13)	0.5028(06)	0.0971(05)	1.0065(12)	7.9(5)
O(14)	0.5016(06)	0.3577(06)	1.4508(10)	8.2(6)
O(21)	0.2216(06)	−0.0671(04)	−0.1546(09)	6.6(5)
O(22)	0.0726(06)	−0.0956(04)	0.3671(11)	7.2(5)
O(23)	0.4092(06)	−0.0939(05)	0.4898(11)	9.3(5)
O(24)	−0.0625(06)	0.1828(05)	0.1148(12)	8.6(5)
C(1)	0.2131(05)	0.2030(05)	0.5231(10)	3.1(4)
C(2)	0.2376(05)	0.2819(04)	0.6422(10)	2.6(4)
C(3)	0.3543(06)	0.2845(05)	0.6545(10)	2.9(4)
C(4)	0.1915(06)	0.3231(04)	0.8458(11)	2.9(4)
C(5)	0.0355(08)	0.3783(07)	1.0372(14)	4.9(6)
C(6)	0.2554(06)	0.3502(05)	0.5258(11)	3.1(4)
C(7)	0.1999(06)	0.4531(05)	0.5834(11)	3.5(4)
C(8)	0.1694(08)	0.6050(06)	0.5062(17)	5.6(6)
C(9)	0.2186(12)	0.6424(08)	0.371(02)	8.7(9)
C(11)	0.3901(07)	0.4452(06)	0.9399(13)	4.9(6)
C(12)	0.5746(07)	0.2809(05)	0.9194(12)	4.0(5)
C(13)	0.4710(07)	0.1757(06)	0.9993(13)	4.7(6)
C(14)	0.4716(07)	0.3400(07)	1.2766(14)	5.4(6)
C(21)	0.2038(07)	−0.0287(05)	0.0063(14)	4.3(5)
C(22)	0.1105(07)	−0.0466(06)	0.3352(14)	5.0(5)
C(23)	0.3252(08)	−0.0464(06)	0.4141(14)	5.3(6)
C(24)	0.0242(08)	0.1289(06)	0.1718(14)	5.3(6)

that in **2**, Re(1)–C(3) = 2.189(7) Å, and the C(2)–C(3) bond is reduced to a single bond, 1.542(9) Å, by the addition of the C(H)CO_2Et grouping. The C(2)–C(6) bond is longer than the C(3)–C(6) bond, 1.534(9) vs 1.49(1) Å, and it is the C(2)–C(6) bond that is cleaved when **5** is transformed to **6**; see below. All of the other bonds in **5** are similar to those in **2**. The cyclopropyl hydrogen atoms on C(3) and C(6) are strongly coupled to each other, δ 3.99 and 2.58 ppm, $^3J_{H\text{-}H}$ = 12.0 Hz. Since the molecule has no symmetry the hydrogen atoms on the methylene group are inequivalent and are coupled to each other and to the methyl group, 4.18 and 4.11 ppm, $^2J_{H\text{-}H}$ = 10.2 Hz, $^3J_{H\text{-}H}$ = 7.2 Hz.

An ORTEP diagram of the molecular structure of **6** is shown in Figure 5. A listing of the final atomic positional parameters is given in Table 6. Compound **6** is somewhat similar to **4a** because in both compounds one of the sulfur atoms of the CS_2 grouping serves as a bridge between the metal atoms. The Re–S and C–S bond distances in **6** are similar to those in **4a**. However, in **6** the methyl carboxylate group is coordinated to one of the metal atoms, Re(2)–O(1) = 2.171(8) Å. The C(H)CO_2Et grouping is bonded solely to the hydrogen substituted carbon C(3), and there is a double bond between these atoms, C(3)–C(6) = 1.33(2) Å. The adjacent C–C bond is essentially single, C(2)–C(3) = 1.47(1) Å. The bond between the CS_2 carbon, C(1), and C(2) is the shortest of all the compounds reported here, C(1)–C(2) = 1.37(1) Å. Since the C(2)–C(4) bond is nearly single, 1.46(1) Å, it seems necessary to assign substantial double bond character to the C(1)–C(2) bond to satisfy its valence requirements.

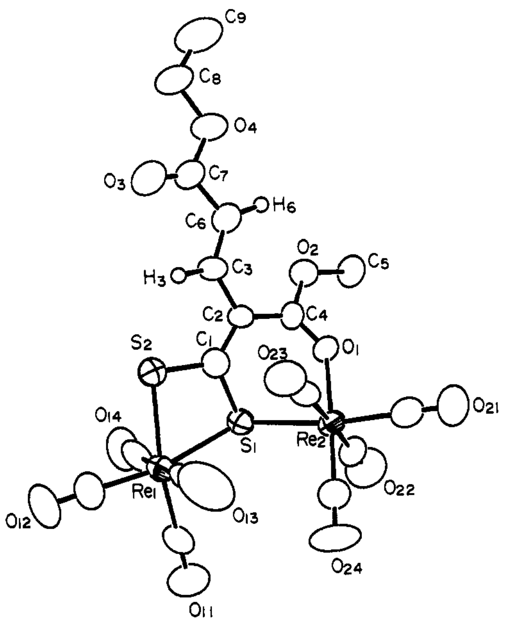


Figure 5. ORTEP diagram of $Re_2(CO)_8[SC(S)C(CHCHCO_2Et)C(OMe)O]$, **6**, showing 50% probability thermal ellipsoids. Selected interatomic distances (Å) and angles (deg) are Re(1)–S(1) = 2.498(3), Re(2)–S(1) = 2.480(3), Re(1)–S(2) = 2.492(4), Re(2)–O(1) = 2.171(8), C(1)–C(2) = 1.37(1), C(2)–C(3) = 1.47(1), C(2)–C(4) = 1.46(1), C(1)–S(1) = 1.77(1), C(1)–S(2) = 1.71(1), C(3)–C(6) = 1.33(2), C(1)–C(2)–C(3) = 119(1), C(1)–C(2)–C(4) = 119(1), C(3)–C(2)–C(4) = 122(1), Re(1)–S(1)–Re(2) = 127.3(1), C(2)–C(3)–C(6) = 131(1), C(3)–C(6)–C(7) = 120(1).

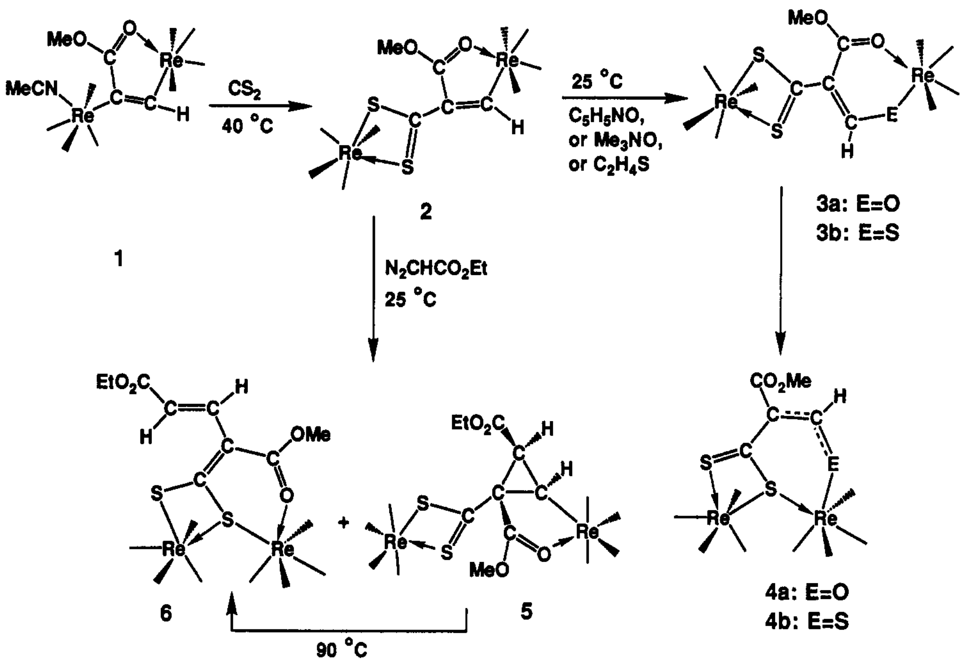
Table 6. Positional Parameters and *B*(eq) for 6

atom	*x*	*y*	*z*	*B*(eq) (Å^2)
Re(1)	0.93990(04)	0.10596(04)	0.702813(19)	4.45(3)
Re(2)	0.91840(03)	0.36911(04)	0.586945(19)	3.73(2)
S(1)	0.9820(02)	0.1982(03)	0.62165(12)	3.9(2)
S(2)	0.8846(03)	0.0003(03)	0.62822(14)	5.2(2)
O(1)	0.9577(05)	0.2830(06)	0.5184(03)	4.0(4)
O(2)	0.9663(05)	0.1613(06)	0.4568(03)	4.4(4)
O(3)	0.7610(10)	−0.1759(09)	0.4797(04)	10.2(8)
O(4)	0.7906(05)	−0.1319(07)	0.4012(03)	5.4(5)
O(11)	1.0198(08)	0.2626(10)	0.7824(04)	9.1(8)
O(12)	0.8804(09)	−0.0481(10)	0.7880(04)	9.9(8)
O(13)	0.7536(07)	0.2244(12)	0.7069(04)	9.9(8)
O(14)	1.1213(08)	−0.0176(10)	0.6943(05)	8.8(8)
O(21)	0.8476(07)	0.5646(08)	0.5261(04)	7.3(7)
O(22)	1.1088(07)	0.4806(10)	0.5916(05)	8.8(7)
O(23)	0.7277(06)	0.2571(08)	0.5918(03)	5.7(5)
O(24)	0.8710(08)	0.4834(10)	0.6867(04)	8.8(8)
C(1)	0.9210(07)	0.0985(09)	0.5872(04)	3.9(6)
C(2)	0.9087(07)	0.0981(09)	0.5356(04)	3.4(6)
C(3)	0.8636(08)	0.0046(10)	0.5122(05)	3.6(6)
C(4)	0.9457(07)	0.1868(09)	0.5052(05)	3.2(6)
C(5)	1.0045(08)	0.2461(11)	0.4252(05)	5.0(7)
C(6)	0.8468(08)	−0.0190(10)	0.4638(05)	4.2(7)
C(7)	0.7971(09)	−0.1182(11)	0.4512(05)	5.1(8)
C(8)	0.7467(11)	−0.2310(14)	0.3845(07)	8(1)
C(9)	0.7412(16)	−0.2338(17)	0.3341(07)	13(2)
C(11)	0.9887(10)	0.2054(12)	0.7534(05)	5.4(8)
C(12)	0.9030(11)	0.0092(12)	0.7554(06)	7(1)
C(13)	0.8231(11)	0.1802(13)	0.7052(05)	6.4(9)
C(14)	1.0550(11)	0.0296(13)	0.6970(05)	6(1)
C(21)	0.8733(09)	0.4922(12)	0.5490(06)	5.2(8)
C(22)	1.0408(10)	0.4365(10)	0.5895(06)	5.3(8)
C(23)	0.7970(09)	0.2981(10)	0.5874(05)	4.4(7)
C(24)	0.8888(10)	0.4419(11)	0.6495(06)	5.6(8)

Discussion

A summary of the results of this study is shown in Scheme 1. We have shown in this and other studies that the carboxylate substituted metal–carbon bond of the dimetalated olefin of **1** is readily functionalized by reaction with CS_2 and other unsaturated molecules (e.g. (aryl)N=C=S and certain alkynes). This occurs by

Scheme 1



displacement of the NCMe ligand and the addition and insertion of the molecule into the carboxylate substituted metal—carbon bond. The insertion of CS_2 into metal—carbon bonds has been observed previously,[11] and Lemke et al. have observed the insertion of CO_2 into one of the metal—carbon bonds of a dimetalated olefin complex.[5b]

We have found in this study that both metal–carbon bonds of the dimetalated olefin complex 1 can be functionalized through a sequence of reactions involving first the insertion of CS_2 and second the insertion of oxygen or sulfur by reaction with the reagents pyridine *N*-oxide, Me_3NO, and ethylene sulfide. Compounds **3a,b** spontaneously isomerize to the more stable compounds **4a,b** by displacement of the carboxylate group by one of the sulfur atoms of the CS_2 grouping. Recently, there has been a flurry of interest in the oxygenation and sulfurization of metal–carbon bonds in organometallic complexes.[12] Curiously, these reactions do not occur with compound 7.

The reaction of 2 with ethyl diazoacetate, $N_2C(H)CO_2Et$, yielded two products **5** and **6**. Compound **6** was formed in competition with **5**. The formation of **6** may proceed initially by the insertion of a carbene into the metal–carbon bond to yield an intermediate that is structurally similar to that of compounds **3a** and **3b**, where the $C(H)CO_2Et$ grouping would occupy the position of the O or S atom, and is then isomerized to the final product.

Compound **5** is believed to have been formed by the addition of the carbene grouping, $C(H)CO_2Et$, to the C–C double bond to form a cyclopropyl grouping. Although it is well-known that carbene sources will convert olefins to cyclopropanes,[13] and it has been shown that diazoalkanes will produce carbene additions to the C–C double bond of bridging vinylidene ligands to yield bridging cyclopropenylidene ligands,[14] this appears to be the first example of the formation of a metalated cyclopropane grouping by this route. Interestingly, compound **5** could be converted to **6** by an opening of the cyclopropane ring, but the conditions for this transformation are much more severe than those of the original synthesis and thus indicate that **5** is not an intermediate in the formation of **6** in the original reaction. Our studies have now demonstrated that dimetalated olefins can be functionalized at both ends. Removal of the metal atoms may yield some unusual new organic molecules.

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Supplementary Material Available: Tables of hydrogen atom positional parameters, bond distances and angles, and anisotropic thermal parameters for all five structural analyses (21 pages). Ordering information is given on any current masthead page.

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