Reactions of a Dicarboxylate-Substituted Allene with Activated Dirhenium Carbonyl Complexes

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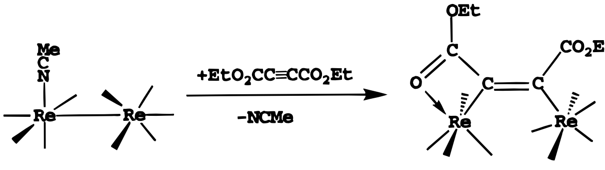
The compound $Re(CO)_4[C(CH_2CO_2Me){=}C(H)CO_2Me]$, **1**, was obtained in 83% yield when a mixture of $Re_2(CO)_9(NCMe)$ and $MeO_2C(H)C{=}C{=}C(H)CO_2Me$ in a hexane solution was heated to reflux for 1.5 h. The addition of one hydrogen atom to the allene grouping was shown to be derived from adventitious water. The reaction of **1** with PMe_2Ph yielded the derivative *fac*-$Re(CO)_3(PMe_2Ph)[C(CH_2CO_2Me){=}C(H)CO_2Me]$, **2**, in 98% yield. The reaction of $Re_2(CO)_8(PMe_2Ph)(NCMe)$ with $MeO_2C(H)C{=}C{=}C(H)CO_2Me$ yielded two isomeric products *mer*-$Re_2(CO)_6(PMe_2Ph)[\mu\text{-}\eta^3\text{-}\eta^1\text{-}MeO_2C(H)CCC(H)CO_2Me]$, **3** (31%), and *fac*-$Re_2(CO)_6(PMe_2Ph)[\mu\text{-}\eta^3\text{-}\eta^1\text{-}MeO_2C(H)CCC(H)CO_2Me]$, **4** (22%), which contain bridging $\eta^3\text{-}\eta^1\text{-}MeO_2C(H)CCC(H)CO_2Me$ dicarboxylateallene ligands and small amounts of three mononuclear nuclear products: *fac*-$Re(CO)_3(PMe_2Ph)[MeO_2CCH_2CC(H)CO_2Me]$, **2** (8%), *mer*-$Re(CO)_3(PMe_2Ph)(MeO_2CCH_2CCHCO_2Me)$, **5** (5%), and a trace of **1**. The carbonyl oxygen atom of one of the carboxylate groups is coordinated to one of the metal atoms in **3** and **4**. Compound **3** slowly isomerizes to **4** at 25 °C, and compound **5** isomerizes to **2** when heated. The reaction of **4** with $EtO_2CN{=}C{=}S$ produced two products: **2** (20%) and *fac*-$Re(CO)_3(PMe_2Ph)[MeO_2CCH_2CC(CO_2Me)C{=}SN(H)CO_2Et]$, **6** (28%). Water may be involved in the formation of both products. Compound **6** contains a $MeO_2CCH_2C{=}C(CO_2Me)C{=}S)N(H)CO_2Et$ grouping that is chelated to the rhenium atom by the sulfur and alkenyl carbon atom to form a five-membered $\overline{Re\text{-}C{=}C{-}C{=}S}$ ring, with Re−S = 2.443(3) Å and Re−C(1) = 2.12(1) Å.

Introduction

In recent studies, we have demonstrated the ability of unsaturated molecules with carboxylate substitutents to insert into the metal−metal bonds of activated dimanganese and dirhenium complexes to yield dimetalated ligands.[1−3] In many cases, a carbonyl oxygen atom of a carboxylate group has become coordinated to one of the metal atoms (e.g. eqs 1 and 2).[2] 1,3-Disubstituted allenes are of synthetic interest because of their intrinsic chirality and potential to form stereogenic centers in reaction products.[4] In order to establish the nature of the interactions of chiral allenes with dimetal centers, we have investigated the reactions of 1,3-bis(methoxycarbonyl)allene, $MeO_2C(H)C{=}C{=}C(H)CO_2Me$, with $Re_2(CO)_9(NCMe)$ and $Re_2(CO)_8(PMe_2Ph)(NCMe)$. Details of this study are reported here.



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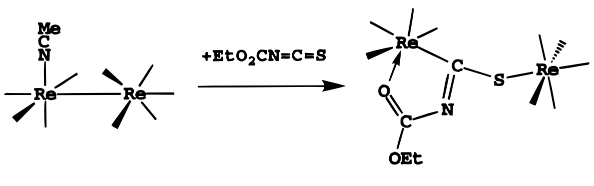

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Experimental Section

Unless specified otherwise, all reactions were carried out under an atmosphere of nitrogen. All solvents were appropriately dried and degassed prior to use. Dimethylphenylphosphine and ethoxycarbonyl isothiocyanate were purchased from Aldrich. 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 5DXBO FT-IR spectrophotometer. ^1H NMR spectra were taken at 400 MHz on a Bruker AM-400 NMR spectrometer. Elemental analyses were performed by Desert Analytics, Tucson, AZ. Mass spectra were performed by direct inlet using electron impact ionization. $Re_2(CO)_9(NCMe)$,[5] $Re_2(CO)_8(PMe_2Ph)(NCMe)$,[6] and $MeO_2C(H)C{=}C{=}C(H)CO_2Me$[7] were prepared by literature methods.

Reaction of $Re_2(CO)_9(NCMe)$ with $MeO_2C(H)C{=}C{=}C(H)CO_2Me$. Method a. A 20.0-mg amount (0.030 mmol) of $Re_2(CO)_9(NCMe)$ and a 15.0-μL amount (0.096 mmol) of $MeO_2C(H)C{=}C{=}C(H)CO_2Me$ were dissolved in 25 mL of hexane. The solution was heated to reflux for 1.5 h. After the solvent was removed in vacuo, the residue was separated by TLC using a 2/1 hexane/CH_2Cl_2 solvent mixture. This yielded the following in order of elution: 0.5 mg of $Re_2(CO)_{10}$, 0.6 mg of unreacted $Re_2(CO)_9(NCMe)$, and 11.3 mg of colorless $Re(CO)_4[C(CH_2CO_2Me){=}C(H)CO_2Me]$, **1**, 83% yield. Spectral

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(1) Adams, R. D. *Chem. Soc. Rev.* **1994**, 335.

(2) (a) Adams, R. D.; Chen, L. *Organometallics* **1994**, *13*, 1264. (b) Adams, R. D.; Chen, L; Wu, W. *Organometallics* **1993**, *12*, 1257.

(3) Adams, R. D.; Huang, M. *Chem. Ber.* **1996**, *129*, 485.

(4) (a) Schuster, H. F. *Allenes in Organic Synthesis*; Wiley: New York, 1984. (b) Aso, M.; Ikeda, I.; Kawabe, T.; Shiro, M.; Kanematsu, K. *Tetrahedron Lett.* **1992**, *33*, 5787. (c) Corey, E. J.; Boaz, N. W. *Tetrahedron Lett.* **1984**, *25*, 3059.

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data for **1** are as follows. IR (ν_{CO} in hexane, cm^{-1}): 2099 (w, br), 2005 (s), 1994 (s), 1985 (s), 1942 (s), 1749 (w, br), 1584 (w, br). ^{1}H NMR (δ in CDCl$_3$, ppm): 6.72 (t, $^4J_{H-H} = 1.0$ Hz, 1H, CH), 3.89 (s, 3H, OCH$_3$), 3.86 (d, $^4J_{H-H} = 1.0$ Hz, 2H, CH$_2$), 3.72 (s, 3H, OCH$_3$). Anal. Calcd (found): C, 29.01 (28.97); H, 1.99 (2.05). MS: parent ion $m/e = 456$ (for ^{187}Re) and ions corresponding to the loss of each of the four carbonyl ligands.

Method b. In the presence of D$_2$O. A 54.0-μL amount of D$_2$O was added to a solution of a 20.0-mg amount (0.030 mmol) of Re$_2$(CO)$_9$(NCMe) and a 15.0-μL amount (0.096 mmol) of MeO$_2$C(H)C=C=C(H)CO$_2$Me in 25 mL of hexane. The solution was heated to reflux for 1.5 h. After the solvent was removed in vacuo, and the residue was separated by TLC using a 2/1 hexane/CH$_2$Cl$_2$, solvent mixture. This yielded the following in order of elution: 0.7 mg of Re$_2$(CO)$_{10}$, 2.0 mg of unreacted Re$_2$(CO)$_9$(NCMe), and 7.0 mg of colorless Re(CO)$_4$[C(CHDCO$_2$Me)=C(H)CO$_2$Me] in 51% yield.

Reaction of 1 with PMe$_2$Ph. A 10.0-mg amount (0.022 mmol) of **1** and a 4.0-μL amount (0.026 mmol) of PMe$_2$Ph were dissolved in 15 mL of hexane. The solution was heated to reflux for 30 min. After cooling, the solvent was removed in vacuo and the residue was separated by TLC using a 2/1 hexane/CH$_2$Cl$_2$, solvent mixture to give 12.2 mg of pale yellow *fac*-Re(CO)$_3$(PMe$_2$Ph)[MeO$_2$CCH$_2$CC(H)CO$_2$Me], **2**, in 98% yield. Spectral data for **2** are as follows. IR (ν_{CO} in hexane, cm^{-1}): 2019 (s), 1935 (s), 1896 (s), 1740 (w, br), 1581 (w, br). ^{1}H NMR (δ in CDCl$_3$, ppm): 7.40−7.30 (m, 5H, C$_6$H$_5$), 6.54 (m, 1H, CH), 3.70 (s, 3H, OCH$_3$), 3.69 (m, 2H, CH$_2$), 3.44 (s, 3H, OCH$_3$), 1.81 (d, $^3J_{P-H} = 8.4$ Hz, 3H, PCH$_3$), 1.71 (d, $^3J_{P-H} = 8.4$ Hz, 3H, PCH$_3$). MS: parent ion $m/e = 566$ plus ions corresponding to the loss of each of the three carbonyl ligands.

Reaction of Re$_2$(CO)$_9$(PMe$_2$Ph) with MeO$_2$C(H)C=C=C(H)CO$_2$Me. A 90.0-mg amount (0.12 mmol) of Re$_2$(CO)$_8$(PMe$_2$Ph)(NCMe) and a 60.0-μL amount (0.38 mmol) of MeO$_2$C(H)C=C=C(H)CO$_2$Me were dissolved in 100 mL of hexane. The solution was heated to reflux for 1 h. After cooling, the solvent was removed in vacuo and the residue was separated by TLC using a 2/1 hexane/CH$_2$Cl$_2$ solvent mixture. This yielded the following in order of elution: 12.8 mg of Re$_2$(CO)$_9$(PMe$_2$Ph), 1.5 mg of **1**, 4.9 mg of pale yellow **2** (8% yield), 3.4 mg of *mer*-Re(CO)$_3$(PMe$_2$Ph)(MeO$_2$CCH$_2$CCHCO$_2$Me), **5** (5% yield), 30.0 mg of *mer*-Re$_2$(CO)$_6$(PMe$_2$Ph)[μ-η^3-η^1-MeO$_2$C(H)CCC(H)CO$_2$Me], **3** (31% yield), and 21.6 mg of *fac*-Re$_2$(CO)$_6$(PMe$_2$Ph)[μ-η^3-η^1-MeO$_2$C(H)CCC(H)CO$_2$Me], **4** (22% yield). Spectral data for **3** are as follows. IR (ν_{CO} in hexane, cm^{-1}): 2045 (w), 2025 (s), 2023 (s), 1953 (s), 1946 (s), 1936 (sh), 1914 (w, br), 1900 (w, br), 1715 (w, br), 1537 (w, br). ^{1}H NMR (δ in CDCl$_3$, ppm): 7.47 (m, 5H, *Ph*), 5.86 (s, 1H, C*H*), 5.23 (s, 1H, C*H*), 3.64 (s, 3H, O*Me*), 3.58 (s, 3H, O*Me*), 2.08 (d, $^3J_{P-H} = 9.3$ Hz, 3H, P*Me*), 2.01 (d, $^3J_{P-H} = 9.3$ Hz, 3H, P*Me*). Anal. Calcd (found): C, 30.22 (30.48); H, 2.29 (2.08). Spectral data for **4** are as follows. IR (ν_{CO} in hexane, cm^{-1}): 2045 (s), 2020 (s), 2013 (s), 1949 (vs), 1939 (s), 1919 (w), 1898 (w, br), 1711 (w, br), 1543 (w, br). ^{1}H NMR (δ in CDCl$_3$, ppm): 7.45 (m, 5H, *Ph*), 5.65 (s, 1H, C*H*), 4.96 (s, 1H, C*H*), 3.63 (s, 3H, O*Me*), 3.39 (s, 3H, O*Me*), 2.11 (d, $^3J_{P-H} = 9.4$ Hz, 3H, P*Me*), 2.10 (d, $^3J_{P-H} = 9.4$ Hz, 3H, P*Me*). Anal. Calcd (found): C, 30.22 (30.40); H, 2.29 (2.23). Spectral data for **5** are as follows. IR (ν_{CO} in hexane, cm^{-1}): 2041 (w, br), 1940 (s), 1899 (m), 1747 (w, br), 1577 (w, br). ^{1}H NMR (δ in CDCl$_3$, ppm): 7.58−7.36 (m, 5H, *Ph*), 6.59 (m, 1H, C*H*), 3.99 (m, 2H, C*H$_2$*), 3.72 (s, 3H, O*Me*), 3.68 (s, 3H, O*Me*), 1.98 (d, $^3J_{P-H} = 8.0$ Hz, 6H, P*Me$_2$*). Anal. Calcd (found): C, 38.23 (38.42); H, 3.56 (3.33).

Conversion of 3 to 4. Method a. A 5.0-mg amount of **3** and 0.6 mL of CDCl$_3$ were placed in a 5-mm NMR tube at room temperature. Compound **3** was slowly transformed to **4**. After 7 days, the **4/3** ratio was 2/1, as determined by ^{1}H NMR spectroscopy.

Method b. A 5.0-mg amount of **4** and 0.6 mL of CDCl$_3$ were placed in a 5-mm NMR tube at room temperature. The transformation was monitored by ^{1}H NMR spectroscopy. After 7 days, the formation of **3** was not detected.

Reaction 4 with H$_2$O. A 10.0-mg amount (0.035 mmol) of **4** and a 50.0-μL amount of distilled H$_2$O were dissolved in 15 mL of CHCl$_3$. The solution was heated to reflux for 22 h. After the solvent was removed via rotary evaporation, the residue was separated by TLC using a 2/1 hexane/CH$_2$Cl$_2$ solvent mixture. This yielded the following in order of elution: 3.1 mg of **2** in 46% yield and 2.9 mg of unreacted starting material.

Conversion of 5 to 2. A 17.0-mg amount (0.070 mmol) of **5** was dissolved in 15 mL of heptane. The solution was heated to reflux for 3 h. After the solvent was removed via rotary evaporation, the residue was separated by TLC using a 2/1 hexane/CH$_2$Cl$_2$, solvent mixture. This yielded the following in order of elution: 8.7 mg of **2** in 51% yield and 1.9 mg of unreacted starting material.

Reaction 4 with EtO$_2$CNCS. A 29.0-mg amount (0.035 mmol) of **4** and a 200.0-μL amount (1.66 mmol) of EtO$_2$CN=C=S were dissolved in 10 mL of heptane. The solution was heated to reflux for 15 h. After cooling, the solvent was removed via rotary evaporation, and the unreacted EtO$_2$CN=C=S was removed in vacuo. The residue was separated by TLC using a 1/1 hexane/CH$_2$Cl$_2$, solvent mixture. This yielded the following in order of elution: 3.9 mg of **2** in 20% yield and 6.8 mg of orange *fac*-Re(CO)$_3$(PMe$_2$Ph)[MeO$_2$CCH$_2$CC(CO$_2$Me)C=SN(H)CO$_2$Et], **6**, in 28% yield. Spectral data for **6** are as follows. IR (ν_{CO} in hexane, cm^{-1}): 2019 (vs), 1944 (s), 1914 (s), 1769 (w, br), 1740 (w, br), 1677 (w, br). ^{1}H NMR (δ in CDCl$_3$, ppm): 11.60 (s, br, 1H, N*H*), 7.31 (m, 5H, *Ph*), 4.46 (dd, $^2J_{H-H} = 15.9$, 2H, C*H$_2$*), 4.28 (q, $^3J_{H-H} = 7.1$ Hz, 2H, OC*H$_2$*Me), 3.71 (s, 3H, O*Me*), 3.65 (s, 3H, O*Me*), 1.77 (d, $^3J_{P-H} = 8.6$ Hz, 3H, P*Me*), 1.76 (d, $^3J_{P-H} = 8.6$ Hz, 3H, P*Me*), 1.34 (t, $^3J_{H-H} = 7.1$ Hz, 3H, *Me*). Anal. Calcd (found): C, 37.93 (37.89); H, 3.62 (3.48); N, 2.01 (2.07).

Crystallographic Analyses. Crystals of **1** suitable for X-ray diffraction analysis were obtained from crystallization of a Et$_2$O solution at −14 °C. Crystals of **3** suitable for X-ray diffraction analysis were obtained by cooling a solution in diethyl ether solvent to −14 °C. Crystals of **4** suitable for X-ray diffraction analysis were obtained by slow evaporation of solvent from a solution in a 1/1 hexane/Et$_2$O solvent mixture at room temperature. Crystals of **5** suitable for X-ray diffraction analysis were obtained by cooling a solution in a 1/1 hexane/Et$_2$O solvent mixture to −20 °C. Crystals of **6** suitable for X-ray diffraction analysis were obtained by cooling a solution in a 1/2 hexane/Et$_2$O solvent mixture at −20 °C. The crystals used in intensity measurements were mounted in thin-walled glass capillaries. Diffraction measurements were made on a Rigaku AFC6S fully automated four-circle diffractometer using graphite-monochromated Mo Kα radiation. The unit cells were determined and refined from 15 randomly selected reflections obtained by using the AFC6S automatic search, center, index, and least-squares routines. Crystal data, data collection parameters, and results of these analyses are listed in Table 1. All data processing was performed on a Digital Equipment Corp. VAXstation 3520 computer or an SGI Indigo2 computer by using the TEXSAN structure solving program libraries obtained from the Molecular Structure Corp., The Woodlands, TX. Neutral atom scattering factors were calculated by the standard procedures.[8a] Anomalous dispersion corrections were applied to all non-hydrogen atoms.[8b] Lorentz−polarization (*Lp*) and absorption corrections were applied in each analysis. Full-matrix least-squares refinements minimized the following function: $\sum_{hkl} w(|F_o| - |F_c|)^2$, where $w = 1/\sigma(F)^2$, $\sigma(F) = \sigma(F_o^2)/2F_o$, and $\sigma(F_o^2) = [\sigma(I_{raw})^2 + (0.02I_{net})^2]^{1/2}/Lp$.

Compounds **1**, **3**, and **5** crystallized in the triclinic crystal system. The space group $P\bar{1}$ was assumed and confirmed in each case by the successful solution and refinement of the structures. The structures were solved by a combination of

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(8) (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.

Table 1. Crystallographic Data for Compounds 1 and 3−6

	compd				
	1	**3**	**4**	**5**	**6**
formula	$ReO_8C_{11}H_9$	$Re_2PO_{10}C_{21}H_{19}$	$Re_2PO_{10}C_{21}H_{19}$	$RePO_7C_{18}H_{20}$	$ReSPO_9NC_{22}H_{25}$
fw	455.39	834.76	834.76	565.53	696.68
cryst system	triclinic	triclinic	orthorhombic	triclinic	monoclinic
lattice params					
a (Å)	9.473(4)	11.306(2)	17.585(3)	11.153(2)	10.775(3)
b (Å)	9.893(3)	12.009(2)	27.585(5)	11.290(2)	12.646(2)
c (Å)	7.536(4)	10.501(2)	10.709(2)	9.610(1)	10.973(3)
α (deg)	96.70(3)	103.89(1)	90.00	114.42(1)	90.00
β (deg)	96.07(4)	94.80(1)	90.00	92.86(1)	116.08(2)
γ (deg)	91.02(3)	67.82(1)	90.00	71.51(1)	90.00
V (Å^3)	697.1(5)	1281.6(4)	5194.7(14)	1040.2(3)	1343.0(6)
space group	$P\bar{1}$ (No. 2)	$P\bar{1}$ (No. 2)	$Pbca$ (No. 61)	$P\bar{1}$ (No. 2)	$P2_1$ (No. 4)
Z	2	2	8	2	2
ρ_{calc} (g/cm^3)	2.17	2.16	2.14	1.81	1.72
μ(Mo Kα) (cm^{-1})	87.52	95.53	94.27	59.55	47.11
temp (°C)	20	20	20	20	20
$2\theta_{max}$ (deg)	44	42	44	42	41
no. of observns ($I > 3\sigma$)	1595	2307	1946	2081	2429
goodness of fit	2.06	1.70	1.52	1.95	1.38
residuals:[a] R; R_w	0.039; 0.049	0.022; 0.025	0.034; 0.033	0.023; 0.027	0.028; 0.028
abs cor	Difabs	empirical	Difabs	empirical	difabs
largest peak in final diff map (e/Å^3)	0.89	0.92	0.69	1.33	0.77

[a] $R = \sum_{hkl}(||F_o| - |F_c||)/\sum_{hkl}|F_o|$; $R_w = [\sum_{hkl}w(|F_o| - |F_c|)^2/\sum_{hkl}wF_o^2]^{1/2}$, $w = 1/\sigma^2(F_o)$; GOF $= [\sum_{hkl}(w(|F_o| - |F_c|)^2)^2)/(n_{data} - n_{vari})]^{1/2}$.

direct methods (MITHRIL) and difference Fourier syntheses. For all three analyses all non-hydrogen atoms were refined with anisotropic thermal parameters, and except for the hydrogen atoms H(2) and H(3) in the analysis of **3**, the positions of the hydrogen atoms on the ligands in each analysis were calculated by assuming idealized geometries with all C−H distances at 0.95 Å. Their contributions were added to the structure factor calculations, but their positions were not refined.

Compound **4** crystallized in the orthorhombic crystal system. The patterns of systematic absences in the data were uniquely consistent with the space group *Pbca*. The structure was solved by a combination of direct methods (MITHRIL) and difference Fourier syntheses. All non-hydrogen atoms were refined with anisotropic thermal parameters, and the positions of the hydrogen atoms on the ligands were calculated by assuming idealized geometries with all C−H distances at 0.95 Å. Their contributions were added to the structure factor calculations, but their positions were not refined.

The systematic absences for compound **6**, $0k0$, $k = 2n + 1$, are consistent with the space groups $P2_1$ and $P2_1/m$. Attempts to solve the structure in the centrosymmetric space group $P2_1/m$ were unsuccessful. An acceptable solution was obtained in the noncentric space group $P2_1$. The structure was solved by a combination of direct methods (MITHRIL) and difference Fourier syntheses. Except for the carbons C(10) and C(22), all non-hydrogen atoms were refined with anisotropic thermal parameters. The positions of the hydrogen atoms on the ligands were calculated by assuming idealized geometries with all C−H distances at 0.95 Å. The scattering contributions of the hydrogen atoms were added to the structure factor calculations, but their positions were not refined. The enantiomorph was determined by inverting the coordinates of all atoms and refining again. This calculation produced significantly higher R-factors and was then discarded in favor of the original coordinates of the original solution.

Results

The compound $Re(CO)_4[C(CH_2CO_2Me){=}C(H)CO_2Me]$, **1**, was obtained in 83% yield from the reaction of $Re_2(CO)_9(NCMe)$ with $MeO_2C(H)C{=}C{=}C(H)CO_2Me$ in refluxing hexane solvent. The product was characterized by a combination of IR, ^{1}H NMR, and elemental and single-crystal X-ray diffraction analyses. An ORTEP drawing of the molecular structure of **1** is shown in Figure 1. The compound contains one rhenium atom with four linear terminal carbonyl ligands. The most interesting ligand is a 1,3-bis(methoxycarbonyl)propenyl grouping that is σ-bonded to the rhenium atom at the 2-position, C(1), with Re−C(1) = 2.19(1) Å. The carbonyl oxygen of one of the carboxylate groups is coordinated to the rhenium atom to form a five-membered ring, Re−O(1) = 2.189(8) Å. The C(1)−C(2) bond is double, C(1)−C(2) = 1.35(2) Å, and the C(1)−C(3) bond is single at 1.48(2) Å. The ^{1}H NMR spectrum shows a long-range coupling between the alkenyl proton H(2) at 6.72 ppm and the methylene protons at 3.86 ppm ($^4J_{H-H}$ = 1.0 Hz). The compound can be viewed as a combination of one $Re(CO)_4$ grouping with 1 equiv of $MeO_2C(H)$-

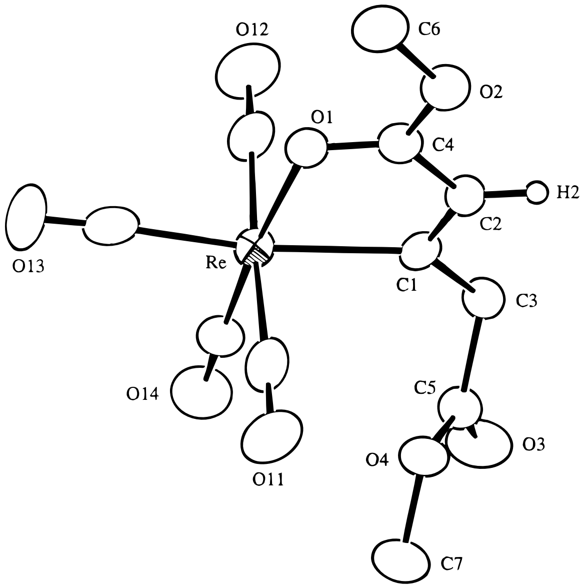

Figure 1. ORTEP diagram of $Re(CO)_4[C(CH_2CO_2Me){=}C(H)CO_2Me]$, **1**, showing 40% probability thermal ellipsoids. Selected interatomic distances (Å) and angles (deg): Re−O(1) = 2.189(8), Re−C(1) = 2.19(1), C(1)−C(2) = 1.35(2), C(2)−C(4) = 1.41(1), C(1)−C(3) = 1.48(2), C(4)−O(1) = 1.23(1); Re(1)−C(1)−C(3) = 128.0(8).

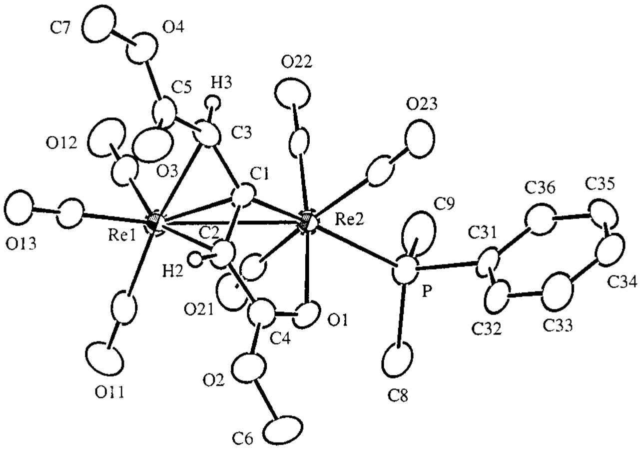

Figure 2. ORTEP diagram of *mer*-$\mathrm{Re_2(CO)_6(PMe_2Ph)[\mu\text{-}\eta^3\text{-}\eta^1\text{-}MeO_2C(H)CCC(H)CO_2Me]}$, **3**, showing 40% probability thermal ellipsoids. Selected interatomic distances (Å) and angles (deg): Re(1)−Re(2) = 2.9727(3), Re(1)−C(1) = 2.089(8), Re(1)−C(2) = 2.331(8), Re(1)−C(3) = 2.358(8), Re(2)−C(1) = 2.156(7), Re(2)−O(1) = 2.192(6), Re(2)−P = 2.443(2), C(1)−C(2) = 1.42(1), C(1)−C(3) = 1.41(1), C(2)−C(4) = 1.43(1), C(4)−O(1) = 1.25(1), C(5)−O(3) = 1.21(1); C(2)−C(1)−C(3) = 121.6(8), C(1)−Re(2)−P = 158.9(2), Re(1)−Re(2)−P = 148.15(6).

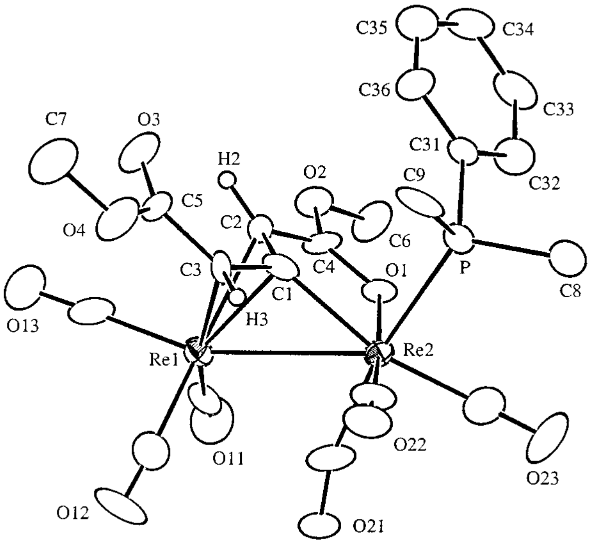

Figure 3. ORTEP diagram of *fac*-$\mathrm{Re_2(CO)_6(PMe_2Ph)[\mu\text{-}\eta^3\text{-}\eta^1\text{-}MeO_2C(H)CCC(H)CO_2Me]}$, **4**, showing 40% probability thermal ellipsoids. Selected interatomic distances (Å) and angles (deg): Re(1)−Re(2) = 3.0069(9), Re(1)−C(1) = 2.14(1), Re(1)−C(2) = 2.31(1), Re(1)−C(3) = 2.39(1), Re(2)−C(1) = 2.15(2), Re(2)−O(1) = 2.20(1), Re(2)−P = 2.474(4), C(1)−C(2) = 1.47(2), C(1)−C(3) = 1.40(2), C(2)−C(4) = 1.44(2), C(4)−O(1) = 1.23(2), C(5)−O(3) = 1.18(2); C(2)−C(1)−C(3) = 119(2), C(1)−Re(2)−P = 80.9(4), Re(1)−Re(2)−P = 126.0(1).

$\mathrm{C{=}C{=}C(H)CO_2Me}$ and one hydrogen atom. One equivalent of $\mathrm{Re(CO)_5}$ was eliminated and was not recovered. The source of the additional hydrogen atom has been traced to water presumably present in small amounts in the reagents and/or reaction apparatus. This was indicated by performing the reaction in the presence of added $\mathrm{D_2O}$. In this case the product was identified as $\mathrm{Re(CO)_4[C(CHDCO_2Me){=}C(H)CO_2Me]}$ by the expected decrease in the intensity of the methylene resonance at 3.86 ppm. It was anticipated that there might have been some interaction of the allene with the dirhenium grouping prior to the hydrogen addition and loss of the $\mathrm{Re(CO)_5}$ grouping. In an effort to test for this we investigated the reaction of $\mathrm{Re_2(CO)_8(PMe_2Ph)(NCMe)}$ with $\mathrm{MeO_2C(H)C{=}C{=}C(H)CO_2Me}$ in hexane solvent. When the solution was heated to reflux for 1 h, five products were obtained: *mer*-$\mathrm{Re_2(CO)_6(PMe_2Ph)[\mu\text{-}\eta^3\text{-}\eta^1\text{-}MeO_2C(H)CCC(H)CO_2Me]}$, **3** (31% yield), and *fac*-$\mathrm{Re_2(CO)_6(PMe_2Ph)[\mu\text{-}\eta^3\text{-}\eta^1\text{-}MeO_2C(H)CCC(H)CO_2Me]}$, **4** (22% yield), and small amounts of three mononuclear rhenium products *fac*-$\mathrm{Re(CO)_3(PMe_2Ph)[MeO_2CCH_2CC(H)CO_2Me]}$, **2** (8% yield), *mer*-$\mathrm{Re(CO)_3(PMe_2Ph)(MeO_2CCH_2CCHCO_2Me)}$, **5** (5% yield), and a trace of **1**.

Compounds **3** and **4** were both characterized crystallographically. ORTEP drawings of the molecular structures of **3** and **4** are shown in Figures 2 and 3, respectively. Compounds **3** and **4** are isomers, and both compounds contain a bridging η^3-η^1-$\mathrm{MeO_2C(H)CCC(H)CO_2Me}$ allene ligand in which the oxygen atom of one of the carboxylate groups is coordinated to the rhenium atom containing the phosphine ligand, Re(2)−O(1) = 2.192(6) Å [2.20(1) Å]. In all cases the value in brackets corresponds to that of compound **4**. In each complex the metal Re(1) contains only three carbonyl ligands and three of the carbon atoms of allene are coordinated to this metal atom. Exempting the metal−metal bond, Re(2) has a coordination of six: three CO groups, the phosphine ligand, the oxygen atom of the carboxylate group, and the central carbon atom of the allene ligand. The isomers are distinguished by the arrangement of ligands on Re(2). In **3** the three of the carbonyl ligands lie in a plane (i.e. a *mer*-geometry). In **4** all three carbonyl ligands are mutually *cis*, a *fac*-geometry. In the absence of a metal−metal bond atom Re(1) formally has 16 valence electrons and Re(2) has 18. Thus, a donor/acceptor bond Re(2)→Re(1) is formed, 2.9727(3) Å [3.0069(9) Å], and both metal atoms achieve 18 electron confirgurations. These distances are slightly shorter than that found in $\mathrm{Re_2(CO)_{10}}$, 3.041(1) Å, which contains a normal Re−Re single bond.[9] This shortening may be produced by the presence of the bridging allene ligand. In each compound, one of the carbonyl ligands, C(21)−O(21), on Re(2) has adopted a weak semibridging coordination to the Re−Re bond, Re−C(21)−O(21) = 167.4(9)° [165(2)°]. This effect is commonly found in complexes containing donor/acceptor metal−metal bonds.[10] Compound **3** slowly isomerizes to **4** at 25 °C. After 7 days, the **4**/**3** ratio was 2/1 as determined by ^{1}H NMR spectroscopy indicating that **4** is the more stable of the two. Solutions of **4** showed no detectable formation of **3** after 7 days at room temperature.

Compound **4** was found to react with $\mathrm{H_2O}$ in chloroform solvent at reflux to yield compound **2**, 46% yield. Compound **2** is simply a phosphine derivative of **1** and can be obtained essentially quantitatively from **1** by reaction with $\mathrm{PMe_2Ph}$. Compound **2** shows three strong absorptions in its IR spectrum, 2019 (s), 1935 (s), and 1896 (s) cm^{-1}; thus, it is assigned a *fac*-structure.

Compound **5** is the one remaining compound obtained from the reaction of $\mathrm{Re_2(CO)_8(PMe_2Ph)(NCMe)}$ with $\mathrm{MeO_2C(H)C{=}C{=}C(H)CO_2Me}$. Compound **5** was characterized crystallographically, and an ORTEP diagram of its molecular structure is shown in Figure 4. Com-

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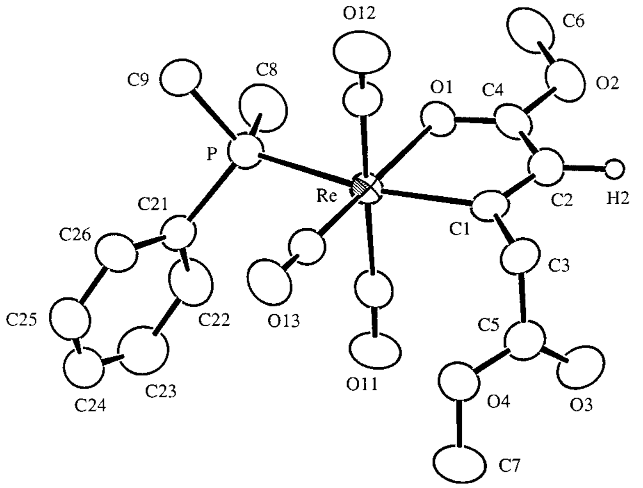


Figure 4. ORTEP diagram of *mer*-Re(CO)$_3$(PMe$_2$Ph)[C(CH$_2$CO$_2$Me)=C(H)CO$_2$Me], **5**, showing 40% probability thermal ellipsoids. Selected interatomic distances (Å) and angles (deg): Re—O(1) = 2.204(4), Re—P = 2.419(2), Re—C(1) = 2.149(6), C(1)—C(2) = 1.357(9), C(2)—C(4) = 1.43(1), C(1)—C(3) = 1.518(9), C(4)—O(1) = 1.249(8); P—Re—C(1) = 164.5(2), Re(1)—C(1)—C(3) = 127.4(5).

pound **5** is the *mer*-isomer of **2** in which the phosphine ligand lies *trans* to the rhenium—carbon bond to the bis(methoxycarbonyl)propenyl grouping. Interestingly, the Re—C bond to the bis(methoxycarbonyl)propenyl grouping is significantly shorter than that in **1**, Re—C(1) = 2.149(6) Å, which is consistent with the poorer *trans* directing influence of the phosphine ligand relative to CO. Compound **5** isomerizes to **2** when solutions in heptane solvent are heated to reflux for 3 h, yield 51%.

The reaction of **4** with EtO$_2$CN=C=S (in large excess) produced two products **2** (20% yield) and *fac*-Re(CO)$_3$(PMe$_2$Ph)[MeO$_2$CCH$_2$CC(CO$_2$Me)C=SN(H)CO$_2$Et], **6** (28% yield). The formation of **2** again seems to be related to the presence of traces of H$_2$O in the reaction mixture. Compound **6** was characterized crystallographically, and an ORTEP diagram of its molecular structure is shown in Figure 5. The complex contains three carbonyl ligands (*fac*-arrangement) and one PMe$_2$Ph ligand. The most interesting ligand is a MeO$_2$CCH$_2$CC(CO$_2$Me)C=SN(H)CO$_2$Et grouping, which has some features in common with the bis(methoxycarbonyl)propenyl ligand in **5**. The difference is that the alkenyl hydrogen atom of the bis(methoxycarbonyl)propenyl ligand is replaced by a S=CN(H)CO$_2$Et grouping. The CO$_2$Me group is not coordinated, but the sulfur atom is, Re—S = 2.443(3) Å and C(4)—S = 1.69(1) Å, and a five-membered Re—C=C—C=S ring was formed. The C(1)—C(2) bond is double, 1.39(1) Å, and C(2)—C(4) bond is single, 1.47(2) Å. There is a hydrogen atom on the nitrogen atom (located but not refined crystallographically), $\delta = 11.60$ ppm. The source of this hydrogen may again be adventitious H$_2$O in the reaction mixture. Because of the similarities between **5** and **6**, efforts were made to try to obtain **6** from **5** by reaction with S=C=NCO$_2$Et; however, no **6** could be obtained by using even large excesses of S=C=NCO$_2$Et and heating to reflux in heptane solvent for 2 days.

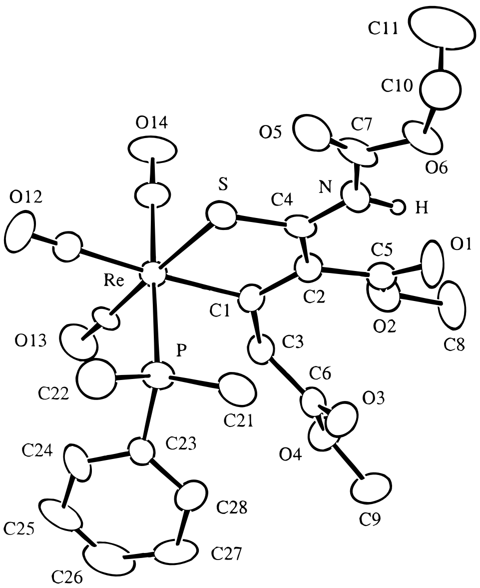
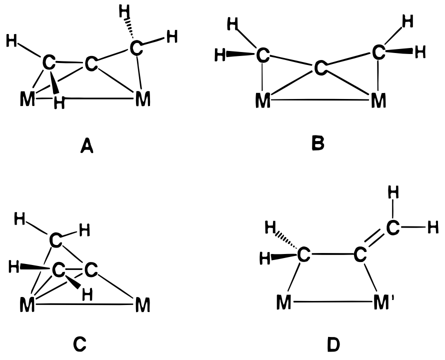


Figure 5. ORTEP diagram of *mer*-Re(CO)$_3$(PMe$_2$Ph)[MeO$_2$CCH$_2$CC(CO$_2$Me)C=SN(H)CO$_2$Et], **6**, showing 40% probability thermal ellipsoids. Selected interatomic distances (Å) and angles (deg): Re—S = 2.443(3), Re—C(1) = 2.12(1), Re—P = 2.468(3), C(1)—C(2) = 1.39(1), C(1)—C(3) = 1.52(2), C(2)—C(4) = 1.47(2), C(4)—S = 1.69(1), C(4)—N = 1.39(1), C(7)—N = 1.39(1); Re—C(1)—C(2) = 121(1), C(1)—C(2)—C(4) = 118(1), Re—S—C(4) = 101.2(4), S—C(4)—C(2) = 118.7(9), C(2)—C(4)—N = 119(1).

Discussion

Allenes have been shown to bridge pairs of metal atoms in four different ways. There are two μ-η^2-η^2 forms, a C_2 form **A**[11] and symmetric C_{2v} form **B**,[12] and one μ-η^1-η^3 form **C**,[13] which has C_s symmetry. There is at least one example of a μ-η^1-η^1 form **D**, which has C_s symmetry reported for a mixed-metal complex.[14] Substituted bridging allenes usually assume one of these basic forms with the introduction of some distortion caused by the effects of the substituents.[15]



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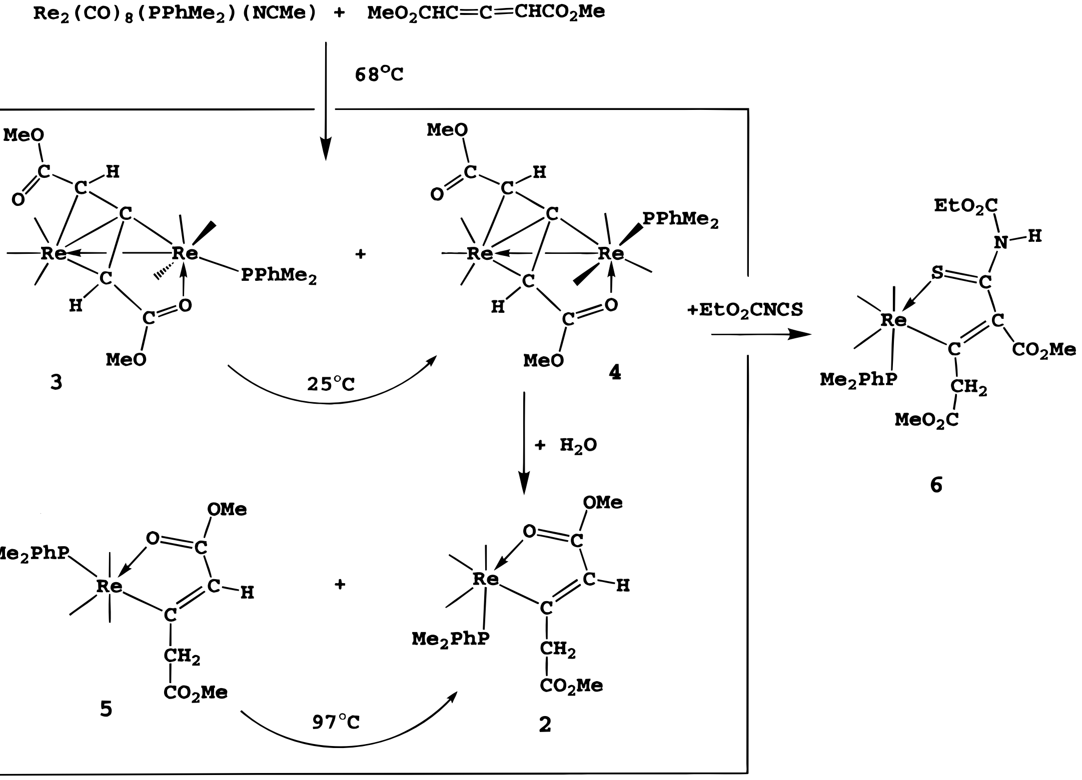
Scheme 1

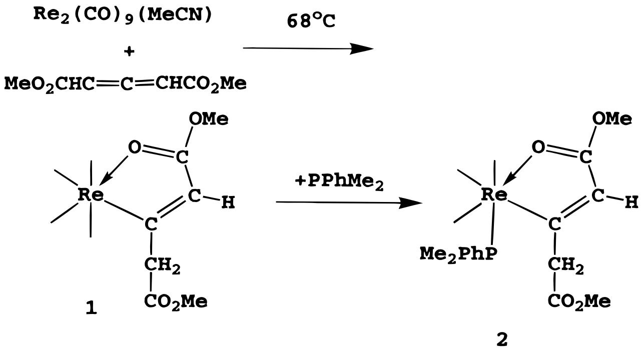


Allene has been shown to coordinate to $M_2(CO)_8$ groupings, M = Mn and Re, in the μ-η^2-η^2 form **A**.[11e−f] We were not able to isolate any π-allene complexes from the reaction of $Re_2(CO)_9(NCMe)$ with $MeO_2C(H)C{=}C{=}C(H)CO_2Me$. In contrast, when $Re_2(CO)_8(PMePh)(NCMe)$ was substituted for $Re_2(CO)_9(NCMe)$, two isolable dirhenium complexes **3** and **4** having allene ligands in the μ-η^3-η^1 coordination mode **C** were formed. The adoption of the **C** coordination mode in **3** and **4** may be strongly influenced by the coordination of one of the carboxylate groups of the allene. It is generally accepted that metal−metal bond formation is strongest when the metal atoms are in low oxidation states. Perhaps the increases in electron density at the metal atoms produced by the substitution of a CO ligand for a PMe_2Ph ligand enhanced the stablization of the dirhenium complexes to the point that they could be isolated (see Scheme 1).

Compound **4** reacts with water to form the monorhenium complex **2** containing a chelating 1,3-bis(methoxycarbonyl)propenyl grouping by addition of a hydrogen atom to the allene and the loss of a rhenium grouping. Its less stable isomer compound **5** is believed to be formed similarly. The formation of compound **1** in the reaction of $Re_2(CO)_9(NCMe)$ with $MeO_2C(H)C{=}C{=}C(H)CO_2Me$ probably takes place via a similar sequence of transformations although the allene intermediate was not observed in this reaction (see Scheme 2).

The reaction of **4** with $EtO_2CN{=}C{=}S$ yields the compound **6** by the coupling of the $EtO_2CN{=}C{=}S$ carbon atom to one of the carboxylate-substituted carbon atoms of the coordinated allene. The allene hydrogen atom is removed from that carbon atom, and hydrogen atoms are added to the nitrogen atom and the other carboxylate-substituted carbon of the allene. It is not known at this time which of these two or if either was the one derived from the carbon to which the $EtO_2CN{=}C{=}S$ has become coordinated. Certainly, there are similarities in this reaction to those of the reaction of the allene complexes **3** and **4** with H_2O, including the loss of a rhenium grouping and formation of a (methoxycarbonyl)methyl group, but we have not yet been able to sort out the details of the overall mechanism as it pertains to the formation of **6**.

Scheme 2



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Supporting Information Available: Tables of atomic positional and *B* parameters, bond distances, bond angles, and anisotropic thermal parameters for all 10 structural analyses (34 pages). Ordering information is given on any current masthead page.

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