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Reactions of Alkynes Having Electron-Withdrawing Substituents with $Re_2(CO)_9(NCMe)$. Formation of Trans Dimetalated Olefins by Alkyne Insertion into an Re–Re Bond

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The reaction of the dirhenium complex $Re_2(CO)_9(NCMe)$, **1**, with electrophilic alkynes, $RC{\equiv}CCO_2R'$, proceeds by displacement of the NCMe ligand and addition of the alkyne with insertion into the rhenium–rhenium bond to yield the dimetalated olefin complexes, $Re(CO)_4[trans\text{-}\mu\text{-}RC{=}C(CO_2R')]Re(CO)_5$, R = H, R′ = Me, **2a**, R = Me, R′ = Me, **2b**, and R = CO_2Et, R′ = Et, **2c**, that have a trans stereochemistry at the C–C double bond. The carboxylate group is coordinated to one of the rhenium atoms through the ketonic oxygen atom to form a metallacycle. The reaction is insensitive to radical scavengers, solvent polarity, and light. The absence of crossover in a reaction of a mixture of labeled and unlabeled **1** is consistent with the insertion of the alkyne into the metal–metal bond by an intramolecular mechanism. Compound **2a** was found to add CO (reversibly) to open the metallacycle and form the simple dimetalated olefin complex $Re(CO)_5[trans\text{-}\mu\text{-}HC{=}C(CO_2Me)]Re(CO)_5$, **3**. When irradiated, **2a** underwent a shift of the alkenyl hydrogen atom to the carboxylate-substituted carbon atom to form the carboxylate-substituted vinylidene complex $Re_2(CO)_8[\mu\text{-}C{=}CH(CO_2Me)]$, **4**, in which the ketonic oxygen atom of the carboxylate group is coordinated to one of the metal atoms. The metal–metal bond in **4** was cleaved (reversibly) by addition of CO at 1 atm/25 °C to yield the complex $Re_2(CO)_9[\mu\text{-}C{=}CH(CO_2Me)]$, **5**, and under a high pressure of CO (1000 psi/100 °C), compound **5** underwent a CO insertion (reversible) into one of the Re–C bonds to form the complex $Re(CO)_4[\mu\text{-}O{=}CC{=}CH(CO_2Me)]Re(CO)_5$, **6**. Compounds **1**, **2a**, and **3**–**6** were characterized by single-crystal X-ray diffraction analysis. Crystal data are as follows. For **1**: space group = $P2_1/c$, a = 7.126(1) Å, b = 30.083(4) Å, c = 15.008(2) Å, β = 93.71(1)°, Z = 8, 2731 reflections, R = 0.035. For **2a**: space group = $P2_1/n$, a = 6.644(1) Å, b = 30.005(8) Å, c = 18.036(2) Å, β = 96.09(1)°, Z = 8, 2468 reflections, R = 0.033. For **3**: space group = $P\bar{1}$, a = 10.730(2) Å, b = 11.533(2) Å, c = 9.544(2) Å, α = 114.14(1)°, β = 114.93(2)°, γ = 90.68(2)°, Z = 2, 2012 reflections, R = 0.039. For **4**: space group = $P\bar{1}$, a = 8.563(1) Å, b = 11.632(2) Å, c = 8.237(2) Å, α = 102.81(1); β = 96.47(1)°, γ = 89.10(1); Z = 2, 1636 reflections, R = 0.022. For **5**: space group = $P\bar{1}$, a = 10.553(2) Å, b = 11.588(1) Å, c = 7.3536(9) Å, α = 104.228(9); β = 90.31(1)°, γ = 84.13(1); Z = 2, 1760 reflections, R = 0.025. For **6**: space group = $P\bar{1}$, a = 9.894(1) Å, b = 12.434(2) Å, c = 8.748(2) Å, α = 108.98(1)°, β = 113.593(9)°, γ = 77.69(1)°, Z = 2, 2067 reflections, R = 0.032.

Introduction

There have been relatively few studies of reactions of dirhenium carbonyl complexes with alkynes.[1-3] Alkyne coupling has been observed for the reactions with internal alkynes.[1,2] Terminal alkynes have been found to engage in CH bond cleavage reactions involving the acetylenic hydrogen atom.[3]

In most dinuclear metal complexes, alkyne ligands adopt bridging coordinations using the $\mu\text{-}\perp$ coordination mode A[4] and serve as four-electron donors.[5] There are some examples of the $\mu\text{-}\|$ coordination mode B[6] where the alkyne serves as a two-electron donor. In the absence of a metal–metal bond these complexes are described as "dimetalated olefins", C–D.[7-9] Although most dimetalated olefin complexes exhibit the cis stereochemistry C,[8] there are a few examples that have trans stereochemistry, D.[9] A system-

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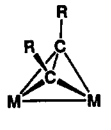
atic route to trans dimetalated olefins involves the backside addition of a nucleophilic metal center to a metal-coordinated alkyne.[9a]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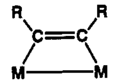
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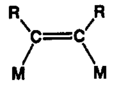
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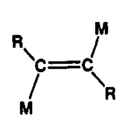
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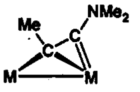
To date there have been no reports of examples of any of these coordination modes where M = Re. We have recently prepared the dirhenium ynamine complex $Re_2(CO)_8(\mu\text{-}MeCNMe_2)$[2] where the ynamine bridges the two metal atoms in an asymmetrical fashion. This distortion appears to be a result of interactions of the lone pair of electrons on the nitrogen atom with the alkyne carbon atom to which it is bonded.[10]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In this report we describe our studies of the reactions of the activated dirhenium complex $Re_2(CO)_9(NCMe)$,[11] **1**, with the electrophilic alkynes, $HC{\equiv}CCO_2Me$, $MeC{\equiv}CCO_2Me$, and $EtO_2CC{\equiv}CCO_2Et$. These reactions proceed by displacement of the NCMe ligand and addition and insertion of the alkyne into the metal–metal bond to yield the dimetalated olefin complexes, $Re(CO)_4$[*trans*-μ-$RC{=}C(CO_2R')]Re(CO)_5$, R = H, R′ = Me, **2a**, R = Me, R′ = Me, **2b**, and R = CO_2Et, R′ = Et, **2c**, of the type D that have a trans stereochemistry at the C–C double bond. A preliminary report of some of these results has been published.[12] We have also studied the transformations of **2a** by thermal and photolytic activation and its reactions with carbon monoxide.

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. Other reagent-grade solvents were stored over 4-Å molecular sieves. 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 and 10% ^{18}O was obtained from Dr. Istvan Horvath of Exxon Research & Engineering Co., Annandale, NJ. UV irradiations were performed by using an externally positioned 360-W high-pressure mercury lamp obtained from Gates Engineering (Long Island, NY) on solutions in Pyrex glassware. 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. ^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. $Re_2(CO)_9(MeCN)$,[11] **1**, and $[NBu_4]_2Re_2Cl_8$[13] were prepared by literature methods.

Preparation of $(OC)_4Re$[*trans*-μ-$HC{=}C(CO_2Me)]Re(CO)_5$, 2a. A 200-mg amount (0.301 mmol) of $Re_2(CO)_9(MeCN)$ and a 40-μL amount (0.451 mmol) of $HC{\equiv}CCO_2Me$ were dissolved in 100 mL of hexane. The solution was heated to reflux for 2 h. After cooling to room temperature, the solution was concentrated, and 172 mg of $(OC)_4Re$[*trans*-μ-$HC{=}C(CO_2Me)]Re(CO)_5$, **2a**, 81%, precipitated as pale yellow crystals. The crystals were washed with two portions of 5 mL of hexane and dried under vacuum. IR (ν_{CO} in hexane, cm^{-1}): 2134 (w), 2090 (m), 2024 (s), 1991 (sh), 1986 (sh), 1982 (s), 1937 (s), 1541 (w, br). ^1H NMR (δ in $CDCl_3$): 3.90 (3 H, s, Me), 10.42 (1 H, s, CH). Anal. Calcd (found): C, 22.02 (22.36); H, 0.56 (0.46). The mass spectrum showed the parent ion m/e = 708 and ions corresponding to the loss of each of the nine carbonyl ligands.

Reaction of $Re_2(CO)_9(MeCN)$, 1, with $HC{\equiv}CCO_2Me$ in the Absence of Light. A flask equipped with a reflux condensor containing a solution consisting of a 20-mg amount (0.030 mmol) of **1** and a 4.0-μL amount (0.045 mmol) of $HC{\equiv}CCO_2Me$ and 40 mL of hexane was wrapped completely with aluminum foil and was then heated to reflux for 2 h. After cooling to room temperature, the solvent was removed, and the residue was separated by TLC using a CH_2Cl_2/hexane, 1/3, solvent mixture to yield 17.6 mg of **2a**, 83%.

When this reaction was conducted in the dark at 25 °C for 24 h, the yield of **2a** was 2.6 mg and 13.9 mg of starting material was recovered.

When the reaction solution was irradiated with room light at 25 °C for 24 h, 1.6 mg of **2a** was obtained and 12.1 mg of starting material was recovered.

Reaction of $Re_2(CO)_9(MeCN)$ with $HC{\equiv}CCO_2Me$ in the Presence of Radical Scavengers. (1) With 2,6-Di-*tert*-butylphenol. A 20-mg amount (0.030 mmol) of **1**, a 4.0-μL amount (0.045 mmol) of $HC{\equiv}CCO_2Me$, and a 59.8-mg amount (0.300 mmol) of 2,6-di-*tert*-butylphenol were dissolved in 40 mL of hexane. The solution was then heated to reflux for 2 h. After cooling the solvent was evaporated to dryness and the residue was separated by TLC using a CH_2Cl_2/hexane, 1/4, solvent mixture to give 16.8 mg of **2a**, 79%.

(2) With Duroquinone. When the reaction was performed with the substitution of 148 mg (0.900 mmol) of duroquinone for the 2,6-di-*tert*-butylphenol, 16.0 mg of **2a**, 75%, was obtained.

(3) With O_2 (Air). Under an atmosphere of air, a 20-mg amount (0.030 mmol) of **1** and a 20-μL amount (0.225 mmol) of $HC{\equiv}CCO_2Me$ was dissolved in 40 mL of hexane. The solution was heated to reflux, and air was purged through the solution for 2 h. After cooling, the solvent was evaporated and the residue was separated by TLC to yield 18.0 mg of **2a**, 89% yield.

Effect of Solvent on the Reaction of 1 with $HC{\equiv}CCO_2Me$. (a) In Hexane. A 20-mg amount (0.030 mmol) of **1** in 40 mL of hexane was allowed to react with a 10-μL amount (0.112 mmol) of $HC{\equiv}CCO_2Me$ at 40 °C for 12.5 h. After cooling, the solvent was evaporated to dryness, and the residue was separated by TLC using a CH_2Cl_2/hexane, 1/3, solvent mixture to yield 10.6 mg of **2a** and 7.1 mg of starting material.

(b) In CH_2Cl_2. When this reaction was carried out at reflux (40 °C) in 40 mL of CH_2Cl_2 for 12.5 h, the yield of **2a** was 10.3 mg, and 5.8 mg of starting material was recovered.

Preparation of $Re_2(^{13}CO)_{10}$ and $Re_2(^{13}CO)_9(MeCN)$. A 150-mg amount (6.25 mmol) of sodium was dissolved in 1 mL of Hg in a three-necked flask. After the mixture was cooled to room temperature, 30 mL of CH_2Cl_2 was introduced into the flask. The flask was connected to a gas disperser with a 4-mm diameter that was extended into the mercury pool, and ^{13}CO was then slowly purged through the solution for 5 min. A 700-mg (5.24-mmol) portion of $AlCl_3$ was then added under the ^{13}CO atmosphere. The mixture was stirred for 2 min, and a gray solid formed. A 200-mg amount (0.175 mmol) of $[NBu_4]_2Re_2Cl_8$ was then added to the reaction mixture under the atmosphere of ^{13}CO. The mixture was stirred at 25 °C for 2 h. The orange solution was transferred under nitrogen by cannula to another flask containing 310 mg (1.74 mmol) of $C_7H_7BF_4$ and was stirred under nitrogen at 25 °C for 3 h. The excess $AlCl_3$ was then removed from the solution by passing over a column of silica gel. The solvent was evaporated, and the residue was separated by TLC using hexane

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as the elution solvent to yield 15.1 mg of $Re_2(^{13}CO)_{10}$. IR for $Re_2(^{13}CO)_{10}$ (ν_{CO} in hexane, cm^{-1}): 2020 (m), 1971 (s), 1959 (m, sh), 1933 (m), 1914 (w), 1897 (w) (for $Re_2(^{12}CO)_{10}$: 2071 (m), 2016 (s), 2005 (m, sh), 1978 (m), 1960 (w), 1943 (w). The mass spectrum showed the parent ion m/e = 664 (2 amu greater than that expected for $Re_2(^{13}CO)_{10}$ due to the presence of the 10% ^{18}O in the CO) and ions corresponding to the loss of each of the nine $^{13}C^{16}O$ and one $^{13}C^{18}O$ ligand.

The $Re_2(^{13}CO)_{10}$ was converted to $Re_2(^{13}CO)_9(MeCN)$ by the literature procedure.[11] The IR spectrum of this sample of $Re_2(^{13}CO)_9(MeCN)$ showed absorptions at 2053 (w), 2049 (w), 1998 (m), 1992 (sh), 1966 (m), 1946 (s), 1920 (m), and 1906 (m) cm^{-1} in hexane solvent. IR absorptions for $Re_2(CO)_9(MeCN)$ at natural isotopic abundances were 2103 (w), 2047 (m), 2012 (m), 1991 (s), 1965 (m), and 1942 (m) cm^{-1}.

Crossover Reaction. A 5.5-mg amount (0.008 mmol) of $Re_2(^{13}CO)_9(MeCN)$ and a 5.5-mg amount (0.008 mmol) of $Re_2(^{12}CO)_9(MeCN)$ were dissolved in 20 mL of hexane. A 2.0-μL amount (0.023 mmol) of $HC{\equiv}CCO_2Me$ was added. The solution was refluxed for 30 min and then cooled to room temperature. The solution was concentrated, and 7.0 mg of pale yellow crystals precipitated. The mass spectrum of the product showed ions with the natural dirhenium isotope distributions centered at m/e 708 and second cluster of ions centered at m/e 719 (11 amu higher than expected for unlabeled **2a** due to the presence of the 10% ^{18}O in the CO) with the isotope pattern similar to that observed for the $Re_2(^{13}CO)_{10}$. 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 713 and 714 which would have been prominantly displayed if the crossover products $Re(^{13}CO)_4[\mu\text{-}HC{=}C(CO_2Me)]Re(CO)_5$ and $Re(CO)_4[\mu\text{-}HC{=}C(CO_2Me)]Re(^{13}CO)_5$ would have been present.

Reaction of 2a with CO at High Pressure. (a) At 25 °C. A 40-mg amount (0.056 mmol) of **2a** was dissolved in 4 mL of CH_2Cl_2 and placed in a Parr high-pressure reaction vessel. The vessel was pressurized to 1200 psi with CO and stirred at 25 °C for 7 days. After venting, the solvent was removed and the residue was separated by TLC using a CH_2Cl_2/hexane, 1/1, solvent mixture to yield 31.0 mg of unreacted **2a** and 4.5 mg of $(OC)_5Re[\textit{trans}\text{-}\mu\text{-}HC{=}C(CO_2Me)]Re(CO)_5$, **3**, 11% yield as colorless crystals. IR (ν_{CO} in hexane) for **3**: 2124 (w), 2062 (w), 2046 (w), 2025 (s), 1983 (s), 1685 (w, br, in CH_2Cl_2). ^1H NMR (δ in $CDCl_3$) for **3**: 7.65 (1 H, s, CH), 3.67 (3 H, s, Me). Anal. Calcd (Found): C, 22.83 (22.76); H, 0.54 (0.59).

(b) At 103 °C. A 200-mg amount (0.282 mmol) of **2a** in 10 mL of hexane was placed in a Parr high-pressure reaction vessel. The vessel was pressurized to 1100 psi with CO and stirred at 103 °C for 11 h. After cooling to room temperature, the solvent was removed and the residue separated by TLC using a CH_2Cl_2/hexane, 1/4, solvent mixture to yield in order of elution: 1.9 mg of $Re_2(CO)_{10}$; 30.0 mg of colorless $Re_2(CO)_9[\mu\text{-}C{=}CH(CO_2Me)]$, **5**, 15% yield; 45.0 mg of starting material; 20.0 mg of orange $Re(CO)_4[\mu\text{-}O{=}CC{=}CH(CO_2Me)]Re(CO)_5$, **6**, 8% yield; and 29.5 mg of **3**, 14% yield. IR (ν_{CO} in hexane) for **5**: 2131 (w), 2087 (m), 2025 (s), 2024 (s), 1993 (m), 1984 (s), 1925 (m), 1568 (w, br). IR (ν_{CO} in hexane) for **6**: 2134 (w), 2102 (w), 2065 (w), 2047 (m), 2027 (s), 2020 (s), 2004 (s), 1984 (s), 1960 (w, sh), 1951 (m), 1575 (w, br). ^1H NMR (δ in $CDCl_3$) for **5**: 10.43 (1 H, s, CH), 3.90 (3 H, s, Me). ^1H NMR (δ in $CDCl_3$) for **6**: 6.23 (1 H, s, CH), 3.92 (3 H, s, Me). The mass spectrum for **6** showed the parent ion m/e 736 and ions corresponding to the loss of each of the eight carbonyl ligands. Anal. Calcd (Found) for **5**: C, 23.26 (23.01); H, 0.83 (0.56).

Decarbonylation of 3. An 11.0-mg amount (0.015 mmol) of **3** was dissolved in 15 mL of hexane, and the solution was heated to reflux for 30 min. After cooling, the solvent was removed in vacuo, and the residue was separated by TLC by using a CH_2Cl_2/hexane, 1/3, solvent mixture to yield 8.5 mg of **2a**, 80% yield.

Photolysis of 2a. A 50-mg amount (0.070 mmol) of **2a** was dissolved in 80 mL of hexane under an atmosphere of CO. This solution was then irradiated (UV) in the presence of slow purge with CO at 25 °C for 100 min. After reaction the solvent was removed in vacuo, and the residue was separated by TLC using a CH_2Cl_2/hexane, 1/4, solvent mixture to yield 10.1 mg of orange $Re_2(CO)_8[\mu\text{-}C{=}CH(CO_2Me)]$, **4**, 21% yield; 25.2 mg of $Re_2(CO)_9[\mu\text{-}C{=}CH(CO_2Me)]$, **5**, 50% yield; and 3.5 mg of unreacted **2**. Note: compound **4** is not stable on silica gel in the air, and the chromatography should be completed as quickly as possible. IR (ν_{CO} in hexane) for **4**: 2110 (w), 2076 (m), 2016 (s), 1998 (s), 1982 (w), 1774 (w), 1960 (s), 1942 (m), 1734 (w, br). ^1H NMR for **4** (δ in $CDCl_3$): 6.79 (1 H, s, CH), 3.91 (3 H, s, Me). Anal. Calcd (Found) for **4**: C, 21.18 (21.32); H, 0.59 (0.63).

Photolysis of 5. A 30-mg amount (0.042 mmol) of **5** was dissolved in 70 mL of hexane under an atmosphere of CO. This solution was then irradiated (UV) in the presence of a slow purge with CO at 25 °C for 100 min. The solvent was then removed in vacuo and the residue separated by TLC by using hexane solvent to yield 20.0 mg of **4**, 69% yield, and 9.3 mg of unreacted **5**.

Interconversions of 4 and 5. A 10-mg amount (0.0150 mmol) of **4** was dissolved in 7 mL of hexane and was then slowly purged with CO at 25 °C for 3 h. The solvent was evaporated under a stream of nitrogen, and the residue was separated by TLC using a CH_2Cl_2/hexane, 1/1, solvent mixture to yield 10.2 mg of **5**, 97%.

A 10-mg amount (0.014 mmol) of **5** in 30 mL of heptane was heated to reflux for 10 min; 7.6 mg of **4**, 80% yield, was isolated by TLC.

Carbonylation of 5. A 50-mg amount (0.071 mmol) of **5** in 3 mL of hexane was allowed to react with CO at 1000 psi/100 °C for 11 h in a Parr high-pressure reaction vessel. After cooling to 25 °C and venting, the solvent was evaporated, and the residue was separated by TLC using a CH_2Cl_2/hexane, 1/3, solvent mixture to yield in order of elution 1.5 mg of $Re_2(CO)_{10}$, 29.2 mg of unreacted **5**, and 11.3 mg of **6**, 22% yield.

Decarbonylation of 6. A 10-mg amount (0.014 mmol) of **6** in 10 mL of heptane was refluxed for 30 min. After cooling, the solvent was removed by rotary evaporation, and the residue was separated by TLC by using a CH_2Cl_2/hexane, 1/3, solvent mixture to yield 2.1 mg of **5**, 22% yield, and 1.5 mg of unreacted **6**.

Preparation of $Re(CO)_4[\textit{trans}\text{-}\mu\text{-}MeC{=}C(CO_2Me)]Re(CO)_5$, 2b. A 100-mg amount (0.157 mmol) of **1** and a 23.5-μL amount (0.236 mmol) of $MeC{\equiv}CCO_2Me$ were dissolved in 80 mL of hexane, and the solution was heated to reflux for 8 h. After cooling, the solvent was removed by evaporation, and the residue was separated by TLC by using a hexane/CH_2Cl_2, 4/1, solvent mixture to yield in order of elution 5.0 mg of $Re_2(CO)_{10}$; 10.8 mg of colorless $Re(CO)_4[\textit{trans}\text{-}\mu\text{-}MeC{=}C(CO_2Me)]Re(CO)_5$, **2b**, 10% yield; and 3.0 mg of unreacted **1**. IR (ν_{CO} in hexane) for **2b**: 2132 (w), 2087 (m), 2021 (s), 1990 (sh), 1982 (s), 1935 (s), 1533 (w, br). ^1H NMR (δ in $CDCl_3$) for **2b**: 3.86 (3 H, s, OMe), 2.83 (3 H, s, Me). Anal. for **2b** Calcd (Found): C, 23.26 (23.01); H, 0.83 (0.56).

Preparation of $Re(CO)_4[\textit{trans}\text{-}\mu\text{-}(EtO_2C)C{=}C(CO_2Et)]Re(CO)_5$, 2c. A 50-mg amount (0.0784 mmol) of **1** and 18.8 μL (0.118 mmol) of $EtO_2CC{\equiv}CCO_2Et$ were dissolved in 80 mL of hexane, and the solution was heated to reflux for 1.5 h. After cooling the solvent was removed by evaporation. The residue was redissolved in hexane/CH_2Cl_2, 1/1, solvent mixture and cooled to −14 °C to yield 46.1 mg of $Re_2(CO)_9[C(CO_2Et){=}CC(OEt){=}O]$, **2c** (79%), as colorless crystals. The mother liquor was concentrated and separated by TLC using a hexane/CH_2Cl_2, 1/1 solvent mixture to yield in order of elution 1.9 mg of **1** and 5.7 mg of $Re_2(CO)_7[C(CO_2Et)C(CO_2Et)C(CO_2Et)C(CO_2Et)]$, **7**, 8% yield. IR ($\nu_{CO}$ in hexane) for **2c**: 2139 (w), 2097 (w), 2036 (s), 2028 (s), 1999 (s), 1992 (s), 1986 (s), 1932 (s), 1685 (w, br in CH_2Cl_2), 1526 (w, br in CH_2Cl_2). IR (ν_{CO} in hexane) for **7**: 2103 (m), 2051 (s), 2030 (s), 1992 (s), 1977 (m), 1960 (m), 1746 (w, sh), 1739 (w), 1719 (w). ^1H NMR (δ in $CDCl_3$) for **2c**: 4.17 (2 H, q, $^3J_{H-H}$ = 7.2 Hz, CH_2), 4.16 (2 H, q, $^3J_{H-H}$ = 7.2 Hz, CH_2), 1.31 (3 H, t, $^3J_{H-H}$ = 7.2 Hz, Me), 1.29 (3 H, t, $^3J_{H-H}$ = 7.2 Hz, Me). ^1H NMR (δ in $CDCl_3$) for **7**: 4.17 (4 H, q, $^3J_{H-H}$ = 7.1 Hz, 2 CH_2), 4.16 (4 H, q, $^3J_{H-H}$ = 7.2 Hz, 2 CH_2), 1.31 (6 H, t, $^3J_{H-H}$ = 7.2 Hz, 2 Me), 1.29 (6 H, t, $^3J_{H-H}$ = 7.1 Hz, 2 Me). The mass spectra for **2c** and **7** showed the parent ions at m/e 794 and m/e 908, respectively. Complex

Table I. Crystal Data of Compound 1, 2a, and 3–6

	1	2a	3	4	5	6
formula	$Re_2O_9NC_{11}H_3$	$Re_2O_{11}C_{13}H_4$	$Re_2O_{12}C_{14}H_4$	$Re_2O_{10}C_{12}H_4$	$Re_2O_{10}C_{12}H_4$	$Re_2O_{12}C_{14}H_4$
formula weight	665.56	708.58	736.59	680.57	680.57	736.59
crystal system	monoclinic	monoclinic	triclinic	triclinic	triclinic	triclinic
lattice parameters						
a (Å)	7.126(1)	6.644(1)	10.730(2)	8.563(1)	10.553(2)	9.894(1)
b (Å)	30.083(4)	30.005(8)	11.533(2)	11.632(2)	11.588(1)	12.434(2)
c (Å)	15.008(2)	18.036(2)	9.544(2)	8.237(1)	7.3536(9)	8.748(2)
α (deg)	90.0	90.0	114.14(1)	102.81(1)	104.228(9)	108.98(1)
β (deg)	93.71(1)	96.09(1)	114.93(2)	96.47(1)	90.31(1)	113.593(9)
γ (deg)	90.0	90.0	90.68(2)	89.10(1)	84.13(1)	77.69(1)
V (Å^3)	3210.6(8)	3575(2)	952.8(4)	794.8(4)	866.9(2)	928.3(5)
space group	$P2_1/c$ (No. 14)	$P2_1/n$ (No. 14)	$P\bar{1}$ (No. 2)	$P\bar{1}$ (No. 2)	$P\bar{1}$ (No. 2)	$P\bar{1}$ (No. 2)
Z value	8	8	2	2	2	2
ρ_{calc} (g/cm^3)	2.75	2.63	2.57	2.84	2.71	2.63
μ (Mo Kα) (cm^{-1})	153.2	137.7	129.2	154.7	142.0	132.65
temperature (°C)	20	20	20	20	20	20
$2\theta_{max}$ (°)	43.5	40.0	44.0	44.0	43.0	44.0
no. obs ($I > 3\sigma$)	2731	2468	2012	1636	1760	2067
residuals: R; R_w	0.035; 0.040	0.033; 0.032	0.039; 0.045	0.022; 0.025	0.025; 0.029	0.032; 0.037

7 is believed to have a metallacyclic structure similar to that of related complexes.[2]

Crystallographic Analysis. Pale yellow crystals of **1** were grown by slow evaporation of solvent from a solution in a hexane–CH_2Cl_2 solvent mixture at 25 °C. Crystals of compound **2a** suitable for X-ray diffraction analysis were grown by slow evaporation of solvent from a solution in CH_2Cl_2 solvent at 25 °C. Crystals of compound **3** were grown from a solution in a CH_2Cl_2/hexane solvent mixture by cooling to −14 °C. Crystals of compounds **4**, **5**, and **6** were grown from solutions in a CH_2Cl_2/hexane solvent mixtures by cooling to −3 °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. 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 Molecular Structure Corp. The Woodlands, TX. Neutral atom scattering factors were calculated by the standard procedures.[14a] Anomalous dispersion corrections were applied to all non-hydrogen atoms.[14b] Lorentz/polarization (Lp) and empirical absorption corrections based on three azimuthal scans were applied to the data for each structure. 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 $\sigma(F_o^2) = [\sigma(I_{raw})^2 + (0.02I_{net})^2]^{1/2}/\mathrm{Lp}$.

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 I.

Compounds **1** and **2a** crystallized in a monoclinic crystal system. Their space groups, $P2_1/c$ and $P2_1/n$, respectively, were identified uniquely from the systematic absences in the data. Both complexes crystallize with two independent molecules in the asymmetric crystal unit. For **1** all non-hydrogen atoms were refined anisotropically, and the positions of the methyl hydrogen atoms were calculated by assuming an idealized geometry with C–H = 0.95 Å and employing one located hydrogen H(3) and H(6) in each of the independent molecules. For **2a** all atoms heavier that carbon were refined anisotropically. All carbon atoms were refined with isotropic thermal parameters, and the hydrogen atom positions were calculated by assuming idealized geometries.

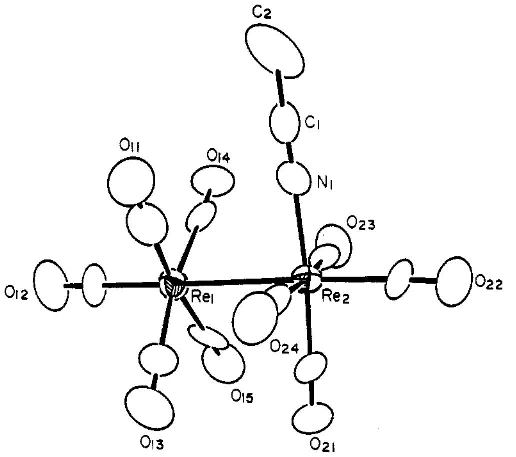

Figure 1. An ORTEP diagram of $Re_2(CO)_9(NCMe)$, **1**, showing 50% probability thermal ellipsoids. Selected intramolecular bond distances (Å) and angles (deg) are as follows: Re(1A)–Re(2A) = 3.309(1), Re(1B)–Re(2B) = 3.309(1), Re(1A)–N(1A) = 2.13(2), Re(1B)–N(1B) = 2.10(2), C(1A)–N(1A) = 1.16(2), C(1B)–N(1B) = 1.11(2), Re(1A)–Re(2A)–N(1A) = 88.4(4), Re(1A)–Re(2A)–N(1A) = 89.8(4).

Compounds **3**–**6** 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 in each case. For compounds **3** and **5** all non-hydrogen atoms were refined with anisotropic thermal parameters, and the alkenyl hydrogen atom was located and refined with an isotropic thermal parameter. The positions of the methyl hydrogen atoms were calculated by assuming idealized geometries. For compounds **4** and **6** all non-hydrogen atoms were refined with anisotropic thermal parameters, and all hydrogen atoms were located and refined with isotropic thermal parameters.

Results and Discussion

To be certain about the coordination geometry of the starting material **1**, a single-crystal X-ray diffraction analysis of this compound was performed. Complex **1** crystallized with two independent molecules in the asymmetric crystal unit. Both molecules are structurally similar, and an ORTEP diagram of the molecular structure of one of the two molecules is shown in Figure 1. The structure of **1** is similar to that of $Re_2(CO)_{10}$ having two square-pyramidal ReL_5 groups joined by a Re–Re single bond. The equatorial ligands adopt a staggered rotational conformation between the two halves of the molecule. The

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[14] (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.

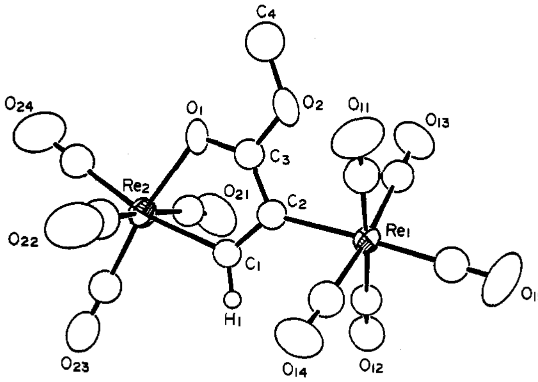

Figure 2. An ORTEP diagram of Re(CO)$_4$[μ-HC=C(CO$_2$Me)]Re(CO)$_5$, **2a**, showing 50% probability thermal ellipsoids. Selected interatomic distances (Å) are Re(1a)–C(2a) = 2.22(2), Re(1b)–C(2b) = 2.21(2), Re(2a)–C(1a) = 2.17(2), Re(2b)–C(1b) = 2.18(1), Re(2a)–O(1a) = 2.16(1), Re(2b)–C(1b) = 2.16(1), C(1a)–C(2a) = 1.37(2), C(1b)–C(2b) = 1.41(2), C(2a)–C(3a) = 1.41(2), C(2b)–C(3b) = 1.40(2), C(3a)–O(1a) = 1.27(2), C(3b)–O(1b) = 1.26(2).

Re–Re bond distance, 3.039(1) Å, is not significantly different than that found for Re$_2$(CO)$_{10}$, 3.041(1) Å.[15] The acetonitrile ligand occupies one of the equatorial coordination sites, Re–N = 2.13(2) Å [2.10(2) Å].

When 1 was allowed to react with the alkynes, HC≡CCO$_2$Me, MeC≡CCO$_2$Me, EtO$_2$CC≡CCO$_2$Et, the products Re(CO)$_4$[*trans*-μ-RC=C(CO$_2$R′)]Re(CO)$_5$, R = H, R′ = Me, **2a**, R = Me, R′ = Me, **2b**, and R = CO$_2$Et, R′ = Et, **2c**, were obtained in the yields 81%, 10%, and 79%, respectively. The three products were characterized by IR and ^{1}H NMR analyses. Compound **2a** was also characterized by a single-crystal X-ray diffraction analysis. An ORTEP drawing of the molecular structure of **2a** is shown in Figure 2. The crystal of **2a** also contains two symmetry independent molecules in the asymmetric crystal unit, and both molecules are structurally similar. Final atomic positional parameters are listed in Table II. The complex can be described as a dimetalated olefin of the type D formed by the insertion of the alkyne between the two metal atoms. The C(1)–C(2) distance, 1.37(2) Å [1.41(2) Å], is indicative of a C–C double bond and thus supports the formulation as a dimetalated olefin. Most interestingly, the rhenium atoms exhibit a trans or *E* stereochemistry with respect to the two carbon atoms. The ketonic oxygen atom O(1) of the ester grouping is coordinated to the metal atom Re(2) to form a five-membered metallacyclic ring, Re(2)–O(1) = 2.16(1) Å [2.16(1) Å]. The hydrogen atom H(2) exhibits a highly deshielded NMR chemical shift, δ = 10.42 ppm.

To obtain information about the mechanism of these reactions, the reaction of 1 with HC≡CCO$_2$Me was studied in detail. It was found that neither the yield nor the rate of the reaction was significantly affected by the presence of room light. Solvent polarity (hexane vs methylene chloride) also had no significant influence upon the reaction. Suspecting that radical intermediates could be involved, efforts were made to test for their presence by performing the reaction in the presence of radical scavengers. However, it was found that the yield and rate of the reaction was *not* significantly affected when the reaction was performed in air, in the presence 2,6-di-*tert*-butylphenol in a 10-fold molar excess, or in the presence duroquinone in a 30-fold molar excess.

To test for molecular fragmentation, the following crossover experiment was performed. A sample of Re$_2$(^{13}CO)$_{10}$ containing 99.9% ^{13}C was prepared and converted to Re$_2$(^{13}CO)$_9$(MeCN) by treatment with Me$_3$NO in MeCN solvent. This compound was mixed with an approximately equimolar amount of unenriched 1, and the mixture was then converted to **2a** by reaction with HC≡CCO$_2$Me. An analysis of the product **2a** by mass spectrometry showed ions due only to the presence of **2a** without ^{13}C enrichment and **2a** having ^{13}C 99.9% at the carbon atoms of the carbonyl ligands. There were *no* significant amounts of the ions attributable to the crossover products, Re(^{13}CO)$_4$[*trans*-μ-HC=C(CO$_2$Me)]Re(CO)$_5$ and Re(CO)$_4$[*trans*-μ-HC=C(CO$_2$Me)]Re(^{13}CO)$_5$. The combination of evidence is consistent with a nondissociative "*intramolecular*" insertion mechanism, but it must be noted that the possibility of dissociative mechanisms in which the fragments remain proximate to one another in tight solvent cages is not ruled out by this data.

Theoretical studies of dimetallated olefins have indicated that the cis/trans isomerization process, C to D, should have a high activation barrier and thus should occur very slowly under the conditions that we have used.[7] Therefore, we have proposed the mechanism shown in Scheme I that avoids traversing an intermediate species, such as C. The first step is a simple substitution of the MeCN ligand and coordination of the C–C triple bond to one of the rhenium atoms, F. An interaction must eventually develop between the second rhenium atom and at least one of the acetylenic carbon atoms of the alkyne ligand. We have chosen the carboxylate-substituted carbon atom for this interaction. As this interaction develops G, the rhenium–rhenium bond will develop a heteropolar (donor/acceptor) character, and in the limit, H, a μ-$\|$ alkyne ligand of the type B would bridge a full heteropolar rhenium–rhenium bond. At some point the metal–metal bond must be cleaved. From H this could be as simple as a withdrawal of both electrons in the metal–metal bond to the Re(CO)$_5$ grouping. To maintain an 18-electron configuration, the Re(CO)$_4$ grouping might then engage two additional electrons from the alkynyl group. This could be achieved through a 90° twist of the MeO$_2$CCRe(CO)$_5$ grouping to form an η^2-alkenyl ligand serving as a three-electron donor, I. Numerous examples of η^2-alkenyl ligands which serve as three-electron donors have been characterized recently.[16] The formation of 2 could be completed by coordination of one of the lone pairs of electrons of the ketonic oxygen atom of the carboxylate group to the Re(CO)$_4$ grouping. The η^2-alkenyl group is then transformed to an η^1-alkenyl group by a further rotation of 90° of the MeO$_2$CCRe(CO)$_5$ group resulting in the observed trans stereochemistry. In all of the intermediates, 18-electron configurations are maintained at both metal atoms. Efforts to produce dimetalated olefin complexes by reactions of 1 with alkynes, such as PhC≡CPh or MeC≡CNMe$_2$, have been unsuccessful, although reactions do take place. It is possible that the stabilizing effect provided by the coordination of the ketonic oxygen atom of the carboxylate grouping is

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[15] Churchill, M. R.; Amoh, K. N.; Wasserman, H. J. *Inorg. Chem.* 1981, *20*, 1609.

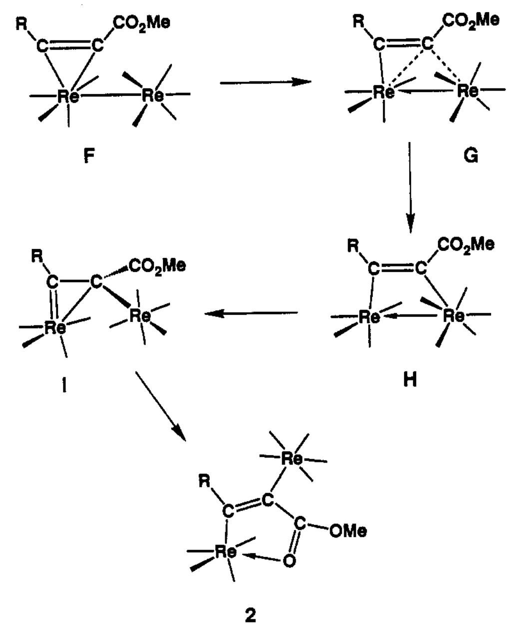
[16] (a) Templeton, J. L. *Adv. Organomet. Chem.* 1989, *29*, 1. (b) Feng, S. G.; Gamble, A. S.; Templeton, J. L. *Organometallics* 1989, *8*, 2024. (c) Pombeiro, A. J. L. *J. Organomet. Chem.* 1988, *358*, 273. (d) Pombeiro, A. J. L.; Hughes, D. L.; Richards, R. L.; Silvestre, J.; Hoffmann, R. *J. Chem. Soc., Chem. Commun.* 1986, 1125. (e) Allen, S. R.; Beevor, R. G.; Green, M.; Norman, N. C.; Orpen, A. G.; Williams, I. D. *J. Chem. Soc., Dalton Trans.* 1985, 435.

Table II. Positional Parameters and B_{eq} Values for $Re_2(CO)_9(HC_2CO_2Me)$, 2a

atom	x	y	z	B_{eq},[a] Å^2	atom	x	y	z	B_{eq},[a] Å^2
Re(1A)	0.44384(12)	0.05347(03)	0.33098(04)	2.85(4)	C(1A)	0.477(03)	0.0923(07)	0.1650(09)	3.6(4)
Re(1B)	0.84801(12)	0.21204(03)	0.84743(04)	2.86(4)	C(1B)	0.882(03)	0.1539(06)	0.6981(08)	2.8(4)
Re(2A)	0.55396(12)	0.08359(03)	0.05191(04)	3.01(4)	C(2A)	0.521(03)	0.0582(07)	0.2147(09)	3.2(4)
Re(2B)	0.97692(12)	0.14829(03)	0.58609(04)	3.19(4)	C(2B)	0.931(03)	0.1942(06)	0.7356(08)	3.1(4)
O(1A)	0.6740(17)	0.0260(04)	0.1127(06)	3.4(6)	C(3A)	0.634(03)	0.0262(07)	0.1800(09)	2.8(4)
O(1B)	1.0948(18)	0.2115(04)	0.6283(05)	3.7(6)	C(3B)	1.048(03)	0.2208(07)	0.6927(10)	3.2(4)
O(2A)	0.7012(19)	−0.0103(05)	0.2208(06)	4.3(7)	C(4A)	0.815(03)	−0.0455(07)	0.1875(10)	4.5(4)
O(2B)	1.108(02)	0.2597(04)	0.7231(06)	4.7(7)	C(4B)	1.211(03)	0.2901(08)	0.6792(11)	5.4(5)
O(11A)	0.875(02)	0.0131(05)	0.3826(07)	5.4(8)	C(11A)	0.716(03)	0.0274(07)	0.3641(09)	3.3(4)
O(11B)	0.436(02)	0.1662(06)	0.7976(08)	7(1)	C(11B)	0.587(03)	0.1832(08)	0.8176(10)	4.5(5)
O(12A)	0.028(02)	0.0925(05)	0.2687(07)	6.1(9)	C(12A)	0.180(03)	0.0788(08)	0.2906(10)	4.7(5)
O(12B)	1.275(02)	0.2550(05)	0.8902(06)	4.7(7)	C(12B)	1.118(03)	0.2390(07)	0.8744(09)	3.3(4)
O(13A)	0.274(02)	−0.0415(05)	0.2854(07)	5.6(8)	C(13A)	0.335(03)	−0.0070(07)	0.3031(09)	3.0(4)
O(13B)	1.024(02)	0.1209(05)	0.9015(07)	5.8(8)	C(13B)	0.959(03)	0.1527(08)	0.8813(10)	3.6(4)
O(14A)	0.626(02)	0.1499(05)	0.3525(08)	7(1)	C(14A)	0.560(03)	0.1129(08)	0.3466(10)	4.1(4)
O(14B)	0.694(03)	0.3021(06)	0.7734(08)	8(1)	C(14B)	0.746(03)	0.2689(08)	0.8010(10)	4.4(5)
O(15A)	0.314(02)	0.0481(05)	0.4910(06)	6.0(8)	C(15A)	0.364(03)	0.0506(07)	0.4322(10)	3.6(4)
O(15B)	0.723(02)	0.2368(06)	1.0031(07)	8(1)	C(15B)	0.767(03)	0.2268(07)	0.9454(11)	4.4(5)
O(21A)	0.126(02)	0.0412(05)	0.0224(07)	5.9(9)	C(21A)	0.287(03)	0.0547(07)	0.0320(09)	3.8(4)
O(21B)	0.785(02)	0.0583(05)	0.5427(07)	7(1)	C(21B)	0.862(03)	0.0920(07)	0.5581(09)	3.5(4)
O(22A)	0.957(02)	0.1347(05)	0.0913(07)	5.5(8)	C(22A)	0.815(03)	0.1148(07)	0.0773(09)	3.7(4)
O(22B)	0.561(03)	0.1910(07)	0.5311(09)	10(1)	C(22B)	0.714(04)	0.1773(09)	0.5497(11)	5.6(5)
O(23A)	0.370(02)	0.1699(05)	−0.0106(08)	7(1)	C(23A)	0.436(03)	0.1372(08)	0.0109(10)	4.2(5)
O(23B)	1.141(02)	0.1567(05)	0.4318(07)	7(1)	C(23B)	1.076(03)	0.1538(07)	0.4877(10)	3.8(4)
O(24A)	0.684(02)	0.0522(06)	−0.0992(07)	7(1)	C(24A)	0.636(03)	0.0639(07)	−0.0448(10)	3.9(4)
O(24B)	1.366(03)	0.0977(06)	0.6539(08)	8(1)	C(24B)	1.224(03)	0.1176(07)	0.6295(10)	4.1(4)

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

Scheme I



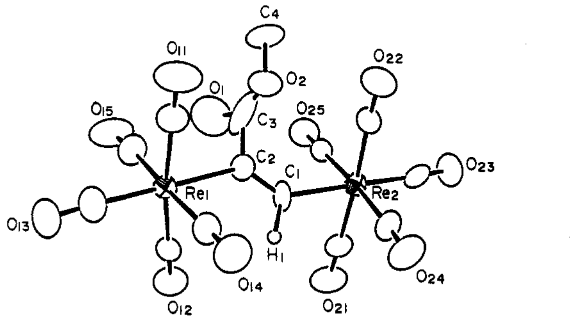


Figure 3. An ORTEP diagram of $Re(CO)_5[\textit{trans}\text{-}\mu\text{-}HC{=}C(CO_2Me)]Re(CO)_5$, **3**, showing 50% probability thermal ellipsoids. Selected intramolecular bond distances (Å) and angles (deg) are as follows: Re(1)–C(2) = 2.22(1), Re(2)–C(1) = 2.24(1), C(1)–C(2) = 1.29(2), Re(2)–C(1)–C(2) = 134(1), Re(1)–C(2)–C(1) = 129(1), Re(1)–C(2)–C(3) = 114(1), C(1)–C(2)–C(3) = 117(1).

essential for the isolation of the dimetalated olefin complexes when only nine carbonyl ligands are present.

In further studies, we investigated the reaction of **2a** with CO, its transformation by UV–vis radiation, and the reaction of the product of this reaction with CO. When **2a** was treated with CO at 1200 psi at 25 °C for 7 days the new CO adduct $(OC)_5Re[\textit{trans}\text{-}\mu\text{-}HC{=}C(CO_2Me)]Re(CO)_5$, **3**, was obtained in 11% yield. Compound **3** was also characterized by a single-crystal X-ray diffraction analysis. An ORTEP drawing of the molecular structure of **3** is shown in Figure 3. Final atomic positional parameters are listed in Table III. The complex is also a dimetalated olefin of the type D. The C(1)–C(2) distance, 1.29(2) Å, appears to be significantly shorter than that in **2a**. The reason for this is not evident, but the distance is clearly consistent with the existence of a C–C double bond between these atoms and thus supports the formulation of **3** as a dimetalated olefin. As in **2a**, the rhenium atoms exhibit a trans or *E* stereochemistry with respect to the two carbon atoms, but the ketonic oxygen atom O(1) of the ester grouping is not coordinated to the metal atom Re(2). The CO addition to form **3** was thus a simple displacement of the ketonic oxygen atom O(1) and an opening of the metallacyclic ring. The hydrogen atom H(1) was located and refined crystallographically. It exhibits a characteristic deshielded NMR chemical shift, $\delta = 7.65$ ppm, but this is significantly less deshielded than that in **2a**. The carbonylation of **2a** is readily reversible. When a solution of **3** in hexane solvent was heated to reflux for 30 min, **2a** was formed in 80% yield.

When **2a** was irradiated (UV–vis) in a hexane solution under an atmosphere of CO for 100 min, two new compounds $Re_2(CO)_8[\mu\text{-}C{=}CH(CO_2Me)]$, **4**, and $Re_2(CO)_9[\mu\text{-}C{=}CH(CO_2Me)]$, **5**, were obtained in the yields 21% and 50%, respectively. Compounds **4** and **5** differ by the amount of one CO ligand, and they are readily interconvertible. Compound **4** was converted to **5** in 97% yield in 3 h by reaction with CO (1 atm) at 25 °C. When **5** was heated to reflux for 10 min in heptane solution **4** was

Table III. Positional Parameters and B_{eq} Values for $Re_2(CO)_{10}(HC_2CO_2Me)$, 3

atom	*x*	*y*	*z*	B_{eq},[a] Å^2
Re(1)	0.08584(05)	0.22181(06)	0.41369(07)	3.03(2)
Re(2)	0.65452(05)	0.31953(06)	0.70729(07)	3.15(2)
O(1)	0.284(02)	0.030(02)	0.238(03)	12(1)
O(2)	0.369(02)	0.214(03)	0.255(02)	13(1)
O(11)	0.0530(18)	0.3436(17)	0.163(02)	8.9(7)
O(12)	0.1667(14)	0.1115(14)	0.6848(17)	6.8(6)
O(13)	−0.2264(13)	0.2011(16)	0.3370(18)	8.2(7)
O(14)	0.1816(15)	0.5060(14)	0.7106(18)	6.6(5)
O(15)	0.002(02)	−0.0643(16)	0.1259(19)	9.7(8)
O(21)	0.6571(17)	0.2190(14)	0.9627(17)	7.6(6)
O(22)	0.6236(14)	0.4306(14)	0.4490(18)	6.6(5)
O(23)	0.9795(11)	0.3597(15)	0.8294(17)	7.1(6)
O(24)	0.6661(15)	0.5974(14)	0.9787(17)	7.1(6)
O(25)	0.6169(14)	0.0343(13)	0.4345(17)	6.1(5)
C(1)	0.4221(13)	0.2905(15)	0.620(02)	3.9(5)
C(2)	0.3106(14)	0.2377(16)	0.4712(20)	4.2(5)
C(3)	0.333(02)	0.155(03)	0.299(03)	9(1)
C(4)	0.393(02)	0.135(03)	0.100(02)	9(1)
C(11)	0.0632(17)	0.2992(18)	0.252(02)	5.0(6)
C(12)	0.1365(15)	0.1521(17)	0.588(02)	4.1(5)
C(13)	−0.1088(19)	0.2063(18)	0.361(02)	5.5(7)
C(14)	0.1459(16)	0.4043(17)	0.604(02)	4.5(6)
C(15)	0.0390(19)	0.037(02)	0.229(03)	5.8(7)
C(21)	0.6597(17)	0.2536(17)	0.869(02)	4.6(6)
C(22)	0.6318(15)	0.3883(15)	0.540(02)	4.0(5)
C(23)	0.8622(20)	0.3481(16)	0.7893(19)	4.6(6)
C(24)	0.6663(16)	0.4957(17)	0.880(02)	4.7(6)
C(25)	0.6282(14)	0.1374(17)	0.532(02)	3.6(5)

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

Table IV. Positional Parameters and B_{eq} Values for $Re_2(CO)_8[C_2(H)C(O)OMe]$, 4

atom	*x*	*y*	*z*	B_{eq},[a] Å^2
Re(1)	−0.59383(04)	0.30665(03)	0.63177(04)	2.47(2)
Re(2)	−0.84390(04)	0.16133(03)	0.37269(04)	2.52(2)
O(1)	−0.9871(08)	0.2588(06)	0.2164(07)	3.1(3)
O(2)	−1.0486(08)	0.4369(06)	0.1693(08)	3.6(3)
O(11)	−0.3770(09)	0.1400(07)	0.8064(10)	4.6(3)
O(12)	−0.3516(09)	0.3055(08)	0.3740(10)	5.6(4)
O(13)	−0.8106(09)	0.3156(07)	0.9150(09)	4.5(4)
O(14)	−0.4462(08)	0.5404(07)	0.8348(09)	4.1(3)
O(21)	−1.0428(10)	−0.0539(07)	0.1583(10)	5.7(4)
O(22)	−0.6776(09)	−0.0092(07)	0.5727(09)	4.7(4)
O(23)	−0.5923(11)	0.1228(09)	0.1186(11)	6.2(5)
O(24)	−1.0923(09)	0.2276(08)	0.6277(09)	4.7(4)
C(1)	−0.7661(10)	0.3499(08)	0.4678(10)	2.4(4)
C(2)	−0.8521(11)	0.4208(10)	0.3859(12)	2.9(4)
C(3)	−0.9650(11)	0.3689(10)	0.2542(11)	3.0(4)
C(4)	−1.1650(15)	0.3794(13)	0.0337(15)	4.2(6)
C(11)	−0.4523(13)	0.2021(09)	0.7413(13)	3.6(5)
C(12)	−0.4434(12)	0.3066(09)	0.4647(13)	3.5(5)
C(13)	−0.7359(12)	0.3131(09)	0.8101(12)	3.1(4)
C(14)	−0.4978(11)	0.4499(10)	0.7610(12)	3.1(4)
C(21)	−0.9692(13)	0.0243(10)	0.2350(12)	3.7(5)
C(22)	−0.7339(12)	0.0597(09)	0.5004(12)	3.2(4)
C(23)	−0.6813(14)	0.1363(09)	0.2092(14)	3.8(5)
C(24)	−1.0002(12)	0.2018(09)	0.5343(12)	2.9(4)

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

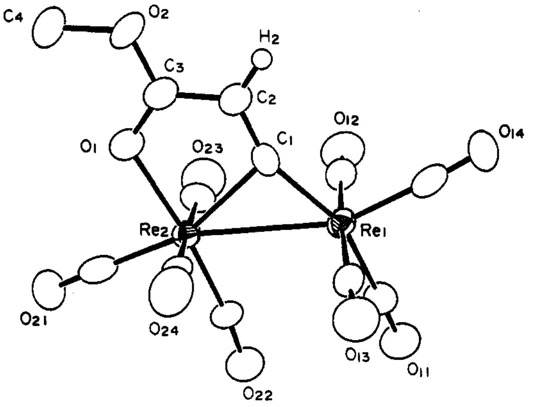


Figure 4. An ORTEP diagram of $Re_2(CO)_8[\mu\text{-}C{=}CH(CO_2Me)]$, 4, showing 50% probability thermal ellipsoids. Selected intramolecular bond distances (Å) and angles (deg) are as follows: Re(1)–Re(2) = 3.0790(7), Re(1)–C(1) = 2.02(1), Re(2)–C(1) = 2.244(9), Re(2)–O(1) = 2.167(6), C(1)–C(2) = 1.34(1), C(2)–C(3) = 1.40(1), C(3)–O(1) = 1.26(1), Re(1)–C(1)–C(2) = 156.7(8), Re(2)–C(1)–C(2) = 111.0(7), Re(1)–C(1)–Re(2) = 92.3(4), C(1)–C(2)–C(3) = 118(1).

regenerated in 80% yield. Both compounds were characterized by IR, ^{1}H NMR and single-crystal X-ray diffraction analyses.

An ORTEP drawing of the molecular structure of 4 is shown in Figure 4. Final atomic positional parameters are listed in Table IV. The complex contains two $Re(CO)_4$ groups joined by a Re–Re single bond, Re(1)–Re(2) = 3.0790(7) Å, which is slightly longer than that in $Re_2(CO)_{10}$ or 1. The two metal atoms are bridged by a methyl carboxylate-substituted vinylidene ligand. The coordination of the bridging carbon atom is slightly asymmetrical, Re(1)–C(1) = 2.02(1) Å and Re(2)–C(1) = 2.244(9) Å. The C(1)–C(2) distance, 1.34(1) Å is indicative of the expected C–C double bond. Interestingly, the ketonic oxygen atom O(1) of the ester grouping is coordinated to the metal atom Re(2) to form a five-membered metallacyclic ring. Re(2)–O(1) = 2.167(1) Å, as found in **2a**. As a consequence the metal–metal bond is formally heteropolar (i.e. Re(2) donates two electrons to Re(1)). The hydrogen atom H(2) was located and refined crystallographically, and it exhibits a characteristic deshielded NMR chemical shift, δ = 6.79 ppm. Bridging vinylidene ligands are not uncommon,[17] and similar carboxylate-substituted alkenylidene ligands having ketonic coordination of the carboxylate groups have been found in the dimanganese complexes $Mn_2(CO)_8[\mu\text{-}C{=}CMe(CO_2Et)]$[18] and $Mn_2(CO)_6(dppm)[\mu\text{-}C{=}CH(CO_2Me)]$.[19]

An ORTEP drawing of the molecular structure of **5** is shown in Figure 5. Final atomic positional parameters are listed in Table V. This complex is very similar to **4**, but has no metal–metal bond, Re(1)···Re(2) = 3.9794(7) Å. The two metal groups are joined only by the bridging carbon atom of the carboxylate-substituted vinylidene ligand, and the coordination is much more symmetrical than in **4**, Re(1)–C(1) = 2.22(1) Å and Re(2)–C(1) = 2.204(8) Å. The C(1)–C(2) distance, 1.34(1) Å, is the same as that in **4**. The ketonic oxygen atom O(1) of the ester grouping is still coordinated to the metal atom Re(2), Re(2)–O(1) = 2.191(1) Å. The hydrogen atom H(2) was again located and refined crystallographically, but its NMR shift is much more deshielded than that in **4**, δ = 10.43 ppm. At 103 °C under a pressure of CO (1100 psi), compound **5** was obtained from **2a** in a 15% yield together with some **3** (14% yield) and a new compound $Re(CO)_4[\mu\text{-}O{=}CC{=}CH(CO_2Me)]Re(CO)_5$, **6**, in an 8% yield. Compound **6** was also obtained directly from **5** under similar conditions (1000 psi/100 °C) for 11 h, but the yield was again low, 22%, and a small amount of $Re_2(CO)_{10}$ was also obtained.

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[18] Adams, R. D.; Chen, G.; Chen, L.; Pompeo, M. P.; Yin, J. *Organometallics* **1992**, *11*, 563.

[19] García Alonso, F. J.; Riera, V.; Ruiz, M. A.; Tiripicchio, A.; Camellini, M. T. *Organometallics* **1992**, *11*, 370.

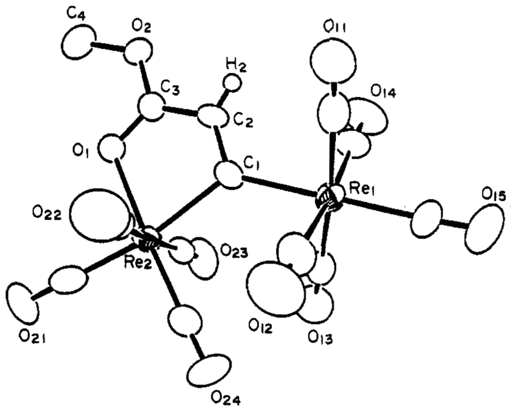


Figure 5. An ORTEP diagram of Re$_2$(CO)$_9$[μ-C=CH(CO$_2$Me)], **5**, showing 50% probability thermal ellipsoids. Selected intramolecular bond distances (Å) and angles (deg) are as follows: Re(1)···Re(2) = 3.9794(7), Re(1)–C(1) = 2.221(1), Re(2)–C(1) = 2.204(8), Re(2)–O(1) = 2.191(6), C(1)–C(2) = 1.34(1), C(2)–C(3) = 1.41(1), C(3)–O(1) = 1.25(1), Re(1)–C(1)–C(2) = 121.2(7), Re(2)–C(1)–C(2) = 110.7(7), Re(1)–C(1)–Re(2) = 128.1(5), C(1)–C(2)–C(3) = 118.3(9).

Table V. Positional Parameters and B_{eq} Values for Re$_2$(CO)$_8$[C$_2$(H)CO$_2$Me], 5

atom	x	y	z	B_{eq},[a] Å^2
Re(1)	0.28192(04)	0.43551(03)	0.72090(06)	3.11(2)
Re(2)	0.20561(04)	0.09659(03)	0.62165(05)	2.63(2)
O(1)	0.0305(06)	0.1111(05)	0.7880(09)	3.0(3)
O(2)	−0.1168(07)	0.2418(05)	0.9704(09)	3.6(3)
O(11)	0.2559(09)	0.5349(07)	1.1565(12)	5.6(5)
O(12)	0.5274(09)	0.2776(09)	0.7902(16)	7.6(6)
O(13)	0.2834(09)	0.3153(07)	0.2883(13)	5.7(5)
O(14)	0.0237(09)	0.5830(07)	0.6748(12)	5.9(5)
O(15)	0.4315(09)	0.6437(09)	0.6756(16)	8.2(6)
O(21)	0.2120(08)	−0.1806(06)	0.4855(12)	5.5(4)
O(22)	0.3718(10)	0.0808(08)	0.9682(12)	6.8(5)
O(23)	0.0596(08)	0.1477(06)	0.2732(12)	5.1(4)
O(24)	0.4488(08)	0.0929(07)	0.3933(12)	5.1(4)
C(1)	0.1674(09)	0.2901(07)	0.7493(13)	2.7(4)
C(2)	0.0611(10)	0.3135(09)	0.8553(15)	3.3(5)
C(3)	−0.0068(09)	0.2169(08)	0.8683(13)	2.7(5)
C(4)	−0.1820(10)	0.1440(09)	0.9884(15)	3.9(5)
C(11)	0.2657(11)	0.5013(09)	1.0001(19)	3.9(6)
C(12)	0.4380(13)	0.3325(10)	0.7613(18)	4.9(6)
C(13)	0.2858(11)	0.3606(09)	0.4455(19)	4.1(6)
C(14)	0.1168(12)	0.5294(09)	0.6915(14)	3.8(5)
C(15)	0.3793(13)	0.5656(10)	0.6886(19)	5.6(7)
C(21)	0.2104(10)	−0.0782(11)	0.5365(14)	3.8(5)
C(22)	0.3109(10)	0.0845(09)	0.8486(16)	3.6(5)
C(23)	0.1071(11)	0.1258(08)	0.4008(16)	3.4(5)
C(24)	0.3597(11)	0.0931(08)	0.4780(14)	3.4(5)
H(2)	0.026(10)	0.376(09)	0.923(14)	4(1)

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

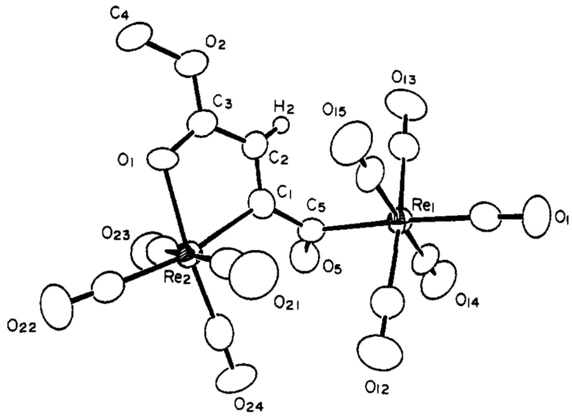


Figure 6. An ORTEP diagram of Re(CO)$_4$[μ-O=CC=CH(CO$_2$Me)]Re(CO)$_5$, **6**, showing 50% probability thermal ellipsoids. Selected intramolecular bond distances (Å) and angles (deg) are as follows: Re(1)–C(5) = 2.23(1), Re(2)–C(1) = 2.16(1), Re(2)–O(1) = 2.170(7), C(1)–C(2) = 1.35(1), C(1)–C(5) = 1.47(1), Re(2)–C(1)–C(2) = 114.6(8), Re(2)–C(1)–C(5) = 123.5(7), Re(1)–C(5)–O(5) = 123.3(8), C(1)–C(2)–C(3) = 115(1), C(2)–C(1)–C(5) = 122(1).

Table VI. Positional Parameters and B_{eq} Values for Re$_2$(CO)$_9$[C(O)CC(H)C(O)OMe], 6

atom	x	y	z	B_{eq},[a] Å^2
Re(1)	0.01508(05)	0.24388(03)	0.24669(05)	2.33(2)
Re(2)	0.39210(05)	0.22531(04)	0.79794(05)	2.41(2)
O(1)	0.5736(08)	0.2609(07)	0.7478(10)	3.2(3)
O(2)	0.6322(08)	0.3478(07)	0.5951(10)	3.8(3)
O(5)	0.0563(09)	0.4057(07)	0.6099(10)	3.9(3)
O(11)	−0.1432(10)	0.0966(07)	−0.1270(11)	4.5(4)
O(12)	−0.0520(12)	0.0758(09)	0.3984(13)	6.2(5)
O(13)	0.0944(12)	0.4299(08)	0.1345(12)	5.5(5)
O(14)	−0.2793(11)	0.3880(08)	0.2696(13)	5.5(4)
O(15)	0.3142(10)	0.1076(08)	0.2228(12)	5.0(4)
O(21)	0.3598(12)	−0.0159(08)	0.5354(13)	5.6(5)
O(22)	0.6030(11)	0.1188(09)	1.0966(14)	6.6(5)
O(23)	0.3718(12)	0.4686(09)	1.0505(13)	6.0(5)
O(24)	0.1149(10)	0.1860(08)	0.8385(12)	4.8(4)
C(1)	0.2861(12)	0.3157(09)	0.5995(13)	2.7(4)
C(2)	0.3802(12)	0.3497(10)	0.5520(15)	2.9(4)
C(3)	0.5312(12)	0.3194(09)	0.6370(15)	2.9(4)
C(4)	0.7873(14)	0.3111(14)	0.676(02)	4.1(6)
C(5)	0.1243(12)	0.3398(09)	0.5222(15)	2.8(4)
C(11)	−0.0873(13)	0.1523(09)	0.0050(16)	2.8(4)
C(12)	−0.0235(14)	0.1330(10)	0.3410(15)	3.5(5)
C(13)	0.0623(13)	0.3652(10)	0.1768(15)	3.3(5)
C(14)	−0.1722(13)	0.3377(09)	0.2625(15)	3.0(5)
C(15)	0.2059(14)	0.1560(10)	0.2325(15)	3.2(5)
C(21)	0.3759(13)	0.0711(11)	0.6261(16)	3.4(5)
C(22)	0.5245(13)	0.1567(11)	0.9851(17)	3.8(5)
C(23)	0.3850(14)	0.3806(11)	0.9596(16)	3.7(5)
C(24)	0.2184(14)	0.1997(10)	0.8221(14)	3.4(5)

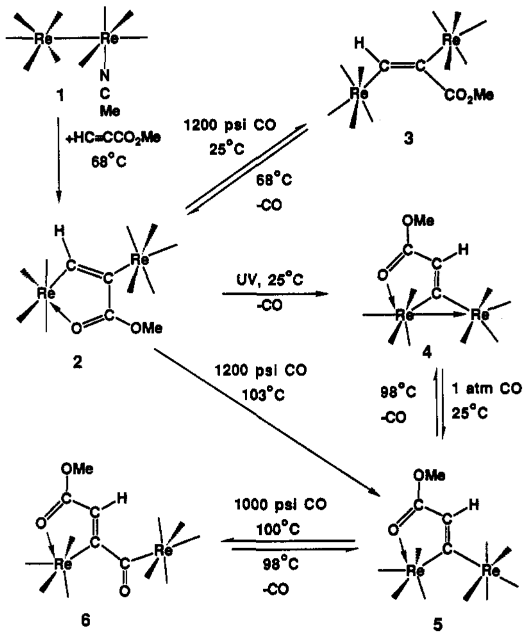
[a] $B_{eq} = (8\pi^2/3) \sum_i^3 \sum_j^3 U_{ij} a_i^* a_j^* \mathbf{\bar{a}}_i \mathbf{\bar{a}}_j$, see: Fischer, R. X.; Tillmanns, E. *Acta Crystallogr.* **1988**, *C44*, 775.

Compound **6** was also characterized by IR, ^{1}H NMR, and single-crystal X-ray diffraction analyses. An ORTEP drawing of the molecular structure of **6** is shown in Figure 6. Final atomic positional parameters are listed in Table VI. This complex is very similar to **5**, except that it contains a carbonyl group, C(5)–O(5) that was inserted into the metal–carbon bond between the bridging vinylidene ligand and the Re(CO)$_5$ group of **5**, Re(1)–C(5) = 2.23(1) Å. This carbonyl group exhibits the expected low-frequency IR absorption at 1575 cm^{-1}. Surprisingly, despite the forcing reaction conditions, the ketonic oxygen atom O(1) of the ester grouping is still coordinated to the metal atom Re(2), Re(2)–O(1) = 2.170(1) Å. The hydrogen atom H(2) was located and refined crystallographically. It exhibits an NMR shift typical of an alkenyl hydrogen, δ = 6.23 ppm. Compound **6** was decarbonylated to **5** at 97 °C (heptane reflux), but the yield of **5** was low, 22%.

Conclusions

A summary of the results of this study is shown in Scheme II. The reactions of **1** with carboxylate-substituted alkynes appear to be the first examples of intramolecular insertion reactions of alkynes into a metal–metal bond to yield dimetalated olefin complexes having trans stereochemistry. A mechanism has been proposed that does not traverse an intermediate having cis stereochemistry. It is possible that this mechanism could be general and could also explain the insertion of alkynes into certain

Scheme II



metal-*ligand* bonds where a trans stereochemistry has been observed.[20]

Compound **2a** undergoes a 1,2-hydrogen shift to form the complexes **4** and **5** that contain a vinylidene ligand bridging the two metal atoms. This transformation may have involved a hydride-containing intermediate.[3] Dimanganese complexes have been observed to produce similar transformations upon terminal alkynes.[19] Compound **4** contains a donor–acceptor metal–metal bond that is very easily and reversibly cleaved by the addition of CO to yield **5**. Ligand-induced cleavage of metal–metal bonds is a principal step of one of the two important mechanisms of ligand substitution in metal cluster complexes.[21] It has also been found that CO can be inserted into one of the metal–carbon bonds of **5** to yield the carbonylated species **6**.

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Supplementary Material Available: Tables of atomic positional parameters, hydrogen atom positional parameters, and anisotropic thermal parameters (22 pages). Ordering information is given on any current masthead page.

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