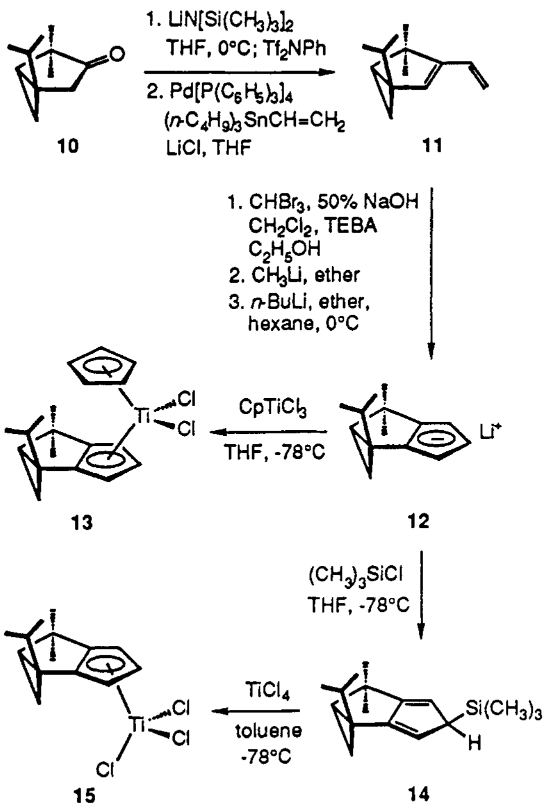

As expected, the silylation of 12 was governed by the same π-facial bias. Admixture of the major silane isomer 14 ($[\alpha]^{20}_D = +11.4°$ ($c = 1.1$, hexane)) with $TiCl_4$ in toluene as before (2 h) with subsequent warming to room temperature (4 h) furnished 15 (70%).[17,18] The powerful deshielding impact of the titanium center in this complex induces a significant downfield shift on the nearby proton of the three-membered ring (δ 0.77).

In summary, this study marks a fundamentally new approach to the preparation from a single precursor of titanocenes that are diastereomeric by virtue of specific π-face complexation. Experiments are in progress to determine the degree to which appreciably enhanced steric compression improves the capacity to function as asymmetric catalysts. The added encumbrance may also provide features more suited to detailed mechanistic clarification.

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[17] As expected, the reactivity of 3, 8, and 14 toward more bulky and less electrophilic reagents[9a,c] such as $CpTiCl_3$ and Cp^*TiCl_3 drops off precipitously.

[18] A prototypical procedure follows. A cold (−78 °C) solution of $TiCl_4$ (1.02 g, 5.4 mmol) in toluene (50 mL) was treated slowly with 8 (1.40 g, 5.4 mmol) dissolved in toluene (30 mL) during 30 min. The red mixture was stirred for 1 h at −78 °C and 48 h at room temperature before being concentrated in vacuo. The residue was dissolved in a small quantity of toluene and cooled to −20 °C to provide bright red crystals of 9 (0.90 g, 49%): mp 136–138 °C (toluene); ^1H NMR (300 MHz, $CDCl_3$) δ 6.80 (s, 1 H), 3.39 (dd, $J = 15.6$, 1.9 Hz, 1 H), 3.24 (t, $J = 5.1$ Hz, 1 H), 2.90 (dd, $J = 14.0$, 3.6 Hz, 1 H), 2.80 (d, $J = 4.9$ Hz, 1 H), 2.39 (s, 3 H), 2.36 (s, 3 H), 2.31 (m, 1 H), 1.43 (s, 3 H), 1.14 (s, 3 H), 0.73 (d, $J = 9.9$ Hz, 1 H); ^{13}C NMR (62.5 MHz, $CDCl_3$) 152.3, 139.8, 137.9, 135.5, 124.6, 44.8, 41.0, 40.8, 36.5, 29.6, 29.1, 28.0, 26.7, 16.0 ppm; HRMS m/z ($M^+ - Cl$) calcd for $C_{14}H_{19}Cl_2Ti$ 304.0265, obsd 304.0293; $[\alpha]^{20}_D = +26.0°$ ($c = 0.3$, toluene).

Insertion of Alkynes with Electron-Withdrawing Substituents into a Rhenium–Rhenium Bond. Evidence for an Intramolecular Insertion with a Trans Stereochemistry

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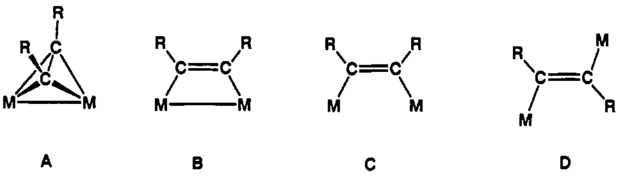
Summary: The reaction of the dirhenium complex $Re_2(CO)_9(NCMe)$ (**1**) with electrophilic alkynes, $R'C{\equiv}CCO_2R$, proceeds by displacement of the NCMe ligand and addition of the alkyne with insertion into the rhenium–rhenium bond to yield the dimetalated olefin complexes $Re(CO)_4[\textit{trans}\text{-}\mu\text{-}R'C{=}C(CO_2R)]Re(CO)_5$ (R = Me, R′ = H (**2a**), Me (**2b**); R = Et, R′ = CO_2Et (**2c**)) having a trans stereochemistry at the C–C double bond. The carboxylate group is coordinated to one of the rhenium atoms to form a metallacycle. Insensitivity to radical scavengers and the absence of crossover in a reaction of a mixture of labeled and unlabeled reagents indicate that the insertion of the alkyne into the metal–metal bond occurs by an intramolecular process. Crystal data for **2a**: space group $P2_1/n$, $a = 6.644$ (1) Å, $b = 30.005$ (8) Å, $c = 18.036$ (2) Å, $\beta = 96.09$ (1)°, $Z = 8$, 2468 reflections, $R = 0.033$.

In most polynuclear metal complexes alkyne ligands adopt bridging coordinations and serve as four-electron donors to the metal atoms.[1] In binuclear metal complexes alkynes usually coordinate in the μ-⊥ coordination mode A,[2] although there are examples of the μ-∥ coordination mode B,[3] where the alkyne serves as a two-electron donor. In the absence of a metal–metal bond these complexes are



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described as "dimetalated olefins" (C, D).[4-6] Although most dimetalated olefin complexes exhibit the cis stereochemistry C,[5] there are a few examples that have the trans stereochemistry D.[6] A systematic route to trans-dimetalated olefins involves the backside addition of a nucleophilic metal center to a metal-coordinated alkyne.[6a]

The paucity of simple alkyne complexes of binuclear manganese and ruthenium carbonyl compounds is surprising and may reflect the fundamentally different chemistry of this binuclear family of complexes.[7] We now wish to report that the reaction of the activated dirhenium complex $\mathrm{Re_2(CO)_9(NCMe)}$[8] (**1**) with the electrophilic alkynes $\mathrm{R'C{\equiv}CCO_2R}$ proceeds by displacement of the NCMe ligand with addition and insertion of the alkyne into the metal–metal bond to yield the dimetalated olefin complexes $\mathrm{Re(CO)_4}$[*trans*-μ-$\mathrm{R'C{=}C(CO_2R)}$]$\mathrm{Re(CO)_5}$ (R = Me, R′ = H, (**2a**), Me (**2b**); R = Et, R′ = $\mathrm{CO_2Et}$ (**2c**)) having a trans stereochemistry at the C–C double bond. We have also obtained evidence which indicates that the insertion of the alkyne into the metal–metal bond occurs by an intramolecular process.

A 200-mg (0.301-mmol) of amount of **1** was allowed to react with 40 μL (0.451 mmol) of $\mathrm{HC{\equiv}CCO_2Me}$ in 100 mL of hexane at reflux for 2 h. The product **2a** was isolated by TLC to yield 170.2 mg (80%).[9] **2b**,**c** were prepared similarly in yields of 10% and 79%, respectively. The molecular structure of **2a** was established by a single-crystal X-ray diffraction analysis,[10] and an ORTEP drawing of its structure is shown in Figure 1. The crystal contains two symmetry-independent molecules in the asymmetric crystal unit, but both molecules are structurally similar. The alkyne was inserted 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. The rhenium atoms exhibit a trans or *E* stereochemistry with respect to the two carbon atoms, and the ketonic oxygen atom O(1) of 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]). To obtain information about the mechanism of the insertion into the metal–metal bond, the following crossover experiment was performed.[11] A

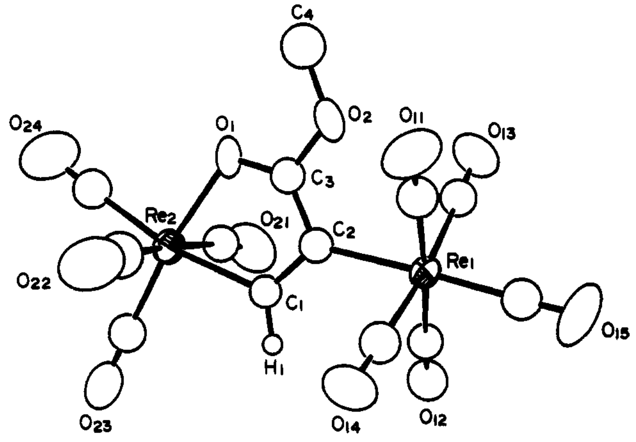
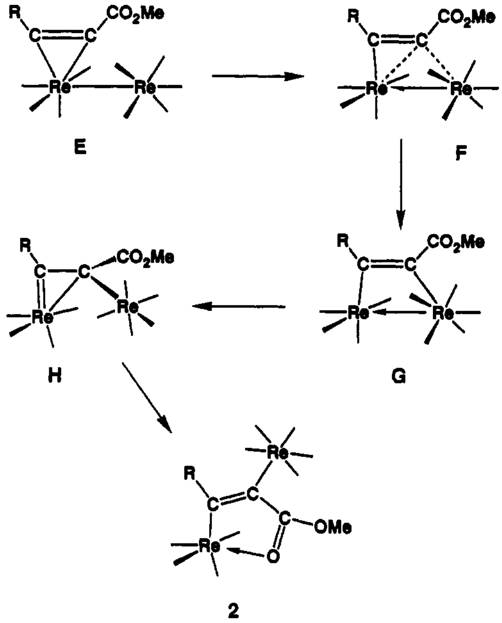


Figure 1. ORTEP diagram of $\mathrm{Re(CO)_4}$[μ-$\mathrm{HC{=}C(CO_2Me)}$]$\mathrm{Re(CO)_5}$ (**2a**). Selected interatomic distances (Å): Re(1a)–C(2a) = 2.22 (2), Re(1b)–C(2b) = 2.21 (2), Re(2a)–C(1a) = 2.17 (2), Re(2b)–C(1b) = 2.18 (1), Re(2a)–O(1a) = 2.16 (1), Re(2b)–C(1b) = 2.16 (1), C(1a)–C(2a) = 1.37 (2), C(1b)–C(2b) = 1.41 (2).

Scheme I



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[9] A 200-mg (0.301-mmol) amount of $\mathrm{Re_2(CO)_9(MeCN)}$[8] was allowed to react with 40 μL (0.451 mmol) of $\mathrm{HC{\equiv}CCO_2Me}$ in 100 mL of hexane at reflux for 2 h. The product $\mathrm{Re_2(CO)_9[C(H){=}CC(OMe){=}O]}$ (**2a**) was isolated by TLC with hexane/$\mathrm{CH_2Cl_2}$ (3/1) as eluent and recrystallization from $\mathrm{CH_2Cl_2}$ to yield 170.2 mg of pale yellow crystals (80% yield). It can be isolated in good purity by simple recrystallization without TLC. IR (ν_{CO} in hexane, cm^{-1}): 2134 (w), 2090 (m), 2024 (s), 1991 (sh), 1986 (sh), 1982 (s), 1937 (s), 1541 (w, br). ^{1}H NMR (δ in $\mathrm{CDCl_3}$): 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 at *m/e* 708 and ions corresponding to the loss of each of the nine carbonyl ligands. For **2b**: IR (ν_{CO} in hexane, cm^{-1}) 2132 (w), 2087 (m), 2021 (s), 1990 (sh), 1982 (s), 1935 (s), 1533 (w, br); ^{1}H NMR (δ in $\mathrm{CDCl_3}$) 3.86 (3 H, s, OMe), 2.83 (3 H, s, Me). For **2c**: IR (ν_{CO} in hexane, cm^{-1}) 2139 (w), 2097 (w), 2036 (s), 2028 (s), 1999 (s), 1992 (s), 1986 (s), 1932 (s), 1685 (w, br, in $\mathrm{CH_2Cl_2}$), 1526 (w, br, in $\mathrm{CH_2Cl_2}$); ^{1}H NMR (δ in $\mathrm{CDCl_3}$) 4.17 (2 H, q, $^3J_{\mathrm{H-H}}$ = 7.2 Hz, $\mathrm{CH_2}$), 4.16 (2 H, q, $^3J_{\mathrm{H-H}}$ = 7.2 Hz, $\mathrm{CH_2}$), 1.31 (3 H, t, $^3J_{\mathrm{H-H}}$ = 7.2 Hz, Me), 1.29 (3 H, t, $^3J_{\mathrm{H-H}}$ = 7.2 Hz, Me).

[10] Crystal data for **2a**: space group $P2_1/n$, a = 6.644 (1) Å, b = 30.005 (8) Å, c = 10.036 (2) Å, β = 96.09 (1)°, Z = 8, 2468 reflections, R = 0.033. Diffraction measurements at 20 °C were made on a Rigaku AFC6S four-circle diffractrometer using Mo Kα radiation. The structure solution and refinement were made by using the TEXSAN structure solving program library (v5.0) of the Molecular Structure Corp., The Woodlands, TX. An empirical absorption correction was applied.

[11] $\mathrm{Re_2(^{13}CO)_9(MeCN)}$ containing 99% ^{13}CO was prepared from $\mathrm{Re_2(^{13}CO)_{10}}$.[8] $\mathrm{Re_2(^{13}CO)_{10}}$ was prepared by the reduction of $\mathrm{[NBu_4]_2[Re_2Cl_8]}$ with Na(Hg) in the presence of $\mathrm{AlCl_3}$ and ^{13}CO. Details of the preparation are provided in the supplementary material accompanying this report. (In fact, the ^{13}CO (obtained from Dr. Istvan Horvath of Exxon Research and Engineering, Clinton, NJ) contained 99.9% ^{13}C ~10% ^{18}O. However, the presence of ^{18}O presented no complications in the interpretation of the crossover experiment, since no crossover actually occurred (see below)). The isotopically enriched $\mathrm{Re_2(^{13}CO)_9(MeCN)}$ was mixed with an equimolar amount (approximately 5 mg) of $\mathrm{Re_2(CO)_9(MeCN)}$ having natural isotopic distributions for all elements. The mixture was then converted to **2a** by reaction with $\mathrm{HC{\equiv}CCO_2Me}$.[9] The mass spectrum of the isolated product showed ions with the natural dirhenium isotope distribution centered at *m/e* 708 and a second cluster of ions centered at *m/e* 719 (11 amu higher than expected for unlabeled **2a** due to the presence of the ^{18}O in the CO) with an isotope pattern similar to that observed for $\mathrm{Re_2(^{13}CO)_{10}}$. 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 mixed ions $\mathrm{Re(^{13}CO)_4}$[μ-$\mathrm{HC{=}C(CO_2Me)}$]$\mathrm{Re(CO)_5}$ and $\mathrm{Re(CO)_4}$[μ-$\mathrm{HC{=}C(CO_2Me)}$]$\mathrm{Re(^{13}CO)_5}$ were present.

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_3NO in MeCN solvent.[12] This compound was mixed with an approximately equimolar amount of unlabeled **1**, and the mixture was then converted to **2a** by reaction with $HC{\equiv}CCO_2Me$ in the above-described manner. 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 99.9% ^{13}C. There were no significant amounts of the ions attributable to the crossover products $Re(^{13}CO)_4[\mu\text{-}HC{=}C(CO_2Me)]Re(CO)_5$ and $Re(CO)_4[\mu\text{-}HC{=}C(CO_2Me)]Re(^{13}CO)_5$. Also, no inhibition in the reaction rate or yield was found when the reaction was performed in the presence of the radical scavengers O_2 (air), 2,6-di-*tert*-butylphenol, and duroquinone in a 30-fold excess. The combination of evidence is most consistent with an *intramolecular* insertion mechanism.[12]

Theoretical studies of dimetalated olefins have indicated that the cis/trans isomerization process (C to D) has a high activation energy and thus would occur very slowly under the conditions that we have used.[4] Accordingly, we propose the mechanism shown in Scheme I, which does not require traversing an intermediate, 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 (E). At some point an interaction must develop between the second rhenium atom and at least one of the acetylenic carbon atoms of the ligand. We have chosen the carboxylate-substituted carbon atom for this interaction. As this interaction develops F, the rhenium–rhenium bond will develop a heteropolar (donor/acceptor) character, and in the limit (G), 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 G this could be as simple as withdrawal of the shared electron pair to the donating $Re(CO)_5$ 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 $MeO_2C{-}C{-}Re(CO)_5$ grouping to form an η^2-alkenyl ligand serving as a three-electron donor (H). Numerous examples of η^2-alkenyl ligands acting as three-electron donors have been characterized recently, although we are not aware of any examples having one of the substituents as a metal-containing group.[13] The formation of **2** is 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, a release of two electrons to the η^2-alkenyl group, and a further rotation of the $MeO_2C{-}C{-}Re(CO)_5$ group to produce the trans stereochemistry. In all of the intermediates 18-electron configurations are maintained at both metal atoms.

This reaction appears to be the first example of an intramolecular insertion reaction of an alkyne into a metal–metal bond that produces a trans stereochemistry. The proposed mechanism which does not traverse the intermediate C, having cis stereochemistry, could also be operative for the insertion of alkynes into metal–ligand bonds where trans stereochemistry has been observed.[14]

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

Supplementary Material Available: Text giving the procedure for the synthesis of $Re_2(^{13}CO)_{10}$, the mass spectrum of the $Re_2(^{13}CO)_{10}$ so obtained, the mass spectrum of the parent ion of **2a** obtained from the crossover experiment, and tables of crystal data, positional parameters, bond distances and angles, and anisotropic thermal parameters for **2a** (15 pages). Ordering information is given on any current masthead page.

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[12] No inhibition in the reaction rate or yield was found when the reaction was performed in the presence of the radical scavengers, duroquinone and 2,6-di-*tert*-butylphenol, but it must be noted that this fact and the lack of crossover do not rule out the possibility of dissociative mechanisms in which the fragments remain proximate to one another in tight solvent cages.

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Metal Transfer and Double Acyl Formation in the Reaction of ((Trimethylsilyl)ethynyl)(Fischer carbene)metal Complexes with $Co_2(CO)_8$

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Summary: A new cobalt carbene complex was obtained and fully characterized in the reaction of ((trimethylsilyl)ethynyl)((diallylamino)carbene)pentacarbonyltungsten with dicobalt octacarbonyl. This complex may be regarded as the consequence of a different evolution of the Pauson–Khand reaction.

Pentacarbonyl(carbene)metal complexes (Fischer complexes) undergo efficient metal-induced cycloadditions.[1] Recently, we reported that alkynyl (allylamino)carbene

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