Reversible "3 + 2 Cycloaddition" of Ethylene to the C=Re≡C Unit in Complexes of the Type Re(C-*t*-Bu)(CHR')(OR)$_2$

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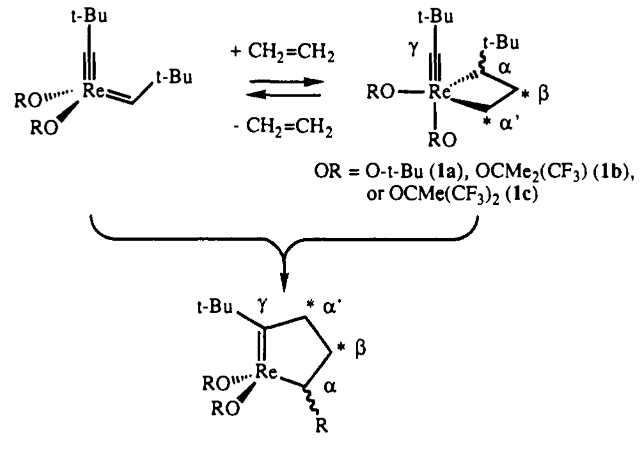
We have synthesized well-characterized rhenium(VII) alkylidene alkylidyne complexes of the type Re(CR')(CHR')(OR)$_2$ (R' = *t*-Bu or CMe$_2$Ph)[1] and have outlined their metathetical reactions with some terminal and internal olefins.[2] Ethylene ultimately behaves differently, however; it adds across the C=Re≡C unit in what is nominally a 3 + 2 cycloaddition reaction.

Ethylene reacts with *syn*-Re(C-*t*-Bu)(CH-*t*-Bu)(O-*t*-Bu)$_2$ below −20 °C to give a compound (**1a**) whose proton NMR spectra are analogous to those of structurally characterized trigonal bipyramidal tungstacyclobutane complexes such as W[CH(*t*-Bu)CH$_2$CH$_2$](NAr)(OR$_{F6}$)$_2$[3-5] (OR$_{F6}$ = OCMe(CF$_3$)$_2$; see figure and Table I in the supplementary material). Upon warming of the reaction mixture to 25 °C, another compound is formed, in which the former neopentylidyne α carbon atom (here labeled γ) and the former neopentylidene α carbon atom are *both* coupled to ^{13}C (when ^{13}CH$_2$^{13}CH$_2$ is employed) by ca. 30 Hz (Table I). We propose that this maroon, pentane-soluble powder is a rhenacyclopentene complex (**2a**; see Scheme I). Usually **1a** is only a minor component of a mixture of **1a** and **2a**, even when the reaction is carried out at low temperatures, and with time **1a** is converted into **2a**. As a solid at −40 °C, **2a** is stable indefinitely, but when a sample is dissolved in C$_6$D$_6$ at room temperature, free ethylene and *syn*-Re(C-*t*-Bu)(CH-*t*-Bu)(O-*t*-Bu)$_2$ (ca. 10% of the initial **2a**) are observed immediately by NMR; the sample then decomposes slowly but steadily to give a complex mixture of products. Analogous reactions involving *syn*-Re(C-*t*-Bu)(CH-*t*-Bu)(OR$_{F3}$)$_2$ (OR$_{F3}$ = OCMe$_2$(CF$_3$)) yield a TBP rhenacyclobutane complex below −50 °C (**1b**) and an analogous rhenacyclopentene complex above ca. −30 °C (**2b**) (See Table I). Compound **2b** decomposes above ca. 5 °C to as yet uncharacterized products. Analogous reactions involving *syn*-Re(C-*t*-Bu)(CH-*t*-Bu)(OR$_{F6}$)$_2$ yield a TBP rhenacyclobutane complex (**1c**) at low temperatures that loses ethylene at 25 °C in solution or in the solid state to re-form Re(C-*t*-Bu)(CH-*t*-Bu)(OR$_{F6}$)$_2$ quantitatively in a few minutes at 25 °C; no rhenacyclopentene complex is observed. Re(C-*t*-Bu)(CHSPh)(THF)$_2$(OR$_{F6}$)$_2$,[1] on the other hand, reacts with ethylene to give a rhenacyclopentene complex (**2d**) that is relatively stable at 25 °C; no TBP rhenacyclobutane complex is observed. Unfortunately, **2d** could be obtained only as an oil, and its slow decomposition at 25 °C foiled attempts at elemental analysis. TBP rhenacyclobutane complexes do not form upon cooling of samples of rhenacyclopentene complexes to a temperature where the rhenacyclobutane complex is known to be stable. All compounds **1** and **2** decompose in the presence of excess ethylene to mixtures of as yet uncharacterized products.

In contrast to **2a** and **2b**, **2d** forms relatively stable monoadducts upon addition of PMe$_3$ or PMe$_2$Ph in which the essential features of the rhenacyclopentene ring are retained (Table I). Crystals of Re[CH(SPh)CH$_2$CH$_2$C(*t*-Bu)](OR$_{F6}$)$_2$(PMe$_2$Ph) were obtained that were suitable for X-ray studies. The compound is roughly a trigonal bipyramid that contains an axial alkoxide and an axial phosphine ligand (P–Re–O(2) = 160.6(3)°; Figure 1). The bond distances and angles in the rhenacyclopentene ring are not unusual; the Re=C(4) bond length (1.90(1) Å) and Re—C(1) bond length (2.14(2) Å) in particular are what one would expect for a double and a single bond, respectively. The geometry around C(4) is planar, as expected for an sp^2-hybridized carbon atom. The metallacycle adopts an open envelope conformation with C(3), C(2), and C(1) being the "flap" of the envelope. The tip of the flap, C(2), is displaced significantly out of the C(1)–Re–C(4) plane, while C(3) is nearly in the plane. An important feature of the structure is the dative Re–S interaction (Re–S = 2.365(5) Å), one that may help to stabilize the complex toward loss of ethylene. We have no reason to believe that the structures of **2a**, **2b**, and **2d** do not contain the essential features of the ReC$_4$ ring found in **3d**, judging from the similarity of the NMR data for all compounds of type **2** (Table I).

Scheme I



OR = O-t-Bu, R = t-Bu (**2a**); OR = OR$_{F3}$, R = t-Bu (**2b**);

OR = OR$_{F6}$, R = SPh (**2d**); * = ^{13}C.

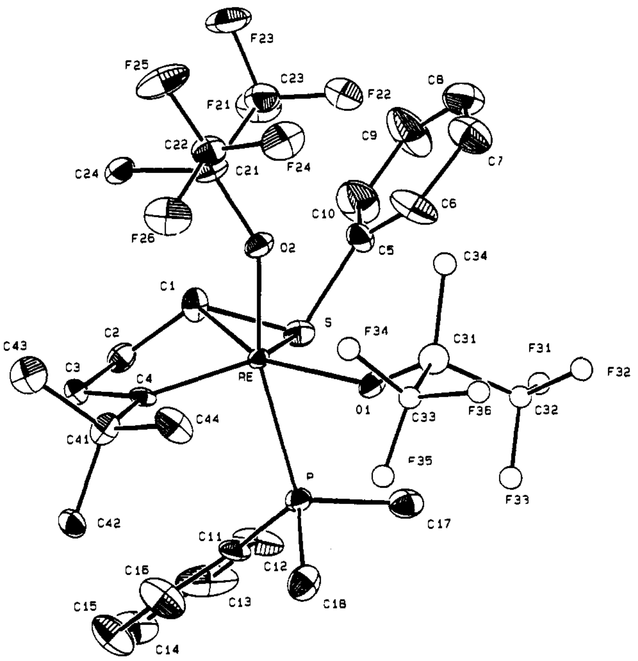


Figure 1. An ORTEP representation of the structure of Re[CH(SPh)CH$_2$CH$_2$C(*t*-Bu)][OCMe(CF$_3$)$_2$]$_2$(PMe$_2$Ph). The CF$_3$ groups were treated as rigid rotors in the final cycles of least squares refinement, and the *B*'s for C(31)–C(34) and F(31)–F(36) were arbitrarily set at 1.2 Å^2.

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The formation of a rhenacyclopentene complex is a fourth documented way in which d^0 metals in well-characterized alkylidene complexes now are known to be reduced, the first three being rearrangement of alkylidenes to olefins (for Nb and Ta), rearrangement of metallacyclobutanes to olefins, and bimolecular coupling of alkylidenes to give olefins.[3] Experiments are under way that should help distinguish between the direct conversion of **1** to **2**, a competition between the parent alkylidyne alkylidene complex and ethylene to form **1** or **2**, or a more convoluted mechanism involving proton migrations in rhenacycle intermediates. So far there is no evidence for H/D scrambling nor, therefore, for the third alternative. A finding that **1** is converted directly to **2** would support a long-standing proposal[6] that four-membered metallacycles are intermediates in 3 + 2 cycloaddition reactions involving olefins and oxo or imido ligands in Os(VIII) complexes.[7]

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Supplementary Material Available: A table of pertinent NMR data for rhenacyclobutane and rhenacyclopentene complexes and a fully labeled ORTEP drawing, final positional parameters, and final thermal parameters for the PMe_2Ph adduct of **2d** (10 pages); final observed and calculated structure factors for the PMe_2Ph adduct of **2d** (39 pages). Ordering information is given on any current masthead page.

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