diastereoselectivity, one can envision simple solutions to a wide range of stereochemical transformations that are currently deemed difficult to accomplish. We are actively pursuing a variety of these. Finally, application of a unique double asymmetric induction phenomenon provides an inroad to even higher diastereoselectivities in nucleophilic addition reactions to carbonyl substrates.

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Supplementary Material Available: Complete experimental details for all reactions reported, as well as ^{1}H and ^{13}C NMR spectra for all compounds (34 pages). Ordering information is given on any current masthead page.

Two Rhenium Complexes That Contain an Unsupported Metal-Metal Double Bond in the Presence of Potentially Bridging Ligands

Robert Toreki, Richard R. Schrock,* and Michael G. Vale

Department of Chemistry, 6-331
Massachusetts Institute of Technology
Cambridge, Massachusetts 02139

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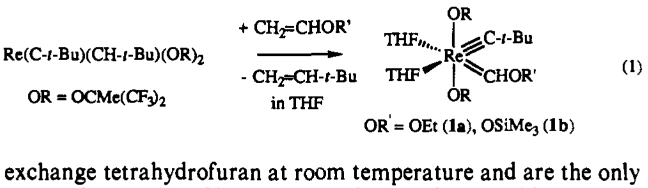
It is not obvious why complexes that contain an unsupported metal-metal double bond (i.e., no bridging ligands) should be so rare, while there are scores of examples of complexes that contain unbridged metal-metal single bonds, or (for molybdenum, tungsten, and rhenium) unbridged triple or quadruple bonds.[1] Two types of complexes that contain an unsupported metal-metal double bond have been reported, $(Me_3SiCH_2)_3(O)Re(\mu\text{-}O)[Re(PMe_3)_4]Re(O)_2(CH_2SiMe_3)$[2] and macrocycle complexes such as [M(octaethylporphyrin)]$_2$ (M = Ru, Os)[3] and $[Ru(C_{22}H_{22}N_4)]_2$.[4] In neither type is there an opportunity for ligands to bridge the metal-metal double bond. We report here the synthesis and structural determination of two complexes that contain an unsupported rhenium-rhenium double bond in the presence of potentially bridging ligands. To our knowledge these are the first such complexes to be synthesized.

Vinyl ethers react smoothly at room temperature in tetrahydrofuran with *syn*-Re(C-*t*-Bu)(CH-*t*-Bu)[OCMe(CF$_3$)$_2$]$_2$,[5,6] to afford **1a**[7] and **1b** quantitatively (eq 1). These species rapidly



exchange tetrahydrofuran at room temperature and are the only reported examples of heteroatom-substituted high oxidation state alkylidene complexes. When analogous reactions in C_6D_6 or CD_2Cl_2 are followed by proton NMR analysis, the base-free

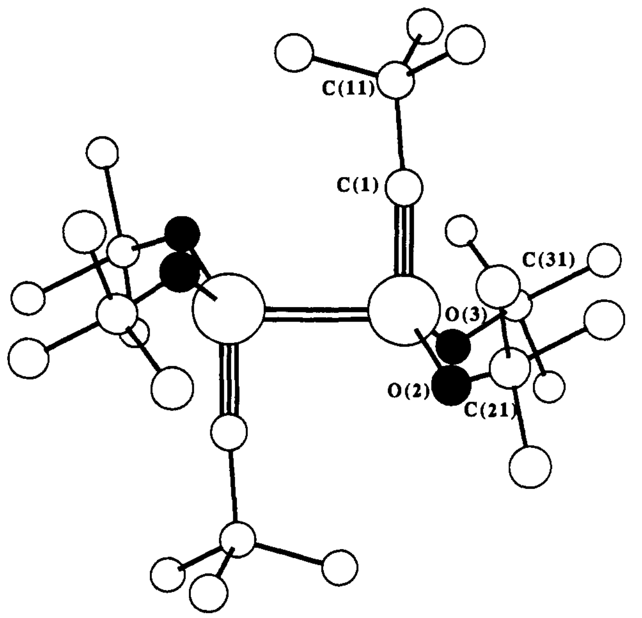


Figure 1. A drawing of the molecular structure of [Re(C-*t*-Bu)(O-*t*-Bu)$_2$]$_2$ (**3b**).

Table I. Selected Bond Distances (Å) and Angles (deg) in **3a** and **3b**

	3a	3b
Re-Re*	2.3836 (8)	2.396 (1)
Re-C(1)	1.728 (8)	1.721 (7)
Re-O(2)	1.925 (5)	1.901 (5)
Re-O(3)	1.932 (5)	1.909 (4)
O(2)-C(21)	1.395 (9)	1.421 (7)
O(3)-C(31)	1.383 (9)	1.425 (8)
Re-Re*-C(1)	90.0 (2)	89.5 (2)
Re-C(1)-C(11)	177.7 (6)	175.6 (5)
Re-O(2)-C(21)	136.9 (5)	135.9 (4)
Re-O(3)-C(31)	140.5 (5)	135.9 (4)
O(2)-Re-O(3)	117.8 (2)	115.1 (2)
O(2)-Re-C(1)	112.8 (3)	114.9 (3)
O(3)-Re-C(1)	113.6 (3)	113.8 (3)

complexes, Re(C-*t*-Bu)(CHOR′)[OCMe(CF$_3$)$_2$]$_2$ [OR′ = OEt (**2a**), OSiMe$_3$ (**2b**)], are observed as a mixture of syn and anti rotamers, the syn/anti ratio varying with reaction conditions and rotameric purity of the starting material. These species decompose if their solutions are concentrated. Re(C-*t*-Bu)(CH-*t*-Bu)(O-*t*-Bu)$_2$[8] reacts slowly with ethyl vinyl ether in dichloromethane over the course of 2 days to give dark red prisms of [Re(C-*t*-Bu)(O-*t*-Bu)$_2$]$_2$ (**3b**)[9] in 50-60% isolated yield, *cis*- and *trans*-3,3-dimethylbutenyl ethyl ether,[10a,b] and neohexene (eq 2).[10c] Concentrated solutions of crude **2a** in dichloromethane, pentane, or toluene decompose in minutes at room temperature to give

$$\mathrm{Re(C\text{-}\mathit{t}\text{-}Bu)(CH\text{-}\mathit{t}\text{-}Bu)(OR)_2 \xrightarrow{+\ xs\ CH_2{=}CHOEt} 1/2\,[Re(C\text{-}\mathit{t}\text{-}Bu)(OR)_2]_2 + CH_2{=}CH\text{-}\mathit{t}\text{-}Bu + EtOCH{=}CH\text{-}\mathit{t}\text{-}Bu} \quad (2)$$

$$\mathrm{OR = OCMe(CF_3)_2\ (\mathbf{3a})}$$
$$\mathrm{OR = O\text{-}\mathit{t}\text{-}Bu\ (\mathbf{3b})}$$

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[6] Syn refers to the rotamer in which the alkylidene substituent points toward the neopentylidyne ligand.

[7] Synthetic procedures, NMR data, and analytical data are available as supplementary material. *syn*-**1a** and *syn*-**1b** isomerize to mixtures of syn and anti rotamers in solution. The structural type shown for **1a** and **1b** is only one of two possibilities, the other being a complex containing cis OR ligands.

[8] Edwards, D. S.; Biondi, L. V.; Ziller, J. W.; Churchill, M. R.; Schrock, R. R. *Organometallics* **1983**, *2*, 1505.

[9] The analogous neophylidyne complex, [Re(CCMe$_2$Ph)(O-*t*-Bu)$_2$]$_2$ (**3c**), also has been prepared. (See supplementary material.)

[10] (a) Identified by ^{1}H NMR comparison with samples prepared via Wittig-like reactions involving tantalum alkylidene complexes.[10b] (b) Schrock, R. R. *J. Am. Chem. Soc.* **1976**, *98*, 5399. (c) Neohexene is formed via metathesis of the vinyl ether with the starting neopentylidene complex as in eq 1. Dimethylbutenyl ethyl ether is apparently formed from reaction of Re(C-*t*-Bu)(CH-*t*-Bu)(OR)$_2$ with **2a** or **3a** as there is not further formation of this olefin once the neopentylidene complex has been consumed. The ratios of product olefins are dependent on the reaction conditions.

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analogous **3a** (30–40% yield), *cis*- and *trans*-diethoxyethylene,[11] and *cis*- and *trans*-3,3-dimethylbutenyl ethyl ether.[10c] We initially believed **3b** to be different in some fundamental way from **3a** since **3b** is extremely soluble in pentane whereas **3a** is only slightly soluble in dichloromethane.

3a and **3b** (Figure 1)[12] are structurally analogous dimers that possess an inversion center, a staggered, ethane-like geometry, and an *unbridged* metal–metal double bond. Bond lengths and angles in the two molecules are compared in Table I. There are no statistically significant differences between the two except a slightly shorter Re=Re bond and larger Re–O–C angles in **3a**. One striking feature is the 90° angle between the alkylidyne ligand and the metal–metal bond. We suspect that the C–Re–C angle in complexes of type **2** also may be 90° and so do not yet ascribe any special significance to the 90° angle in **3**. The rhenium–rhenium bond distances are consistent with their being double bonds on the basis of Re–Re distances of 2.381 (1) Å in $(Me_3SiCH_2)_3(O)Re(\mu\text{-}O)[Re(PMe_3)_4]Re(O)_2(CH_2SiMe_3)^2$ and 2.408 (1) Å in $[Ru(OEP)]_2$.[3] The Re—Re single bond in structurally related species such as $[ReO(Me{\equiv}CMe)_2]_2$ is considerably longer [2.686 (1) Å].[13] A rhenium–rhenium double bond is consistent with the diamagnetism of **3** and is attractive also because of the analogy between the Re=Re bond and the Re=C bond in **2**. The metal–alkylidyne bond lengths are among the shortest known.[14] There is no evidence for hydrides in either **3a** or **3b**.[15]

One equivalent of *syn*-Re(C-*t*-Bu)(CH-*t*-Bu)$[OCMe(CF_3)_2]_2$ in C_6D_6 reacts with **1a** in 4 h at 85 °C to yield **3a** (90%) and *cis*- and *trans*-3,3-dimethylbutenyl ethyl ether as the major olefinic products (eq 3). (Small amounts of *cis*- and *trans*-1,2-diethoxyethylene also are formed.)

$$\textit{syn}\text{-Re(C-}t\text{-Bu)(CH-}t\text{-Bu)[OCMe(CF}_3)_2]_2 + \mathbf{1a} \xrightarrow{C_6D_6} \mathbf{3a} + \underset{\text{(cis and trans)}}{\text{EtOCH=CH-}t\text{-Bu}} \qquad (3)$$

When **1a** is heated in C_6D_6, **3a** and *cis*- and *trans*-1,2-diethoxyethylene are obtained in high yield. Therefore, one mechanism of forming **3a** and **3b** most likely involves coupling two alkylidene ligands in a dimetallacyclobutane complex. Since it has been argued that elimination of an olefin from a 1,2-M_2C_2 core is symmetry forbidden,[16] and formation of a 1,3-M_2C_2 core is more consistent with M=C bond polarity considerations, we suggest that 1,3-dimetallacycles are the precursors to **3a** and **3b**.[17] Subsequent conversion to a dimetallatetrahedrane could then result in extrusion of olefin and direct metal–metal bond formation. Note that samples of *syn*- and *anti*-Re(C-*t*-Bu)(CH-*t*-Bu)$(OR)_2$ [OR = O-*t*-Bu, $OCMe_2(CF_3)$, $OCMe(CF_3)_2$] produce only trace amounts of *trans*-2,2,5,5-tetramethyl-3-hexene in solution at 120 °C, suggesting that coupling is rapid only when heteroatom substituents are present or when at least one of the two alkylidenes involved is relatively small.

We also have preliminary evidence that suggests that complexes of type **3** form when rhenacyclobutane complexes rearrange to give an olefin by a β hydrogen process, i.e., that complexes of type **3** also can form by coupling of monomeric Re(C-*t*-Bu)$(OR)_2$ units. Such d^2 Re(C-*t*-Bu)$(OR)_2$ species would be expected to have trigonal-planar structures by analogy with what are proposed to be isoelectronic trigonal-planar $Ta[OSi(t\text{-}Bu)_3]_3$[18] and W(N-*t*-Bu)$[OSi(t\text{-}Bu)_3]_2$,[19] and crystallographically characterized $Os(N\text{-}2,6\text{-}i\text{-}Pr_2C_6H_3)_3$.[20]

Dimers **3a** and **3b** do not react readily with simple olefins such as ethylene or norbornene, even at 70 °C after several hours. They also do not form stable adducts with pyridine or dimethylphenylphosphine. However, $[Re(CCMe_2Ph)(O\text{-}t\text{-}Bu)_2]_2$ (**3c**) does react rapidly at −40 °C in ether with 2 equiv of I_2 to afford pentane-soluble vermillion crystals consistent with the formulation $Re(CCMe_2Ph)(O\text{-}t\text{-}Bu)_2I_2$ (**4**). In future studies we hope to elucidate these and other reactions and to determine whether unbridged Re=Re double bonds are a general feature of Re(V) chemistry.

Acknowledgment. R.R.S. thanks the National Science Foundation for research support (CHE 88-22508), and R.T. thanks Catalytica, Inc., for financial support. We thank Dr. William M. Davis for crystallographic assistance.

Supplementary Material Available: Synthetic procedures, NMR data, and analytical data for **1a**, **1b**, **2a**, **2b**, **3a–c**, and **4**, description of the X-ray studies of **3a** and **3b**, and labeled ORTEP drawings, final positional parameters, and final thermal parameters for **3a** and **3b** (15 pages); listing of final observed and calculated structure factors for **3a** and **3b** (42 pages). Ordering information is given on any current masthead page.

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(12) Crystals were mounted in a glass fiber. Data were collected on a Rigaku AFC6R diffractometer at −72 ± 1 °C using graphite-monochromated Mo Kα radiation. For **3a** (**3b**), a total of 4778 (4028) reflections $(h,k,\pm l)$ were collected in the range 1.2 (1.2)° < 2θ < 55 (55)° with 3182 (2822) having $I > 3.00\sigma(I)$ being used in the structure refinement by full-matrix least-squares techniques [253 (145) variables] using the TEXSAN crystallographic software package from Molecular Structure Corporation. Final R = 0.036 (0.029), R_w = 0.047 (0.040). Full details can be found in the supplementary material.

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(15) **3a–c** do not react with CCl_4 to produce $CHCl_3$, even upon photolysis. Treatment of **3a** or **3c** with excess HCl(g) in a sealed NMR tube did not produce H_2 (δ 4.45). Low-temperature proton NMR (−77 °C, CD_2Cl_2) with a 5-s pulse delay did not reveal any resonances attributable to hydrides in the range +60 to −45 ppm. For neither structure did crystallographic evidence favor the presence of bridging hydrides. (See supplementary material.)

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Aqueous Ruthenium(II) Complexes of Functionalized Olefins: The X-ray Structure of $Ru(H_2O)_2(\eta^1(O){:}\eta^2(C,C')\text{-}OCOCH_2CH{=}CHCH_3)_2$

Dominic V. McGrath and Robert H. Grubbs*

Contribution No. 8358, Arnold and Mabel Beckman
Laboratory of Chemical Synthesis
Division of Chemistry and Chemical Engineering
California Institute of Technology
Pasadena, California 91125

Joseph W. Ziller

Department of Chemistry, University of California
Irvine, California 92717

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We recently reported the development of a ring-opening metathesis polymerization (ROMP)[1] system based on low valent ruthenium complexes[2] that tolerates many organic functionalities known to deactivate early-transition-metal metathesis catalysts. The coordination compound $Ru^{II}(H_2O)_6(tos)_2$ (tos = *p*-toluene-

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