Synthesis and Reactions of $Cp^*(CO)_2Re{=}Re(CO)_2Cp^*$

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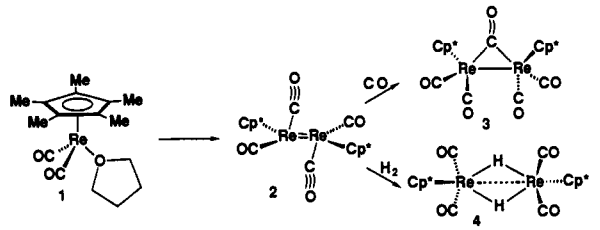
While metal-metal double bonded compounds are quite common,[1] examples which are the formal dimers of 16e d^6 fragments are very rare.[2-4] Here we report that $Cp^*Re(CO)_2(THF)$ (**1**, $Cp^* = C_5Me_5$) loses THF to form the stable isolable diamagnetic rhenium-rhenium double bonded compound $Cp^*(CO)_2Re{=}Re(CO)_2Cp^*$ (**2**). The kinetic reactivity of **2** is extremely high: reaction with CO occurs within seconds at -80 °C to produce the known $Cp^*(CO)_2Re(\mu\text{-}CO)Re(CO)_2Cp^*$ (**3**), and reaction with H_2 also occurs within seconds at -80 °C to produce the new dirhenium dihydride $Cp^*(CO)_2Re(\mu\text{-}H)_2Re(CO)_2Cp^*$ (**4**).



In an effort to prepare rhenium-alkene and alkyne complexes, we photolyzed $Cp^*Re(CO)_3$ in THF solution to obtain a solution of the reactive intermediate $Cp^*Re(CO)_2(THF)$ (**1**), which has been employed as a versatile synthetic intermediate but which had previously been characterized only in solution.[5] Concentration of the solution of **1** and addition of hexane at -80 °C led to the isolation of yellow crystalline **1** in 50% yield.[6] The ^1H NMR spectrum clearly showed a 1:1 ratio of Cp* and complexed THF ligands.

Solid yellow **1** (427 mg, 0.95 mmol) was converted to dark green solid $C_5Me_5(CO)_2Re{=}Re(CO)_2C_5Me_5$ (**2**) (360 mg, 98%)[7] upon storage for 1 week in a glovebox. The ^1H NMR spectrum of **2** in benzene-d_6 showed a new singlet at δ 1.98 for a single compound of >95% purity and no signals for THF. In a separate experiment, free THF evolved from solid **1** over several days and was condensed and analyzed by ^1H NMR. When a solution of **1** in THF-d_8 was monitored by ^1H NMR over 2 days, **2** (δ 2.20), a small amount of $Cp^*Re(CO)_3$ (δ 2.18), and free THF were observed in addition to unreacted **1**. Pure **2** is best obtained from solid-state decomposition of **1**.

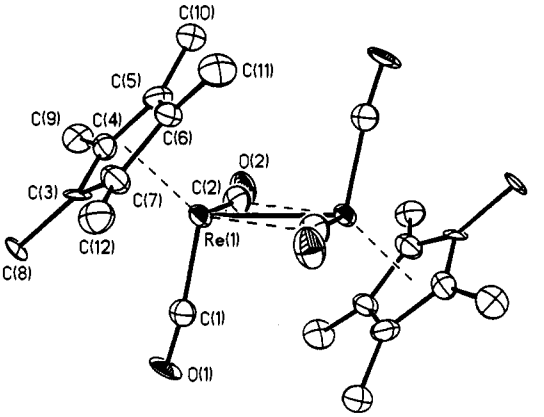


Figure 1. Structure of $Cp^*(CO)_2Re{=}Re(CO)_2Cp^*$ ($\mathbf{2}\cdot C_6D_6$). Selected bond lengths (Å) and angles (deg): Re(1)=Re(1A), 2.723 (1); Re(1)-C(2), 1.921 (9); Re(1A)-C(2), 2.485 (9); Re(1)-C(2)-O(2), 165.2 (8); Re(1)-C(1)-O(1), 173.4 (7); Re(1A)-Re(1)-C(2), 61.9 (3); Re(1A)-Re(1)-C(1), 98.6 (2).

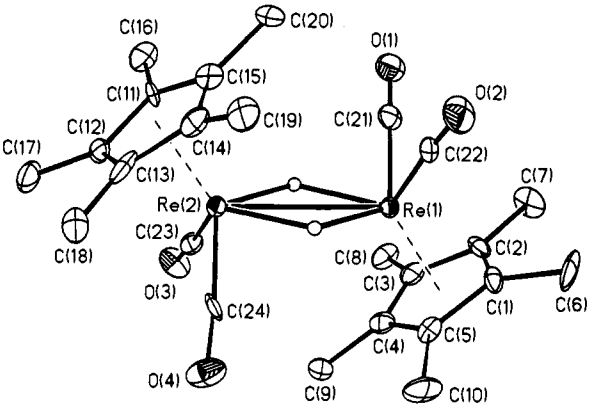


Figure 2. Structure of $Cp^*(CO)_2Re(\mu\text{-}H)_2Re(CO)_2Cp^*$ (**4**). Selected bond lengths (Å) and angles (deg): Re(1)-Re(2), 3.143 (1); Re-(μ-H), 1.840 (20); C(21)-Re(1)-C(22), 86.4 (5); C(23)-Re(2)-C(24), 89.3 (5); Re(2)-Re(1)-C(21), 96.1 (5); Re(1)-Re(2)-C(23), 95.1 (3); Re(2)-Re(1)-H(1), 31.4 (6).

X-ray crystallographic analysis of single crystals of green $\mathbf{2}\cdot C_6D_6$ isolated from benzene-d_6 (Figure 1) showed a centrosymmetric structure having a planar arrangement of two semibridging carbonyls and the two rhenium atoms, with anti Cp* and terminal carbonyl ligands above and below the plane. The Re=Re bond length in $\mathbf{2}\cdot C_6D_6$ of 2.723 (1) Å is 0.234 Å shorter than the 2.957 (1) Å Re—Re single bond of $Cp(CO)_2Re(\mu\text{-}CO)Re(CO)_2Cp$[8] and 0.312 Å longer than the 2.411 (1) Å Re≡Re triple bond of $Cp^*Re(\mu\text{-}CO)_3ReCp^*$.[9] The Re-C distances to the semibridging CO ligands are 1.921 (9) and 2.485 (9) Å, and the Re-C-O angle is 165.2 (8)°; these parameters are similar to those of other linear semibridging carbonyls.[10] In the IR spectrum of **2** in toluene, the terminal and semibridging CO ligands give rise to bands at 1869 and 1824 cm^{-1}, respectively. $Cp^*(CO)_2Re{=}Re(CO)_2Cp^*$ (**2**) has two more valence electrons than the related triple-bonded

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(6) For **1**: ^1H NMR (THF-d_8) δ 3.78 (OCH_2), 1.95 (C_5Me_5), 1.81 (OCH_2CH_2); $^{13}C\{^1H\}$ NMR (toluene-d_8, -80 °C) δ 208.9 (CO), 92.9 (C_5Me_5), 86.4 (OCH_2), 27.3 (OCH_2CH_2), 10.8 (C_5Me_5); IR (THF) 1893 (s), 1823 (s) cm^{-1}.

(7) For **2**: ^1H NMR (C_6D_6) δ 1.98 (C_5Me_5); ^1H NMR (THF-d_8) δ 2.14; ^{13}C NMR (toluene-d_8) δ 209.4 (CO), 103.1 (C_5Me_5), 11.1 (C_5Me_5); IR (toluene) 1869 (s), 1824 (s) cm^{-1}; IR (KBr) 1860 (s), 1809 (s) cm^{-1}; HRMS calcd for $C_{23}H_{30}O_3{}^{187}Re_2$ $(M-CO)^+$ 728.1311, found 728.1353. Anal. Calcd (found) for $C_{24}H_{30}O_4Re_2$: C, 38.19 (37.49); H, 4.01 (4.16).

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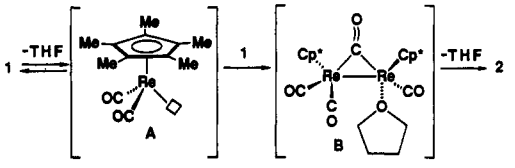
group 6 $Cp^*(CO)_2M{\equiv}M(CO)_2Cp^*$ compounds.[11]

The rhenium-rhenium double bonded compound **2** is extremely reactive in ligand addition and in oxidative addition reactions. When a green solution of **2** in THF at -80 °C was exposed to 1 atm of CO, the color of the solution changed to yellow in less than 1 min. In a preparative reaction, **2** (30 mg, 40 μmol) reacted with CO at room temperature to give the known $Cp^*(CO)_2Re(\mu\text{-}CO)Re(CO)_2Cp^*$ (**3**)[9] in 95% yield after flash chromatography.

Similarly, a green solution of **2** in THF at -80 °C turned yellow in less than 1 min upon exposure to H_2. In a preparative reaction, **2** (30 mg, 40 μmol) in THF reacted with H_2 at room temperature to produce the new dihydride $Cp^*(CO)_2Re(\mu\text{-}H)_2Re(CO)_2Cp^*$ (**4**) in 90% yield after flash chromatography. The ^1H NMR spectrum of **4** established a 1:1 ratio of Cp* to ReH units, and the IR spectrum established that only terminal CO groups were present.[12] An X-ray crystal structure of **4** (Figure 2) showed a long Re-Re distance of 3.143 (1) Å and indicated a staggered arrangement of the Cp* and CO ligands with anti Cp* groups. The arrangement of the Cp* and CO ligands is consistent only with bridging hydride ligands. Symmetrically bridged hydrides were located close to the plane perpendicular to the plane of the Re atoms and the Cp* centroids. **4** has two more valence electrons than the related tungsten compound $Cp^*(CO)_2W(\mu\text{-}H)_2W(CO)_2Cp^*$;[13] this gives **4** an unusual formal electron count of >18e at each Re. The long Re-Re distance is consistent with the presence of two three-center two-electron Re(μ-H)Re bonds and a Re--Re antibond, for a net bond order of 1. This type of bonding was first suggested by Dahl[14] for compounds such as $[L_2H_2Re]_2(\mu\text{-}H)_4$ (**5**)[15] and $[Co_2L_6(\mu\text{-}H)_3]^+$.[16] The bridging hydride ^1H NMR chemical shift of **4** (δ -6.19) is downfield from normal μ-H ligands but is similar to that seen for the unusual μ-H ligands of **5**. The facile oxidative addition of H_2 across multiple metal-metal bonds is unusual, but Sattelberger[17] and Messerle[18] have reported H_2 addition across Ta=Ta double bonds at room temperature.

While Re=Re compound **2** is the formal dimer of the high-energy coordinatively unsaturated 16e d^6 fragment **A**, it is highly unlikely that it is formed by dimerization of **A**. We suggest that



unsaturated intermediate **A** adds to a Re=CO unit of THF complex **1** to form the bridging CO intermediate **B**, which then loses THF to form **2**. The reactions of **2** with CO and other donor ligands may proceed by reactions related to the microscopic reverse of the loss of THF from **B**. We are actively pursuing the reactions of **2** and the synthesis of new M=M systems.

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Supplementary Material Available: X-ray crystallographic data for $2{\cdot}C_6D_6$ and **4** (17 pages); tables of observed and calculated structure factors for $2{\cdot}C_6D_6$ and **4** (24 pages). Ordering information is given on any current masthead page.

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Carbohydrates as Chiral Auxiliaries: Asymmetric Cyclopropanation Reaction of Acyclic Olefins

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The importance of chiral, nonracemic cyclopropane subunits in a number of natural and unnatural products[2] as well as in molecules used to probe biological processes[3] has led to intensive efforts to develop efficient methods for their construction. One synthetic strategy involves the stereoselective cyclopropanation reactions of substituted allylic alcohols or α,β-unsaturated carbonyl compounds linked to a number of well-known chiral auxiliaries.[4] However, in most cases these reactions show some severe drawbacks that include the limited availability of the chiral auxiliary and the general scope of the reaction. A highly diastereoselective cyclopropanation reaction of substituted allylic alcohols linked to a carbohydrate[5] readily available from D-glucose is reported herein.

The design of a new chiral auxiliary for this reaction is based on the observation that oxygen atoms proximal to the alkene can undergo direct attack by the reagent via prior coordination of the zinc atom.[6] It was initially anticipated that a suitably protected carbohydrate derivative would be an ideal chiral template for this purpose since it possesses a number of proximal oxygens that can direct the attack by the reagent. The ability for chelation of the oxygen at the C-2 position can, in principle, be modified by selecting an appropriate protecting group, R'. It was hoped that stereoselective delivery of the reagent from one side of the diastereotopic double bond or the other could be favored by ade-

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