

## Preliminary Communication

### Homonuclear dirhenium complex bridged by CO<sub>2</sub>: molecular structure of a rhenium dimer bridged by CO<sub>2</sub> and a rhenium chloride complex

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#### Abstract

A mononuclear complex (CO)<sub>3</sub>ReL<sub>2</sub>Cl (**1a**) (L = NH<sub>2</sub>CHMe<sub>2</sub>) and a dinuclear CO<sub>2</sub> complex (CO)<sub>3</sub>L<sub>2</sub>Re(μ,η<sup>1</sup>,η<sup>1</sup>-CO<sub>2</sub>)Re(CO)<sub>4</sub>L (**2**) are prepared from the reaction of a carbamoyl complex, (CO)<sub>4</sub>ReL(CONHCHMe<sub>2</sub>) with H<sub>2</sub>O in CHCl<sub>3</sub>. The coupling of a proposed intermediate (CO)<sub>4</sub>LReCOOH with **1a** is a viable process for the formation of complex **2**. The structures of (CO)<sub>3</sub>ReL<sub>2</sub>Cl (**1b**) (L = NH<sub>2</sub>CH<sub>2</sub>CH=CH<sub>2</sub>) and **2** have been established by X-ray diffraction.

**Key words:** Rhenium; Bridging ligand; Carbon dioxide; X-ray diffraction

In the hope of finding appropriate systems for the activation of CO<sub>2</sub> [1], several transition metal complexes containing CO<sub>2</sub> ligand have been characterized in recent years. Although the η<sup>1</sup>-, η<sup>2</sup>-, μ-, and μ<sub>3</sub> bonding types of the CO<sub>2</sub> ligand are known [1e], only a few μ,η<sup>1</sup>,η<sup>1</sup>-CO<sub>2</sub> bridged dinuclear complexes of transition metals have been reported. Examples are the Ir–Os complex [2], the Pt<sub>2</sub> complex [3] and the Fe–Re complex which has been structurally characterized [4]. We report the structure of a homonuclear μ,η<sup>1</sup>,η<sup>1</sup>-CO<sub>2</sub> bridging dirhenium complex.

The reaction of (CO)<sub>5</sub>ReBr with Me<sub>2</sub>CHNH<sub>2</sub> gives a rhenium carbamoyl complex [5], *cis*-(CO)<sub>4</sub>Re(NH<sub>2</sub>-CHMe<sub>2</sub>)(CONHCHMe<sub>2</sub>) [5k]. In the presence of MeOH or H<sub>2</sub>O, this carbamoyl complex was converted to a mixture of a monomeric chloride (CO)<sub>3</sub>ReL<sub>2</sub>Cl (**1a**) (L = NH<sub>2</sub>CHMe<sub>2</sub>), and a dimeric CO<sub>2</sub> complex (CO)<sub>3</sub>L<sub>2</sub>Re(μ,η<sup>1</sup>,η<sup>1</sup>-CO<sub>2</sub>)Re(CO)<sub>4</sub>L (**2**) in chloroform [6\*]. This conversion requires the presence of O<sub>2</sub>. The

major product **1a** is sparingly soluble in organic solvent and is therefore purified by recrystallization from hexane, after separation from **2**. In the IR spectrum of **1a**, three ν(CO) stretches at 2015, 1899 and 1873 cm<sup>-1</sup> are consistent with the facial arrangement of the three CO groups. The analogous complex (CO)<sub>3</sub>Re(NH<sub>2</sub>-CH<sub>2</sub>CH=CH<sub>2</sub>)<sub>2</sub>Cl (**1b**) is similarly prepared from the complex (CO)<sub>4</sub>Re(NH<sub>2</sub>CH<sub>2</sub>CH=CH<sub>2</sub>)(CONHCH<sub>2</sub>-CH=CH<sub>2</sub>). The crystal structure of **1b** is established by a single crystal X-ray diffraction analysis [7\*]. The ORTEP diagram of **1b** is shown in Fig. 1. The core structure around the Re metal centre is virtually octahedral with the Re–Cl distance being 2.471(3) Å. The two amine groups are *cis* to each other and both are *trans* to the carbonyl groups.

Complex **2** is a minor product and attempts to separate **2** from the mixture using column chromatography on silica gel lead to decomposition of both complexes. Complex **2** is separated from a crude mixture containing **1a** and **2** by hexane extraction followed by repeated recrystallization. The isolated yield of **2** is less than 5%. Complex **2** has been characterized by a single crystal X-ray diffraction analysis. Crystals of **2** conform to the space group *P*2<sub>1</sub>/*n* with four molecules in a unit cell [8\*]. The ORTEP diagram of **2** is shown in Fig. 2. It is seen that the CO<sub>2</sub> unit bridges between the two rhenium metal centres through the carbon atom (bound to Re(2)) and one of the oxygen atoms (bound to Re(1)). The three CO groups of Re(1) are in a facial disposition. Other than the oxygen of CO<sub>2</sub> replacing the Cl ligand, the coordination sphere of Re(1) is identical to that of Re in **1b**. The Re(2)–C(1) distance of 2.184(9) Å is much longer than the Re–C bond distances in typical dimeric μ,η<sup>3</sup>-CO<sub>2</sub> Re complexes (2.04(4) [1f]–2.089(9) [1g] Å) and the Re(1)–O(2) distance of 2.117(6) Å is comparable to the corresponding one (2.154(2) Å) in the Fe–Re dimer [4]. The C(1)–O(1) and C(1)–O(2) bond lengths of the bridging CO<sub>2</sub> in **2** are 1.24(1) and 1.30(1) Å, respectively. The difference between these distances is slightly larger than that observed in the dimeric μ,η<sup>3</sup>-CO<sub>2</sub> Re complex (the two C–O distances are 1.28(1), 1.31(1) Å) [1g]. The C(1)–O(1) bond length is slightly longer than that

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\* Reference number with an asterisk indicates a note in the list of references.

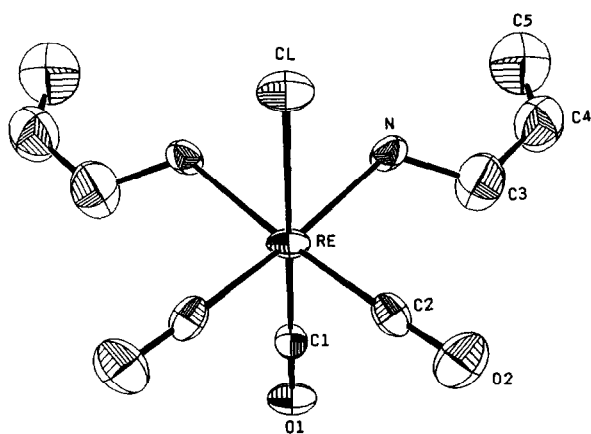


Fig. 1. ORTEP drawing for  $(\text{CO})_3\text{ReL}_2\text{Cl}$  (**1b**) ( $\text{L} = \text{NH}_2\text{CH}_2\text{-CH}=\text{CH}_2$ ), with thermal ellipsoids shown at the 50% probability level. The atoms not labelled were generated by a reflection plane. Selected bond distances (Å) and bond angles (deg) are as follows: Re–N, 2.236(7); Re–Cl, 2.471(3); Re–C(1), 1.88(1); Re–C(2), 1.90(1); C(3)–N, 1.39(2); C(3)–C(4), 1.53(2); C(4)–C(5), 1.28(2); C(1)–O(1), 1.17(2); C(2)–O(2), 1.17(1) Å; N–Re–N, 82.3(3); Cl–Re–N, 82.6(2) $^\circ$ ; Re–N–C(3), 119.5(6) $^\circ$ .

found in the Fe–Re complex of 1.226(3) Å [4]. Typical C(sp<sup>2</sup>)–O single bond and C(sp<sup>2</sup>)=O double bond distances are 1.368(15) and 1.210(8) Å, respectively [9]. The bond angles Re(2)–C(1)–O(1), Re(2)–C(1)–O(2) and O(1)–C(1)–O(2) are 123.8(7) $^\circ$ , 117.2(6) $^\circ$  and 119.0(8) $^\circ$ , respectively. To our knowledge, complex **2** is the first structurally characterized homonuclear com-

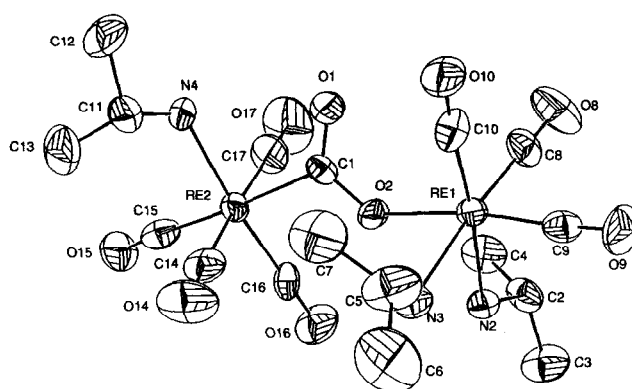
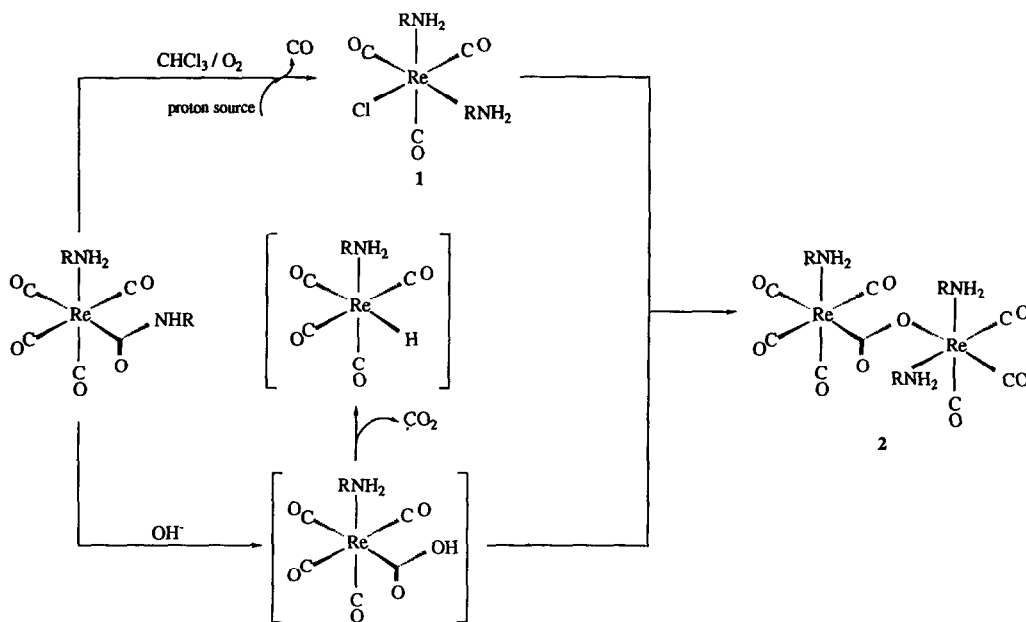


Fig. 2. ORTEP drawing for  $(\text{CO})_3\text{L}_2\text{Re}(\mu,\eta^1,\eta^1\text{-CO}_2)\text{Re}(\text{CO})_4\text{L}$  (**2**) ( $\text{L} = \text{NH}_2\text{CH}(\text{CH}_3)_2$ ), with thermal ellipsoids shown at the 50% probability level. Selected bond distances (Å) and bond angles (deg) are as follows: Re(1)–O(2), 2.117(6); Re(1)–N(2), 2.224(7); Re(1)–N(3), 2.230(8); Re(2)–C(1), 2.184(9); Re(2)–N(4), 2.217(8); C(1)–O(1), 1.24(1); C(1)–O(2), 1.30(1) Å; Re(1)–O(2)–C(1), 134.8(6); Re(2)–C(1)–O(2), 117.2(6) $^\circ$ ; Re(2)–C(1)–O(1), 123.8(7) $^\circ$ ; Re(1)–O(2)–C(1), 134.8(6) $^\circ$ ; N(2)–Re(1)–N(3), 80.7(3) $^\circ$ .

plex where the two metal centres are bridged by a  $\mu,\eta^1,\eta^1\text{-CO}_2$  ligand.

Based on the structural data mentioned above, a mechanism, shown in the Scheme 1, is proposed for the formation of **2**. The formation of **1** which requires the presence of O<sub>2</sub>, possibly proceeds through a radical induced abstraction of a Cl atom from CHCl<sub>3</sub>. And the formation of **2** begins with a nucleophilic attack of water (or OH<sup>−</sup>) at the carbamoyl group



Scheme 1.

forming an intermediate with a carbohydroxy group [10]; coupling of this intermediate with **1** gives **2**. The intermediate is unstable and may lose CO<sub>2</sub> to yield a hydride. This facile process explains the low yield of **2**. The resulting hydride could be sufficiently acidic and may thus be the proton source in the formation of **1**. Several examples are known for the formation of the CO<sub>2</sub> dimer from coordinated CO. The bridging CO<sub>2</sub> ligand of the Ir–Os dinuclear complex [2] was also reported to form from an Ir coordinated CO and an oxygen atom of OsO<sub>4</sub>. Formation of CO<sub>2</sub> molecule through coordination of an oxygen atom to a terminal carbonyl carbon atom is well known in the water gas shift reaction [11]. The transition-metal catalyzed water gas shift reaction has been suggested to involve a nucleophilic attack of OH<sup>−</sup> or water onto the carbon atom of the metal coordinated CO to afford a carbohydroxylate complex [12]. We believe that the formation of **2** should involve the same step. Explorations aiming at improving the yield of **2** and better understanding of the chemical reactivities of **1** and **2** are currently under way.

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- Yield: 71%. Spectroscopic data for **1**: IR (THF): 2015m, 1899vs, 1873vs; <sup>1</sup>H NMR (acetone-*d*<sub>6</sub>, δ): 3.59 (br, NH<sub>2</sub>), 3.21 (m, CH, J(H–H) = 6.2 Hz), 1.28 (d, CH<sub>3</sub>, J(H–H) = 6.2 Hz); Mass (FAB, *m/z*): 423.9 ([M]<sup>+</sup>), 393.3 (M<sup>+</sup> – 2CH<sub>3</sub>).
- Crystal data of **1b**: space group *Pnma*, *a* = 12.344(2), *b* = 19.559(5), *c* = 5.754(1) Å, *V* = 1389.3(5) Å<sup>3</sup>, *Z* = 4. The unit cell constants were consistent with an orthorhombic system, and the space group was subsequently determined to be *Pnma*. Routine 2θ–ω data collection was used to scan the possible 935 reflections in the range from 2° to 45°. The solution procedure for this structure is similar to those for **2** as described in reference 8. The coordinates for C(5) (terminal allylic carbon atom) were fixed and refined isotropically. The final residuals of the refinement were *R* = 0.028 and *R<sub>w</sub>* = 0.023.
- Crystal data: space group *P2<sub>1</sub>/n*, *a* = 11.536(3), *b* = 12.533(3), *c* = 17.695(4) Å, β = 94.856(18)°, *V* = 2549.3(1) Å<sup>3</sup>, *Z* = 4. The unit cell constants were consistent with a monoclinic system, and the space group was subsequently determined to be *P2<sub>1</sub>/n*. Routine 2θ–ω data collection was used to scan the possible 3325 reflections in the range from 2° to 45°. The structure factors were obtained after Lorentz and polarization correction. Empirical absorption corrections, based on azimuthal scans of reflections of Eulerian angle near 90°, were applied to the data. The rhenium atoms were located in a Patterson synthesis and the remaining atoms were found in a series of alternating difference Fourier maps and least-square refinements. Anisotropic thermal parameters were used for all the atoms except the hydrogen atoms. The final residuals of the refinement were *R* = 0.029 and *R<sub>w</sub>* = 0.027.
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