Journal of Organometallic Chemistry, 467 (1994) C6–C8

Preliminary Communication

Homonuclear dirhenium complex bridged by CO_2: molecular structure of a rhenium dimer bridged by CO_2 and a rhenium chloride complex

Yu-Lee Yang, Jhy-Der Chen, Ying-Chih Lin,
Ming-Chu Cheng and Yu Wang

*Department of Chemistry, National Taiwan University, Taipei,
106 (Taiwan)*

(Received September 1, 1993; in revised form October 6, 1993)

Abstract

A mononuclear complex $(CO)_3ReL_2Cl$ (**1a**) ($L = NH_2CHMe_2$) and a dinuclear CO_2 complex $(CO)_3L_2Re(\mu,\eta^1,\eta^1\text{-}CO_2)Re(CO)_4L$ (**2**) are prepared from the reaction of a carbamoyl complex, $(CO)_4ReL(CONHCHMe_2)$ with H_2O in $CHCl_3$. The coupling of a proposed intermediate $(CO)_4LReCOOH$ with **1a** is a viable process for the formation of complex **2**. The structures of $(CO)_3ReL_2Cl$ (**1b**) ($L = NH_2CH_2CH{=}CH_2$) 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_2 [1], several transition metal complexes containing CO_2 ligand have been characterized in recent years. Although the η^1-, η^2-, μ-, and μ_3 bonding types of the CO_2 ligand are known [1e], only a few μ,η^1,η^1-CO_2 bridged dinuclear complexes of transition metals have been reported. Examples are the Ir–Os complex [2], the Pt_2 complex [3] and the Fe–Re complex which has been structurally characterized [4]. We report the structure of a homonuclear μ,η^1,η^1-CO_2 bridging dirhenium complex.

The reaction of $(CO)_5ReBr$ with Me_2CHNH_2 gives a rhenium carbamoyl complex [5], *cis*-$(CO)_4Re(NH_2CHMe_2)(CONHCHMe_2)$ [5k]. In the presence of MeOH or H_2O, this carbamoyl complex was converted to a mixture of a monomeric chloride $(CO)_3ReL_2Cl$ (**1a**) ($L = NH_2CHMe_2$), and a dimeric CO_2 complex $(CO)_3L_2Re(\mu,\eta^1,\eta^1\text{-}CO_2)Re(CO)_4L$ (**2**) in chloroform [6*]. This conversion requires the presence of O_2. 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^{-1} are consistent with the facial arrangement of the three CO groups. The analogous complex $(CO)_3Re(NH_2CH_2CH{=}CH_2)_2Cl$ (**1b**) is similarly prepared from the complex $(CO)_4Re(NH_2CH_2CH{=}CH_2)(CONHCH_2CH{=}CH_2)$. 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 $P2_1/n$ with four molecules in a unit cell [8*]. The ORTEP diagram of **2** is shown in Fig. 2. It is seen that the CO_2 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_2 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^3-CO_2 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_2 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^3-CO_2 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

---

Correspondence to: Dr. Y.-C. Lin.

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

0022-328X/94/$7.00
SSDI 0022-328X(93)24210-V

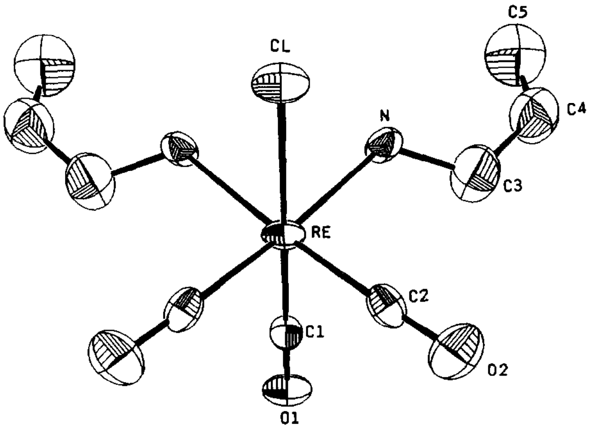


Fig. 1. ORTEP drawing for $(CO)_3ReL_2Cl$ (**1b**) ($L = NH_2CH_2-CH{=}CH_2$), with thermal ellipsoids shown at the 50% probability level. The atoms not labelled were generated by a reflection plane. Selected bond distances (Å) and bond angles (deg) are as follows: Re–N, 2.236(7); Re–Cl, 2.471(3); Re–C(1), 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)°; Re–N–C(3), 119.5(6)°.

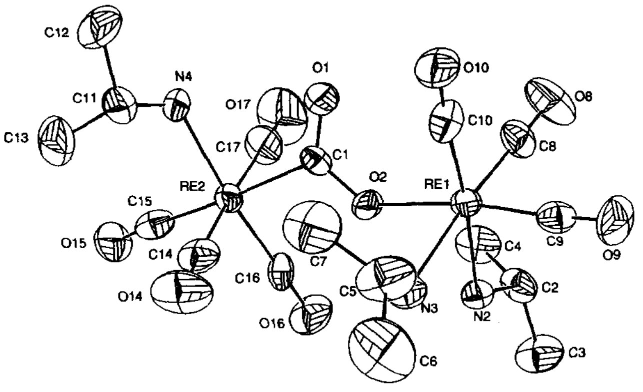
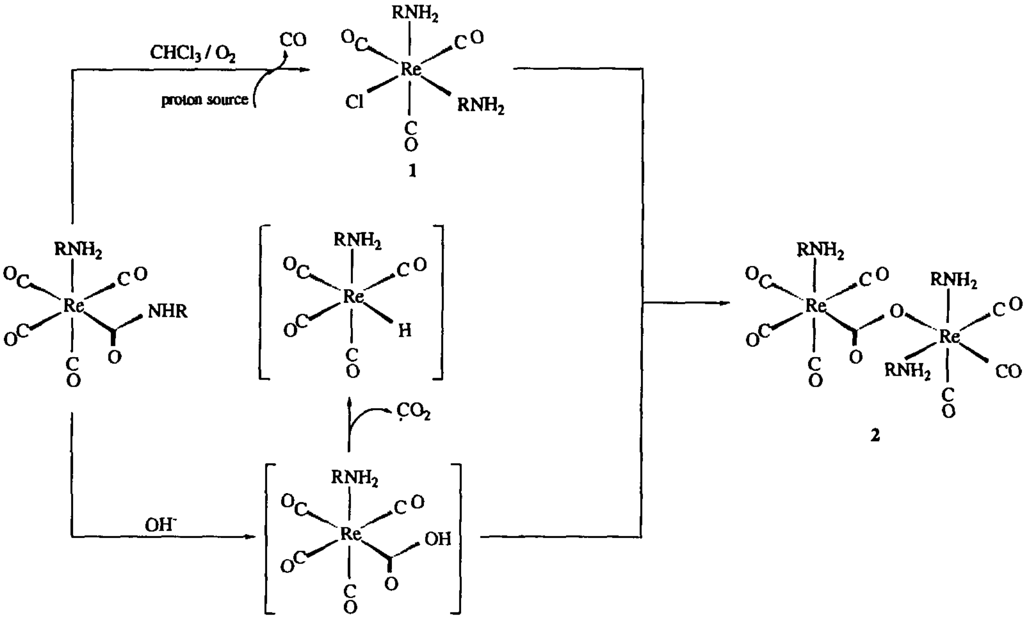


Fig. 2. ORTEP drawing for $(CO)_3L_2Re(\mu,\eta^1,\eta^1\text{-}CO_2)Re(CO)_4L$ (**2**) ($L = NH_2CH(CH_3)_2$), with thermal ellipsoids shown at the 50% probability level. Selected bond distances (Å) and bond angles (deg) are as follows: Re(1)–O(2), 2.117(6); Re(1)–N(2), 2.224(7); Re(1)–N(3), 2.230(8); 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)°; Re(2)–C(1)–O(1), 123.8(7)°; Re(1)–O(2)–C(1), 134.8(6)°; N(2)–Re(1)–N(3), 80.7(3)°.

found in the Fe–Re complex of 1.226(3) Å [4]. Typical $C(sp^2)$–O single bond and $C(sp^2){=}O$ 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)°, 117.2(6)° and 119.0(8)°, respectively. To our knowledge, complex **2** is the first structurally characterized homonuclear complex where the two metal centres are bridged by a μ,η^1,η^1-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_2, possibly proceeds through a radically induced abstraction of a Cl atom from $CHCl_3$. And the formation of **2** begins with a nucleophilic attack of water (or OH^-) 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_2 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_2 dimer from coordinated CO. The bridging CO_2 ligand of the Ir–Os dinuclear complex [2] was also reported to form from an Ir coordinated CO and an oxygen atom of OsO_4. Formation of CO_2 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^- 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.

Acknowledgment

We thank the National Science Council of the Republic of China for financial support.

References and notes

1 (a) A. Behr (ed.), *Carbon Dioxide Activation By Metal Complexes*, VCH Publishers, Weinheim, 1988, (b) P. Braunstein, D. Matt and D. Nobel, *Chem. Rev., 88* (1988) 747; (c) D. Walther, *Coord. Chem. Rev., 79* (1987) 135; (d) D.J. Darensbourg and R.A. Kudaroski, *Adv. Organomet. Chem., 22* (1983) 129; (e) A. Behr, *Angew. Chem., Int. Ed. Engl., 27* (1988) 661; (f) R.S. Pilato, C.E. Housmekerides, P. Jernakoff, D. Rubin, G.L. Geoffroy and A.L. Rheingold, *Organometallics, 9* (1990) 2333; (g) C.E. Housmekerides, D.L. Ramage, C.M. Kretz, J.T. Shontz, R.S. Pilato, G.L. Geoffroy, A.L. Rheingold and B.S. Haggerty, *Inorg. Chem., 32* (1992) 4453; (h) C.T. Tso and A.R. Cutler, *J. Am. Chem. Soc., 108* (1986) 6069; (i) D.R. Senn, J.A. Gladysz, K. Emerson and R.D. Larsen, *Inorg. Chem., 26* (1987) 2737; (j) J.C. Vites, B.D. Steffey, M.E. Giuseppetti-Dery and A.R. Cutler, *Organometallics, 10* (1991) 2827; (k) C. Floriani, *Pure Appl. Chem., 55* (1983) 1; C. Floriani, *Pure Appl. Chem., 54* (1982) 54; (l) G.R. Lee and N.J. Cooper, *Organometallics, 4* (1985) 794; (m) I. Torresan, R.A. Michelin, A. Marsella, A. Zanardo, F. Pinna and G. Strukul, *Organometallics, 10* (1991) 623.

2 J.D. Audett, T.J. Collins, B.D. Santarsiero and G.H. Spies, *J. Am. Chem. Soc., 104* (1982) 7352.

3 M.A. Bennett, G.B. Robertson, A. Rokicki and W.A. Wickramasinghe, *J. Am. Chem. Soc., 110* (1988) 7098.

4 D.H. Gibson, M. Ye and J.F. Richardson, *J. Am. Chem. Soc., 114* (1992) 9716.

5 (a) R.J. Angelici and D.L. Denton, *Inorg. Chim. Acta, 2* (1968) 3; (b) R.J. Angelici, *Chem. Commun.*, (1965) 524; (c) R.B. King, *J. Am. Chem. Soc., 85* (1963) 1918; (d) R.B. King, M.B. Bisnette and A. Fronzaglia, *J. Organomet. Chem., 5* (1966) 341; (e) A. Busetto and R.J. Angelici, *Inorg. Chim. Acta, 2* (1968) 391; (f) H. Behrens, E. Lindner and P. Pässler, *Z. Anorg. Allg. Chem., 365* (1969) 137; (g) H. Behrens, E. Lindner and P. Pässler, *Z. Anorg. Allg. Chem., 361* (1968) 125; (h) R.J. Angelici and A.E. Kruse, *J. Organomet. Chem., 22* (1970) 461; (i) R.D. Adams, D.F. Chodosh and N.M. Golembeski, *Inorg. Chem., 17* (1978) 266; (j) W.-J. Liao, Y.-J. Wang, J.-D. Chen, Y.-C. Lin and L.-K. Liu, *J. Chin. Chem. Soc., 39* (1992) 311; (k) R.J. Angelici, *Acc. Chem. Res., 5* (1972) 335.

6 Yield: 71%. Spectroscopic data for **1**: IR (THF): 2015m, 1899vs, 1873vs; ^1H NMR (acetone-d_6, δ): 3.59 (br, NH_2), 3.21 (m, CH, J(H-H) = 6.2 Hz), 1.28 (d, CH_3, J(H-H) = 6.2 Hz); Mass (FAB, m/z): 423.9 ($[M]^+$), 393.3 ($M^+ - 2CH_3$).

7 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^3, $Z = 4$. The unit cell constants were consistent with an orthorhombic system, and the space group was subsequently determined to be *Pnma*. Routine $2\theta-\omega$ 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 $R_w = 0.023$.

8 Crystal data: space group $P2_1/n$, $a = 11.536(3)$, $b = 12.533(3)$, $c = 17.695(4)$ Å, $\beta = 94.856(18)°$, $V = 2549.3(1)$ Å^3, $Z = 4$. The unit cell constants were consistent with a monoclinic system, and the space group was subsequently determined to be $P2_1/n$. Routine $2\theta-\omega$ 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 $R_w = 0.027$.

9 F.H. Allen, O. Kennard, D.G. Watson, L. Brammer, A.G. Orpen and R. Taylor, *J. Chem. Soc., Perkin Trans. 2*, (1987) S1.

10 (a) C.P. Casey, M.A. Andrews and J.E. Rinz, *J. Am. Chem. Soc., 101* (1979) 741; (b) J.R. Sweet and W.A.G. Graham, *Organometallics, 1* (1982) 982; (c) J.A. Gladysz, *Adv. Organomet. Chem., 20* (1982) 1; (d) D.H. Gibson and T.S. Ong, *J. Am. Chem. Soc., 109* (1987) 7191; (e) D.H. Gibson, T.S. Ong and M. Ye, *Organometallics, 10* (1991) 1811.

11 (a) N. Grice, S.C. Kao and R. Pettit, *J. Am. Chem. Soc., 101* (1979) 1627; (b) P.C. Ford, *Acc. Chem. Res., 14* (1981) 31; (c) P.C. Ford and A. Rokicki, *Adv. Organomet. Chem., 28* (1987) 139.

12 D.J. Darensbourg and J.A. Froelich, *J. Am. Chem. Soc., 99* (1977) 5940.