Organometallics **1997,** *16,* 3089−3090

Formation of a Carbon Dioxide Complex of Rhenium *via* Formal Oxidation of a Carbon Monoxide Ligand

Tein-Fu Wang,* Chong-Chen Hwu, Chia-Wen Tsai, and Kuan-Jiuh Lin

Institute of Chemistry, Academia Sinica, Taipei, Taiwan

Received April 4, 1997[⊗]

Summary: The reaction of aminorhenium carbonyl complex **1** *with MCPBA provides the aminorhenium η^2-CO_2 complex* **2** *in 97% yield. Bromination of* **1** *followed by treatment of the resultant bromide with NaOH also provides* **2** *in 90% yield.*

Oxidation of a carbonyl ligand to CO_2 usually results in a decarbonylation reaction, due to insufficient binding force between metal and CO_2. One notable example is the trimethylamine *N*-oxide promoted ligand substitution reactions of metal carbonyl.[1] However, if the binding force were strong enough to hold the metal and CO_2 together, the resultant CO_2 complex could be isolable, evidenced by the reported η^2-CO_2 complexes (Rh,[2] Nb,[3] and Ta[4]) from an aerobic oxidation of the corresponding metal carbonyl complexes. In our recent study of the reactivity of electron-rich aminorhenium complexes,[5] we have found that the oxidation of an aminorhenium complex with 3-chloroperoxybenzoic acid (MCPBA) resulted in a stable η^2-CO_2 complex. This outcome is quite unusual in organometallic chemistry.

Addition of MCPBA (1 equiv) to a yellow solution of aminorhenium complex $[\eta^5{:}\eta^1\text{-}C_5H_4CH_2CH_2N(CH_3)_2]Re(CO)_2$ (**1**)[6] in CH_2Cl_2 (0 °C) resulted in an immediate deepening of the color with the disappearance of carbonyl absorptions of **1** (1899 and 1828 cm^{-1}) and the concomitant appearance of new intense bands at 1873 and 1725 cm^{-1} which are associated with **2** (see Scheme 1). Solvent evaporation and recrystallization (CH_2Cl_2/hexane) gave yellow crystals of the CO_2 complex $[\eta^5{:}\eta^1\text{-}C_5H_4CH_2CH_2N(CH_3)_2]Re(CO)(\eta^2\text{-}CO_2)$ (**2**; 97%), whose structure was suggested by spectroscopic data[7] and confirmed by X-ray crystallography.[8] Figure 1 is the molecular plot of **2** and clearly shows the η^2-CO_2 binding mode of **2**. The O−C−O angle of 131° is essentially similar to those reported in the literature (124−134°).[9]

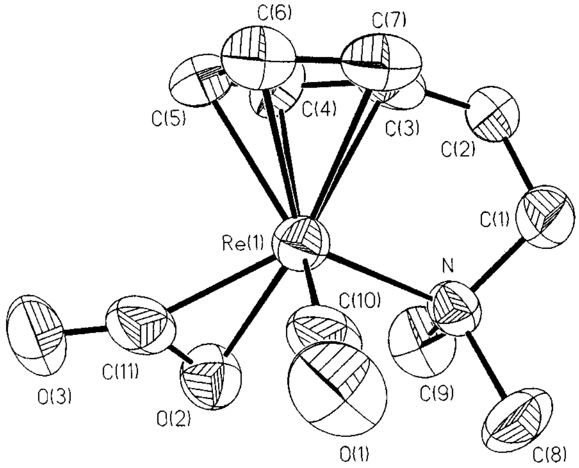
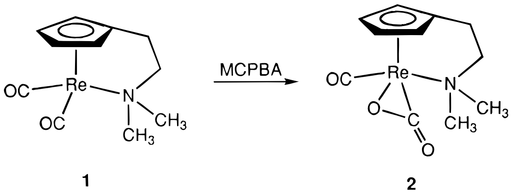


Figure 1.

Scheme 1



Crystals of **2** could be heated up to its melting point (160−165 °C) without decomposition. In $CDCl_3$ or C_3D_6O, the ^1H NMR of **2** remains unchanged after standing overnight at room temperature under air. Treatment of **2** with MCPBA at room temperature for 1 h recovers **2** completely. Compound **2** is less reactive than **1** toward an oxidizing agent, in accordance with respective oxidation potentials that were measured as +0.248 V for **1** and +0.431 V for **2** relative to the Ag/$AgNO_3$ reference electrode.[10] The phase-transfer reaction of **1** with the magnesium salt of monoperoxyphthalic acid (H_2O/CH_2Cl_2) also provides **2**, in 92% yield. Nonetheless, only traces of **2** together with unidentifi-

---

[⊗] Abstract published in *Advance ACS Abstracts,* June 15, 1997.

[1] Albers, M. O.; Coville, N. J. *Coord. Chem. Rev.* **1984**, *53*, 227.

[2] Iwashita, Y.; Hayata, A. *J. Am. Chem. Soc.* **1969**, *91*, 2525.

[3] Fu, P.-F.; Khan, M. A.; Nicholas, K. M. *J. Am. Chem. Soc.* **1992**, *114*, 6579.

[4] Fu, P.-F.; Fazlur-Rahman, A. K.; Nicholas, K. M. *Organometallics* **1994**, *13*, 413.

[5] Wang, T. F.; Lai, C. Y.; Hwu, C. C.; Wen, Y. S. *Organometallics* **1997**, *16*, 1218.

[6] Complex **1** was prepared by irradiation of $[\eta^5\text{-}C_5H_4CH_2CH_2N(CH_3)_2]Re(CO)_3$ in THF. See: Wang, T. F.; Juang, J. P.; Lin, K. J. *Bull. Inst. Chem., Acad. Sin.* **1995**, *42*, 41.

[7] Spectroscopic data for **2** and **3** are given in the Supporting Information.

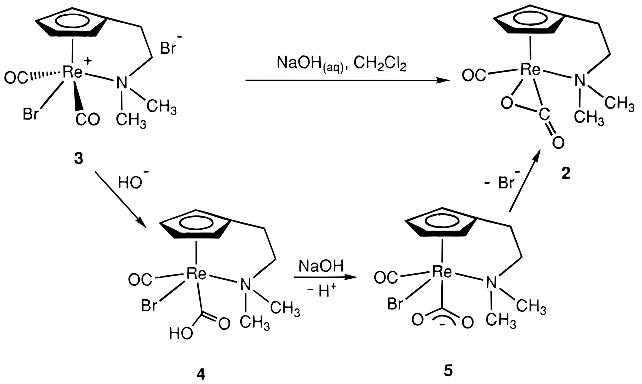
[8] Crystal data for **2**, $C_{11}H_{14}NO_3Re{\cdot}0.5H_2O$: monoclinic, space group *C2/c*; $a = 22.180(4)$, $b = 7.615(2)$, $c = 14.098(3)$ Å; $\beta = 91.35(3)°$; $V = 2380.5(9)$ Å^3; $Z = 8$; $F(000) = 1528$; $D_c = 2.251$ g cm^{-3}; $\mu = 102.06$ cm^{-1}. Diffraction data were collected at room temperature on an Enraf-Nonius CAD4 diffractometer with graphite-monochromated Mo Kα radiation; $\lambda = 0.710\ 69$ Å. The unit cell parameters and orientation matrix were established from a least-squares fit of 25 reflections. Intensity data were collected in the $\omega{-}2\theta$ scanning mode with three standard reflections monitored for intensity variation throughout the experiment. No significant variation in standards was observed. Of the 1554 reflections collected ($2\theta_{max} = 45°$), 1308 unique reflections were considered observed ($I > 2\sigma(I)$) after Lorentz−polarization and empirical absorption corrections. The structure was solved by direct methods using NRCVAX[16] and refined by full-matrix least squares (based on F^2) using SHELXL-93.[17] All non-hydrogen atoms were refined with anisotropic displacement parameters, and all hydrogen atoms were constrained to geometrically calculated positions. The reliability factors converged to R1 = 0.061, wR2(F^2) = 0.183, and GOF = 1.134.

[9] (a) Bristow, G. S.; Hitchcock, P. B.; Lappert, M. F. *J. Chem. Soc., Chem. Commun.* **1981**, 1145. (b) Alvarez, R.; Carmona, E.; Gutierrez-Puebla, E.; Marin, J. M.; Monge, A.; Poveda, M. L. *J. Chem. Soc., Chem. Commun.* **1984**, 1326. (c) Komiya, S.; Akita, M.; Kasuga, N.; Hirano, M.; Fukuoka, A. *J. Chem. Soc., Chem. Commun.* **1994**, 1115. (d) Gambarotta, S.; Floriani, C.; Chiesi-Villa, A.; Guastini, C. *J. Am. Chem. Soc.* **1985**, 107, 2985.

[10] The measurements were performed on a Bioanalytical Systems BAS 100B. The oxidation potentials were obtained in deoxygenated CH_3CN with a platinum working electrode, a platinum-wire auxiliary electrode, and a Ag/$AgNO_3$ reference electrode with 0.1 M tetrabutylammonium perchlorate as supporting electrolyte. The scan rate was 60 mV s^{-1}.

S0276-7333(97)00284-7 CCC: $14.00

Scheme 2



able decomposition mixtures could be observed when **1** reacts with peroxides (*t*-BuOOH, H_2O_2, and O_3). No reaction could be observed between **1** and trimethylamine *N*-oxide.

Interestingly, the CO_2 complex **2** could also be obtained *via* another pathway. Addition of Br_2 to a CH_2Cl_2 soultion of **1** in the presence of pyridine provides the yellow precipitate of **3** (85%, see Scheme 2).[11] The symmetrical spectroscopic data (^1H and ^{13}C) suggest that **3** is the trans isomer.[7] Treatment of **3** with NaOH (H_2O/CH_2Cl_2) provided the CO_2 complex **2** (90%) and a small amount of **1** (5%). The proposed reaction profile is as follows. The Re center of **1** is first oxidized by Br_2, from Re(I) to Re(III), followed by nucleophilic hydroxide addition to the carbonyl group.[12] The carboxylic acid intermediate **4** is deprotonated to give presumably the carboxylate or η^1-CO_2 complex **5**,[13] whereupon the displacement of Br^- by the carboxylate oxygen provided **2**. A formal reduction of the Re center from Re(III) to Re(I) with concomitant formal oxidation of carboxylate to carbon dioxide takes place intramolecularly. It could not be ruled out, however, that the reaction proceeds with a CO_2 expulsion, followed by Br^- elimination and a recapture of CO_2.

We have demonstrated that the oxidation of aminorhenium carbonyl complex **1** with peroxy acids provides the η^2-CO_2 complex **2**. Whether the peroxy acid attacks initially at the metal center or at the amino group may require clarification. Nevertheless, the result suggests that the binding force between the aminorhenium fragment $[\eta^5:\eta^1\text{-}C_5H_4CH_2CH_2N(CH_3)_2]$-Re(CO) and CO_2 is very strong, thereby allowing an isolation of the η^2-CO_2 complex **2**, the first example of a mononuclear Re$-$$CO_2$ complex.[14,15] It is equally interesting that reaction of the bromide **3** with NaOH also provides the η^2-CO_2 complex **2**.

Acknowledgment. Financial support from the National Science Council of the ROC is gratefully acknowledged.

Supporting Information Available: Text giving spectroscopic data for **2** and **3** and tables giving X-ray crystallographic data for **2** (6 pages). Ordering information is given on any current masthead page.

OM9702845

---

[11] Pyridine is essential for obtaining good-quality **3**.

[12] For similar addition reactions see: (a) Sweet, J. R.; Graham, W. A. G. *Organometallics* **1982**, *1*, 982. For reactions using phase-transfer catalysis see: (b) Alper, H. *Adv. Organomet. Chem.* **1981**, *19*, 183. (c) Gibson, D. H.; Hsu, W. L.; Lin, D. S. *J. Organomet. Chem.* **1979**, *172*, C7.

[13] (a) Calabrese, J. C.; Herskovitz, T.; Kinney, J. B. *J. Am. Chem. Soc.* **1983**, *105*, 5914. (b) Tanaka, H.; Nagao, H.; Peng, S.-M.; Tanaka, K. *Organometallics* **1992**, *11*, 1450.

[14] For bimetallic CO_2 complexes containing rhenium, see: (a) Gibson, D. H.; Ye, M.; Richardson, J. F. *J. Am. Chem. Soc.* **1992**, *114*, 9716. (b) Gibson, D. H.; Ye, M.; Richardson, J. F.; Mashuta, M. S. *Organometallics* **1994**, *13*, 4559. (c) Gibson, D. H.; Franco, J. O.; Mehta, J. M.; Mashuta, M. S.; Richardson, J. F. *Organometallics* **1995**, *14*, 5068. (d) Yang, Y.-L.; Chen, J.-D.; Lin, Y.-C.; Cheng, M.-C.; Wang, Y. *J. Organomet. Chem.* **1994**, *467*, C6. (e) Senn, D. R.; Gladysz, J. A.; Emerson, K.; Larsen, R. D. *Inorg. Chem.* **1987**, *26*, 2737. (f) Tso, C. T.; Cutler, A. R. *J. Am. Chem. Soc.* **1986**, *108*, 6069. (g) Pilato, R. S.; Geoffroy, G. L.; Rheingold, A. L. *J. Chem. Soc., Chem. Commun.* **1989**, 1287. (h) Pilato, R. S.; Housmekerides, C. E.; Jernakoff, P.; Rubin, D.; Geoffroy, G. L.; Rheingold, A. L. *Organometallics* **1990**, *9*, 2333. (i) Gibson, D. H.; Mehta, J. M.; Ye, M.; Richardson, J. F.; Mashuta, M. S. *Organometallics* **1994**, *13*, 1070.

[15] For a recent review on the organometallic chemistry of CO_2, see: Gibson, D. H. *Chem. Rev.* **1996**, 96, 2063.

[16] Gabe, E. J.; Lepage, Y.; Charland, J. P.; Lee, F. L.; White, P. S. *J. Appl. Crystallogr.* **1989**, *22*, 384.

[17] Sheldrick, G. M. *SHELXL-93*, Program for Crystal Structure Refinement; University of Gottingen, Gottingen, Germany, 1993.