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Journal of Organometallic Chemistry 689 (2004) 411–418
Journal of Organometallic Chemistry
www.elsevier.com/locate/jorganchem

Aminorhenium carbon dioxide complexes: formal oxidation of a carbon monoxide ligand with peroxy-acids or bromine/hydroxide ☆

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Received 21 August 2003; received in revised form 18 September 2003; accepted 19 September 2003

Abstract

The electron-rich aminorhenium complexes η^5:η^1-$C_5H_4CH_2CH_2NR(CH_3)Re(CO)_2$ (**3a–d**; R = methyl, benzyl, *n*-butyl, *n*-butyl-OH) are easily oxidized with peroxy-acids to give the corresponding η^2-CO_2 complexes η^5:η^1-$C_5H_4CH_2CH_2NR(CH_3)Re(CO)(\eta^2$-$CO_2)$ (**4a–d**) in excellent yield. The resultant η^2-CO_2 complex is predominantly the anti-isomer. The structures of η^2-CO_2 complex η^5:η^1-$C_5H_4CH_2CH_2N(CH_3)$(*n*- $C_4H_8OH)Re(CO)(\eta^2$-$CO_2)$ (**4d-anti**) and the corresponding CO complex **3d** have been confirmed by X-ray crystallography. The η^2-CO_2 complexes **4a–4d** are stable at ambient temperature under air. In addition to peroxy-acid oxidation, bromination of the aminorhenium dicarbonyl complexes followed by base treatment also provided the corresponding η^2-CO_2 complexes. The reaction mechanism for the formation of CO_2 complex from the corresponding dicarbonyl is discussed briefly.

Keywords: Rhenium; Carbon dioxide; Cyclopentadienyl; Amine; Oxidation

1. Introduction

Carbon dioxide was generally considered as a poor ligand in organometallic chemistry. Such a property has been utilized as an advantage in the carbonyl ligand substitution reactions. A notable example is the trimethylamine N-oxide promoted ligand substitution reactions of metal carbonyl [1]. In the reaction, the carbon monoxide ligand was oxidized by N-oxide to a carbon dioxide ligand followed by CO_2 extrusion, due to the insufficient binding force between the metal and the resultant CO_2 ligand. Coordination with a prerequisite ligand completed the ligand substitution. However, if the binding force was strong enough to hold the metal and CO_2 together, the resultant CO_2 complex could be stable and isolable. Mononuclear CO_2 complexes have usually been prepared by direct coordination of CO_2 to a metal complex which has a vacant site or an easily displaced ligand [2]. For example, η^2-CO_2 complex $Ni(CO_2)(PCy_3)_2$ was prepared by $Ni(PCy_3)_3$ or $[Ni(PCy_3)_2]_2$ (μ-N_2) in toluene under an atmospheric pressure of CO_2 [3]. Similarly, $Fe(depe)_2$ (CO_2) was made from $Fe(depe)_2(N_2)$ and CO_2 [4]. There is only few cases of stable η^2-CO_2 complex been resulted by a formal oxidation of metal carbonyl complex. For example, $Cp_2Nb(R)(\eta^2$-$CO_2)$ has been prepared by aerobic oxidation of the corresponding carbonyl complex [5]. Transient CO_2 complex $(\eta^2$-$C_5H_4CH_3)_2Ta(\eta^2$-$CO_2)H$ was formed during the dioxygen oxidation of the corresponding metal carbonyl hydride [6]. Excellent reviews on the coordination chemistry of carbon dioxide have been reported [7].

We have demonstrated that the electron-rich aminorhenium complex reacts readily with a variety of carbon electrophiles. For instance, bidentate complex [η^5:η^1-$C_5H_4CH_2CH_2N(CH_3)_2Re(CO)_2$] reacts with alkyl halides to give the corresponding adduct [η^5:η^1-C_5H_4-$CH_2CH_2N(CH_3)_2Re(CO)_2$ alkyl]$^+X^-$ [8]. We envisioned that if "oxo" electrophiles had been used for the reaction, the resultant "metal-oxo" intermediate might undergo interesting transformations. Indeed, when aminorhenium complex was treated with *m*-chloroperoxybenzoic acid

☆ Supplementary data associated with this article can be found, in the online version at doi:10.1016/j.jorganchem.2003.09.051.

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0022-328X/$ - see front matter © 2003 Elsevier B.V. All rights reserved.
doi:10.1016/j.jorganchem.2003.09.051

(MCPBA), the corresponding η^2-CO_2 complex was obtained [9]. Furthermore, oxidation of the metal center by a bromonium ion followed by base treatment also provides η^2-CO_2 complex. It is quite amazing that same η^2-CO_2 complex could be produced via two completely different approaches. In this report, we want to present such reactions and briefly describe their reaction pathways. The diastereoselectivity of the reaction to give syn- and anti-isomers will also be discussed.

2. Results and discussion

2.1. Preparation of the aminorhenium complexes

Chelated aminorhenium complex **2** was prepared by ultraviolet irradiation of the monomethylamino rhenium tricarbonyl complex η^5-$C_5H_5CH_2CH_2NH(CH_3)$-$Re(CO)_3$ (**1**) in tetrahydrofuran (THF) [6]. About 5–10% of *N*-hydroxybutyl complex **3d** (Scheme 1) was also isolated. Presumably, the photoexcitation of **1** gave rise to an expulsion of a CO ligand. The resultant vacant site was coordinated intramolecularly with the pendent amino group to form the chelated complex **2**, or stabilized with the solvent to form the THF coordinated **A**. The intermediate **A** could then undergo intramolecular ligand exchange to give **2**. Alternatively, under irradiation condition, **A** could also undergo ring-opening of the coordinated THF by the amino group intramolecularly to give the minor compound **3d**. Irradiation of the purified chelated complex **2** in THF also gave **3d**, however, in low yield along with decomposition. Various *N*-substituted aminorhenium complexes **3a**–**3c** were obtained by deprotonation of the methylaminorhenium complex **2** with *n*-butyllithium followed by alkylation with alkyl halides (CH_3I; $C_6H_5CH_2Br$; *n*-C_4H_9Br) [8,10]. The yellow solids of **3a**–**3d** are stable at room temperature under air.

Characterization of the reaction products could be easily accomplished spectroscopically. Upon coordination, the *N*-methyl groups downfield shift to about δ 3.03 compared to the free amine at δ 2.44 in the ^{1}H NMR spectra. Owing to the nitrogen chiral center, the cyclopentadienyl protons of **3b**–**3d** appear as four discrete resonances and the methylene protons of the side chain appear diastereotopically. The terminal carbonyl groups of **3b**–**3d** are non-equivalent, as shown by the different resonance frequencies of the carbonyl carbons in the ^{13}C NMR spectra. Compound **3d** has also been characterized by X-ray crystallography and the ORTEP drawing is shown in Fig. 1.

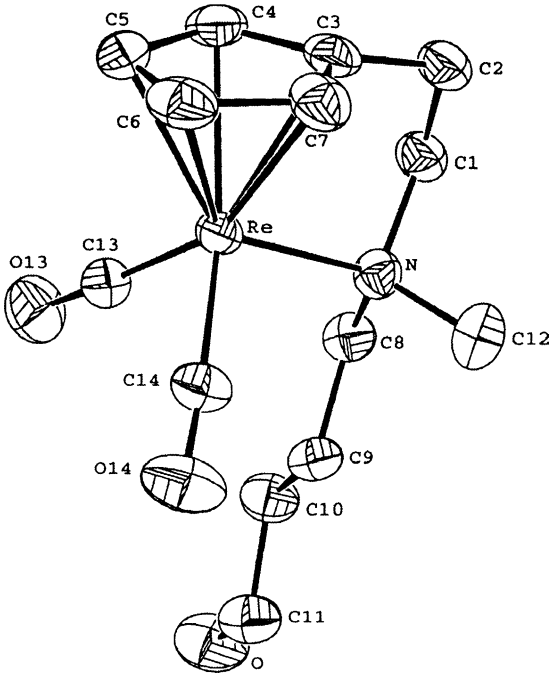
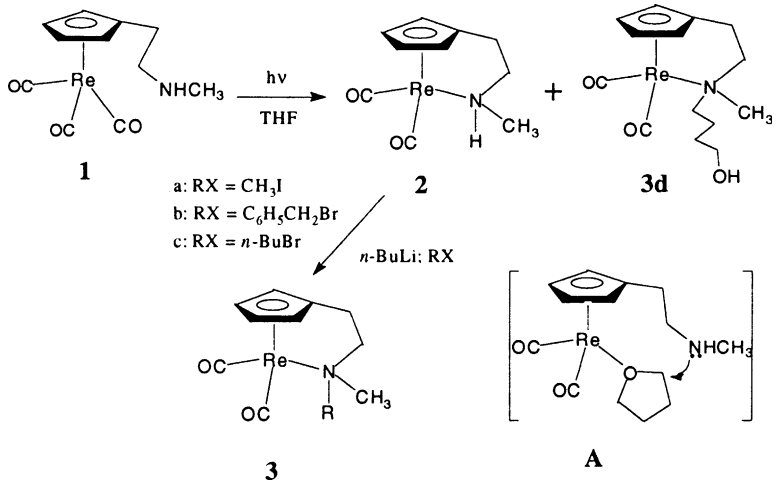


Fig. 1. An ORTEP drawing of **3d**.



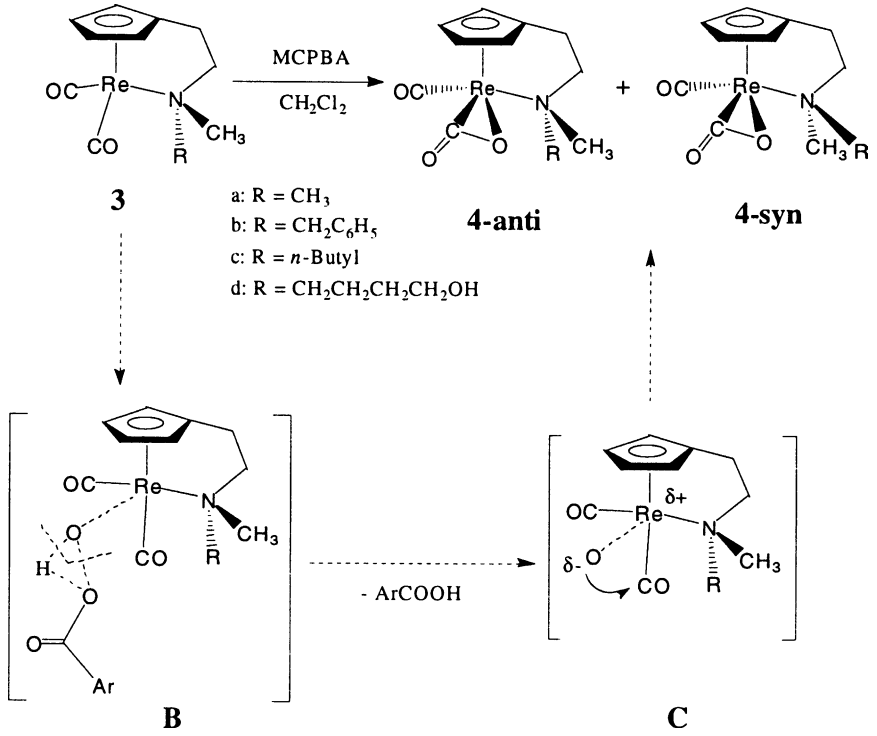
Scheme 1.

2.2. Reaction with peroxy-acids

In general, low valent organometallic complexes are vulnerable to oxidation. Therefore, we thought at begining that the reaction of aminorhenium complex with "oxo" electrophiles might provide rheniumoxides or messy complexes. To our surprise, addition of one equivalent of MCPBA to a yellow solution of *N*,*N*-dimethylaminorhenium complex **3a** in CH_2Cl_2 at 0 °C resulted in an immediate deepening of the color with the disappearance of carbonyl absorptions of **3a** (1899 and 1828 cm^{-1}) and the concomitant appearance of new intense bands at 1873 and 1725 cm^{-1} which are assigned to the terminal carbonyl and η^2-CO_2 absorptions of the carbon dioxide complex **4a**. The structure had been confirmed by X-ray crystallographic study to show that the carbon dioxide ligand is coordinated to the rhenium in a η^2-fashion with the O–C–O angle of 131° [9].

Chiral complexes **3b**–**3d** also reacted with MCPBA smoothly to provide the corresponding η^2-CO_2 complexes as a mixture of diastereomers (Scheme 2). Examination of the crude ^{1}H NMR spectra showed that there are two sets of Cp protons and two well separated *N*-methyl signals. The major component which the *N*-methyl resonance appear at around δ 2.8 was assigned to the anti-isomer **4-anti** (the η^2-CO_2 ligand and the bigger substituent of the amino ligand are anti-orientation) based upon the X-ray crystallographic analysis (see below). Accordingly, the minor component that the *N*-methyl resonance appears at around δ 3.3 was assigned to the syn-isomer **4-syn**. The ratios were determined by integration of the individual protons and are shown in Table 1.

Single crystals of the major isomer **4d-anti** from the reaction of **3d** with MCPBA were obtained from a solution of CH_2Cl_2 and hexane. Fig. 2 shows the molecular structure of **4d-anti**. The CO_2 ligand located at the anti-position of the hydroxybutyl group along the Re–N axis. The binding of the CO_2 ligand to the metal is η^2-fashion with the O–C–O angle of 133°, similar to those η^2-CO_2 complexes reported in the literature (124–134°) [11]. It is worth noting that the core structures of **4d-anti**



Scheme 2.

Table 1
The ratio of **4-anti**:**4-syn** and yields in parenthesis for various reaction conditions

Reagents	4a	4b	4c	4d
MCPBA	(97)	67:33 (96)	70:30 (91)	72:28 (98)
MMPP	(92)	64:36 (95)	63:37 (96)	64:36 (75)
Br_2/NaOH	18:1 (95)[a]	33:22:45 (70)[b]	39:38:23 (75)[b]	26:23:51 (45)[b]

[a] The ratio represents **4a**:**3a** and the yield is the total isolated yield of **4a** + **3a**.
[b] The ratio represents **4-anti**:**4-syn**:**3** and the yield is the total isolated yield of **4** + **3**.

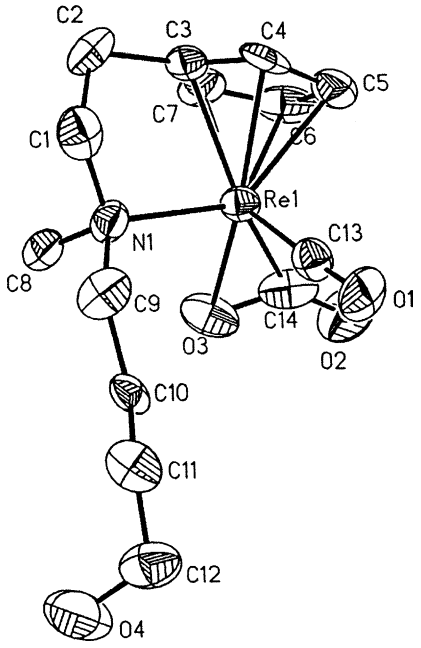


Fig. 2. An ORTEP drawing of **4d-anti**. There are two essentially independent molecules within the unit cell. Only one molecule is shown.

and the corresponding CO complex **3d** are quite similar. The bond lengths of Re–N (2.23 Å for **3d** and 2.20 Å for **4d-anti**) and Re–CO (1.88 Å for **3d** and 1.87 Å for **4d-anti**), and the bond angles of N–Re–CO (97.6° for **3d** and 96.0° for **4d-anti**) of both **3d** and **4d-anti** are very close (see Table 2).

In addition to the homogeneous reaction with MCPBA, the phase-transfer reaction (H_2O/CH_2Cl_2) of **3** with the magnesium salt of monoperoxyphthalic acid (MMPP) also provides **4** in good yield. The diastereomeric ratios and chemical yields (Table 1) are comparable to those of the MCPBA reaction. Other peroxide oxidants (*t*-BuOOH, H_2O_2, and O_3) also gave carbon dioxide complex **4**, however, in only trace amount together with unidentifiable decomposition mixtures. Oxidation of the monomethylaminorhenium complex **2** gave decomposition or complex mixture only. Pure **4d-anti** compound does not isomerized to the corresponding **4d-syn** under the oxidation reaction condition and the syn- and anti-isomers once formed the ratio stayed unchanged, suggesting that the formation of **4-syn** and **4-anti** isomers are under kinetic control.

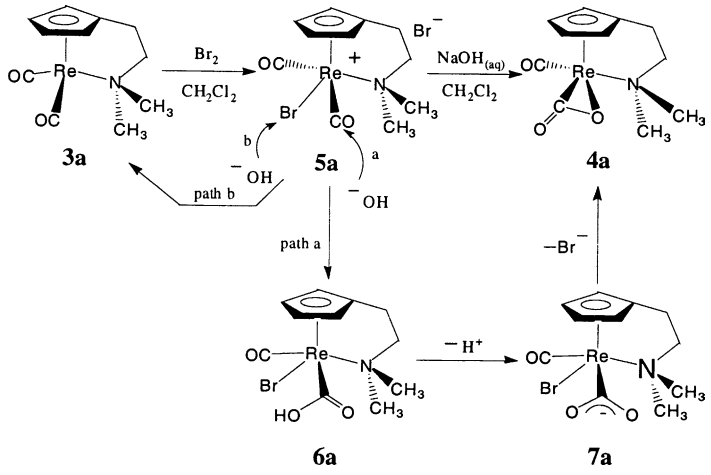
It is conceivable that the interaction of electron-rich rhenium metal center with the electrophilic oxygen was the first step for the reaction of aminorhenium complex **3** with peroxy-acid. The rhenium-oxo complex **C** was, therefore, proposed as the transient intermediate which then underwent intramolecular cyclization to give the carbon dioxide complex.

2.3. Bromination followed by base treatment

It has been reported that the bromination of $CpRe(CO)_3$ resulted in extrusion of a carbonyl ligand to give the dibromo complex $CpRe(CO)_2Br_2$ [12]. Interestingly, in the presence of electron donating amino

Table 2
Selected bond lengths (Å) and angles (°) for **3d** and **4d-anti**

3d		**4d-anti**	
Re–N	2.232(4)	Re1–N1	2.20(2)
Re–C3	2.277(5)	Re1–C3	2.26(2)
Re–C6	2.247(5)	Re1–C6	2.26(2)
Re–C7	2.285(5)	Re1–C7	2.32(2)
Re–C13	1.876(5)	Re1–C13	1.87(2)
Re–C14	1.877(5)	Re1–C14	2.01(2)
N–C1	1.521(6)	Re1–O3	2.12(1)
N–C8	1.498(6)	N1–C1	1.45(3)
N–C12	1.481(7)	N1–C8	1.48(3)
O13–C13	1.165(6)	O1–C13	1.19(2)
O14–C14	1.165(7)	C14–O2	1.23(3)
N–Re–C3	78.9(2)	N1–Re1–C3	78.9(6)
N–Re–C5	135.1(2)	N1–Re1–C5	133.5(7)
N–Re–C6	134.0(2)	N1–Re1–C6	132.6(8)
N–Re–C7	97.5(2)	N1–Re1–C7	98.0(7)
N–Re–C13	97.6(2)	N1–Re1–C13	96.0(7)
N–Re–C14	100.1(2)	N1–Re1–C14	123.9(9)
C3–Re–C13	134.3(2)	N1–Re1–O3	88.0(6)
C3–Re–C14	136.0(2)	C3–Re1–C13	127.8(7)
Re–C13–O13	176.2(4)	C3–Re1–C14	137.6(8)
Re–C14–O14	174.3(5)	C3–Re1–O3	131.8(6)
Re–N–C1	105.5(3)	Re1–C13–O1	178(2)
Re–N–C8	115.6(3)	Re1–C14–O2	151(2)
Re–N–C12	113.5(3)	O2–C14–O3	133(2)



Scheme 3.

ligand, bromination of aminorhenium complex **3a** provides the corresponding cationic monobromo complex **5a** without extrusion of any ligands (Scheme 3). The symmetrical spectroscopic data (^{1}H and ^{13}C NMR) suggest that **5a** is a *trans* isomer. Graham and co-workers [13] have reported that terminal carbonyl ligand of cationic nitrosyl complex $[CpRe(NO)(CO)_2]^+$ reacts with hydroxide ion to give the corresponding adduct CpRe(NO)(CO)COOH, which upon loss of CO_2 providing rhenium hydride complex CpRe(NO)(CO)H. However, treatment of the CH_2Cl_2 solution of **5a** with aqueous sodium hydroxide provided the CO_2 complex **4a** (90%) together with a small amount of **3a** (5%). The reaction could be proceeding via the addition of hydroxide to one of the carbonyl ligand to give the corresponding carboxylic acid **6a**, similar to that described by Graham and co-workers [13]. In the basic reaction condition, the carboxylic acid was deprotonated to give presumably the carboxylate or η^1-CO_2 complex **7a** [14], whereupon the displacement of Br^- by the carboxylate oxygen provided **4a**. In the reaction, the initial Re(I) of complex **3a** was oxidized by bromine to Re(III). Upon displacement of Br^- by the carboxylate, a formal reduction of Re(III) back to Re(I) took place intramolecularly with concomitant formal oxidation of carboxylate to carbon dioxide. It could not be ruled out that the reaction proceeded with a CO_2 expulsion, followed by Br^- elimination and a recapture of CO_2. The formation of a small amount of **3a** was resulted by the hydroxide ion attacks on the Br ligand of complex **5a**.

Reactions proceeded similarly for **3b**–**3d** to provide a mixture of anti- and syn-η^2-CO_2 complexes and recovered **3**. The ratios of anti- and syn-isomers are listed in Table 1. Higher percentage of the recovery of **3b**–**3d** than that of **3a** could be arising from the decreasing rate of hydroxide ion attacked on the carbonyl ligand owing to the bulkier substituent on the amino group. Therefore, the relative rate of the hydroxide attacked on Br ligand increases substantially and a significant amount of recovered **3** resulted.

3. Experimental

General information has been reported previously [8,15]. For the assignment of ^{1}H and ^{13}C NMR data, the carbon bound to the nitrogen was designated as C_1 and the hydrogens on C_1 were designated as H_{1a} and H_{1b}. The next carbon was designated as C_2, and the hydrogens on C_2 were designated as H_{2a} and H_{2b}.

*3.1. Preparation of η^5:η^1-$C_5H_4CH_2CH_2NH(CH_3)Re(CO)_2$ (**2**) and η^5:η^1-$C_5H_4CH_2CH_2N(CH_3)$(n-BuOH)-$Re(CO)_2$ (**3d**)*

Literature procedure [6] for the preparation of **2** was followed, except that the more polar portion of **3d** was collected. That is, after irradiation of the complex **1** (6.326 g, 16.12 mmol) in THF (500 ml) at 0 °C for 2 h, solvent was evaporated. The residue was chromatographed on silica gel with 30% ethyl acetate in hexanes as eluent followed by 50% and then 100% ethyl acetate. The first yellow band ($R_f = 0.38$, 30% EtOAc in hexane) was collected and concentrated to give 3.78 g of **2** as yellow powders (64% yield). The second yellow band at $R_f = 0.18$ (tailing, 50% EtOAc in hexane) was collected and concentrated to give 0.452 g (6.6% yield) of **3d** as yellow powders. The physical data of **3d** are recorded as follows. M.p. 100–101 °C. IR (CH_2Cl_2): 1893, 1815 cm^{-1}. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 5.23–5.21 (1H, m, Cp), 5.15–5.13 (1H, m, Cp), 4.91–4.89 (1H, m, Cp), 4.88–4.86 (1H, m, Cp), 3.73 (2H, t, $J = 6.1$ Hz), 3.42–3.26 (2H, m), 3.08 (1H, td, $J = 12.0$, 4.0 Hz), 3.03 (3H, s, N–CH_3), 2.82 (1H, td, $J = 11.6$, 5.2 Hz), 2.34 (1H, ddd, $J = 14.6$, 10.7, 5.7 Hz), 2.23–2.02 (2H, m), 1.94–1.79 (1H, m), 1.68–1.59 (2H, m). ^{13}C NMR ($CDCl_3$, 75

MHz): δ 205.8 (CO), 205.4 (CO), 119.8 (C, Cp), 82.4 (CH, Cp), 79.7 (CH_2), 77.9 (CH, Cp), 76.0 (CH, Cp), 73.7 (CH, Cp), 73.2 (CH_2), 62.0 (CH_2), 58.4 (CH_3), 29.7 (CH_2), 25.1 (CH_2), 24.4 (CH_2). (Found: C, 38.49; H, 4.61; N, 3.42$C_{14}H_{20}NO_3Re$ requires: C, 38.52; H, 4.62; N, 3.21.)

3.2. Preparation of η^5:η^1-$C_5H_4CH_2CH_2N(CH_3)(n\text{-}Bu)Re(CO)_2$ (**3c**)

To a stirred solution of **2** (456 mg, 1.25 mmol) in THF (10 ml) was added a hexane solution of *n*-BuLi (1.6 M, 0.95 ml, 1.5 mmol) over a period of 3 min at −78 °C. After the solution was stirred for an additional 10 min, *n*-BuBr (0.5 ml) was added. The cool bath was removed and the solution stirred at room temperature for 30 min. The residue after evaporation of solvents was chromatographed on silica gel using 20% EtOAc in hexanes as eluent. A yellow band at $R_f = 0.39$ (20% EtOAc in hexane) was collected and concentrated to give, after recrystallization from a solution of CH_2Cl_2 and hexane, 0.358 g (68% yield) of **3c** as yellow crystals. M.p. 101–102 °C. IR (CH_2Cl_2): 1895, 1818 cm^{-1}. ^1H NMR ($CDCl_3$, 300 MHz): δ 5.21–5.19 (1H, m, Cp), 5.15–5.13 (1H, m, Cp), 4.90–4.88 (1H, m, Cp), 4.87–4.85 (1H, m, Cp), 3.41–3.29 (2H, m), 3.06 (1H, td, $J = 11.9$, 4.2 Hz), 3.03 (3H, s), 2.80 (1H, td, $J = 11.6$, 5.0 Hz), 2.32 (1H, ddd, $J = 14.5$, 10.4, 5.8 Hz), 2.18 (1H, ddd, $J = 14.5$, 5.2, 3.4 Hz), 2.04–1.89 (1H, m), 1.73–1.60 (1H, m), 1.49–1.29 (2H, m), 0.98 (3H, t, $J = 7.3$ Hz). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 205.9 (CO), 204.9 (CO), 119.5 (C, Cp), 82.2 (CH, Cp), 79.6 (CH_2), 77.9 (CH, Cp), 75.8 (CH, Cp), 73.6 (CH, Cp), 73.5 (CH_2), 58.4 (CH_3), 30.4 (CH_2), 24.5 (CH_2), 20.1 (CH_2), 14.0 (CH_3). (Found: C, 40.02; H, 4.68; N, 3.60%. $C_{14}H_{20}NO_2Re$ requires: C, 39.99; H, 4.79; N, 3.33.)

3.3. Reaction of **3a–d** with m-chloroperoxybenzoic acid. Preparation of η^5:η^1-$C_5H_4CH_2CH_2NR(CH_3)Re(CO)(\eta^2\text{-}CO_2)$ (**4a–d**; R = methyl, benzyl, n-butyl, n-butyl-OH)

To a stirred solution of **3a**–**d** (1 mmol) in CH_2Cl_2 (20 ml) at 0 °C was added MCPBA (237 mg, 80%, 1.1 mmol). The yellow color of the solution turned deeper immediately. After stirring for 20 min, CH_2Cl_2 was evaporated. The residual solids were washed three times with diethyl ether to give analytically pure **4a**–**d** as yellow powders.

3.3.1. η^5:η^1-$C_5H_4CH_2CH_2N(CH_3)_2Re(CO)(\eta^2\text{-}CO_2)$ (**4a**)

97% yield. M.p. 160–165 °C. IR (CH_2Cl_2): 1873, 1725, 1120 cm^{-1}. ^1H NMR (C_3D_6O, 300 MHz): δ 5.69–5.67 (1H, m, Cp), 5.48–5.46 (1H, m, Cp), 5.29–5.27 (1H, m, Cp), 5.08–5.06 (1H, m, Cp), 3.90 (1H, ddd, $J = 12.0$, 10.0, 5.5 Hz, H_{1a}), 3.62 (1H, ddd, $J = 12.0$, 5.4, 4.4 Hz, H_{1b}), 3.43 (3H, s, N–CH_3), 2.89 (3H, s, N–CH_3), 2.67 (1H, ddd, $J = 14.5$, 10.0, 5.4 Hz, H_{2a}), 2.47 (1H, ddd, $J = 14.5$, 5.5, 4.4 Hz, H_{2b}). ^{13}C NMR (C_3D_6O, 75 MHz): δ 204.4 (CO), 182.2 (CO_2), 126.6 (C, Cp), 93.1 (CH, Cp), 90.9 (CH, Cp), 79.3 (CH_2), 77.0 (CH, Cp), 73.4 (CH, Cp), 61.5 (CH_3), 52.1 (CH_3), 25.9 (CH_2). (Found: C, 33.18; H, 3.29; N, 3.37%. $C_{11}H_{14}NO_3Re$ requires: C, 33.50; H, 3.58; N, 3.55.)

3.3.2. η^5:η^1-$C_5H_4CH_2CH_2N(CH_3)(CH_2Ph)Re(CO)(\eta^2\text{-}CO_2)$ (**4b**)

96% yield (anti/syn: 67/33). The physical data were recorded by using a mixture of anti- and syn-isomers. M.p. 145–148 °C (decomp.). IR (CH_2Cl_2): 1873, 1727, 1112 cm^{-1}. ^1H NMR (C_3D_6O, 300 MHz, **4b-anti**): δ 7.52–7.23 (5H, m, Ph), 5.75–5.73 (1H, m, Cp), 5.52–5.50 (1H, m, Cp), 5.30–5.28 (1H, m, Cp), 5.14–5.12 (1H, m, Cp), 4.93 (1H, d, $J = 13.4$ Hz, benzylic-H_a), 4.72 (1H, d, $J = 13.4$ Hz, benzylic-H_b), 4.00 (1H, td, $J = 11.5$, 5.7 Hz, H_{1a}), 3.43 (1H, ddd, $J = 12.0$, 5.2, 3.3 Hz, H_{1b}), 2.78 (3H, s, N–CH_3), 2.61 (1H, ddd, J = 14.6, 11.0, 5.2 Hz, H_{2a}), 2.54–2.44 (1H, m, H_{2b}). ^1H NMR (C_3D_6O, 300 MHz, **4b-syn**): δ 7.52–7.23 (5H, m, Ph), 5.72–5.70 (1H, m, Cp), 5.63–5.61 (1H, m, Cp), 5.35–5.33 (1H, m, Cp), 5.10–5.08 (1H, m, Cp), 4.45 (1H, d, $J = 13.4$ Hz, benzylic-H_a), 4.37 (1H, d, $J = 13.4$ Hz, benzylic-H_b), 3.76–3.59 (2H, m, H_1's), 3.31 (3H, s, N–CH_3), 2.90–2.82 (1H, m, H_{2a}), 2.54–2.44 (1H, m, H_{2b}). ^{13}C NMR (C_3D_6O, 75 MHz, **4b-anti**): δ 204.9 (CO), 182.2 (CO_2), 133.6 (C, Ph), 133.1 (CH_2, Ph), 130.1 (CH, Ph), 129.2 (CH x 2, Ph), 126.2 (C, Cp), 93.6 (CH, Cp), 90.7 (CH, Cp), 76.3 (CH, Cp), 75.8 (CH, Cp), 73.5 (CH_2), 56.6 (CH_3), 46.9 (CH_2), 25.7 (CH_2). (Found: C, 43.18; H, 3.88; N, 3.14%. $C_{17}H_{18}NO_3Re$ requires: C, 43.39; H, 3.86; N, 2.98.)

3.3.3. η^5:η^1-$C_5H_4CH_2CH_2N(CH_3)(n\text{-}C_4H_9)Re(CO)(\eta^2\text{-}CO_2)$ (**4c**)

91% yield (anti/syn: 70/30). The physical data were recorded by using a mixture of anti- and syn-isomers. M.p. 143–145 °C (decomp.). IR (CH_2Cl_2): 1873, 1728, 1122 cm^{-1}. ^1H NMR (C_3D_6O, 300 MHz, **4c-anti**): δ 5.62–5.60 (1H, m, Cp), 5.51–5.49 (1H, m, Cp), 5.25–5.23 (1H, m, Cp), 5.10–5.08 (1H, m, Cp), 3.84 (1H, td, $J = 12.2$, 5.5 Hz, H_{1a}), 3.59 (1H, ddd, $J = 12.2$, 5.4, 1.4 Hz, H_{1b}), 3.41–3.18 (2H, m), 2.89–2.76 (1H, m), 2.84 (3H, s, N–CH_3), 2.36 (1H, dd, J = 14.5, 5.5 Hz), 1.87–1.60 (2H, m), 1.47–1.25 (2H, m), 0.89 (3H, t, $J = 7.4$ Hz). ^1H NMR (C_3D_6O, 300 MHz, **4c-syn**, partial): δ 5.70–5.68 (1H, m, Cp), 5.51–5.49 (1H, m, Cp), 5.35–5.33 (1H, m, Cp), 5.10–5.08 (1H, m, Cp), 3.33 (3H, s, N–CH_3). ^{13}C NMR (C_3D_6O, 75 MHz, **4c-anti**): δ 204.3 (CO), 183.0 (CO_2), 126.2 (C, Cp), 93.9 (CH, Cp), 90.0 (CH, Cp), 77.4 (CH_2), 75.1 (CH, Cp), 74.0 (CH, Cp), 73.0 (CH_2), 47.4 (CH_3), 29.6 (CH_2), 25.4 (CH_2), 20.7

(CH_2), 14.2 (CH_3). (Found: C, 38.50; H, 4.71; N, 3.35%. $C_{14}H_{20}NO_3Re$ requires: C, 38.52; H, 4.62; N, 3.21.)

3.3.4. η^5:η^1-$C_5H_4CH_2CH_2N(CH_3)(n\text{-}C_4H_8OH)Re(CO)(\eta^2\text{-}CO_2)$ (**4d**)

98% yield (anti/syn: 72/28). The physical data were recorded by using a mixture of anti- and syn-isomers. M.p. 120–125 °C. IR (CH_2Cl_2): 1873, 1728, 1122 cm^{-1}. ^1H NMR (C_3D_6O, 300 MHz, **4d-anti**): δ 5.60–5.58 (1H, m, Cp), 5.49–5.47 (1H, m, Cp), 5.23–5.21 (1H, m, Cp), 5.11–5.09 (1H, m, Cp), 3.85 (1H, td, $J = 12.2$, 5.6 Hz, H_{1a}), 3.62–3.50 (2H, m), 3.43–3.27 (2H, m), 2.84 (3H, s, N–CH_3), 2.84–2.75 (2H, m), 2.37 (1H, ddd, $J = 14.4$, 5.5, 1.4 Hz), 1.88–1.78 (2H, m), 1.56–1.46 (2H, m). ^1H NMR (C_3D_6O, 300 MHz, **4d-syn**, partial): δ 5.69–5.67 (1H, m, Cp), 5.49–5.47 (1H, m, Cp), 5.34–5.32 (1H, m, Cp), 5.09–5.07 (1H, m, Cp), 3.34 (3H, s, N–CH_3). ^{13}C NMR (C_3D_6O, 75 MHz, **4d-anti**): δ 204.5 (CO), 181.8 (CO_2), 125.9 (C, Cp), 93.8 (CH, Cp), 90.0 (CH, Cp), 77.3 (CH_2), 75.0 (CH, Cp), 74.1 (CH, Cp), 73.2 (CH_2), 60.1 (CH_2), 47.2 (CH_3), 31.0 (CH_2), 25.4 (CH_2), 24.4 (CH_2). (Found: C, 37.19; H, 4.38; N, 3.02%. $C_{14}H_{20}NO_4Re$ requires C, 37.16; H, 4.45; N, 3.10.)

3.4. Two phase reactions of **3** with magnesium monoperoxyphthalate (MMPP)

To a stirred solution of **3a**–**d** (0.5 mmol) in CH_2Cl_2 (10 ml) at 0 °C was added a water solution of MMPP (2 ml, 0.3M). The yellow color of the CH_2Cl_2 layer turned deeper immediately. After stirring for 20 min, CH_2Cl_2 layer was separated and evaporated. The residual solids were washed three times with diethyl ether to give **4a**–**d** as yellow powders. See Table 1 for yields and the anti to syn ratios.

3.5. Preparation of {[η^5:η^1-$C_5H_4CH_2CH_2N(CH_3)_2$]Re(CO)$_2$Br}$^+$Br$^-$ (**5a**)

To a stirred solution of **3a** (175 mg, 0.46 mmol) and pyridine (0.05 mL) in CH_2Cl_2 (30 ml) at 0 °C was added a solution of bromine in CH_2Cl_2 (0.5 M, 1.2 ml) slowly over 5 min. After stirring for another 20 min, the yellow powders were collected and washed once with a small amount of CH_2Cl_2. Evaporation under reduced pressure gave 210 mg (85% yield) of **5a** as yellow powders. M.p. 92–95 °C (decomp.). IR (CH_3OH): 2064, 2001 cm^{-1}. ^1H NMR (CD_3OD, 300 MHz): δ 7.14 (2H, t, $J = 2$ Hz, Cp H), 5.80 (2H, t, $J = 2$ Hz, Cp H), 4.05 (2H, t, $J = 6.4$ Hz, H_1's), 3.48 (6H, s), 2.61 (2H, t, $J = 6.4$ Hz, H_2's). ^{13}C NMR (CD_3OD, 75 MHz): δ 192.2 (CO 2×), 133.6 (C, Cp), 97.2 (CH 2×, Cp), 93.9 (CH 2×, Cp), 88.9 (CH_2, C_1), 64.5 (CH_3 2×), 25.4 (CH_2, C_2). (Found: C, 24.60; H, 2.92; N, 2.96%. $C_{11}H_{14}Br_2NO_2Re$ requires: C, 24.55; H, 2.62; N, 2.60.)

3.6. Crystal structure of η^5:η^1-$C_5H_4CH_2CH_2N(CH_3)(n\text{-}C_4H_8OH)Re(CO)_2$ (**3d**) and η^5:η^1-$C_5H_4CH_2CH_2N(CH_3)(n\text{-}C_4H_8OH)Re(CO)(\eta^2\text{-}CO_2)$ (**4d-anti**)

Single crystals of **3d** and **4d-anti** were obtained by slow diffusion of each individual CH_2Cl_2 solution into hexane at room temperature. Diffraction measurements were made on an Enraf-Nonius CAD-4 automated diffractometer by use of a graphite-monochromated Mo Kα radiation ($\lambda = 0.710\,69$ Å) with θ–2θ scan mode. The unit cells were determined and refined using 25 randomly selected reflections obtained with the automatic search, center, index, and least-squares routines. Lorentz/polarization and empirical absorption corrections based on three azimuthal scans were applied to the data. The space groups ($P\bar{1}$ for **3d** and $Pbn2_1$ for **4d-anti**) were determined from the systematic absences observed during data collection. All data reduction and refinements were carried out on a DecAlpha 3400/400 computer using the NRCVX program [16]. The structures were solved by direct methods and refined by a full-matrix least-squares routine [17] with anisotropic thermal parameters for all non-hydrogen atoms. The structures were refined by minimizing $\sum w|F_o - F_c^2|$, where $w = (1/\sigma^2)F_o$ was cal-

Table 3
Crystallographic data and structure refinements for **3d** and **4d-anti**

Compound	**3d**	**4d-anti**
Formula	$C_{14}H_{20}NO_3Re$	$C_{14}H_{20}NO_4Re$
Formula weight	436.52	452.52
Crystal size (mm)	$0.41 \times 0.19 \times 0.38$	$0.30 \times 0.18 \times 0.16$
Color	yellow	orange
Temperature (K)	293	293
Crystal system	triclinic	orthorhombic
Space group	$P\bar{1}$	$Pbn2_1$
a (Å)	7.4028(7)	8.4343(14)
b (Å)	8.2371(15)	15.989(2)
c (Å)	12.879(3)	21.802(4)
α (°)	94.231(17)	90
β (°)	90.694(15)	90
γ (°)	114.564(13)	90
V (Å^3)	711.5(2)	2940.1(8)
Z	2	8
D_c (g cm^{-3})	2.038	2.036
$F(000)$	418	1736
λ(Mo Kα) (Å)	0.71069	0.71069
μ(Mo Kα) (cm^{-1})	86.585	82.75
$T_{min,max}$	0.453, 1.00	0.50, 1.00
Scan rate (deg min^{-1})	0.824–2.06	0.824–2.747
$\theta/2\theta$ scan width (°)	$0.80 + 0.35\tan\theta$	$0.75 + 0.35\tan\theta$
$2\theta_{max}$ (°)	50	45
h, k, l range	(−8; 7), (0; 9), (−15; 15)	(0; 9), (0; 17), (0; 23)
Unique reflections	2498	1973
Observed reflections ($I > 2.0\sigma(I)$)	2345	1728
Refined parameters	173	360
R; wR	0.020; 0.026	0.0320; 0.0803
S	1.69	1.024
$(\Delta\rho)_{max,min}$ (e Å^{-3})	0.930; −0.890	1.813; −1.343

culated from the counting statistics. Hydrogens were included in the structure factor calculations in their expected positions on the basis of idealized bonding geometry but not refined in least-squares. The final cell parameters and data collection parameters are listed in Table 3. The ORTEP drawings are shown in Fig. 1 for **3d** and Fig. 2 for **4d-anti**.

4. Conclusion

We have demonstrated that the aminorhenium carbon dioxide complex could be easily obtained from the corresponding carbonyl complex via a formal oxidation of the carbon monoxide ligand. The diastereoselectivity of the resultant η^2-CO_2 complex is predominantly the anti-isomer. Two approaches for the formation of CO_2 complexes from the corresponding CO complexes have been realized. The peroxy-acids (MCPBA and MMPP) methodology provided direct access to the high yielded CO_2 complexes. The two steps approach, bromination followed by hydroxide treatment, gave us a clearer picture of the reaction pathway on the formation of CO_2 complexes. The presence of the electron donating amino ligand may be an important factor for the preparation of CO_2 complexes been successful. In the course of oxidation, the amino ligand stabilized the developing positive charge, thereby allowing the subsequent transformations proceeded smoothly to give the CO_2 complex.

Acknowledgements

We are grateful to the National Science Council of Taiwan for financial support.

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