Articles

Insertion Reactions of CO into the Rhenium−Nitrogen Bond. η^2-Carbamoyl Complexes and Their Reactions

Tein-Fu Wang,* Chong-Chen Hwu, Chia-Wen Tsai, and Yuh-Sheng Wen

Institute of Chemistry, Academia Sinica, Taipei, Taiwan 115, Republic of China

Received June 27, 1997[⊗]

Deprotonation of $[(CO)_2RReNH(CH_3)CH_2CH_2(\eta^5\text{-}C_5H_4)]^+X^-$ (R = CO_2Me, CO_2Et; X = Br) followed by heating under a CO atmosphere yields the corresponding CO insertion compound $(CO)_2RReC(=O)N(CH_3)CH_2CH_2(\eta^5\text{-}C_5H_4)$. An anologous insertion reaction proceeds more rapidly for the complexes $[(CO)_2XReNH(CH_3)CH_2CH_2(\eta^5\text{-}C_5H_4)]^+Y^-$ (X = Br, I, PhS, and PhSe) in which X is a strong electron-withdrawing group. Without the presence of external ligands, the oxygen of the resultant carbamoyl group binds to the rhenium to fulfill the 18-electron rule. The η^2-carbamoyl selenolate complex $[(CO)PhSeRe(\eta^2\text{-}C{=}O)N(CH_3)CH_2CH_2(\eta^5\text{-}C_5H_4)]$ (**9b**) has been characterized by X-ray crystallography. Upon addition of two-electron-donor ligands, such as CO, isocyanides, and trialkyl phosphites, the η^2-carbamoyl complexes convert cleanly to the corresponding η^1-carbamoyl complexes.

Introduction

The migratory insertion of carbon monoxide into a metal−ligand bond is an important reaction.[1] The insertion of carbon monoxide into a metal−carbon bond has attracted the most attention.[2] By comparison, not much is known about the insertion of carbon monoxide into a metal−nitrogen bond.[3] We are interested in organometallic complexes that have an amino ligand.[4] With certain cationic aminorhenium complexes,[5] we found that removal of a N−H proton by a base results in migratory insertion of the CO ligand into the rhenium−nitrogen bond. The resultant carbamoyl ligand binds to the rhenium in an η^2-fashion to fulfill the usual 18-electron count. The η^2-carbamoyl complexes readily convert to η^1-carbamoyl complexes by adding two-electron-donor ligands such as CO, isocyanides, and trialkyl phosphites. A description of these reactions is presented herein.

Results and Discussion

A. CO Insertion Reactions of the Aminorhenium Complexes 2. We reported[5] that reaction of **1** with carbon electrophiles provides cationic aminorhenium complexes **2** (see Scheme 1). The N−H proton of **2** could be removed by base to give the corresponding neutral species **3**. Upon exposure to moisture, **3** recaptures a proton and regenerates cationic **2**. Heating the neutral complexes **3a**−**d** gave either recovery of **2a**−**d** or decomposition mixtures. However, when **3e** and **3f** were heated, CO insertion occurred, providing **4e** and **4f**, respectively. In order to improve the yields, the reactions were performed under a CO atmosphere. Thus, **2e** and **2f** were deprotonated with NaH in THF, followed by heating under 1 atm of CO at 45 °C. Complexes **4e** and **4f** were isolated in 70−77% yield.

The terminal CO stretches of **4e** and **4f** occur as strong bands at 2029−2030 and 1955−1956 cm^{-1}. The carbonyl stretches of the ester groups of **4e** and **4f** were observed as moderate intensity bands at 1687−1697 cm^{-1}, compared to 1735 cm^{-1} for the normal ester groups of organic compounds.[5,6] The CO stretch of the η^1-carbamoyl group was observed at 1557−1558 cm^{-1} as moderate bands. Symmetrical ^1H and ^{13}C NMR data for both **4e** and **4f** suggests that they are both *trans* isomers. The resultant *N*-methyl of the carbamoyl

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

(1) For a review, see: Durfee, L. D.; Rothwell, I. P. *Chem. Rev.* **1988**, *88*, 1059.

(2) (a) Conejo, M. M.; Pizzano, A.; Sanchez, L. J.; Carmona, E. *J. Chem. Soc., Dalton Trans.* **1996**, 3687. (b) Gomez, M.; Gomez-Sal, P.; Jimenez, G.; Martin, A.; Royo, P.; Sanchez-Nieves, J. *Organometallics* **1996**, *15*, 3579. (c) Contreras, L.; Pizzano, A.; Sanchez, L.; Carmona, E. *J. Organomet. Chem.* **1995**, *500*, 61. (d) Giannini, L.; Solari, E.; Angelis, S. D.; Ward, T. R.; Floriani, C.; Chiesi-Villa, A.; Rizzoli, C. *J. Am. Chem. Soc.* **1995**, *117*, 5801. (e) Angelis, S. D.; Solari, E.; Floriani, C.; Chiesi-Villa, A.; Rizzoli, C. *Organometallics* **1995**, *14*, 4505. (f) Gamble, A. S.; White, P. S.; Templeton, J. L. *Organometallics* **1991**, *10*, 693.

(3) (a) Rahim, M.; Ahmed, K. J. *Organometallics* **1994**, *13*, 1751. (b) Chisholm, M. H.; Hammond, C. E.; Huffman, J. C. *Organometallics* **1987**, *6*, 210. (c) Ahmed, K. J.; Chisholm, M. H. *Organometallics* **1986**, *5*, 185. (d) Fagan, P. J.; Manriquez, J. M.; Vollmer, S. H.; Day, C. S.; Day, V. W.; Marks, T. J. *J. Am. Chem. Soc.* **1981**, *103*, 2206.

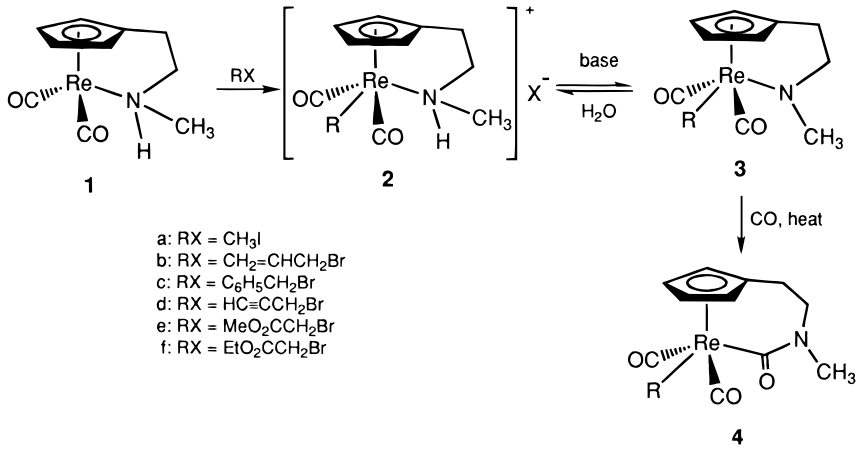
(4) (a) Wang, T. F.; Lai, C. Y.; Wen, Y. S. *J. Organomet. Chem.* **1996**, *523*, 187. (b) Wang, T. F.; Wen, Y. S. *J. Organomet. Chem.* **1992**, *439*, 155. (c) Wang, T. F.; Lee, C. Y.; Wen, Y. S.; Liu, L. K. *J. Organomet. Chem.* **1991**, *403*, 353.

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

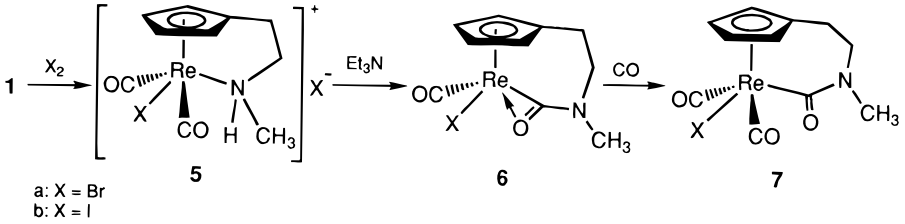
(6) Silverstein, R. M.; Bassler, G. C.; Morrill, T. C. *Spectroscopic Identification of Organic Compounds*, 5th ed.; John Wiley & Sons: New York, 1991; pp 113−123.

S0276-7333(97)00544-X CCC: $15.00
Publication on Web 01/19/1998

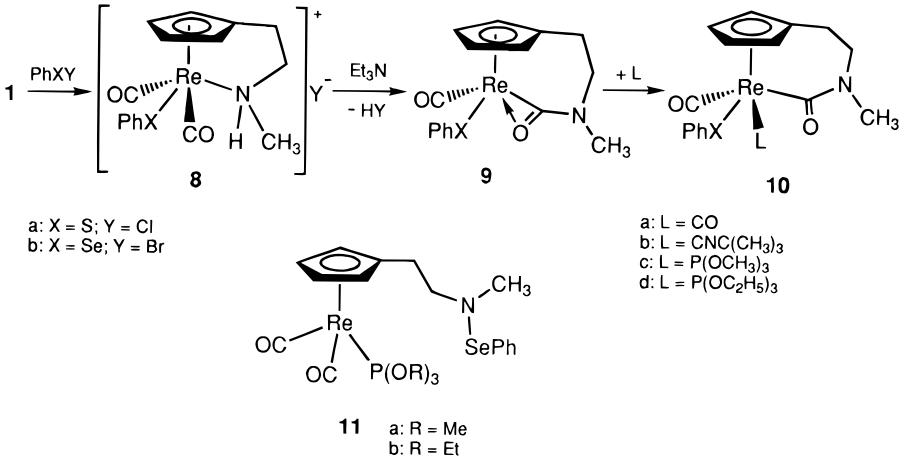
Scheme 1



Scheme 2



Scheme 3



group was observed at δ 3.00 as a singlet for both compounds, compared to a doublet for the *N*-methyl group of **2**. Complexes derived from the CO insertion into the Re−R bonds were not observed in the reactions.

B. Insertion Reactions of the Aminorhenium Halides 5. In view of the ease of the CO insertion for **3e** and **3f** relative to that for **3a**−**d**, we felt that the insertion reaction may have something to do with the nature of the R group. It seemed that the more electronegative the R group, the faster the insertion of CO into the Re-N bond. In order to test this, we studied the reactions of the halides **5a** and **5b**, which contain much more electronegative groups compared to the ester groups of **2e** and **2f**.

Complex **1** reacted readily with Br_2 and I_2, providing the bromide **5a** and iodide **5b** in nearly quantitative yield (see Scheme 2). Formation of the cationic halides **5a** and **5b** could be easily characterized by the terminal CO stretches in the IR. Upon halogenation, the CO stretches shift from 1893 and 1816 cm^{-1} for **1** to 2069 and 2001 cm^{-1} for **5a** and 2058 and 1992 cm^{-1} for **5b**. As a result of the electron-withdrawing nature of the halide ligand, the N−H protons of **5a** and **5b** are quite acidic and a weak base, such as Et_3N, is strong enough to remove it. Slow addition of Et_3N to each individual CH_2Cl_2 solution of **5a** and **5b** resulted in an immediate disappearance of the terminal carbonyl absorptions and the concomitant appearance of two new carbonyl bands. One band is due to a terminal CO (1905 cm^{-1}) and the other band (1642 cm^{-1}) is associated with the carbamoyl stretch. In the ^1H NMR spectra, the Cp protons of both products moved upfield relative to that for **5a** and **5b** and the *N*-methyl groups were observed as singlets at δ 3.31 and δ 3.34, respectively. These spectroscopic data suggest that the reaction products are the η^2-carbamoyl complexes **6a** and **6b**. Complexes **6a** and **6b** decomposed slowly in solution, and attempts of recrystallization were unsuccessful.

Upon exposure to CO, **6a** and **6b** converted to η^1-carbamoyl complexes **7a** and **7b**. Two terminal carbonyl

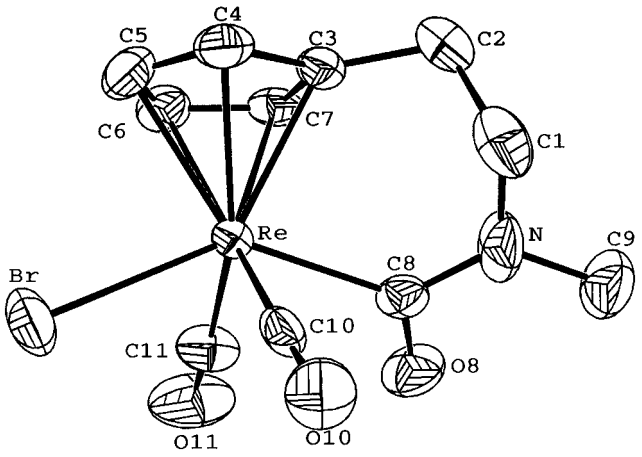


Figure 1. ORTEP drawing of **7a**.

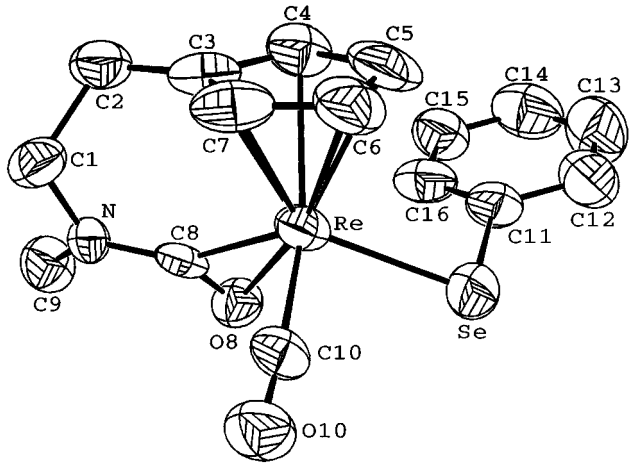


Figure 2. ORTEP drawing of **9b**.

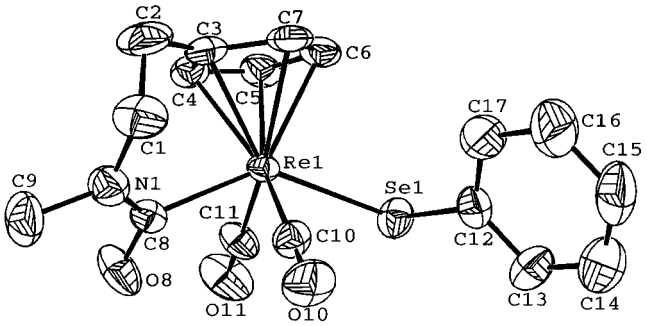


Figure 3. ORTEP drawing of **10ba**. There are two essentially independent molecules within the unit cell. Only one molecule is shown.

streches were observed at 2052 and 1982 cm^{-1} for **7a** and at 2042 and 1972 cm^{-1} for **7b**. The carbamoyl absorption occurred at 1569 cm^{-1} for **7a** and 1570 cm^{-1} for **7b**. In the ^1H NMR spectra, four Cp protons displayed as an AA′BB′ pattern at δ 5.88 and 5.78 for **7a** and δ 5.75 and 5.49 for **7b**. The ^{13}C NMR spectra of both **7a** and **7b** showed that the two terminal carbonyls are identical (δ 188.5 for **7a**; δ 186.8 for **7b**) and the Cp carbons are symmetrical. The symmetrical ^1H and ^{13}C data suggests that **7a** and **7b** are both *trans* isomers. Definite assignment of **7a** has been accomplished by an X-ray analysis. Figure 1 shows that the two terminal carbonyls are in a *trans* orientation with an angle of 102° (C_{10}−Re−C_{11}). The *trans* Br and the η^1-carbamoyl define an angle of 138° (Br−Re−C_8).

C. η^2-Carbamoyl Complexes of Rhenium Selenolate and Rhenium Thiolate. In addition to carbon and halogen electrophiles, we also examined the reactions of **1** with electrophiles derived from the group 16 elements. Rhenium−sulfur and rhenium−selenium bonds[7] were formed easily *via* the reaction of **1** with phenylsulfenyl chloride (PhSCl) and phenylselenenyl bromide (PhSeBr), respectively. The reactions proceeded instantly, providing **8a** and **8b** in nearly quantitative yield (see Scheme 3). Terminal carbonyl stretches appearing at 2052 and 1986 cm^{-1} for **8a** and 2042 and 1978 cm^{-1} for **8b** are characteristic for this type of complex.[5] Addition of Et_3N to a CH_2Cl_2 solution of **8a** resulted in an immediate disappearance of the terminal carbonyl absorptions and the concomitant appearance of a new intense band at 1900 cm^{-1} and a medium band at 1605 cm^{-1} that are associated with the η^2-carbamoyl complex **9a**. Reaction of **8b** with Et_3N proceeded similarly, providing the η^2-carbamoyl complex **9b**. The *N*-methyl groups of **9a** and **9b** appeared as singlets at δ 3.26 and 3.23 in the ^1H NMR spectra, similar to those for **6a** and **6b**. Remarkably, η^2-carbamoyl complexes **9a** and **9b** are quite stable and could be purified chromatographically with silica gel.

A single crystal of **9b** was obtained from a solution of CH_2Cl_2 in hexane and analyzed by crystallography. The molecular structure of **9b** (Figure 2) shows that the carbamoyl group binds to the rhenium in an η^2-mode with bond distances of 2.01 Å for Re−C8 and 2.37 Å for Re−O8. The rhenium−carbon bond distance is 0.18 Å shorter than that for the η^1-carbamoyl **5a** (2.19 Å for Re−C8) and 0.20 Å shorter for the η^1-carbamoyl **10ba** (2.21 Å for Re−C8, see below). The CO bond length for the η^2-carbamoyl group of **9b** is 1.26 Å, not much different from those for the η^1-carbamoyls **5a** (1.22 Å) and **10ba** (1.22 Å, see below).

D. Conversion of η^2-Carbamoyl Complexes to η^1-Carbamoyl Complexes by Addition of Two-Electron-Donor Ligands. When CO gas was introduced into individual solutions of **9a** and **9b**, dicarbonyl complexes **10aa** and **10ba** were obtained (see Scheme 3). Formation of **10aa** and **10ba** could be easily characterized by the terminal carbonyl stretches. Two carbonyl stretches observed at 2036 and 1966 cm^{-1} for **10aa** and 2027 and 1959 cm^{-1} for **10ba** are characteristic of this type of dicarbonyl complex. Symmetrical ^1H and ^{13}C NMR data suggest that **10aa** and **10ba** are *trans* isomers. Figure 3 shows the molecular structure of **10ba**. Two terminal carbonyl groups are in a *trans* orientation with an angle of 99.1°. The angle of the selenolate and the carbamoyl groups is 137.9°. It is worth noting that the atoms attached to the carbamoyl group, namely, C1, C9, N1, C8, O8, and Re1, lie in the same plane. Similarly, in **7a**, the C1, C9, N, C8, O8, and Re atoms are essentially planar.

Addition of *tert*-butyl isocyanide to a solution of **9a** and **9b** resulted in immediate coordination of isocyanide to the rhenium, providing **10ab** and **10bb**, respectively.

(7) Preparation of transition-metal selenolate complexes have been reported, see: (a) Eikens, W.; Jager, S.; Jones, P. G.; Thone, C. *J. Organomet. Chem.* **1996**, *511*, 67. (b) Eikens, W.; Kienitz, C.; Jones, P. G.; Thone, C. *J. Chem. Soc., Dalton Trans.* **1994**, 3329. (c) Lau, P.; Huttner, G.; Zsolnai, L. *J. Organomet. Chem.* **1992**, *440*, 41. (d) Winter, A.; Huttner, G.; Gottlieb, M.; Jibril, I. *J. Organomet. Chem.* **1985**, *286*, 317.

Strong bands appearing at 2156 cm^{-1} for **10ab** and 2150 cm^{-1} for **10bb** are characteristic of an isocyanide stretch. A strong and a medium band at 1954 and 1554 cm^{-1} for **10ab** and 1947 and 1553 cm^{-1} for **10bb** are assigned to the terminal carbonyl and the η^1-carbamoyl stretches, respectively.

In addition to CO and isocyanide, trialkyl phosphites also add to η^2-carbamoyl **9a** and **9b** to give the corresponding η^1-carbamoyl complexes **10** (L = $P(OR)_3$). Addition of $P(OMe)_3$ or $P(OEt)_3$ to a solution of **9a** resulted in an immediate color change from red to yellow. The terminal carbonyl stretch shifted from 1900 to 1935 cm^{-1} for **10ac** and to 1930 cm^{-1} for **10ad**. Incorporation of a phosphite ligand was verified by ^{31}P chemical shifts, which appeared at δ 93.0 for **10ac** and δ 88.4 for **10ad**. The reaction of **9b** with phosphites proceeded similarly to that for **9a**. Phosphite complexes with thiolate **10ac** and **10ad** are not stable in solution and slowly decomposed to an unidentifiable mixture. The corresponding selenolate complexes **10bc** and **10bd** are much more labile than the thiolate complexes **10ac** and **10ad**, converting *via* an unclear pathway to **11a** and **11b** with a half-life of about 5 min at room temperature. Complexes **11a** and **11b** were characterized spectroscopically. In the infrared spectra, two terminal carbonyl stretchings appeared with equal intensities at 1941 and 1868 cm^{-1} for **11a** and 1938 and 1866 cm^{-1} for **11b** and the coordinated phosphite ligand was observed at δ 140.1 for **11a** and δ 136.2 for **11b**.

Conclusion

Removal of the N−H proton of cationic aminorhenium complexes results in a CO insertion into the Re−N bond, as demonstrated by the halides **5a**,**b**, thiolate **8a**, and selenolate **8b**. The resultant carbamoyl group binds to the Re in an η^2-mode. Remarkably, η^2-carbamoyl complexes **9a** and **9b** are stable, as shown by their stability toward column chromatography. In the presence of two-electron-donor ligands, such as CO, isocyanides, and phosphites, the η^2-carbamoyl complexes readily convert to the corresponding η^1-carbamoyl complexes. The nature of the R group affects the insertion reaction. For complexes that having a strong electron-withdrawing R group, such as **5a**, **5b**, **8a**, and **8b**, the insertion reaction proceeds rapidly at low temperature (0 °C). When R is an ester group, such as **2e** and **2f**, the insertion reaction requires a higher temperature (45 °C) and longer time (several hours). No insertion reactions were observed when the R group was alkyl, allyl, benzyl, and propargyl (**2a**−**d**).

From these results, it can be concluded that two conditions are required for the insertion reaction: removal of the N−H proton and an electron-withdrawing R group. Removal of the N−H proton results in a free electron-pair on the nitrogen. This may allow the resultant nonbonding electrons of the nitrogen to interact with the nearby CO ligand. The electron-withdrawing nature of the R group may lower the π^* orbital of the CO ligand, thereby reducing the energy gap between the π^* orbital of CO and the nonbonding orbital of the nitrogen. This may account for the rapid reaction of **5a**, **5b**, **8a**, and **8b**, slow reaction of **2e** and **2f**, and nonreactivity of **2a**−**d**.

Experimental Section

Reactions that required anhydrous conditions were performed under an argon atmosphere by means of Schlenk-tube techniques. Infrared solution spectra were recorded on a Perkin-Elmer 882 infrared spectrophotometer using 0.1 mm cells with CaF_2 windows. Melting points were determined by using a Yanaco model MP micro melting point apparatus and were uncorrected. ^1H NMR (300 MHz) and ^{13}C NMR (75 MHz) were obtained with a Bruker AC-300 FT spectrophotometer. For the assignment of the ^1H 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}. All chemical shifts are reported in parts per million (ppm) relative to Me_4Si. Elemental analyses were obtained on a Perkin-Elmer 2400 CHN elemental analyzer. Mass spectra were recorded on a VG 70-250S mass spectrophotometer.

Preparation of $(CO)_2RReC(=O)N(CH_3)CH_2CH_2(\eta^5\text{-}C_5H_4)$ (4e, R = CH_2CO_2Me; 4f, R = CH_2CO_2Et). A two-necked, 100 mL flask equipped with a stir bar was charged with NaH (95 mg, 60% dispersion in mineral oil). Mineral oils were removed by washing 3 times with hexane under nitrogen. Nitrogen was evacuated and replaced with CO gas. THF (20 mL) was then added. A suspension of **2e** or **2f** (0.55 mmol) in THF (20 mL) was added at room temperature over 5 min. The resultant mixture was heated in an oil bath at 45 °C for 16 h. The mixture was then filtered through Celite. The filtrates were concentrated and chromatographed on silica gel, using 50% ethyl acetate in hexane as the eluent followed by 100% ethyl acetate. A pale yellow band was collected and concentrated to give **4e** or **4f**.

$(CO)_2(CH_2CO_2Me)ReC(=O)N(CH_3)CH_2CH_2(\eta^5\text{-}C_5H_4)$ (4e): yellow crystal (77% yield). Mp: 141−144 °C. IR (CH_2Cl_2): 2030 (s), 1956 (s), 1697(m), 1558 (m) cm^{-1}. ^1H NMR ($CDCl_3$, 300 MHz): δ 5.41 (2H, t, J = 2.0 Hz, Cp H), 5.36 (2H, t, J = 2.0 Hz, Cp H), 3.62 (3H, s, OCH_3), 3.36 (2H, t, J = 5.4 Hz), 3.00 (3H, s, $N-CH_3$), 2.40 (2H, s, $Re-CH_2CO_2Me$), 2.35 (2H, t, J = 5.5 Hz). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 193.9 (CO × 2), 182.0 (C, CO_2Me), 173.3 (C, ReCON), 106.5 (C, Cp), 94.3 (CH × 2, Cp), 86.7 (CH × 2, Cp), 59.9 (CH_2, C_1), 50.8 (CH_3, OCH_3), 34.8 (CH_3, $N-CH_3$), 25.5 (CH_2, C_2), −17.9 (CH_2, $Re-CH_2CO_2Me$). MS (FAB, ^{187}Re; *m*/*e* (relative intensity)): 465 (60, M^+), 409 (95), 392 (60), 367 (100), 336 (85). Anal. Calcd for $C_{14}H_{16}NO_5Re$: C, 36.20; H, 3.47; N, 3.02. Found: C, 36.15; H, 3.35; N, 2.84.

$(CO)_2(CH_2CO_2Et)ReC(=O)N(CH_3)CH_2CH_2(\eta^5\text{-}C_5H_4)$ (4f): yellow crystal (70% yield). Mp: 116−118 °C. R_f = 0.36 (100% EtOAc, SiO_2). IR (CH_2Cl_2): 2029 (s), 1955 (s), 1687 (m), 1557 (m) cm^{-1}. ^1H NMR ($CDCl_3$, 300 MHz): δ 5.39 (2H, t, J = 2.0 Hz, Cp H), 5.36 (2H, t, J = 2.0 Hz, Cp H), 4.07 (2H, q, J = 7.1 Hz, OEt), 3.36 (2H, t, J = 5.5 Hz, H_1), 3.00 (3H, s, $N-CH_3$), 2.39 (2H, s, $Re-CH_2CO_2Et$), 2.34 (2H, t, J = 5.5 Hz, H_2), 1.26 (3H, t, J = 7.1 Hz, OEt). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 193.9 (CO × 2), 181.4 (C, CO_2Et), 173.4 (C, ReCON), 106.5 (C, Cp), 94.2 (CH × 2, Cp), 86.6 (CH × 2, Cp), 59.9 (CH_2), 59.5 (CH_2), 34.7 (CH_3, $N-CH_3$), 25.4 (CH_2, C_2), 14.2 (CH_3, OEt), −17.7 (CH_2, $Re-CH_2CO_2Et$). MS (FAB, ^{187}Re; *m*/*e* (relative intensity)): 480 (80, $M^+ + 1$), 423 (88), 392 (100, $M^+ - CH_2CO_2Et$), 364 (82), 336 (70). Anal. Calcd for $C_{15}H_{18}NO_5Re$: C, 37.65; H, 3.79; N, 2.93. Found: C, 37.68; H, 3.69; N, 2.79.

Preparation of $[(CO)_2XReNH(CH_3)CH_2CH_2(\eta^5\text{-}C_5H_4)]^+X^-$ (5a, X = Br; 5b, X = I). A 100 mL flask was charged with aminorhenium complex **1** (364 mg, 1 mmol) followed by CH_2Cl_2 (20 mL) and pyridine (0.2 mL). The resultant yellow solution was cooled in an ice-water bath. A CH_2Cl_2 solution of halogen (0.25 M for Br_2 or 0.04 M for I_2, 1 mmol) was added over 5−10 min. After the mixture was stirred for an additional 5 min, hexane (5 mL) was added. The volume of the solvents was reduced to about 10−15 mL by evaporation under reduced

pressure. The resultant red precipitates were collected and washed twice with ether to give red powders of **5a** (82%) or **5b** (92%). **5a** and **5b** are stable in the solid state. While in solution, they decomposed gradually at room temperature.

[(CO)$_2$BrReNH(CH$_3$)CH$_2$CH$_2$(η^5-C$_5$H$_4$)]$^+$Br$^-$ (5a): red crystal (82% yield). Mp: 100−103 °C. IR (CH_2Cl_2): 2069 (s), 2001 (s) cm^{-1}. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 9.83 (1H, br, N−H), 7.52 (1H, br s, Cp H), 6.56 (1H, br s, Cp H), 5.85 (1H, br s, Cp H), 5.41 (1H, br s, Cp H), 4.45−4.38 (1H, m, H_{1a}), 3.48−3.38 (1H, m, H_{1b}), 3.15−3.04 (1H, m, H_{2a}), 2.99 (3H, d, J = 5.6 Hz, N−CH_3), 2.24−2.16 (1H, m, H_{2b}). MS (FAB, ^{81}Br, ^{187}Re; *m*/*e* (relative intensity)): 446 (12, M^+). Anal. Calcd for $C_{10}H_{12}Br_2NO_2Re$: C, 22.91; H, 2.31; N, 2.67. Found: C, 22.66; H, 2.49; N, 2.32.

[(CO)$_2$IReNH(CH$_3$)CH$_2$CH$_2$(η^5-C$_5$H$_4$)]$^+$I$^-$ (5b): red crystal (92% yield). Mp: 126 °C (dec). IR (CH_2Cl_2): 2058 (s), 1992 (s) cm^{-1}. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 8.79 (1H, br, N−H), 7.34 (1H, br s, Cp H), 6.34 (1H, br s, Cp H), 5.94 (1H, br s, Cp H), 5.72 (1H, br s, Cp H), 4.47−4.40 (1H, m, H_{1a}), 3.50−3.37 (1H, m, H_{1b}), 3.28−3.15 (1H, m, H_{2a}), 2.98 (3H, d, J = 5.7 Hz, N−CH_3), 2.27−2.21 (1H, m, H_{2b}). ^{1}H NMR (CD_3OD, 300 MHz): δ 6.84 (1H, br s, Cp H), 6.62 (1H, br s, Cp H), 6.02 (1H, br s, Cp H), 5.99 (1H, br s, Cp H), 4.19−4.12 (1H, m, H_{1a}), 3.81−3.72 (1H, m, H_{1b}), 3.06 (3H, s, N−CH_3), 2.44−2.36 (2H, m, H_2). MS (FAB, ^{187}Re; *m*/*e* (relative intensity)): 492 (52, M^+), 365 (12, M^+ − I). Anal. Calcd for $C_{10}H_{12}I_2NO_2Re$: C, 19.43; H, 1.96; N, 2.26. Found: C, 19.68; H, 2.05; N, 2.02.

Preparation of [(CO)XRe(η^2-C=O)N(CH$_3$)CH$_2$CH$_2$(η^5-C$_5$H$_4$)] (6a,b; X = Br, I). To a stirred yellow solution of **1** (364 mg, 1 mmol) in CH_2Cl_2 (20 mL) at 0 °C was added a CH_2Cl_2 solution of halogen (0.25 M for Br_2 or 0.04 M for I_2, 1 mmol) over 5−10 min. After the mixture was stirred for an additional 5 min, a solution of triethylamine (0.3 mL) in CH_2Cl_2 (10 mL) was then added slowly over 1 h by using a syringe pump. The cool bath was removed, and the red solution was concentrated. The resultant red solids were washed three 3 with ether. The residue was then extracted with THF twice to give a red liquid after evaporation (70−80% yield). The ^{1}H NMR spectra of the liquid showed that it contained 85% of **6** and 15% of **7**. Small amounts of pure samples of **6a** and **6b** were obtained, respectively, by recrystallization of the each individual mixture mentioned above from a solution of CH_2Cl_2 and hexane.

[(CO)BrRe(η^2-C=O)N(CH$_3$)CH$_2$CH$_2$(η^5-C$_5$H$_4$)] (6a): red powder. Mp: 113 °C (dec). IR (CH_2Cl_2): 1905 (s), 1642 (m) cm^{-1}. ^{1}H NMR (C_3D_6O, 300 MHz): δ 6.07−6.05 (m, 1H, Cp H), 5.80−5.78 (m, 1H, Cp H), 5.41−5.39 (m, 1H, Cp H), 5.04−5.02 (m, 1H, Cp H), 3.69 (1H, ddd, J = 13.9, 4.1, 3.0 Hz, H_{1a}), 3.56 (1H, ddd, J = 13.9, 12.4, 2.3 Hz, H_{1b}), 3.31 (3H, s, N−CH_3), 2.92 (1H, dt, J = 14.3, 2.6 Hz, H_{2a}), 2.53 (1H, ddd, J = 14.3, 12.4, 4.1 Hz, H_{2b}). Anal. Calcd for $C_{10}H_{11}BrNO_2Re$: C, 27.09; H, 2.50; N, 3.16. Found: C, 26.82; H, 2.48; N, 2.95.

[(CO)IRe(η^2-C=O)N(CH$_3$)CH$_2$CH$_2$(η^5-C$_5$H$_4$)] (6b): orange crystal. Mp: 117−118 °C (dec). IR (CH_2Cl_2): 1905 (s), 1642 (m) cm^{-1}. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 6.14−6.12 (m, 1H, Cp H), 5.68−5.66 (m, 1H, Cp H), 5.15−5.13 (m, 1H, Cp H), 4.83−4.81 (m, 1H, Cp H), 3.68−3.49 (2H, m), 3.34 (3H, s, N−CH_3), 2.86 (1H, dt, J = 14.4, 2.5 Hz, H_{2a}), 2.38 (1H, ddd, J = 14.4, 12.4, 4.3 Hz, H_{2b}). MS (FAB, ^{187}Re; *m*/*e* (relative intensity)): 492 (10, M^+ + 1), 463 (10, M^+ − CO). Anal. Calcd for $C_{10}H_{11}INO_2Re$: C, 24.50; H, 2.26; N, 2.86. Found: C, 24.46; H, 2.28; N, 2.62.

Preparation of [(CO)$_2$XReC(=O)N(CH$_3$)CH$_2$CH$_2$(η^5-C$_5$H$_4$)] (7a, X = Br; 7b, X = I). The procedure is similar to that for the preparation of **6** except that a carbon monoxide gas was bubbling through a needle while adding the triethylamine solution. After concentration, the residue was flash-chromatographed on silica gel with 50% ethyl acetate in hexane as the eluent followed by 100% ethyl acetate. The first orange band was collected and concentrated to give **7a** or **7b**. Analytical pure samples were obtained by recrystallization of the individual complex from dichloromethane and hexane.

[(CO)$_2$BrReC(=O)N(CH$_3$)CH$_2$CH$_2$(η^5-C$_5$H$_4$)] (7a): orange crystal (78% yield). Mp: 125−130 °C. R_f = 0.46 (100% EtOAc, SiO_2). IR (CH_2Cl_2): 2052 (s), 1982 (s), 1569 (m) cm^{-1}. ^{1}H NMR (C_3D_6O, 300 MHz): δ 5.88 (2H, t, J = 2.2 Hz, Cp H), 5.78 (2H, t, J = 2.2 Hz, Cp H), 3.45−3.41 (2H, m), 2.87 (3H, s, N−CH_3), 2.46−2.42 (2H, m). ^{1}H NMR ($CDCl_3$, 300 MHz): δ 5.68 (2H, t, J = 2.2 Hz, Cp H), 5.55 (2H, t, J = 2.2 Hz, Cp H), 3.44−3.40 (2H, m), 2.98 (3H, s, N−CH_3), 2.36−2.32 (2H, m). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 188.5 (CO × 2), 168.0 (C, Re−CON), 104.9 (C, Cp), 98.3 (CH × 2, Cp), 86.5 (CH × 2, Cp), 60.2 (CH_2, C_1), 35.1 (CH_3, N−CH_3), 25.2 (CH_2, C_2). MS (FAB, ^{187}Re; *m*/*e* (relative intensity)): 473 (45, M^+), 445 (38, M^+ − CO), 417 (50, M^+ − 2CO), 392 (100, M^+ − Br), 364 (35, M^+ − Br − CO), 336 (25, M^+ − I − 2CO). Anal. Calcd for $C_{11}H_{11}BrNO_3Re$: C, 28.03; H, 2.35; N, 2.97. Found: C, 28.25; H, 2.38; N, 2.62.

[(CO)$_2$IReC(=O)N(CH$_3$)CH$_2$CH$_2$(η^5-C$_5$H$_4$)] (7b): orange crystal (85% yield). Mp: 122−125 °C (dec). R_f = 0.47 (100% EtOAc, SiO_2). IR (CH_2Cl_2): 2042 (s), 1972 (s), 1570 (m) cm^{-1}. ^{1}H NMR (C_3D_6O, 300 MHz): δ 5.75 (2H, t, J = 2.2 Hz, Cp H), 5.49 (2H, t, J = 2.2 Hz, Cp H), 3.46−3.42 (2H, m), 3.02 (3H, s, N−CH_3), 2.38−2.34 (2H, m). ^{1}H NMR ($CDCl_3$, 300 MHz): δ 5.75 (2H, t, J = 2.2 Hz, Cp H), 5.50 (2H, t, J = 2.2 Hz, Cp H), 3.46−3.42 (2H, m), 3.02 (3H, s, N−CH_3), 2.39−2.35 (2H, m). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 186.8 (CO × 2), 166.0 (C, Re−CON), 105.6 (C, Cp), 95.0 (CH × 2, Cp), 86.5 (CH × 2, Cp), 60.0 (CH_2, C_1), 35.3 (CH_3, N−CH_3), 25.4 (CH_2, C_2). MS (FAB, ^{187}Re; *m*/*e* (relative intensity)): 520 (80, M^+ + 1), 491 (52, M^+ − CO), 463 (60, M^+ − 2CO), 392 (100, M^+ − I), 364 (38, M^+ − I − CO), 336 (28, M^+ − I − 2CO). Anal. Calcd for $C_{11}H_{11}INO_3Re$: C, 25.49; H, 2.14; N, 2.70. Found: C, 25.40; H, 2.08; N, 2.59.

Preparation of [(CO)$_2$PhXReNH(CH$_3$)CH$_2$CH$_2$(η^5-C$_5$H$_4$)]$^+$Y$^-$ (8a, X = S, Y = Cl; 8b, X = Se, Y = Br). A CH_2Cl_2 solution of PhSCl (0.2 M, 5 mL) or PhSeBr (0.2 M, 5 mL) was added to a stirred yellow solution of **1** (364 mg, 1 mmol) in CH_2Cl_2 (20 mL) at 0 °C over 5 min. After the mixture was stirred for an additional 5 min, the resultant red solution was concentrated under reduced pressure to about 3 mL. The residual solution was then added slowly to ether (60 mL). The precipitates were collected and washed twice with ether to give **8a** or **8b**.

[(CO)$_2$PhSReNH(CH$_3$)CH$_2$CH$_2$(η^5-C$_5$H$_4$)]$^+$Cl$^-$ (8a): hygroscopic orange powder (98% yield). IR (CH_2Cl_2): 2052(s), 1986 (s) cm^{-1}. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 10.0 (1H, br, N−H), 7.32−7.25 (5H, m, Ph), 7.17−7.15 (1H, m, Cp H), 6.43−6.41 (1H, m, Cp H), 5.65−5.63 (1H, m, Cp H), 5.33−5.31 (1H, m, Cp H), 4.27−4.22 (1H, m, H_{1a}), 3.40−3.32 (1H, m, H_{1b}), 3.14−3.04 (1H, m, H_{2a}), 3.01 (3H, d, J = 5.5 Hz, N−CH_3), 2.26 (1H, dd, J = 13.2, 6.3 Hz, H_{2b}). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 191.8 (CO), 189.1 (CO), 140.2 (C, Ph), 132.4 (CH × 2, Ph), 128.6 (CH × 2, Ph), 126.9 (C, Cp), 126.0 (CH, Ph), 99.7 (CH, Cp), 92.3 (CH, Cp), 91.2 (CH, Cp), 88.3 (CH, Cp), 77.4 (CH_2, C_1), 48.5 (CH_3, N−CH_3), 24.4 (CH_2, C_2). MS (FAB, ^{187}Re; *m*/*e* (relative intensity)): 474 (52, M^+), 446 (100, M^+ − CO), 365 (25, M^+ − SPh). Anal. Calcd for $C_{16}H_{17}ClNO_2ReS$: C, 37.75; H, 3.37; N, 2.75. Found: C, 37.28; H, 3.51; N, 2.47.

[(CO)$_2$PhSeReNH(CH$_3$)CH$_2$CH$_2$(η^5-C$_5$H$_4$)]$^+$Br$^-$ (8b): hygroscopic orange powder (99% yield). IR (CH_2Cl_2): 2042 (s), 1978 (s) cm^{-1}. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 9.32 (1H, br, N−H), 7.46−7.40 (2H, m, Ph), 7.29−7.24 (3H, m, Ph), 7.16−7.14 (1H, m, Cp H), 6.29−6.27 (1H, m, Cp H), 5.55−5.53 (1H, m, Cp H), 5.42−5.40 (1H, m, Cp H), 4.29−4.22 (1H, m, H_{1a}), 3.43−3.30 (1H, m, H_{1b}), 3.15 (1H, td, J = 12.8, 6.1 Hz, H_{2a}), 3.01 (3H, d, J = 5.7 Hz, N−CH_3), 2.22 (1H, dd, J = 13.3, 6.1 Hz, H_{2b}). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 191.5 (CO), 189.0 (CO), 135.1 (CH × 2, Ph), 129.9 (C, Ph or Cp), 128.9 (CH × 2, Ph), 128.1 (C, Cp or Ph), 127.6 (CH, Ph), 96.8 (CH, Cp), 91.0 (CH, Cp), 89.4 (CH, Cp), 87.5 (CH, Cp), 77.9 (CH_2, C_1), 48.8 (CH_3, N−CH_3), 24.5 (CH_2, C_2). Anal. Calcd for $C_{16}H_{17}BrNO_2ReSe$: C, 32.01; H, 2.85; N, 2.33. Found: C, 31.67; H, 2.98; N, 2.30.

Preparation of [(CO)PhXRe(η^2-C=O)N(CH$_3$)CH$_2$CH$_2$-

(η^5-C_5H_4)] (9a, X = S; 9b, X = Se). A solution of triethylamine (0.3 mL) in CH_2Cl_2 (3 mL) was added over 3 min to a stirred solution of **8a** or **8b** (1 mmol) in CH_2Cl_2 (25 mL) at 0 °C. The cool bath was removed. After the mixture was stirred at room temperature for 10 min, the solution was concentrated and the residue was flash-chromatographed on silica gel with 50% ethyl acetate in hexane as the eluent followed by 90% ethyl acetate in hexane. A red band was collected and concentrated to give **9a** or **9b**.

[(CO)PhSRe(η^2-C=O)N(CH_3)CH_2CH_2(η^5-C_5H_4)] (9a): red crystal (63% yield). Mp: 112−115 °C (dec). IR (CH_2Cl_2): 1900 (s), 1605 (w) cm^{-1}. ^1H NMR ($CDCl_3$, 300 MHz): δ 7.44−7.40 (2H, m, Ph), 7.21−7.14 (2H, m, Ph), 7.08−7.02 (1H, m, Ph), 5.53−5.51 (1H, m, Cp H), 5.27−5.25 (1H, m, Cp H), 5.11−5.09 (1H, m, Cp H), 4.76−4.74 (1H, m, Cp H), 3.53 (1H, ddd, J = 13.8, 12.2, 2.2 Hz, H_{1a}), 3.43 (1H, ddd, J = 13.8, 3.9, 3.2 Hz, H_{1b}), 3.26 (3H, s, N−CH_3), 2.86 (1H, dt, J = 14.2, 2.7 Hz, H_{2a}), 2.33 (1H, ddd, J = 14.2, 12.2, 3.9 Hz, H_{2b}). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 207.8 (CO), 199.1 (CO), 153.0 (C, Ph), 132.5 (CH × 2, Ph), 127.6 (CH × 2, Ph), 124.9 (CH, Ph), 109.9 (C, Cp), 104.2 (CH, Cp), 96.9 (CH, Cp), 74.4 (CH, Cp), 69.5 (CH, Cp), 55.1 (CH_2, C_1), 36.2 (CH_3, N−CH_3), 28.2 (CH_2, C_2). MS (FAB, ^{187}Re; *m*/*e* (relative intensity)): 474 (85, M^+ + 1), 445 (38, M^+ − CO), 364 (20, M^+ − SPh). Anal. Calcd for $C_{16}H_{16}NO_2ReS$: C, 40.66; H, 3.41; N, 2.96. Found: C, 40.74; H, 3.47; N, 2.80.

[(CO)PhSeRe(η^2-C=O)N(CH_3)CH_2CH_2(η^5-C_5H_4)] (9b): orange crystal (65% yield). Mp: 120 °C (dec). R_f = 0.70 (100% EtOAc, SiO_2). IR (CH_2Cl_2): 1897 (s), 1610 (m) cm^{-1}. ^1H NMR ($CDCl_3$, 300 MHz): δ 7.56−7.52 (2H, m), 7.18−7.09 (3H, m), 5.45−5.43 (m, 1H, Cp H), 5.23−5.21 (m, 1H, Cp H), 5.14−5.12 (m, 1H, Cp H), 4.68−4.66 (m, 1H, Cp H), 3.60 (1H, td, J = 13.2, 2.1 Hz, H_{1a}), 3.46 (1H, dt, J = 13.6, 3.4 Hz, H_{1b}), 3.29 (3H, s, N−CH_3), 2.85 (1H, dt, J = 14.2, 2.4 Hz, H_{2a}), 2.35 (1H, ddd, J = 14.2, 12.6, 3.8 Hz, H_{2b}). ^1H NMR (CD_3CN, 300 MHz): δ 7.44−7.40 (2H, m, Ph), 7.16−7.08 (3H, m, Ph), 5.63−5.61 (m, 1H, Cp H), 5.26−5.24 (m, 1H, Cp H), 5.18−5.16 (m, 1H, Cp H), 4.69−4.67 (m, 1H, Cp H), 3.57−3.52 (2H, m), 3.23 (3H, s, N−CH_3), 2.81 (1H, dt, J = 14.2, 2.4 Hz, H_{2a}), 2.40 (1H, ddd, J = 14.2, 12.6, 3.8 Hz, H_{2b}). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 205.4 (CO), 199.1 (CO), 142.8 (C, Ph), 134.1 (CH × 2, Ph), 127.5 (CH × 2, Ph), 125.0 (CH, Ph), 109.9 (C, Cp), 102.9 (CH, Cp), 96.2 (CH, Cp), 72.7 (CH, Cp), 69.5 (CH, Cp), 55.0 (CH_2, C_1), 36.2 (CH_3, N−CH_3), 28.0 (CH_2, C_2). Anal. Calcd for $C_{16}H_{16}NO_2ReSe$: C, 36.99; H, 3.10; N, 2.70. Found: C, 37.05; H, 3.02; N, 2.61.

Preparation of [(CO)(L)PhSReC(=O)N(CH_3)CH_2CH_2-(η^5-C_5H_4)] (10aa−ad (L = CO, $(CH_3)_3CNC$, P(OMe)$_3$, P(OEt)$_3$). For L = CO, the CO gas was allowed to bubble through a CH_2Cl_2 solution of **9a** (236 mg, 0.5 mmol) at 0 °C until the 1900 cm^{-1} absorption disappeared in the IR spectrum. For L = $(CH_3)_3CNC$, P(OMe)$_3$, and P(OEt)$_3$, a CH_2Cl_2 solution of L (1 equiv) was added to a stirred red solution of **9a** (236 mg, 0.5 mmol) in CH_2Cl_2 (20 mL) at 0 °C over 2 min. After the mixture was stirred for another 2 min, the CO stretch of **9a** (1900 cm^{-1}) disappeared. Hexane (10 mL) was added to the resultant yellow solution and then evaporated under reduced pressure to about 5 mL of solvents. Yellow precipitates were collected and washed twice with hexane to give **10aa−ad**. Analytically pure samples were obtained by recrystallization of the individual compound from dichloromethane and hexane.

[(CO)$_2$PhSReC(=O)N(CH_3)CH_2CH_2(η^5-C_5H_4)] (10aa): yellow crystal (100% yield). Mp: 121−124 °C (dec). IR (CH_2Cl_2): 2036 (s), 1966 (s), 1567 (m) cm^{-1}. ^1H NMR ($CDCl_3$, 300 MHz): δ 7.38−7.34 (2H, m, Ph), 7.21−7.14 (2H, m, Ph), 7.11−7.05 (1H, m, Ph), 5.59 (2H, t, J = 2.2 Hz, Cp H), 5.49 (2H, t, J = 2.2 Hz, Cp H), 3.42 (2H, t, J = 5.5 Hz), 2.99 (3H, s, N−CH_3), 2.35 (2H, t, J = 5.5 Hz). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 190.0 (CO), 171.1 (CO, ReCON), 142.1 (C, Ph), 133.1 (CH × 2, Ph), 128.1 (CH × 2, Ph), 124.9 (CH, Ph), 106.8 (C, Cp), 98.2 (CH × 2, Cp), 86.9 (CH × 2, Cp), 60.3 (CH_2, C_1), 34.9 (CH_3, N−CH_3), 25.3 (CH_2, C_2). MS (FAB, ^{187}Re; *m*/*e* (relative intensity)): 501 (12, M^+). Anal. Calcd for $C_{17}H_{16}NO_3ReS$: C, 40.79; H, 3.22; N, 2.80. Found: C, 41.11; H, 3.27; N, 2.68.

[(CO)(($CH_3)_3CNC$)PhSReC(=O)N(CH_3)CH_2CH_2(η^5-C_5H_4)] (10ab): yellow crystal (94% yield). Mp: 115−119 °C (dec). IR (CH_2Cl_2): 2156 (m), 1954 (s), 1554 (m) cm^{-1}. ^1H NMR ($CDCl_3$, 300 MHz): δ 7.37−7.33 (2H, m, Ph), 7.14−7.09 (2H, m, Ph), 6.98−6.93 (1H, m, Ph), 5.53−5.51 (1H, m, Cp H), 5.41−5.39 (1H, m, Cp H), 5.38−5.36 (1H, m, Cp H), 5.29−5.27 (1H, m, Cp H), 3.55−3.38 (2H, m), 2.98 (3H, s, N−CH_3), 2.46 (1H, ddd, J = 13.4, 7.0, 3.5 Hz, H_{2a}), 2.22 (1H, ddd, J = 13.4, 7.5, 3.8 Hz, H_{2b}), 1.26 (9H, s, ^{t}Bu). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 197.4 (CO), 176.9 (CO, ReCON), 144.5 (C, Ph), 135.9 (C, ReCN^{t}Bu), 131.9 (CH × 2, Ph), 127.5 (CH × 2, Ph), 122.8 (CH, Ph), 103.8 (C, Cp), 99.5 (CH, Cp), 92.8 (CH, Cp), 87.4 (CH, Cp), 83.6 (CH, Cp), 59.5 (CH_2, C_1), 57.4 (C, ^{t}Bu), 34.7 (CH_3, N−CH_3), 30.2 (CH_3 × 3, ^{t}Bu), 25.9 (CH_2, C_2). Anal. Calcd for $C_{21}H_{25}N_2O_2ReS$: C, 45.39; H, 4.53; N, 5.04. Found: C, 45.76; H, 4.79; N, 4.81.

[(CO)(P(OMe)$_3$)PhSReC(=O)N(CH_3)CH_2CH_2(η^5-C_5H_4)] (10ac): unstable yellow crystal (95% yield). Mp: 118−124 °C (dec). IR (CH_2Cl_2): 1935 (s), 1577 (w), 1550 (w) cm^{-1}. ^1H NMR ($CDCl_3$, 300 MHz): δ 7.45−7.41 (2H, m, Ph), 7.16−7.11 (2H, m, Ph), 7.04−6.98 (1H, m, Ph), 5.62−5.60 (1H, m, Cp H), 5.38−5.36 (1H, m, Cp H), 5.24−5.22 (1H, m, Cp H), 5.20−5.18 (1H, m, Cp H), 3.78 (9H, d, J = 11.5 Hz, P(OMe)$_3$), 3.40−3.35 (2H, m), 2.94 (3H, s, N−CH_3), 2.61−2.54 (1H, m, H_{2a}), 2.05−2.00 (1H, m, H_{2b}). ^{31}P NMR ($CDCl_3$): δ 93.0. Anal. Calcd for $C_{19}H_{25}NO_5PReS$: C, 38.25; H, 4.22; N, 2.35. Found: C, 38.02; H, 4.08; N, 2.32.

[(CO)(P(OEt)$_3$)PhSReC(=O)N(CH_3)CH_2CH_2(η^5-C_5H_4)] (10ad): unstable yellow crystal (82% yield). Mp: 92−94 °C (dec). IR (CH_2Cl_2): 1930 (s), 1577 (w), 1548 (w), 1472 (w) cm^{-1}. ^1H NMR ($CDCl_3$, 300 MHz): δ 7.43−7.37 (2H, m, Ph), 7.15−7.09 (2H, m, Ph), 7.02−6.97 (1H, m, Ph), 5.57−5.55 (1H, m, Cp H), 5.27−5.25 (2H, m, Cp H), 5.18−5.16 (1H, m, Cp H), 4.24−4.06 (6H, m, OEt), 3.39−3.31 (2H, m), 2.91 (3H, s, N−CH_3), 2.52−2.45 (1H, m, H_{2a}), 2.09 (1H, ddd, J = 13.2, 9.2, 4.5 Hz, H_{2b}), 1.37−1.22 (9H, m, OEt). ^{31}P NMR ($CDCl_3$): δ 88.4. MS (FAB, ^{187}Re; *m*/*e* (relative intensity)): 640 (10, M^+ + 1), 611 (35, M^+ − CO), 530 (100, M^+ − SPh), 502 (80, M^+ − SPh − CO). Anal. Calcd for $C_{22}H_{31}NO_5PReS$: C, 41.37; H, 4.89; N, 2.19. Found: C, 41.37; H, 4.96; N, 2.12.

Reaction of 9b with L (L = CO, $(CH_3)_3CNC$, P(OMe)$_3$, P(OEt)$_3$). The respective procedures are analogous to the preparation of **10aa−ad**. Complexes **10bc** and **10bd** are hygroscopic and unstable at room temperature. They readily converted to **11a** and **11b**, respectively, in solution with a room temperature with a half-life of about 5 min.

[(CO)$_2$PhSeReC(=O)N(CH_3)CH_2CH_2(η^5-C_5H_4)] (10ba): orange crystal (98% yield). Mp: 140 °C (dec). R_f = 0.46 (100% EtOAc, SiO_2). IR (CH_2Cl_2): 2027 (s), 1959 (s), 1567 (m) cm^{-1}. ^1H NMR ($CDCl_3$, 300 MHz): δ 7.53−7.49 (2H, m), 7.19−7.13 (3H, m), 5.57 (2H, t, J = 2.2 Hz, Cp H), 5.38 (2H, t, J = 2.2 Hz, Cp H), 3.40 (2H, t, J = 5.5 Hz, H_1's), 3.01 (3H, s, N−CH_3), 2.33 (2H, t, J = 5.5 Hz, H_2's). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 190.0 (CO), 170.0 (CO, ReCON), 135.2 (CH × 2, Ph), 131.9 (C, Ph), 128.4 (CH × 2, Ph), 126.4 (CH, Ph), 106.7 (C, Cp), 96.4 (CH × 2, Cp), 86.7 (CH × 2, Cp), 60.2 (CH_2, C_1), 34.9 (CH_3, N−CH_3), 25.4 (CH_2, C_2). Anal. Calcd for $C_{17}H_{16}NO_3ReSe$: C, 37.30; H, 2.94; N, 2.56. Found: C, 37.58; H, 2.90; N, 2.42.

[(CO)(($CH_3)_3CNC$)PhSeReC(=O)N(CH_3)CH_2CH_2(η^5-C_5H_4)] (10bb): yellow crystal (95% yield). Mp: 60 °C (dec). IR (CH_2Cl_2): 2150 (s), 1947 (s), 1553 (m), 1472 (m) cm^{-1}. ^1H NMR ($CDCl_3$, 300 MHz): δ 7.52−7.47 (2H, m), 7.13−7.03 (3H, m), 5.39−5.36 (2H, m, Cp H), 5.33−5.31 (1H, m, Cp H), 5.20−5.18 (1H, m, Cp H), 3.48 (1H, ddd, J = 13.8, 7.3, 3.7 Hz, H_{1a}), 3.40 (1H, ddd, J = 13.8, 7.1, 3.7 Hz, H_{1b}), 3.00 (3H, s, N−CH_3), 2.39 (1H, ddd, J = 13.4, 7.3, 3.7 Hz, H_{2a}), 2.24 (1H, ddd, J = 13.4, 7.1, 3.7 Hz, H_{2b}), 1.31 (9H, s, ^{t}Bu). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 197.3 (CO), 175.5 (CO, ReCON), 135.6 (C, ReCN^{t}Bu), 134.2 (C, Ph), 133.7 (CH × 2, Ph), 127.8 (CH × 2, Ph), 124.3

Table 1. Crystallographic Data and Structure Refinements for 7a, 9b, and 10ba

compound	**7a**	**9b**	**10ba**
formula	$C_{11}H_{11}BrNO_3Re$	$C_{16}H_{19}NO_2ReSe$	$C_{34}H_{32}N_2O_6Re_2Se_2$
fw	471.32	522.50	1094.97
cryst size (mm)	0.41 × 0.38 × 0.28	0.25 × 0.13 × 0.13	0.26 × 0.19 × 0.19
cryst syst	triclinic	monoclinic	triclinic
space group	$P\bar{1}$	$P2_1/a$	$P\bar{1}$
a (Å)	6.8954(12)	11.3724(11)	7.7076(13)
b (Å)	9.4283(9)	8.2498(7)	9.4299(14)
c (Å)	10.2745(12)	17.3955(19)	23.1581(23)
α (deg)	102.620(10)	90	90.513(10)
β (deg)	93.576(12)	99.787(9)	90.879(11)
γ (deg)	107.518(11)	90	93.963(13)
V (Å^3)	615.7(1)	1608.3(3)	1678.9(4)
Z	2	4	2
D_c (g cm^{-3})	2.542	2.158	2.166
F(000)	433	988	1032
λ(Mo Kα) (Å)	0.710 69	0.710 69	0.710 69
μ(Mo Kα) (cm^{-1})	132.129	99.028	94.959
transmissn	0.841; 1.000	0.829; 1.000	0.869; 1.000
scan speed (deg min^{-1})	2.06−8.24	1.65−8.24	1.65−8.24
$\theta/2\theta$ scan width (deg)	2(0.70 + 0.35 tan θ)	2(0.70 + 0.35 tan θ)	2(0.75 + 0.35 tan θ)
$2\theta_{max}$ (deg)	45.0	50.0	45.0
unit cell detn: no.; 2θ range (deg)	25; 14.75−32.73	25; 14.72−34.38	25; 14.84−33.44
hkl range	−7 to 7, 0 to 10, −11 to 10	−13 to 13, 0 to 9, 0 to 20	−8 to 8, 0 to 10, −24 to 24
no. of collected reflns	1770	2925	4770
no. of unique reflns	1608	2827	4376
no. of obsd reflns ($I > 2.0\sigma(I)$)	1528	1635	3658
no. of refined params	154	190	415
R_f;[a] R_w[b]	0.031; 0.041	0.036, 0.037	0.025, 0.031
GOF	2.91	1.16	1.62
weight modifier k in kF_o^2	0.000 100	0.000 100	0.000 100
$\Delta\rho$ (max, min; e Å^{-3})	+0.800; −1.880	+0.840; −0.800	+0.720; −1.190

[a] $R_f = \sum(F_o - F_c)/\sum(F_o)$. [b] $R_w = [\sum w(F_o - F_c)^2/\sum wF_o^2]^{1/2}$.

(CH, Ph), 103.6 (C, Cp), 97.0 (CH, Cp), 92.0 (CH, Cp), 86.9 (CH, Cp), 83.2 (CH, Cp), 59.2 (CH_2, C_1), 57.3 (C, ^{t}Bu), 34.6 (CH_3, N−CH_3), 30.2 (CH_3 × 3, ^{t}Bu), 25.8 (CH_2, C_2). Anal. Calcd for $C_{21}H_{25}N_2O_2ReSe$: C, 41.86; H, 4.18; N, 4.65. Found: C, 42.08; H, 4.32; N, 4.55.

[(CO)(P(OMe)$_3$)PhSeReC(=O)N(CH$_3$)CH$_2$CH$_2$(η^5-C$_5$H$_4$)] (10bc): unstable hygroscopic yellow powder. IR (CH_2Cl_2): 1933 (s) cm^{-1}. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.58−7.54 (2H, m, Ph), 7.12−7.09 (3H, m, Ph), 5.36−5.34 (2H, m, Cp H), 5.29−5.27 (1H, m, Cp H), 5.15−5.13 (1H, m, Cp H), 3.77 (9H, d, J = 11.5 Hz, P(OMe)$_3$), 3.38−3.34 (2H, m), 2.95 (3H, s, N−CH_3), 2.56−2.48 (1H, m, H_{2a}), 2.16−1.99 (1H, m, H_{2b}). ^{31}P NMR ($CDCl_3$): δ 99.8.

[(CO)(P(OEt)$_3$)PhSeReC(=O)N(CH$_3$)CH$_2$CH$_2$(η^5-C$_5$H$_4$)] (10bd): unstable hygroscopic yellow powder. IR (CH_2Cl_2): 1927 (s) cm^{-1}. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.57−7.53 (2H, m, Ph), 7.12−7.09 (3H, m, Ph), 5.36 (1H, s, Cp H), 5.25 (1H, s, Cp H), 5.23 (1H, s, Cp H), 5.15 (1H, s, Cp H), 4.19−4.06 (6H, m, P(OEt)$_3$), 3.38−3.31 (2H, m), 2.92 (3H, s, N−CH_3), 2.48−2.42 (1H, m, H_{2a}), 2.12−2.03 (1H, m, H_{2b}), 1.36 (9H, t, J = 7.2 Hz, P(OEt)$_3$). ^{31}P NMR ($CDCl_3$): δ 98.0.

(CO)$_2$(P(OMe)$_3$)Re(η^5-C$_5$H$_4$CH$_2$CH$_2$N(CH$_3$)SePh) (11a): yellow liquid (92% yield from **9b**). IR (CH_2Cl_2): 1941 (s), 1868 (s) cm^{-1}. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.63−7.59 (2H, m, Ph), 7.28−7.24 (3H, m, Ph), 5.13 (2H, t, J = 2 Hz, Cp H), 5.05 (2H, t, J = 2 Hz, Cp H), 3.54 (9H, d, J = 12.4 Hz, P(OMe)$_3$), 2.75 (2H, t, J = 6.8 Hz), 2.59 (2H, d, J = 6.8 Hz), 2.46 (3H, s, N−CH_3). ^{31}P NMR ($CDCl_3$): δ 140.1. Anal. Calcd for $C_{19}H_{25}NO_5PReSe$: C, 35.46; H, 3.92; N, 2.18. Found: C, 35.58; H, 3.96; N, 2.05.

(CO)$_2$(P(OEt)$_3$)Re(η^5-C$_5$H$_4$CH$_2$CH$_2$N(CH$_3$)SePh) (11b): yellow liquid (93% yield from **9b**). IR (CH_2Cl_2): 1938 (s), 1866 (s) cm^{-1}. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.64−7.58 (2H, m, Ph), 7.33−7.24 (3H, m, Ph), 5.09 (2H, t, J = 2 Hz, Cp H), 5.02 (2H, t, J = 2 Hz, Cp H), 3.90 (6H, dq, J = 14.6, 7.2 Hz, P(OEt)$_3$), 2.73 (2H, t, J = 7.5 Hz), 2.57 (2H, d, J = 7.5 Hz), 2.44 (3H, s, N−CH_3), 1.29 (9H, t, J = 7.2 Hz, P(OEt)$_3$). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 200.8 (CO × 2, d, J_{CP} = 35 Hz), 135.5 (C, Ph), 131.5 (CH × 2, Ph), 129.1 (CH × 2, Ph), 127.7 (CH, Ph), 105.3 (C, Cp), 82.4 (CH × 2, Cp), 82.2 (CH × 2, Cp), 61.0 (CH_2 × 3, P(OEt)$_3$), 53.7 (CH_2), 36.1 (CH_3, N−CH_3), 28.6 (CH_2), 16.0 (CH_3 × 3, P(OEt)$_3$). ^{31}P NMR ($CDCl_3$): δ 136.2. Anal. Calcd for $C_{22}H_{31}NO_5PReSe$: C, 38.54; H, 4.56; N, 2.04. Found: C, 358.28; H, 4.39; N, 2.32.

Table 2. Selected Bond Lengths (Å) and Bond Angles (deg) for 7a, 9b, and 10ba

	7a	**9b**	**10ba**
Re−Br(Se)	2.613(1)	2.500(2)	2.591(1)
Re−C(8)	2.19(1)	2.02(1)	2.213(9)
Re−O(8)		2.37(1)	
Re−C(10)	1.93(1)	1.88(1)	1.93(1)
Re−C(11)	1.95(1)		1.93(1)
C(8)−O(8)	1.22(1)	1.26(1)	1.22(1)
Br(Se)−Re−C(8)	138.7(3)	121.2(4)	137.9(2)
Br(Se)−Re−O−(8)		89.2(2)	
Br(Se)−Re−C(10)	77.8(3)	90.0(4)	76.2(3)
Br(Se)−Re−C(11)	80.2(4)		77.8(3)
Re−C(8)−O(8)	121.7(8)	89.8(8)	120.6(7)
O(8)−Re−C(8)		32.0(4)	
O(8)−Re−C(10)		92.3(4)	
C(8)−Re−C(10)	73.3(4)	90.7(5)	74.0(4)
C(8)−Re−C(11)	77.8(5)		78.3(4)
C(10)−Re−C(11)	102.0(4)		99.1(4)
Cp(cent.)−Re−Br(Se)	111.53(4)	117.14(4)	112.46(3)
Cp(cent.)−Re−C(8)	109.7(3)	109.9(3)	109.6(2)
Cp(cent.)−Re−O(8)		131.8(2)	
Cp(cent.)−Re−C(10)	134.5(3)	124.7(3)	136.5(3)
Cp(cent.)−Re−C(11)	123.3(3)		124.3(3)

Crystal Structures of [(CO)$_2$BrReC(=O)N(CH$_3$)CH$_2$CH$_2$-(η^5-C$_5$H$_4$)] (7a), [(CO)PhSeRe(η^2-C=O)N(CH$_3$)CH$_2$CH$_2$(η^5-C$_5$H$_4$)] (9b), and [(CO)$_2$PhSeReC(=O)N(CH$_3$)CH$_2$CH$_2$(η^5-C$_5$H$_4$)] (10ba). Single crystals of **7a**, **9b**, and **10ba** were obtained from each individual solution of CH_2Cl_2 and hexane at 5 °C for several days. Diffraction measurements were made on an Enraf-Nonius CAD-4 automated diffractometer by use of a graphite-monochromated Mo Kα radiation (λ = 0.710 69 Å) with the $\theta-2\theta$ 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 **7a** and **10ba**; $P2_1/a$ for **9b**) 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 NRCVAX program.[8] The structures were solved by direct methods and refined by a full-matrix least-squares routine[9] 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 calculated 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 1, and selected bond distances and angles in Table 2.

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

Supporting Information Available: Tables of data collection parameters, bond lengths and bond angles, fractional atomic coordinates, and anisotropic thermal parameters for **7a**, **9b**, and **10ba** (11 pages). Ordering information is given on any current masthead page.

OM970544I

(8) Gabe, E. J.; LePage, Y.; Charland, J. P.; Lee, F. L; White, P. S. *J. Appl. Crystallogr.* **1989**, *22*, 384.

(9) Main, P. In *Crystallographic Computing 3: Data Collection, Structure Determination, Proteins and Databases*, Sheldrick, G. M., Krueger, C., Goddard, R., Eds.; Clarendon Press: Oxford, 1985; pp 206−215.