Reaction of the Half-Sandwich Cationic Aminorhenium Complex with Amines. Preparation of Rhenium Bis(amine) Hydride and Rhenium Isocyanate Complexes

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

Institute of Chemistry, Academia Sinica, Taipei, Taiwan

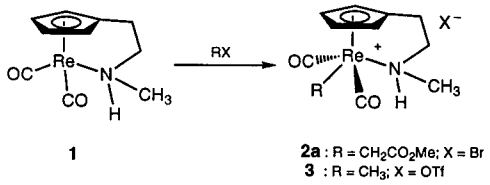
Received December 8, 1998

The aminorhenium ester complex {[η^5:η^1-$C_5H_4CH_2CH_2NH(CH_3)$]$Re(CO)_2(CH_2CO_2CH_3)$}$^+$-Br^- (**2a**) reacts with *n*-butylamine in refluxing CH_2Cl_2 solution, giving the *n*-butylamine coordinated complex {[η^5:η^1-$C_5H_4CH_2CH_2NH(CH_3)$]$Re(CO)(CH_2CO_2CH_3)$(*n*-$BuNH_2$)}$^+Br^-$ (**6a**), which was derived via rhenium−carbamoyl bond cleavage of the intermediate. In contrast, the slightly electron-rich methyl complex {[η^5:η^1-$C_5H_4CH_2CH_2NH(CH_3)$]$Re(CO)_2$-(CH_3)}$^+CF_3SO_3^-$ (**3**) reacts with *n*-butylamine, giving the *n*-butylamine hydride complex {[η^5:η^1-$C_5H_4CH_2CH_2NH(CH_3)$]$ReH(CO)$(*n*-$BuNH_2$)}$^+CF_3SO_3^-$ (**7a**), which was derived via the coupling of the carbamoyl and the methyl groups followed by an amine coordination. Methyl complex **3** also reacts with *tert*-butylamine, diethylamine, and ammonia to give the corresponding amine hydride complexes. The presence of an Re−H bond is evidenced by the characteristic hydride resonance in the ^{1}H NMR spectra. The *tert*-butylamine hydride complex **7b** has been characterized by an X-ray analysis. The reaction of both **2** and **3** with hydrazine proceeds via a net loss of 1 mol of ammonia to give isocyanate complexes **12a** and **12b**, respectively. The structure of **12a** is supported by single-crystal X-ray analysis.

Introduction

Amines are the classic ligands of coordination chemistry, but they have not often been used with organotransition-metal compounds.[1] Unlike ligands containing the heavier group 15 atoms, amines show no π-acceptor ability. Therefore, they coordinate only weakly to the low-valent transition metals and form relatively labile complexes.[2] However, through intramolecular chelation, stable amino group chelation complexes of manganese,[3] molybdenum,[4] and rhenium[5] have been prepared.[6] Strong σ donation of the amino ligand to the low-valent transition metals makes the metal center much more electron-rich, thereby enhancing the ability of the metal to undergo nucleophilic reactions. We have reported such a reaction that is derived from an aminorhenium complex with various electrophiles.[5b] Complex **1** reacts with alkylating agents, giving the exclusive rhenium−alkyl complex **2a** and **3** (see Scheme 1). The carbonyl stretchings of the aminorhenium complex **1** appear at 1893 and 1816 cm^{-1}. Upon rhenium alkylation, the carbonyl stretchings shift to higher frequencies at about 2034 and 1966 cm^{-1}. High frequencies of the carbonyl stretchings suggests that the carbonyl ligands are relatively labile. Nucleophilic addition to this type of labile carbonyl ligand is not uncommon.[7] However, it might be of interest to find out what the effect of the electron-donating amino ligand might have on the subsequent reactions. The carbon nucleophile, which is also a strong base, deprotonates the N−H protons of **2a** and **3** only. Therefore, a nucleophile that has low basicity but is still nucleophilic enough for addition to the carbonyl ligand is required. In this study, we choose amines as nucleophiles to react with the activated carbonyl ligand and found some interesting reactions. The results are presented in the following.

Scheme 1



1 **2a** : R = CH_2CO_2Me; X = Br
3 : R = CH_3; X = OTf

Results and Discussion

A. Reaction of the Ester Complex 2 with *n*-Butylamine. Addition of *n*-butylamine to a solution of **2a** (see Scheme 2) resulted in an immediate disappear-

(1) (a) Collman, J. P.; Hegedus, L. S.; Norton, J. R.; Finke, R. G. *Principles and Applications of Organotransition Metal Chemistry*, 2nd ed.; University Science Books: Mill Valley, CA, 1987; p 64. (b) Cotton, F. A.; Wilkinson, G. *Advanced Inorganic Chemistry*, 5th ed.; Wiley: New York, 1988; p 36.

(2) (a) Jutzi, P.; Dahlhaus, J.; Kristen, M. O. *J. Organomet. Chem.* **1993**, *450*, C1−C3. (b) Sellmann, D.; Mueller, J. *J. Organomet. Chem.* **1985**, *281*, 249−262. (c) Sellmann, D.; Mueller, J.; Hofmann, P. *Angew. Chem., Int. Ed. Engl.* **1982**, *21*, 691.

(3) Wang, T. F.; Lee, T. Y.; Wen, Y. S.; Liu, L. K. *J. Organomet. Chem.* **1991**, *403*, 353.

(4) (a) Wang, T. F.; Wen, Y. S. *J. Organomet. Chem.* **1992**, *439*, 155. (b) Wang, T. F.; Lee, T. Y.; Chou, J. W.; Ong, C. W. *J. Organomet. Chem.* **1992**, *423*, 31.

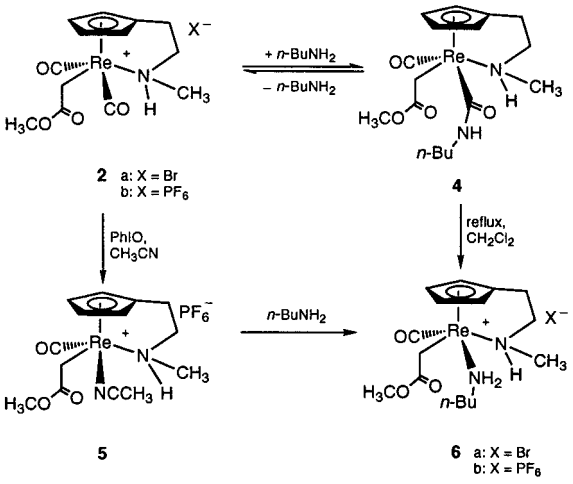
(5) (a) Wang, T. F.; Juang, J. P.; Wen, Y. S. *Bull. Inst. Chem., Acad. Sin.* **1995**, *42*, 41. (b) Wang, T. F.; Lai, C. Y.; Hwu, C. C.; Wen, Y. S. *Organometallics* **1997**, *16*, 1218. (c) Wang, T. F.; Hwu, C. C.; Tsai, C. W.; Wen, Y. S. *Organometallics* **1998**, *17*, 131.

(6) For a review of aminoethyl-functionalized cyclopentadienyl complexes, see: Jutzi, P.; Redeker, T. *Eur. J. Inorg. Chem.* **1998**, 663.

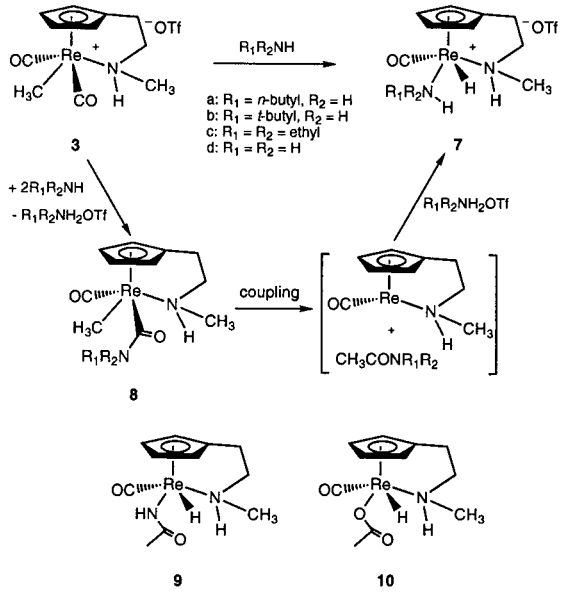
(7) Cotton, F. A.; Wilkinson, G. *Advanced Inorganic Chemistry*, 5th ed.; Wiley: New York, 1988; p 1048.

10.1021/om980998v CCC: $18.00
Publication on Web 03/26/1999

Scheme 2



Scheme 3



ance of the carbonyl bands of **2a** with concomitant appearance of a new intense band at 1888 cm^{-1}. However, upon removal of the excess *n*-butylamine, **2a** was regenerated. Examination of the reaction intermediate by ^1H NMR spectroscopy showed that the methyl group of the amino ligand appeared as a doublet (δ 2.94), indicating that the N−H proton is intact. The Cp protons resonate at positions that are normally those of a neutral compound. These data are in accordance with the proposed carbamoyl complex **4**. When the reaction mixture was heated in CH_2Cl_2 under reflux, the bis(amine) complex **6a** was obtained, presumably derived from the Re−carbamoyl bond cleavage of **4** followed by amine coordination. To confirm the assignment, **6a** was converted to the corresponding hexafluorophosphate **6b** and compared with the compound that is synthesized via an explicit pathway. Anion exchange of **2a** to the corresponding hexafluorophosphate **2b** followed by reaction with iodosobenzene in CH_3CN provided the acetonitrile complex **5**. The labile acetonitrile ligand was then displaced with *n*-butylamine to give **6b**, whose spectroscopic data are identical with those of the compound obtained by the reaction of **2a** with *n*-butylamine in refluxing CH_2Cl_2 and an anion exchange.

The other pathway for the formation of **6a** via decarbonylation of **2a** followed by coordination with *n*-butylamine was ruled out, since heating a CH_2Cl_2 solution of **2a** alone resulted in recovery of **2a** quantitatively.

B. Reaction of the Methyl Complex 3 with Amines. Astonishingly, the reaction of methyl complex **3** with amines gave a completely different type of compound. For example, treatment of **3** with *n*-butylamine provided the bis(amine) hydride complex **7a** (see Scheme 3). The reaction presumably proceeded via the carbamoyl intermediate **8**, similar to the reaction of the ester complex **2** with *n*-butylamine, followed by coupling between the carbamoyl and methyl groups and then ligation of 1 mol of *n*-butylamine to the resultant vacant site. The proposed carbamoyl **8** was not observed due to the facile coupling reaction. The byproduct, *N*-butylacetamide, was not isolated but was evidenced by the resonance of the methyl ketone group at δ 1.97 in the ^1H NMR spectrum (lit.[8] δ 1.95). The reaction of **3** with *tert*-butylamine and diethylamine proceeded similarly, giving bis(amine) hydride complexes **7b** and **7c**, respectively.

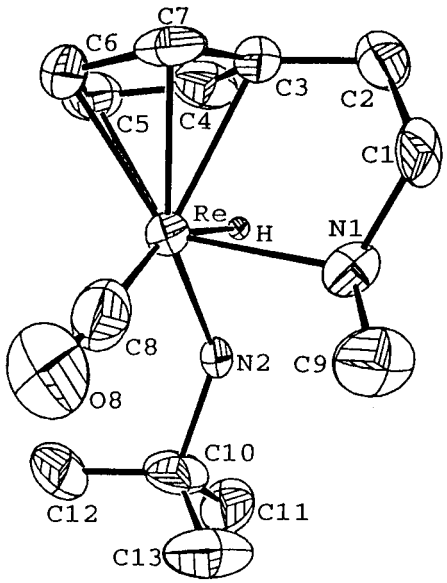


Figure 1. ORTEP drawing of **7b**. $CF_3SO_3^-$ is omitted for simplicity.

The presence of the Re−H moiety of complexes **7a**−**c** could be confirmed by the hydride resonances at δ −5.15, −5.11, and −4.46, respectively, in the ^1H NMR spectra. Further support for the structural assignments has been accomplished by an X-ray analysis of **7b**. Figure 1 shows that the hydride is located trans to the carbonyl group in a distorted four-legged piano-stool geometry. The distances of rhenium to both nitrogens (2.25 and 2.21 Å, respectively; see Table 1) are similar to the reported Re−N bond distance (2.22 Å).[5b] The alkyl tether is bent down 8.2° from the cyclopentadienyl ring toward rhenium (Cp*−C(3)−C(2) = 171.8° (Cp* denotes the centroid of the cyclopentadienyl ring)). The bond angle of Cp*−Re−N(1) (chelate) is 107.3°, much smaller than the 125° of Cp*−Re−N(2) (nonchelate).

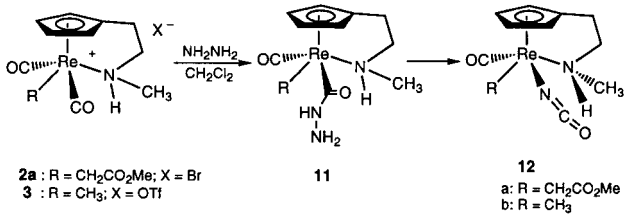
(8) Yang, S.-H.; Wang, H.-M.; Chen, L.-C. *J. Chin. Chem. Soc.* **1995**, *42*, 585.

Table 1. Selected Bond Lengths (Å) and Bond Angles (deg) for 7b and 12a[a]

7b		12a	
Re−Cp*	1.90(1)	Re−Cp*	1.94(1)
Re−N(1)	2.25(1)	Re−N(1)	2.23(1)
Re−N(2)	2.21(1)	Re−N(10)	2.10(1)
Re−C(8)	1.84(2)	Re−C(9)	1.85(1)
C(8)−O(8)	1.17(2)	C(9)−O(9)	1.17(1)
		Re−C(11)	2.24(1)
		N(10)−C(10)	1.13(1)
		C(10)−O(10)	1.20(1)
Cp*−Re−N(1)	107.3(2)	Cp*−Re−N(1)	104.0(2)
Cp*−Re−N(2)	125.0(2)	Cp*−Re−N(10)	128.8(2)
Cp*−Re−C(8)	126.0(5)	Cp*−Re−C(9)	123.4(2)
Cp*−Re−H	81.5(1)	Cp*−Re−C(11)	107.8(2)
Cp*−C(3)−C(2)	171.8(8)	Cp*−C(3)−C(2)	173.9(7)
N(1)−Re−N(2)	82.5(4)	N(1)−Re−N(10)	74.6(2)
N(1)−Re−C(8)	89.4(6)	N(1)−Re−C(9)	88.1(3)
N(2)−Re−C(8)	107.6(6)	N(1)−Re−C(11)	146.4(2)
Re−C(8)−O(8)	176.5(15)	N(10)−Re−C(9)	107.8(3)
		N(10)−Re−C(11)	77.3(2)
		C(9)−Re−C(11)	83.3(3)
		Re−C(9)−O(9)	173.5(6)
		Re−N(10)−C(10)	175.1(6)
		N(10)−C(10)−O(10)	178.0(8)

[a] Cp* denotes the centroid of the cyclopentadienyl ring.

Scheme 4



In addition to the primary and secondary amines, **3** also reacts with ammonia to give the corresponding ammonia hydride complex **7d** (see Scheme 3). When the reaction was conducted in dioxane, the acetamido hydride complex **9** was also observed by its distinctive hydride (δ −4.98) and acetamide ligand (δ 2.10) resonances in the ^{1}H NMR spectrum. The acetamido hydride **9** is unstable in solution at room temperature and converted to **7d** gradually in the reaction media. Two-phase (H_2O and CH_2Cl_2) reaction of **3** with ammonia−water gave three compounds, **7d**, **9**, and **10**, in a ratio of 3:80:17. This procedure allows the isolation and characterization of the neutral acetamido hydride species **9** as an orange crystalline compound in 32% yield. The formation of **9** is presumably derived from the coupling of the methyl and the carbamoyl groups of the proposed intermediate **8d**, followed by coordination of the resultant vacant site with the newly formed acetamide that is in the close vicinity of the vacant site.

The acetate hydride **10** is apparently derived from the reaction of **3** with hydroxide ion that exists in the aqueous ammonia solution. The complex **10** has also been synthesized independently from **3** with aqueous sodium carbonate and characterized spectroscopically.

C. Reactions with Hydrazine. The reaction of both **2** and **3** with hydrazine proceeded instantly to give the corresponding hydrazide **11** (Scheme 4), as suggested by the infrared spectra, which show only one terminal carbonyl band at 1892 cm^{-1} for **11a** and 1874 cm^{-1} for **11b**. Upon further reaction, another absorption band at about 2238 cm^{-1}, corresponding to an isocyanate group, grows gradually and reaches the maximum in 1 h. The products were isolated and examined spectroscopically. The combination of IR and ^{1}H NMR data suggests that all of the ligands are intact, except one of the carbonyl ligands was tranformed into an isocyanate group. Therefore, **12a** and **12b** were proposed for the reaction products, respectively. To confirm the assignment, **12a** was subjected to crystallographic analysis.

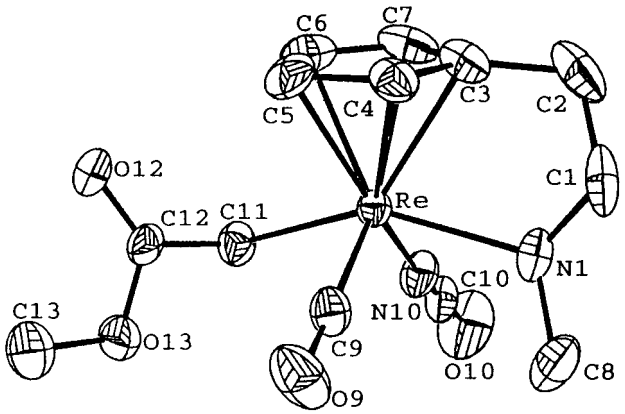


Figure 2. ORTEP drawing of **12a**.

Figure 2 shows that the isocyanate ligand[9] is located trans to the carbonyl ligand in a distorted four-legged piano-stool geometry. The bond distance of rhenium to the nitrogen of isocyanate is 2.10 Å, shorter than the 2.23 Å distance of the rhenium to the amine nitrogen. The N−C distance (1.13 Å) of the isocyanate group is shorter than the C−O distance (1.20 Å) and implies some triple-bond character. The rhenium−isocyanate linkage is approximately linear, 175.1° for Re−N−C and 178.0° for N−C−O angles. These features are in accordance with the reported N-bonded isocyanate of titanocene,[10] zirconocene,[10] and nitrosylchromium[11] complexes.[12] The alkyl tether is bent down 6.1° from the cyclopentadienyl ring toward rhenium. The amine and ester ligands are held upward, while the isocyanate and carbonyl ligands are held downward from a normal four-legged piano-stool geometry. The angles from the center of the Cp ring (Cp*) and rhenium to the four legs are 104° for the amine ligand, 107.8° for the ester ligand, 128.8° for the isocyanate, and 123.4° for the carbonyl ligands.

Conclusion

We have demonstrated that the reaction of aminorhenium complexes **2** and **3** with amines proceeds instantly, giving the corresponding carbamoyl intermediate. Sub-

(9) Initially, the O-bonded cyanate group was assumed. Least-squares refinement gave final $R = 0.026$ and a goodness of fit value of 1.43. However, the bond lengths of O−C (1.166 Å) and C−N (1.161 Å) seem unlikely for the bond order of a cyanate group (O−C≡N). Reversal of N and O gave improved final $R = 0.023$ and GOF = 1.18. The bond lengths of the isocyanate group (N−C = 1.129 Å and C−O = 1.198 Å) fit the bond order of N=C=O.

(10) Anderson, S. J.; Brown, D. S.; Finney, K. J. *J. Chem. Soc., Dalton Trans.* **1979**, 152.

(11) Bush, M. A.; Sim, G. A. *J. Chem. Soc. A* **1970**, 605.

(12) For other cyanate and isocanate organometallic complexes, see: (a) Herrmann, W. A.; Jung, K. A.; Herdtweck, E. *Chem. Ber.* **1989**, *122*, 2041. (b) Burmeister, J. L.; Deardorff, E. A.; Jensen, A.; Christiansen, V. H. *Inorg. Chem.* **1970**, *9*, 58. (c) Paul, D. K.; McKee, M. L.; Worley, S. D.; Hoffman, N. W.; Ash, D. H.; Gautney, J. *J. Phys. Chem.* **1989**, *93*, 4598. (d) Veszpremi, T.; Pasinszki, T.; Feher, M. *J. Am. Chem. Soc.* **1994**, *116*, 6303.

sequent reaction of the carbamoyl intermediate is dependent on the electronic nature of the metal and/or the ligands. The ester complex **4** undergoes bond cleavage of the rhenium−carbamoyl bond, while the slightly more electron-rich methyl complex **8** undergoes coupling reaction of the methyl and the carbamoyl groups. It is noteworthy that the slight difference in the electronic properties induced a dramatic difference in the reaction pathways. The reactions of **2** and **3** with hydrazine gave products that are quite different from those resulting from the reactions with amines. The hydrazide intermediate **11** undergoes rearrangement and a net loss of 1 mol of ammonia to give an isocyanate complex. The mechanism for this unique transformation is not clear yet.

Experimental Section

General experimental equipment and instrumentations were reported previously.[5c] 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}.

Preparation of {[η^5:η^1-$C_5H_4CH_2CH_2NH(CH_3)$]Re(CO)($CH_2CO_2CH_3$)(CH_3CN)}$^+$$PF_6^-$ (5). To a stirred solution of **2a** (1.55 g, 3 mmol) in CH_3CN (100 mL) was added NH_4PF_6 (1 g, 6 mmol). After the mixture was stirred at room temperature for 20 min, CH_3CN was evaporated. The solid residue was extracted with CH_2Cl_2 to give the hexafluorophosphate salt **2b** as a yellow powder which exhibits the following spectroscopic data. IR (CH_3CN): 2053 (s), 1981 (s), 1708 (m) cm^{-1}. ^{1}H NMR (C_3D_6O, 300 MHz): δ 6.99 (1H, br s, N−H), 6.79−6.77 (1H, m, Cp H), 6.55−6.53 (1H, m, Cp H), 5.30−5.28 (1H, m, Cp H), 5.26−5.24 (1H, m, Cp H), 4.29−4.22 (1H, m, H_{1a}), 3.91−3.80 (1H, m, H_{1b}), 3.59 (3H, s, $-OCH_3$), 3.12 (3H, d, J = 5.7 Hz, N−CH_3), 3.14−3.08 (1H, m, H_{2a}), 2.62 (2H, s, Re−CH_2R), 2.55−2.49 (1H, m, H_{2b}). ^{13}C NMR (C_3D_6O, 75 MHz): δ 197.6 (CO), 196.5 (CO), 179.7 (C, ester), 131.9 (C, Cp), 93.8 (CH, Cp), 91.3 (CH, Cp), 90.5 (CH, Cp), 89.5 (CH, Cp), 79.2 (CH_2, C_1), 51.4 (CH_3, $-OCH_3$), 50.2 (CH_3, N−CH_3), 25.7 (CH_2, C_2), −11.9 (CH_2, Re−CH_2R).

The yellow powder **2b** was dissolved in CH_3CN (30 mL), followed by cooling of the resultant solution in an ice−water bath. The white powder PhIO (0.8 g, 3.6 mmol) was then added in one portion, and the mixture was stirred at 0 °C for 1.5 h. After this mixture was filtered through Celite, the resultant yellow solution was concentrated and the residue was dissolved in CH_2Cl_2 (10 mL). The CH_2Cl_2 solution was then added to a solution of hexane (60 mL) to effect precipitation. The yellow powders were collected and washed twice with hexane to give 1.61 g (90% yield) of **5**. An analytically pure sample was obtained by recrystallization of the yellow powders from acetone and hexane. Mp: 116−120 °C. IR (CH_2Cl_2): 1930 (m), 1635 (s) cm^{-1}. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 6.13 (1H, Cp H), 5.73 (1H, Cp H), 5.38 (1H, Cp H), 5.28 (1H, br s, N−H), 4.57 (1H, Cp H), 3.91−3.85 (1H, m, H_{1a}), 3.61 (3H, s, $-OCH_3$), 3.20−3.10 (1H, m, H_{1b}), 3.03 (3H, d, J = 5.8 Hz, N−CH_3), 2.86 (3H, s, Re−NCCH_3), 2.75 (1H, d, J = 9.3 Hz, Re−CH_{2a}R), 2.76−2.64 (1H, m, H_{2a}), 2.44 (1H, d, J = 9.3 Hz, Re−CH_{2b}R), 2.09 (1H, dd, J = 14.2, 5.4 Hz, H_{2b}). ^{13}C NMR (C_3D_6O, 75 MHz): δ 208.0 (CO), 180.9 (C, ester), 137.1 (C, Re−NCCH_3), 129.5 (C, Cp), 98.6 (CH, Cp), 96.3 (CH, Cp), 80.9 (CH, Cp), 78.4 (CH, Cp), 72.3 (CH_2, C_1), 50.7 (CH_3, $-OCH_3$), 48.8 (CH_3, N−CH_3), 26.4 (CH_2, C_2), 4.3 (CH_3, Re−NCCH_3), −9.4 (CH_2, Re−CH_2R). Mass spectrum (FAB, ^{187}Re; *m/e* (relative intensity (%)): 451 (100, M^+). Anal. Calcd for $C_{14}H_{20}F_6N_2O_3PRe$: C, 28.24; H, 3.38; N, 4.70. Found: C, 28.08; H, 3.48; N, 4.82.

Reaction of 2a with *n*-Butylamine. To a stirred solution of **2a** (50 mg) in CH_2Cl_2 (10 mL) was added *n*-butylamine (0.5 mL) at room temperature. After the mixture was stirred for 3 min, the infrared spectrum showed only one peak at 1888 cm^{-1} in the terminal carbonyl absorption region, suggesting that the carbamoyl complex **4** was formed. Upon removal of CH_2Cl_2 and the excess *n*-butylamine, the complex **2a** was regenerated, as suggested by the ^{1}H NMR and IR spectra. Addition of *n*-butylamine (ca. 0.1 mL) to a solution of **2a** (ca. 3 mg) in $CDCl_3$ (0.5 mL) in an NMR tube allowed us to record the ^{1}H NMR spectrum of **4**. Because of serious overlapping of the *n*-butylamine signals with some signals of **4**, only a partial spectrum is reported as follows. ^{1}H NMR: δ 5.77 (1H, Cp H), 5.59 (1H, Cp H), 4.86 (1H, Cp H), 4.51 (1H, Cp H), 3.62 (3H, s, $-OCH_3$), 2.94 (3H, d, J = 5.8 Hz, N−CH_3).

Preparation of {[η^5:η^1-$C_5H_4CH_2CH_2NH(CH_3)$]Re(CO)($CH_2CO_2CH_3$)(*n*-$BuNH_2$)}$^+$$Br^-$ (6a). To a stirred solution of **2a** (121 mg, 0.23 mmol) in CH_2Cl_2 (20 mL) was added *n*-butylamine (0.3 mL). The resultant solution was then heated under reflux for 16 h. The solvent was evaporated to dryness. The residue was dissolved in CH_2Cl_2 (2 mL) and added to hexane (30 mL). The clear hexane layer was decanted, and the oily precipitates were dissolved in CH_2Cl_2 (2 mL) again. Ether (40 mL) was added. The resultant cloudy solution was filtered through Celite and concentrated to give **6a** as an oil (109 mg, 83% yield, 95% purity). Further attempts to purify the sample for elemental analysis were not successful.

For characterization purposes, **6a** was dissolved in acetone and treated with NH_4PF_6 at room temperature for 10 min. Acetone was evaporated, and the product was taken up with CH_2Cl_2. Spectroscopic data of this compound are identical with those of **6b**, whose synthesis is described below.

The spectroscopic data of **6a** are as follows. IR (CH_2Cl_2): 1905 (s), 1670 (m) cm^{-1}. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 8.17 (1H, br s, N−H), 6.30 (1H, br s, $BuNH_{2a}$), 6.17−6.15 (1H, m, Cp H), 5.76−5.74 (1H, m, Cp H), 5.09 (1H, br s, $BuNH_{2b}$), 4.98−4.96 (1H, m, Cp H), 4.60−4.58 (1H, m, Cp H), 3.91−3.86 (1H, m, H_{1a}), 3.67 (3H, s, $-OCH_3$), 3.30−2.95 (4H, m), 2.97 (3H, d, J = 5.8 Hz, N−CH_3), 2.31 (1H, d, J = 9.6 Hz, Re−CH_{2a}), 2.07 (1H, d, J = 9.6 Hz, Re−CH_{2b}), 2.06−1.99 (1H, m, H_{2b}), 1.83−1.75 (2H, m, butyl), 1.48−1.38 (2H, m, butyl), 0.96 (3H, t, J = 7.2 Hz, butyl).^{13}C NMR ($CDCl_3$, 100 MHz): δ 211.4 (CO), 184.8 (C, ester), 126.9 (C, Cp), 95.1 (CH, Cp), 95.0 (CH, Cp), 79.2 (CH, Cp), 76.2 (CH, Cp), 71.2 (CH_2, C_1), 53.4 (CH_2, butyl), 51.0 (CH_3, $-OCH_3$), 48.7 (CH_3, N−CH_3), 35.4 (CH_2, butyl), 26.5 (CH_2, C_2), 19.8 (CH_2, butyl), 13.8 (CH_3, butyl), −0.8 (CH_2, Re−CH_2R).

Preparation of {[η^5:η^1-$C_5H_4CH_2CH_2NH(CH_3)$]Re(CO)($CH_2CO_2CH_3$)(*n*-$BuNH_2$)}$^+$$PF_6^-$ (6b). To a stirred solution of **5** (182 mg, 0.30 mmol) in CH_2Cl_2 (10 mL) was added *n*-butylamine (0.5 mL). After the mixture was stirred at room temperature for 10 min, the solvent was evaporated. The residue was dissolved in CH_2Cl_2 (3 mL), and the resultant solution was added to hexane (50 mL). The yellow powder was collected and washed twice with hexane to give the hygroscopic yellow powder **6b** (187 mg, 97% yield). IR (CH_2Cl_2): 1911 (s), 1672 (m) cm^{-1}. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 6.06−6.04 (1H, m, Cp H), 5.86 (1H, br s, $BuNH_{2a}$), 5.82−5.80 (1H, m, Cp H), 5.42 (1H, br s, N−H), 4.98−4.96 (1H, m, Cp H), 4.67−4.65 (1H, m, Cp H), 4.02 (1H, br s, $BuNH_{2b}$), 3.95−3.89 (1H, m, H_{1a}), 3.69 (3H, s, $-OCH_3$), 3.30−3.10 (2H, m, H_{1b} & $RCH_{2a}NH_2$), 2.99 (3H, d, J = 5.8 Hz, N−CH_3), 3.00−2.90 (1H, m, RCH_{2b}-NH_2), 2.71−2.62 (1H, m, H_{2a}), 2.46 (1H, d, J = 9.6 Hz, Re−CH_{2a}), 2.13−2.07 (1H, m, H_{2b}), 1.85 (1H, d, J = 9.6 Hz, Re−CH_{2b}), 1.79−1.71 (2H, m, butyl), 1.49−1.40 (2H, m, butyl), 0.96 (3H, t, J = 7.2 Hz, butyl). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 209.9 (CO), 184.5 (C, ester), 127.1 (C, Cp), 96.1 (CH, Cp), 95.4 (CH, Cp), 79.6 (CH, Cp), 76.7 (CH, Cp), 71.4 (CH_2, C_1), 54.1 (CH_2, butyl), 51.0 (CH_3, $-OCH_3$), 48.9 (CH_3, N−CH_3), 35.4 (CH_2, butyl), 26.1 (CH_2, C_2), 19.4 (CH_2, butyl), 13.7 (CH_3, butyl), −0.4 (CH_2, Re−CH_2R). Mass spectrum (FAB, ^{187}Re; *m/e* (relative intensity (%)): 483 (28, M^+), 410 (100, $M^+ - C_4H_9NH_2$ and/or

$M^+ - CH_2CO_2CH_3$). Anal. Calcd for $C_{16}H_{28}F_6N_2O_3PRe$: C, 30.62; H, 4.50; N, 4.46. Found: C, 30.31; H, 4.58; N, 4.10.

Genaral Procedure for the Preparation of {[η^5:η^1-$C_5H_4CH_2CH_2NH(CH_3)$]ReH(CO)(R_1R_2NH)}$^+CF_3SO_3^-$ (7a, R_1 = *n*-Butyl, R_2 = H; 7b, R_1 = *tert*-Butyl, R_2 = H; 7c, R_1 = R_2 = Ethyl). A 50 mL flask was charged with the cationic methyl complex **3** (264 mg, 0.5 mmol) followed by CH_2Cl_2 (15 mL) and the corresponding amine (1.5 mL). The resultant solution was stirred at room temperature, and the progress of the reaction was monitored by infrared spectroscopy. After the terminal carbonyl bands of **3** disappeared (0.5−6 h), the solution was evaporated to dryness. The residue was dissolved in CH_2Cl_2 and added to hexane. The precipitates were collected to give the corresponding hydride complexes **7a**−**c**. Analytically pure samples were obained by recrystallization of the individual compounds from dichloromethane and hexane.

{[η^5:η^1-$C_5H_4CH_2CH_2NH(CH_3)$]ReH(CO)(*n*-$BuNH_2$)}$^+CF_3SO_3^-$ (7a): yellow crystal (92% yield). Mp: 119−126 °C. IR (CH_2Cl_2): 1895 (s) cm^{-1}. ^1H NMR ($CDCl_3$, 300 MHz): δ 5.75 (1H, Cp H), 5.57 (1H, Cp H), 5.55 (1H, br s, N−H), 5.23 (1H, Cp H), 4.72 (1H, br s, N−H), 4.35 (1H, Cp H), 3.90−3.84 (1H, m, H_{1a}), 3.82 (1H, br s, N−H), 3.34−3.21 (1H, m, H_{1b}), 3.15−2.93 (2H, m, butyl), 3.02 (3H, d, J = 5.8 Hz, N−CH_3), 2.66 (1H, ddd, J = 14.2, 13.2, 5.6 Hz, H_{2a}), 2.13 (1H, ddd, J = 14.2, 5.6, 4.6 Hz, H_{2b}), 1.69−1.57 (2H, m, butyl), 1.44−1.32 (2H, m, butyl), 0.94 (3H, t, J = 7.3 Hz, butyl), −5.15 (1H, s, Re−H). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 207.6 (CO), 127.8 (C, Cp), 120.2 (q, J_{CF} = 317 Hz, triflate), 91.5 (CH, Cp), 75.9 (CH, Cp), 71.4 (CH, Cp), 70.9 (CH_2, C_1), 69.8 (CH, Cp), 58.7 (CH_2, butyl), 48.1 (CH_3, N−CH_3), 35.1 (CH_2, butyl), 26.7 (CH_2, C_2), 19.5 (CH_2, butyl), 12.6 (CH_3, butyl). Mass spectrum (FAB, ^{187}Re; *m*/*e* (relative intensity (%)): 411 (100, M^+), 338 (35, $M^+ - BuNH_2$). Anal. Calcd for $C_{14}H_{24}F_3N_2O_4ReS$: C, 30.05; H, 4.32; N, 5.00. Found: C, 30.10; H, 4.33; N, 4.91.

{[η^5:η^1-$C_5H_4CH_2CH_2NH(CH_3)$]ReH(CO)(*t*-$BuNH_2$)}$^+CF_3SO_3^-$ (7b): yellow crystal (95% yield). Mp: 170−185 °C dec. IR (CH_2Cl_2): 1898 (s) cm^{-1}. ^1H NMR ($CDCl_3$, 300 MHz): δ 5.77 (1H, Cp H), 5.68 (1H, Cp H), 5.65 (1H, Cp H), 5.40 (1H, br s, N−H), 5.16 (1H, br s, N−H), 4.52 (1H, Cp H), 4.46 (1H, br s, N−H), 3.92−3.84 (1H, m, H_{1a}), 3.68−3.56 (1H, m, H_{1b}), 3.10 (3H, d, J = 5.8 Hz, N−CH_3), 2.50 (1H, ddd, J = 14.2, 10.6, 5.6 Hz, H_{2a}), 2.36 (1H, ddd, J = 14.2, 5.0, 4.4 Hz, H_{2b}), 1.33 (9H, s, *tert*-butyl), −5.11 (1H, s, Re−H). ^{13}C NMR (C_3D_6O, 100 MHz): δ 210.3 (CO), 130.1 (C, Cp), 121.8 (q, J_{CF} = 317 Hz, triflate), 92.4 (CH, Cp), 77.8 (CH, Cp), 73.0 (CH, Cp), 71.9 (CH_2, C_1), 69.9 (CH, Cp), 56.1 (C, *tert*-butyl), 49.0 (CH_3, N−CH_3), 29.8 (CH_3, *tert*-butyl), 27.1 (CH_2, C_2). Anal. Calcd for $C_{14}H_{24}F_3N_2O_4ReS$: C, 30.05; H, 4.32; N, 5.00. Found: C, 29.92; H, 4.28; N, 5.04.

{[η^5:η^1-$C_5H_4CH_2CH_2NH(CH_3)$]ReH(CO)(Et_2NH)}$^+CF_3SO_3^-$ (7c): yellow crystal (85% yield). Mp: 117−119 °C. IR (CH_2Cl_2): 1898 (s) cm^{-1}. ^1H NMR ($CDCl_3$, 300 MHz): δ 5.93 (1H, br s, N−H), 5.49 (1H, Cp H), 5.47 (1H, Cp H), 5.18 (1H, Cp H), 4.62 (1H, br s, N−H), 4.42 (1H, Cp H), 3.95−3.88 (1H, m, H_{1a}), 3.60−3.47 (1H, m, ethyl), 3.47−3.35 (1H, m, ethyl), 3.35−3.22 (1H, m, H_{1b}), 3.19−3.06 (2H, m, ethyl), 3.02 (3H, d, J = 5.7 Hz, N−CH_3), 2.68 (1H, td, J = 13.8, 5.5 Hz, H_{2a}), 2.15 (1H, ddd, J = 13.8, 5.2, 1.6 Hz, H_{2b}), 1.23 (3H, t, J = 7.0 Hz, ethyl), 1.20 (3H, t, J = 7.0 Hz, ethyl), −4.46 (1H, s, Re−H). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 207.3 (CO), 128.0 (C, Cp), 120.1 (q, J_{CF} = 317 Hz, triflate), 92.2 (CH, Cp), 76.8 (CH, Cp), 71.0 (CH_2, C_1), 70.3 (CH, Cp), 69.4 (CH, Cp), 55.6 (CH_2, ethyl), 54.4 (CH_2, ethyl), 48.0 (CH_3, N−CH_3), 26.6 (CH_2, C_2), 12.9 (CH_2, ethyl), 12.4 (CH_3, ethyl). Mass spectrum (FAB, ^{187}Re; *m*/*e* (relative intensity (%)): 411 (100, M^+), 338 (40, $M^+ - Et_2NH$). Anal. Calcd for $C_{14}H_{24}F_3N_2O_4ReS$: C, 30.05; H, 4.32; N, 5.00. Found: C, 29.89; H, 4.17; N, 4.87.

Reaction of 3 with Ammonia. Preparation of {[η^5:η^1-$C_5H_4CH_2CH_2NH(CH_3)$]ReH(CO)(NH_3)}$^+CF_3SO_3^-$ (7d). A 50 mL flask was charged with complex **3** (132 mg, 0.25 mmol) and dioxane (10 mL). Ammonia gas was bubbled through the resultant solution for 5 min, and then the solution was kept under an atmosphere of ammonia at room temperature. The progress of the reaction was monitored by ^1H NMR spectroscopy. Two compounds, **7d** and **9**, were observed. Complex **9** is not stable at room temperature and gradually converted to **7d** in the reaction media. After it was stirred for 20 h, the solution was evaporated to dryness. The residue was dissolved in CH_2Cl_2 and the solution filtered through Celite into a hexane solution to produce oily precipitates. The solvents were decanted, and the oil was dried under vacuum overnight to remove acetamide. The residual yellow oil **7d** (95 mg, 75% yield) was 95% pure, as ascertained by its ^1H NMR spectrum. Unfortunately, we have been unable to obtain an analytically pure sample of **7d**. The spectroscopic properties of **7d** are as follows. IR (CH_2Cl_2): 1900 cm^{-1}. ^1H NMR ($CDCl_3$, 300 MHz): δ 5.73 (1H, Cp H), 5.63 (1H, Cp H), 5.28 (1H, Cp H), 5.15 (1H, br, N−H), 4.35 (1H, Cp H), 3.84 (4H, br, NH_3 & H_{1a}), 3.40−3.27 (1H, m, H_{1b}), 3.04 (3H, d, J = 5.8 Hz, N−CH_3), 2.59 (1H, ddd, J = 14.2, 12.5, 5.5 Hz, H_{2a}), 2.16 (1H, ddd, J = 14.2, 5.2, 1.8 Hz, H_{2b}), −5.35 (1H, s, Re−H). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 207.9 (CO), 127.8 (C, Cp), 121.2 (q, J_{CF} = 317 Hz, triflate), 92.2 (CH, Cp), 76.1 (CH, Cp), 71.9 (CH, Cp), 70.9 (CH_2, C_1), 69.8 (CH, Cp), 48.1 (CH_3, N−CH_3), 26.6 (CH_2, C_2). Mass spectrum (FAB, ^{187}Re; *m*/*e* (relative intensity (%)): 355 (100, M^+), 338 (25, $M^+ - NH_3$).

Reaction of 3 with Ammonium Hydroxide. Preparation of [η^5:η^1-$C_5H_4CH_2CH_2NH(CH_3)$]ReH(CO)($NHCOCH_3$) (9). To a solution of **3** (253 mg, 0.48 mmol) in CH_2Cl_2 (60 mL) at 0 °C was added a solution of ammonia in water (10 mL, 32%). The resultant mixture was stirred vigorously at 0 °C for 2 h. The CH_2Cl_2 layer was then filtered through a pad of anhydrous $MgSO_4$. After concentration, ^1H NMR of the crude product showed a mixture of three compounds, **7d**, **9**, and **10**, in a ratio of 3:80:17. The mixture was dissolved in CH_2Cl_2 (2 mL). Hexane (6 mL) was added. Compound **7d**, which precipitates, was removed by filtration. The filtrate was concentrated to give a mixture of **9** and **10** (165 mg, 87% yield). Pure **9** (61 mg, 32% yield) as orange crystals was obtained by recrystallization of the mixture from CH_2Cl_2 and hexane in a refrigerator and exhibited the following properties. Mp: 121−124 °C dec. IR (CH_2Cl_2): 1865 (s), 1569 (w) cm^{-1}. ^1H NMR ($CDCl_3$, 300 MHz): δ 8.02 (1H, br s, N−H), 6.09 (1H, br s, N−H, acetamido), 5.82 (1H, Cp H), 5.44 (1H, Cp H), 5.31 (1H, Cp H), 4.27 (1H, Cp H), 3.59−3.52 (1H, m, H_{1a}), 3.17−3.00 (1H, m, H_{1b}), 2.85 (3H, d, J = 5.8 Hz, N−CH_3), 2.63 (1H, td, J = 13.7, 5.5 Hz, H_{2a}), 2.10 (3H, s, acetamide), 2.05 (1H, dd, J = 13.7, 5.3 Hz, H_{2b}), −4.98 (1H, s, Re−H). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 214.1 (CO), 178.0 (C, amide), 126.7 (C, Cp), 92.0 (CH, Cp), 75.8 (CH, Cp), 72.3 (CH, Cp), 70.6 (CH, Cp), 68.6 (CH_2, C_1), 46.2 (CH_3, N−CH_3), 26.7 (CH_2, C_2), 26.3 (CH_3, amide). Anal. Calcd for $C_{11}H_{17}N_2O_2Re$: C, 33.41; H, 4.33; N, 7.08. Found: C, 33.36; H, 4.17; N, 6.86.

Reaction of 3 with Aqueous Sodium Carbonate. Preparation of [η^5:η^1-$C_5H_4CH_2CH_2NH(CH_3)$]ReH(CO)(OAc) (10). To a solution of **3** (223 mg, 0.42 mmol) in CH_3OH (20 mL) at 30 °C was added a saturated Na_2CO_3 aqueous solution (5 mL). After the mixture was stirred at 30 °C for 2 h, methanol and water were evaporated to dryness. The residue was extracted with CH_2Cl_2 and flash-chromatographed on aluminum oxide (activity V, 1.5 cm × 10 cm), using 2% of CH_3OH in ethyl acetate as the eluent. The yellow band was collected and concentrated to give 82 mg (49% yield) of **10** as a yellow liquid. IR (CH_2Cl_2): 1873 (s), 1587 (m) cm^{-1}. ^1H NMR ($CDCl_3$, 300 MHz): δ 6.25 (1H, br, N−H), 5.74 (1H, Cp H), 5.67 (1H, Cp H), 5.15 (1H, Cp H), 4.30 (1H, Cp H), 3.68−3.61 (1H, m, H_{1a}), 3.30−3.16 (1H, m, H_{1b}), 3.01 (3H, d, J = 5.9 Hz, N−CH_3), 2.58 (1H, ddd, J = 14.0, 12.8, 5.6 Hz, H_{2a}), 2.15 (1H, ddd, J = 14.0, 5.3, 1.6 Hz, H_{2b}), 2.12 (3H, s, OAc), −3.01 (1H, s, Re−H). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 211.3 (CO), 180.2 (C, OAc), 125.5 (C, Cp), 94.1 (CH, Cp), 76.9 (CH, Cp), 69.9 (CH, Cp), 68.3 (CH, Cp), 67.8 (CH_2, C_1), 46.1 (CH_3, N−CH_3), 26.8 (CH_2, C_2), 23.2

(CH_3, OAc). Anal. Calcd for $C_{11}H_{16}NO_3Re$: C, 33.32; H, 4.07; N, 3.53. Found: C, 33.15; H, 4.21; N, 3.42.

Reaction of 2 and 3 with Hydrazine. Preparation of [η^5:η^1-$C_5H_4CH_2CH_2NH(CH_3)$]Re(CO)(NCO)(R) (12a,b; R = $CH_2CO_2CH_3$, CH_3). To a solution of complex **2** or **3** (0.5 mmol) in CH_2Cl_2 (30 mL) at 0 °C was added hydrazine monohydrate (1 mL). The mixture was stirred vigorously for 1 h. The CH_2Cl_2 layer was passed through a pad of anhydrous $MgSO_4$. The solution was concentrated to about 10 mL. Hexane (60 mL) was added to effect precipitation. The orange powders were collected and washed twice with hexane to give **12a** and **12b**, respectively. Analytically pure samples were obtained by recrystallization of the individual complex from dichloromethane and hexane.

[η^5:η^1-$C_5H_4CH_2CH_2NH(CH_3)$]Re(CO)(NCO)($CH_2CO_2CH_3$) (12a): orange crystal (95% yield). Mp: 195−197 °C dec. IR (CH_2Cl_2): 2238 (s), 1892 (s) cm^{-1}. ^1H NMR [$(CD_3)_2CO$, 300 MHz]: δ 6.01 (1H, Cp H), 5.89 (1H, Cp H), 5.48 (1H, Cp H), 5.16 (1H, br, N−H), 4.51 (1H, Cp H), 3.87−3.79 (1H, m, H_{1a}), 3.59−3.50 (1H, m, H_{1b}), 3.47 (3H, s, OCH_3), 2.99 (1H, d, J = 8.8 Hz, Re−CH_{2a}), 2.99 (3H, d, J = 6.0 Hz, N−CH_3), 2.53 (1H, d, J = 8.8 Hz, Re−CH_{2b}), 2.40 (1H, ddd, J = 13.7, 9.5, 5.8 Hz, H_{2a}), 2.28 (1H, dt, J = 13.7, 5.2 Hz, H_{2b}). ^{13}C NMR [$(CD_3)_2CO$, 75 MHz]: δ 217.6 (CO), 181.5 (C, ester), 128.2 (C, Cp), 100.7 (CH, Cp), 97.5 (CH, Cp), 79.5 (CH, Cp), 78.0 (CH, Cp), 70.8 (CH_2, C_1), 50.3 (CH_3), 47.5 (CH_3), 26.6 (CH_2, C_2), 2.0 (CH_2, Re−CH_2). The isocyanate carbon was not observed due to the poor solubility of the sample and limited accumulation time. Anal. Calcd for $C_{13}H_{17}N_2O_4Re$: C, 34.58; H, 3.80; N, 6.20. Found: C, 34.41; H, 3.89; N, 6.37.

[η^5:η^1-$C_5H_4CH_2CH_2NH(CH_3)$]Re(CO)(NCO)(CH_3) (12b): orange crystal (93% yield). Mp: 179−182 °C dec. IR (CH_2Cl_2): 2235 (s), 1874 (s) cm^{-1}. ^1H NMR ($CDCl_3$, 300 MHz): δ 5.61 (1H, Cp H), 5.58 (1H, Cp H), 4.81 (1H, Cp H), 4.54 (1H, Cp H), 4.24 (1H, br, N−H), 3.68−3.59 (1H, m, H_{1a}), 3.29−3.16 (1H, m, H_{1b}), 3.04 (3H, d, J = 5.9 Hz, N−CH_3), 2.28 (1H, ddd, J = 14.2, 10.8, 5.6 Hz, H_{2a}), 2.13 (1H, ddd, J = 14.2, 5.4, 3.8 Hz, H_{2b}), 1.05 (3H, s, Re−CH_3). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 217.2 (CO), 130.5 (NCO), 121.3 (C, Cp), 98.2 (CH, Cp), 94.5 (CH, Cp), 78.1 (CH, Cp), 74.4 (CH, Cp), 68.0 (CH_2, C_1), 47.6 (CH_3, N−CH_3), 26.7 (CH_2, C_2), −14.6 (CH_3, Re−CH_3). Mass spectrum (FAB, ^{187}Re; *m/e* (relative intensity (%)): 394 (22, M^+), 366 (12, M^+ − CO), 154 (100). Anal. Calcd for $C_{11}H_{15}N_2O_2Re$: C, 33.58; H, 3.84; N, 7.12. Found: C, 33.45; H, 3.84; N, 6.90.

Crystal Structure of {[η^5:η^1-$C_5H_4CH_2CH_2NH(CH_3)$]ReH(CO)(*t*-$BuNH_2$)}$^+CF_3SO_3^-$ (7b) and [η^5:η^1-$C_5H_4CH_2CH_2NH(CH_3)$]Re(CO)(NCO)($CH_2CO_2CH_3$) (12a). Single crystals of **7b** and **12a** were obtained from each individual solution of CH_2Cl_2 and hexane at 5 °C. Diffraction measurements were made on an Enraf-Nonius CAD-4 automated diffractometer by use of graphite-monochromated Mo Kα radiation (λ = 0.710 69 Å) with the 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 group *Pcab* for **12a** was 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.[13] The structures were solved by direct methods and refined by a full-matrix least-squares routine[14] 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 2, and selected bond distances and angles are given in Table 1.

Table 2. Crystallographic Data and Structure Refinement Details for 7b and 12a

	7b	12a
formula	$C_{14}H_{24}F_3N_2O_4ReS$	$C_{13}H_{17}N_2O_4Re$
fw	559.61	451.49
cryst size (mm)	0.13 × 0.19 × 0.19	0.19 × 0.25 × 0.31
cryst syst	triclinic	orthorhombic
space group	$P\bar{1}$	*Pcab*
a (Å)	9.4094(15)	11.0812(13)
b (Å)	10.1445(16)	15.0577(18)
c (Å)	11.6322(18)	16.6725(19)
α (deg)	81.700(13)	90
β (deg)	67.406(12)	90
γ (deg)	68.828(13)	90
V (Å^3)	955.9(3)	2781.9(6)
Z	2	8
D_c (g cm^{-3})	1.944	2.156
F(000)	542	1719
λ(Mo Kα) (Å)	0.710 69	0.710 69
μ(Mo Kα) (cm^{-1})	65.941	88.684
transmissn	0.777; 1.000	0.549; 1.000
scan speed (deg min^{-1})	2.06−8.24	2.06−8.24
$\theta/2\theta$ scan width (deg)	2(0.90 + 0.35 tan θ)	2(0.70 + 0.35 tan θ)
$2\theta_{max}$ (deg)	50.0	50.0
unit cell detn: no.; 2θ range (deg)	25; 15.09−33.86	25; 15.05−33.31
hkl range	0−11, 0−12, 0−13	0−13, 0−17, 0−19
no. of collected rflns	1498	2436
no. of unique reflns	1498	2436
no. of obsd reflns ($I > 2.0\sigma(I)$)	1285	1769
no. of refined params	226	182
R_F;[a] R_w[b]	0.027; 0.030	0.023, 0.026
GOF	1.41	1.18
weight modifier *k* in kF_o^2	0.000 100	0.000 100
$\Delta\rho$(max; min) (e Å^{-3})	+0.680; −0.570	+0.900; −0.920

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

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

Supporting Information Available: Tables of bond lengths and bond angles, fractional atomic coordinates, and anisotropic thermal parameters for **7b** and **12a**. This material is available free of charge via the Internet at http://pubs.acs.org.

OM980998V

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

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