Half-Sandwich Aminorhenium Complexes: Preparation and Regioselective N-*versus* Re-Alkylations

Tein-Fu Wang,* Ching-Yih Lai, Chong-Chen Hwu, and Yuh-Sheng Wen

Institute of Chemistry, Academia Sinica, Taipei, Taiwan

Received November 19, 1996[⊗]

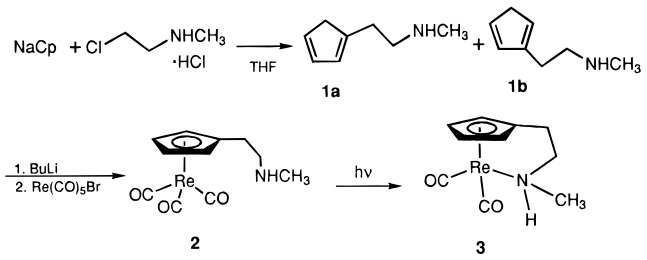
The aminorhenium complex $(CO)_2ReNH(CH_3)CH_2CH_2(\eta^5\text{-}C_5H_4)$ (**3**), in which the ligating amino group is connected to the cyclopentadienyl ligand, was prepared by irradiation of $(\eta^5\text{-}C_5H_4CH_2CH_2NHCH_3)Re(CO)_3$ (**2**) in THF. Alkylation of the corresponding anion $[(CO)_2ReN(CH_3)CH_2CH_2(\eta^5\text{-}C_5H_4)]^-Li^+$ (**4**) as well as the neutral aminorhenium complex **3** with a variety of electrophiles has been studied. The anion **4** reacted with electrophiles, such as CH_3I, $CH_2{=}CHCH_2Br$, $C_6H_5CH_2Br$, and $HC{\equiv}CCH_2Br$, at the nitrogen center to provide $(CO)_2ReNR(CH_3)CH_2CH_2(\eta^5\text{-}C_5H_4)$ (**5a**−**d**). However, **4** reacted with electrophiles having a carbonyl group or a nitrile group next to the electrophilic carbon, such as $BrCH_2CO_2CH_3$, $BrCH_2CO_2C_2H_5$, and $BrCH_2CN$, to give rhenium alkylation compounds $[(CO)_2(R)ReNH(CH_3)CH_2CH_2(\eta^5\text{-}C_5H_4)]^+Br^-$ (**7e**−**g**) after protonation. The neutral aminorhenium complex **3** reacted with the electrophiles mentioned above to provide exclusive Re-alkylation compounds **7a**−**g**. The structure of the tetraphenylborate salt of **7c**, $[(CO)_2(C_6H_5CH_2)ReNH(CH_3)CH_2CH_2(\eta^5\text{-}C_5H_4)]^+BPh_4^-$ (**8**), has been determined by X-ray diffraction.

Introduction

Transition-metal complexes with an amino group tethered to the cyclopentadienyl ligand have attracted attention recently.[1] Most of the investigations have concentrated on the early-transition-metal compounds for application as metallocene catalysts in olefin polymerization.[2] There has not been much study on the middle-[3] and late-transition-metal[4] compounds. Strong σ donation of the amino ligand to the low-valent transition metals may make the metal center electron-rich, thereby enhancing the ability of the metal to undergo nucleophilic reactions. This property is quite interesting. Therefore, we wish to explore some of their chemistry. Here, we report our results on the synthesis and alkylation reactions of aminorhenium complexes.

Deprotonation of an aminorhenium complex such as **3** provides the anion **4**. Nucleophilic reaction of **4** with an electrophile may occur at either rhenium or nitrogen. The behavior resembles the C- versus O-alkylation of an enolate anion.[5] The site of alkylation depends on the nature of the alkylating agent. However, reaction of the neutral aminorhenium complex **3** gives exclusive Re selectivity. The details are reported as follows.

Scheme 1



Results and Discussion

A. Synthesis of Aminorhenium Complex 3. Addition of an excess of NaCp to $ClCH_2CH_2NHCH_3{\cdot}HCl$ in THF provides a useful route to the substituted-cyclopentadienyl compound $C_5H_5CH_2CH_2NHCH_3$ (**1**), which was obtained as a 1:1 mixture of the double-bond isomers **1a** and **1b**.[2c,3c] Subsequent deprotonation with *n*-BuLi gave a homogeneous cyclopentadienyl anion. Reaction of the anion with $Re(CO)_5Br$ in refluxing THF provided the half-sandwich rhenium tricarbonyl **2** (see Scheme 1) in 82% yield as a pale yellow oil after column chromatography and vacuum distillation. When stored in a freezer, **2** became a waxy solid. The terminal carbonyl stretchings of **2** appeared at 2021 and 1926 cm^{-1} as a strong and a broad strong bands, respectively, in the infrared spectra, similar to those for the unsubstituted $CpRe(CO)_3$. The methylamino group appeared at δ 2.44, as is usual for amines, in the ^1H NMR spectra.

Irradiation of a THF solution of **2** at 0 °C gave **3** as a yellow powder in 64% yield. Presumably, carbon monoxide was extruded upon irradiation followed by intramolecular amino group coordination; alternatively,

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

(1) For a brief review on functionalized cyclopentadienyl ligands, see: Okuda, J. *Comments Inorg. Chem.* **1994**, 16, 185.

(2) (a) Shapiro, P. J.; Bunel, E.; Schaefer, W. P.; Bercaw, J. E. *Organometallics* **1990**, 9, 867. (b) Shapiro, P. J.; Cotter, W. D.; Schaefer, W. P.; Labinger, J. A.; Bercaw, J. E. *J. Am. Chem. Soc.* **1994**, *116*, 4623. (c) Hughes, A. K.; Meetsma, A.; Teuben, J. H. *Organometallics* **1993**, *12*, 1936. (d) Okuda, J.; Schattenmann, F. J.; Wocadlo, S.; Massa, W. *Organometallics* **1995**, *14*, 789. (e) Flores, J. C.; Chien, J. C. W.; Rousch, M. D. *Organometallics* **1994**, *13*, 4140, (f) Jutzi, P.; Kleimeier, J. *J. Organomet. Chem.* **1995**, *486*, 287. (g) Herrmann, W. A.; Morawietz, M. J. A.; Priermeier, T.; Mashima, K. *J. Organomet. Chem.* **1995**, *486*, 291. (h) Herrmann, W. A.; Anwander, R.; Munck, F. C.; Scherer, W. *Chem. Ber.* **1993**, *126*, 331. (i) van der Hende, J. R.; Hitchcock, P. B.; Lappert, M. F.; Nile, T. A. *J. Organomet. Chem.* **1994**, *472*, 79.

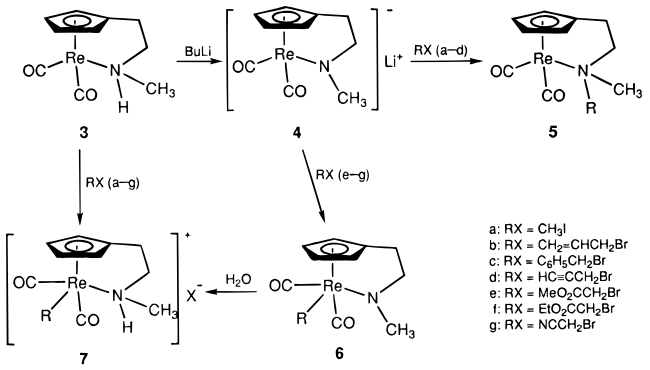
(3) (a) Wang, T. F.; Lee, T. Y.; Wen, Y. S.; Liu, L. K. *J. Organomet. Chem.* **1991**, *403*, 353. (b) Wang, T. F.; Wen, Y. S. *J. Organomet. Chem.* **1992**, *439*, 155. (c) Wang, T. F.; Lee, T. Y.; Chou, J. W.; Ong, C. W. *J. Organomet. Chem.* **1992**, *423*, 31.

(4) (a) Jutzi, P.; Kristen, M. O.; Dahlhaus, J.; Neumann, B.; Stammler, H. G. *Organometallics* **1993**, *12*, 2980. (b) Jutzi, P.; Dahlhaus, J.; Kristen, M. O. *J. Organomet. Chem.* **1993**, *450*, C1.

(5) Carey, F. A.; Sundberg, R. J. *Advanced Organic Chemistry, Part B: Reactions and Synthesis,* 3rd ed.; Plenum Press: New York, 1990; pp 23−27.

S0276-7333(96)00980-6 CCC: $14.00

Scheme 2



THF might fill the vacant site first[6] followed by pendant amino group substitution to give **3**. The terminal carbonyl stretchings of **3** appeared at 1893 and 1816 cm^{-1}, much lower frequencies than those for $CpRe(CO)_2L$ compounds (L = THF,[6] N_2,[7] carbene,[8] alkyne,[9] and thiophene[10]). This indicates that the Re to CO π^* back-bonding for the aminorhenium complex **3** is much stronger than that of the other complexes with ligands other than the amino group. The amino group ligation is further suggested by the downfield shift (0.71 ppm) of the *N*-methyl resonance in the ^1H NMR spectrum. Due to vicinal coupling with the N−H proton, the *N*-methyl appeared at δ 3.15 as a doublet (J = 6 Hz). The N−H proton appeared at δ 4.46 as a broad signal and remained unchanged after shaking with D_2O. Yellow powders of **3** could be stored under air in a refrigerator for several months without noticeable decomposition. In solution, however, minor decomposition was observed after 24 h at room temperature in air.

B. Reaction of the Anion 4: Re- ***versus*** **N-Alkylations.** Although the N−H proton of **3** does not exchange with D_2O, it could be removed by *n*-BuLi to give the anion **4**, which showed characteristic low CO stretching frequencies at 1836 and 1708 cm^{-1}. Treatment of **4** with CH_3I gave the *N*,*N*-dimethyl complex **5a** (see Scheme 2) in 72% yield. Having a plane of symmetry, **5a** showed quite simple ^1H and ^{13}C NMR spectra. **5a** has been obtained previously by irradiation of the dimethylamino compound $[\eta^5\text{-}C_5H_4CH_2CH_2N(CH_3)_2]Re(CO)_3$ in THF.[11] Reaction of the anion **4** with other electrophiles, such as $CH_2{=}CHCH_2Br$, $C_6H_5CH_2Br$, and $HC{\equiv}CCH_2Br$, also provided exclusive N-alkylation compounds (**5b**−**d**) in comparable yields (67−78%). The spectroscopic properties (IR, ^1H and ^{13}C NMR) of **5b**−**d** are not much different from those of **3**. The terminal carbonyl stretchings were evident around 1898 (±4) cm^{-1} and 1822 (±5) cm^{-1}. In the ^1H NMR spectra, cyclopentadienyl protons appeared between δ 5.27 and 4.85 for compounds **5a**−**d**.

When the anion **4** was allowed to react with electrophiles having a carbonyl or a nitrile group next to the electrophilic carbon, such as $BrCH_2CO_2CH_3$, $BrCH_2CO_2C_2H_5$, and $BrCH_2CN$, alkylation occurred exclusively at rhenium to give **6e**−**g**, respectively. Because they are very sensitive to moisture, **6e**−**g** are protonated upon exposure to moisture. Therefore, a small amount of water was added after alkylation to provide cationic **7e**−**g** (see Scheme 2), respectively, in 62−98% yield. The neutral amido intermediates **6e**−**g** could be observed in the infrared spectra, which displayed low terminal carbonyl stretchings at 1896 and 1824 cm^{-1}. The carbonyl stretchings of **7e**−**g** appeared at much higher frequencies, around 2052 (±3) and 1980 (±5) cm^{-1}. In the ^1H NMR spectra, all four Cp protons of compounds **7e**−**g** split into four different resonances, and one of the resonances appeared below δ 7.00. Due to the vicinal coupling with the N−H proton, the *N*-methyl group appeared at δ 2.93 (±0.02) as a doublet (J = 5.7 Hz). However, unlike **3**, the signal of the N−H proton (δ 9.49−9.04) disappeared upon shaking with D_2O.

The effect of alkylating agent on the site selectivity can be rationalized by use of the hard−soft acid−base principle.[12] The alkylating agents CH_3I, $CH_2{=}CHCH_2Br$, $C_6H_5CH_2Br$, and $HC{\equiv}CCH_2Br$ favor the N-alkylation complex **5**, while the "softer" alkylating agents $BrCH_2CO_2CH_3$, $BrCH_2CO_2C_2H_5$, and $BrCH_2CN$ choose the "softer" rhenium as the reaction site to provide exclusively the Re-alkylation complex **7**. Cationic complexes **7e**−**g** could also be obtained by direct reaction of **3** with the corresponding alkylating agents and will be discussed in the following section.

C. Reaction of the Neutral Aminorhenium Complex 3 with Electrophiles: Exclusive Re-Alkylations. As described previously, the ligated amino group could be making the rhenium center much more electron rich, thereby enhancing the ability of the metal to react with electrophiles. Indeed, the neutral aminorhenium complex **3** is reactive enough toward electrophiles. For example, **3** reacted with CH_3I without addition of a solvent gave exclusively the Re-alkylation compound **7a** in 97% yield. The addition product could be easily characterized by the terminal CO stretchings. High CO stretching frequencies appearing at 2040 and 1971 cm^{-1} for the reaction product suggest that the cationic Re-alkylation compound **7a** was obtained instead of the neutral N-alkylation compound **5a**. Similarly, reaction of **3** with electrophiles such as $CH_2{=}CHCH_2Br$, $C_6H_5CH_2Br$, $HC{\equiv}CCH_2Br$, $BrCH_2CO_2CH_3$, $BrCH_2CO_2C_2H_5$, and $BrCH_2CN$, also provided exclusive Re-alkylation compounds **7b**−**g** in good yields (74 − 98%). None of the N-alkylation compounds were observed. Because the N−H is tightly bonded in complex **3**, the nitrogen is now fully substituted and has no room for accepting an electrophile. This may be the rationale for the observation of exclusive Re selectivity. A total of three isomers, one trans and two cis, is possible for the Re-alkylation reactions. However, only one isomer was obtained. The rhenium tricarbonyl complex $CpRe(CO)_3$ does not show similar reactivity. When it was treated with the reagents mentioned above, only $CpRe(CO)_3$ was recovered.

(6) Barrientos-Penna, C. F.; Einstein, F. W. B.; Jones, T.; Sutton, D. *Inorg. Chem.* **1982**, *21*, 2578.
(7) (a) Einstein, F. W. B.; Klahn-Oliva, A. H.; Sutton, D.; Tyers, K. G. *Organometallics* **1986**, 5, 53. (b) Sellmann, D. *J. Organomet. Chem.* **1972**, *36*, C27.
(8) (a) Casey, C. P.; Vosejpka, P. C.; Askham, F. R. *J. Am. Chem. Soc.* **1990**, *112*, 3713. (b) Casey, C. P.; Czerwinki, C. J.; Hayashi, R. K. *J. Am. Chem. Soc.* **1995**, *117*, 4189.
(9) (a) Einstein, F. W. B.; Tyers, K. G.; Sutton, D. *Organometallics* **1985**, *4*, 489. (b) Casey, C. P.; Yi, C. S. *J. Am. Chem. Soc.* **1992**, *114*, 6597.
(10) Choi, M. G.; Angelici, R. J. *J. Am. Chem. Soc.* **1989**, *111*, 8753.
(11) Wang, T. F.; Juang, J. P.; Lin, K. J. *Bull. Inst. Chem., Acad. Sin.* **1995**, *42*, 41.
(12) (a) Pearson, R. G. *J. Am. Chem. Soc.* **1963**, *85*, 3533. (b) Pearson, R. G. *J. Chem. Educ.* **1968**, *45*, 581. (c) Pearson, R. G. *J. Chem. Educ.* **1968**, *45*, 643. (d) Pearson, R. G.; Songstad, J. *J. Am. Chem. Soc.* **1967**, *39*, 1827. (e) Ho, T. L. *Tetrahedron* **1985**, *41*, 3.

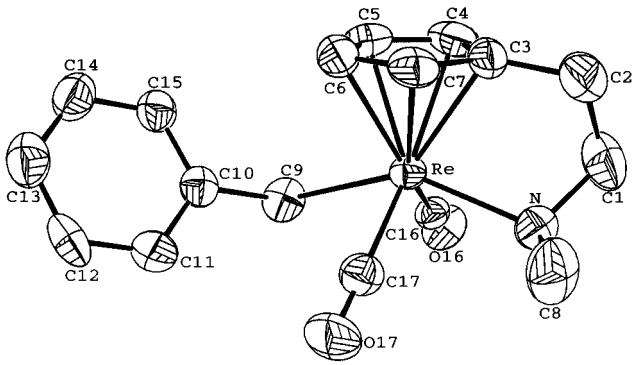


Figure 1. ORTEP drawing of **8**. BPh_4^- is omitted for simplicity.

Treatment of **7c** with sodium tetraphenylborate in methanol provided the anion-exchanged compound **8**. The structure of **8** was determined unambiguously by an X-ray diffraction study. Crystals of **8** were obtained by slow diffusion of a CH_2Cl_2 solution of **8** into hexane. Figure 1 shows that the benzyl group is trans to the amino group with an angle of 144.6° (N−Re−C(9)). The trans terminal CO groups have an angle of 103.2° (C(16)−Re−C(17)), much smaller than that of N−Re−C(9). These angles are close to the 138.9° value for the angle methyl carbon−Re−acyl carbon and 101.2° for the angle CO carbon−Re−CO′ carbon seen in the untethered four-legged piano-stool complex *trans*-$CpRe(CO)_2(COCH_3)(CH_3)$.[13] The alkyl tether of **8** is bent down 6.7° from the cyclopentadienyl ring toward rhenium (C(2)−C(3)−Cp(centroid) = 173.3°). This angle is smaller than that of the tethered methoxycarbene complex $(CO)_2Re{=}C(OCH_3)CH_2CH_2(\eta^5\text{-}C_5H_4)$,[8b] in which the alkyl tether is bent down 9°. This may suggest that the strain introduced by tethering a ligand to the cyclopentadienyl ligand is smaller for a tethered four-legged piano-stool complex, such as **8**, than that of the tethered three-legged piano stool complex, such as $(CO)_2Re{=}C(OCH_3)CH_2CH_2(\eta^5\text{-}C_5H_4)$.

Conclusion

We have demonstrated that a stable aminorhenium complex could easily be prepared when the amino group was tethered to the cyclopentadienyl ligand. The amino ligand is an important element for promoting the rhenium complex reactivity toward carbon electrophiles. Alkylation of the neutral aminorhenium complex **3** gives exclusive Re selectivities. The resulting cationic complex **7** provides, further opportunity for studying the reactivity of half-sandwich rhenium complexes, such as ligand exchanges, electrophilic reactions, and others. Alkylation of the anionic **4** with electrophiles provides either Re- or N-alkylation complexes. The regioselectivity is dependent on the nature of the electrophiles and can be explained by use of the hard−soft acid−base principle.[12]

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 (200 or 300 MHz) and ^{13}C NMR (50 or 75 MHz) were obtained with Bruker AC-200 FT and AC-300 FT spectrophotometers. For the assignment of ^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 $C_5H_5CH_2CH_2NHCH_3$ (1). A THF solution of sodium cyclopentadienide (2 M, 190 mL, 0.38 mol) was added to a stirred suspension of 2-(methylamino)ethyl chloride hydrochloride (19.5 g, 0.15 mol) in THF (100 mL) and HMPA (45 mL) at 0 °C over 20 min. The resulting mixture was heated under reflux for 4 h. The resulting brown solution was concentrated under water aspirator pressure. To the residue was added water (500 mL), which was then extracted twice with pentane (800 mL). The pentane layer was washed once with water and then concentrated under water aspirator pressure. The residue was then distilled (Kugelrohr), using a dry ice cooling device, at 0.5 Torr and 40 °C. Colorless distillates were collected to give 10.3 g of **1** (55% yield) as a 1:1 mixture of double-bond isomers. ^1H NMR ($CDCl_3$, 200 MHz): δ 6.45−6.07 (3H, m), 2.97−2.87 (2H, m), 2.82−2.73 (2H, m), 2.64−2.57 (2H, m), 2.44 (3H, s).

The cyclopentadiene species **1** (10.3 g, 83.6 mmol) was dissolved in THF (104 mL). The solution was cooled in an ice−water bath. A hexane solution of *n*-BuLi (1.6 M, 53 mL) was then added over a period of 40 min. The resulting suspension was 0.5 M $(C_5H_4CH_2CH_2NHCH_3)^-Li^+$ and was ready for the next reaction.

Preparation of $(\eta^5\text{-}C_5H_4CH_2CH_2NHCH_3)Re(CO)_3$ (2). A suspension of $(C_5H_4CH_2CH_2NHCH_3)^-Li^+$ in THF (0.5 M, 45 mL) was added to a stirred suspension of $Re(CO)_5Br$ (7.98 g, 19.65 mmol) in THF (100 mL) at room temperature. The resulting orange solution was then heated under reflux for 20 h. The resulting brown solution was concentrated. The residue was then chromatographed on neutral aluminum oxide (activity V). The nonpolar fraction, possibly rhenium carbonyl, was removed by using 5% ethyl acetate in hexanes. The desired yellow band was collected by eluting with 100% ethyl acetate. The yellow liquid that remained after solvents were removed was distilled (Kugelrohr) at 0.5 Torr. A fraction boiling at 130−140 °C was collected to give 6.326 g of **2** (82% yield) as a pale yellow liquid at room temperature: mp 10.5 °C. IR (CH_2Cl_2): 2021 (s), 1926 (br s) cm^{-1}. ^1H NMR ($CDCl_3$, 300 MHz): δ 5.30 (2H, t, J = 2.0 Hz, Cp H), 5.24 (2H, t, J = 2.0 Hz, Cp H), 2.72 (2H, t, J = 6.8 Hz), 2.57 (2H, t, J = 6.8 Hz), 2.44 (3H, s). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 194.2 (CO × 3), 108.5 (C, Cp), 83.6 (CH × 2, Cp), 83.4 (CH × 2, Cp), 53.5 (CH_2), 36.2 (CH_3), 28.4 (CH_2). Anal. Calcd for $C_{11}H_{12}NO_3Re$: C, 33.67; H, 3.08; N, 3.57. Found: C, 33.42; H, 3.35; N, 3.82.

Preparation of $(CO)_2ReNH(CH_3)CH_2CH_2(\eta^5\text{-}C_5H_4)$ (3). Complex **2** (6.326 g, 16.12 mmol) was placed in a cylindrical borosilicate reaction vessel. THF (500 mL) was added. The vessel containing the pale yellow solution was evacuated and flushed with argon. Argon was then kept flowing during the course of the reaction. The reaction vessel was immersed in an ice−water bath. An irradiation source (Hanovia 450 W medium-pressure Hg lamp) with a quartz filter was placed in the middle of the reaction vessel. The reaction was monitored by examining the carbonyl absorption in the infrared spectra. After 2 h, about 30% of **2** remained unreacted. Prolonged irradiation resulted in formation of side products. Therefore, the reaction was terminated at this point and the resulting yellow-brown solution was concentrated. The residue was then flash-chromatographed on silica gel, with 50% ethyl acetate in hexanes as eluent followed by 100% ethyl acetate. The first

(13) Goldberg, K. I.; Bergman, R. G. *J. Am. Chem. Soc.* **1989**, *111*, 1285.

yellow band was collected and concentrated to give 3.78 g of **3** (64% yield) as a yellow powder: mp 110 °C (dec). IR (CH_2Cl_2): 1893 (s), 1816 (s) cm^{-1}. ^1H NMR ($CDCl_3$, 300 MHz): δ 5.28−5.26 (1H, m, Cp H), 5.23−5.21 (1H, m, Cp H), 5.05−5.03 (1H, m, Cp H), 4.88−4.86 (1H, m, Cp H), 4.46 (1H, br, −NH), 3.69−3.61 (1H, m), 3.15 (3H, d, J = 6.0 Hz), 3.19−3.07 (1H, m), 2.15 (1H, dt, J = 14.4, 4.7 Hz), 1.98 (1H, ddd, J = 14.4, 10.4, 5.3 Hz). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 205.3 (CO), 205.1 (CO), 121.4 (C, Cp), 81.2 (CH, Cp), 78.0 (CH, Cp), 76.6 (CH, Cp), 74.0 (CH, Cp), 72.8 (CH_2), 52.4 (CH_3), 26.0 (CH_2). Mass spectrum (FAB, ^{187}Re; *m/e* (relative intensity (%)): 365 (100, M^+). Anal. Calcd for $C_{10}H_{12}NO_2Re$: C, 32.96; H, 3.32; N, 3.84. Found: C, 32.69; H, 3.41; N, 3.57.

General Procedure for the Preparation of $(CO)_2ReNR(CH_3)CH_2CH_2(\eta^5\text{-}C_5H_4)$ (5a−d; R = Methyl, Allyl, Benzyl, Propargyl). Over a period of 3 min, a hexane solution of *n*-BuLi (1.6 M, 0.75 mL, 1.2 mmol) was added to a stirred solution of **3** (365 mg, 1.0 mmol) in THF (15 mL) at −78 °C. After the mixture was stirred for an additional 10 min, an electrophile (CH_3I, $CH_2{=}CHCH_2Br$, $C_6H_5CH_2Br$, or $HC{\equiv}CCH_2Br$; 2−3 mmol) was added. After another 5 min of stirring, the cool bath was removed and the solution was stirred at room temperature for 20−30 min. The resulting yellow-brown solution was concentrated and flash-column-chromatographed on silica gel (230−400 mesh) upon elution with 10−30% EtOAc in hexanes. The first yellow band was collected and concentrated to provide the desired product in 67−78% yield.

$(CO)_2ReN(CH_3)_2CH_2CH_2(\eta^5\text{-}C_5H_4)$ (5a): pale yellow crystal (72% yield). Mp: 195 °C dec. This compound has been reported previously.[11]

$(CO)_2ReN(CH_3)(CH_2CH{=}CH_2)CH_2CH_2(\eta^5\text{-}C_5H_4)$ (5b): yellow crystal (78% yield). Mp: 86−88 °C. IR (CH_2Cl_2): 1898 (s), 1823 (s) cm^{-1}. ^1H NMR ($CDCl_3$, 300 MHz): δ 6.26−6.13 (1H, m, internal olefinic H), 5.43 (1H, doublets of multiplet, J = 9.9 Hz, terminal olefinic H_c), 5.32 (1H, doublets of multiplet, J = 17 Hz, terminal olefinic H_t), 5.23−5.21 (1H, m, Cp H), 5.17−5.15 (1H, m, Cp H), 4.90−4.87 (1H, m, Cp H), 4.88−4.85 (1H, m, Cp H), 3.86 (1H, dd, J = 12.8, 5.6 Hz, allylic H_a), 3.54 (1H, dd, J = 12.8, 8.2 Hz, allylic H_b), 3.44−3.28 (2H, m, H_1's), 3.07 (3H, s, N−CH_3), 2.35−2.15 (2H, m, H_2's). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 205.5 (CO), 205.0 (CO), 133.6 (CH, internal olefin), 122.1 (CH_2, terminal olefin), 119.6 (C, Cp), 82.0 (CH, Cp), 78.8 (CH_2, C_1), 78.2 (CH, Cp), 75.9 (CH_2, Re−CH_2), 75.7 (CH, Cp), 73.9 (CH, Cp), 58.9 (CH_3), 24.7 (CH_2, C_2). Mass spectrum (FAB, ^{187}Re; *m/e* (relative intensity (%)): 406 (80, $M^+ + 1$), 404 (100), 377 (86, $M^+ - CO$), 362 (16, $M^+ - CO - CH_3$), 349 (68, $M^+ - 2CO$), 334 (20, $M^+ - 2CO - CH_3$). Anal. Calcd for $C_{13}H_{16}NO_2Re$: C, 38.60; H, 3.99; N, 3.46. Found: C, 38.72; H, 4.15; N, 3.13.

$(CO)_2ReN(CH_3)(CH_2C_6H_5)CH_2CH_2(\eta^5\text{-}C_5H_4)$ (5c): yellow crystal (75% yield). Mp: 167 °C dec. IR (CH_2Cl_2): 1897 (s), 1821 (s) cm^{-1}. ^1H NMR ($CDCl_3$, 300 MHz): δ 7.39−7.30 (3H, m), 7.23−7.19 (2H, m), 5.28−5.26 (1H, m, Cp H), 5.22−5.20 (1H, m, Cp H), 4.90−4.88 (1H, m, Cp H), 4.88−4.86 (1H, m, Cp H), 4.65 (1H, d, J = 13.8 Hz, benzylic H_a), 4.59 (1H, d, J = 13.8 Hz, benzylic H_b), 3.45−3.36 (1H, m, H_{1a}), 3.21−3.14 (1H, m, H_{1b}), 3.14 (3H, s), 2.30 (1H, dt, J = 14.6, 5.5 Hz, H_{2a}), 2.19 (1H, ddd, J = 14.6, 8.7, 5.1 Hz, H_{2b}). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 205.4 (CO × 2), 132.6 (C, Ph), 131.6 (CH × 2, Ph), 128.6 (CH, Ph), 128.3 (CH × 2, Ph), 119.7 (C, Cp), 81.1 (CH, Cp), 79.2 (CH, Cp), 77.2 (CH_2, benzylic), 75.0 (CH, Cp), 74.9 (CH_2, C_1), 74.2 (CH, Cp), 58.1 (CH_3), 24.9 (CH_2, C_2). Mass spectrum (FAB, ^{187}Re; *m/e* (relative intensity (%)): 455 (100, M^+), 364 (60, M^+ − benzyl). Anal. Calcd for $C_{17}H_{18}NO_2Re$: C, 44.92; H, 3.99; N, 3.08. Found: C, 44.63; H, 3.82; N, 2.94.

$(CO)_2ReN(CH_3)(CH_2C{\equiv}CH)CH_2CH_2(\eta^5\text{-}C_5H_4)$ (5d): yellow liquid (67% yield). IR (CH_2Cl_2): 3300 (w), 1902 (s), 1825 (s) cm^{-1}; terminal acetylenic absorption was not observed. ^1H NMR ($CDCl_3$, 300 MHz): δ 5.24−5.22 (1H, m, Cp H), 5.19−5.17 (1H, m, Cp H), 4.89−4.85 (2H, m, Cp H's), 4.19 (1H, dd, J = 17, 2.5 Hz, acetylenic H_a), 4.17 (1H, dd, J = 17, 2.5 Hz, acetylenic H_b), 3.62−3.53 (1H, m, H_{1a}), 3.49−3.41 (1H, m, H_{1b}), 3.34 (3H, s), 2.49 (1H, t, J = 2.5 Hz, −C≡CH), 2.25−2.20 (2H, m, H_2's). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 204.8 (CO), 204.7 (CO), 119.7 (C, Cp), 80.5 (CH, Cp), 79.7 (CH, Cp), 77.3 (C, −C≡), 76.3 (CH, ≡CH), 76.0 (CH_2, C_1), 74.9 (CH_2, Cp), 74.5 (CH, Cp), 62.8 (CH_2, Re−CH_2), 59.3 (CH_3), 24.8 (CH_2, C_2). Mass spectrum (FAB, ^{187}Re; *m/e* (relative intensity (%)): 403 (80, M^+), 375 (100, $M^+ - CO$), 347 (38, $M^+ - 2CO$). Anal. Calcd for $C_{13}H_{14}NO_2Re$: C, 38.80; H, 3.51; N, 3.48. Found: C, 38.56; H, 3.82; N, 3.71.

General Procedure for the Preparation of $[(CO)_2(R)ReNH(CH_3)CH_2CH_2(\eta^5\text{-}C_5H_4)]^+Br^-$ (7e−g; R = $CH_2CO_2CH_3$, $CH_2CO_2C_2H_5$, CH_2CN). Over a period of 3 min, a hexane solution of *n*-BuLi (1.6 M, 0.75 mL, 1.2 mmol) was added to a stirred solution of **3** (365 mg, 1.0 mmol) in THF (15 mL) at −78 °C. After the mixture was stirred for an additional 10 min, an electrophile ($BrCH_2CO_2CH_3$, $BrCH_2CO_2C_2H_5$, or $BrCH_2CN$; 2−3 mmol) was added. The cool bath was removed, and the resulting solution was stirred at room temperature for 20−30 min. The infrared spectra showed the terminal carbonyl stretching frequencies at 1896 and 1824 cm^{-1}, suggesting that the intermediate is the neutral amidorhenium complex **6**. One drop of water was then added. Solvents were evaporated to dryness. The resulting yellow-brown solids were extracted with CH_2Cl_2. After filtration, CH_2Cl_2 was evaporated until about 10 mL was left. Ether was added to effect precipitation. Solids were collected and washed twice with ether to give **7e−g** in 53−80% yield.

$[(CO)_2(CH_2CO_2CH_3)ReNH(CH_3)CH_2CH_2(\eta^5\text{-}C_5H_4)]^+Br^-$ (7e): yellow crystal (80% yield). Mp: 148 °C dec. IR (CH_2Cl_2): 2051 (s), 1975 (s), 1696 (m) cm^{-1}. ^1H NMR ($CDCl_3$, 300 MHz): δ 9.16−9.04 (1H, br s, N−H), 7.11−7.09 (1H, m, Cp H), 6.45−6.43 (1H, m, Cp H), 5.14−5.12 (1H, m, Cp H), 5.02−5.00 (1H, m, Cp H), 4.34−4.28 (1H, m, H_{1a}), 3.65 (3H, s, −OCH_3), 3.62−3.46 (1H, m, H_{1b}), 3.07 (1H, ddd, J = 13.4, 12.8, 6.3 Hz, H_{2a}), 2.94 (3H, d, J = 5.6 Hz, N−CH_3), 2.56 (2H, s, Re−CH_2R), 2.33 (1H, dd, J = 13.4, 6.2 Hz, H_{2b}). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 196.9 (CO), 193.7 (CO), 179.3 (−$COOCH_3$), 130.4 (C, Cp), 93.6 (CH, Cp), 91.0 (CH, Cp), 88.5 (CH, Cp), 87.4 (CH, Cp), 79.3 (CH_2, C_1), 51.2 (CH_3, −OCH_3), 48.7 (CH_3, N−CH_3), 24.3 (CH_2, C_2), −12.7 (CH_2, Re−CH_2R). Mass spectrum (FAB, ^{187}Re; *m/e* (relative intensity (%)): 438 (100, M^+), 410 (13, $M^+ - CO$). Anal. Calcd for $C_{13}H_{17}BrNO_4Re$: C, 30.18; H, 3.31; N, 2.71. Found: C, 29.85; H, 3.35; N, 2.93.

$[(CO)_2(CH_2CO_2C_2H_5)ReNH(CH_3)CH_2CH_2(\eta^5\text{-}C_5H_4)]^+Br^-$ (7f): hygroscopic solid (75% yield). IR (CH_2Cl_2): 2050 (s), 1981 (s), 1695 (m) cm^{-1}. ^1H NMR ($CDCl_3$, 300 MHz): δ 9.35−9.25 (1H, br s, N−H), 7.20−7.18 (1H, m, Cp H), 6.25−6.23 (1H, m, Cp H), 5.18−5.16 (1H, m, Cp H), 5.03−5.01 (1H, m, Cp H), 4.37−4.30 (1H, m, H_{1a}), 4.11 (1H, dq, J = 10.9, 7.0 Hz, −OEt), 4.07 (1H, dq, J = 10.9, 7.0 Hz, −OEt), 3.51−3.37 (1H, m, H_{1b}), 3.15 (1H, td, J = 13.0, 6.3 Hz, H_{2a}), 2.93 (3H, d, J = 5.7 Hz, N−CH_3), 2.54 (2H, s, Re−CH_2), 2.24 (1H, dd, J = 13.4, 6.3 Hz, H_{2b}), 1.28 (3H, t, J = 7.0 Hz, −OEt). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 196.7 (CO), 193.8 (CO), 178.6 (−CO_2Et), 130.2 (C, Cp), 93.5 (CH, Cp), 90.5 (CH, Cp), 88.6 (CH, Cp), 87.1 (CH, Cp), 79.1 (CH_2, C_1), 59.9 (CH_2, −OEt), 48.5 (CH_3, N−CH_3), 24.1 (CH_2, C_2), 13.9 (CH_3, −OEt), −12.7 (CH_2, Re−CH_2). Mass spectrum (FAB, ^{187}Re; *m/e* (relative intensity (%)): 452 (100, M^+), 424 (16, $M^+ - CO$). Anal. Calcd for $C_{14}H_{19}BrNO_4Re$: C, 31.64; H, 3.60; N, 2.64. Found: C, 31.18; H, 3.75; N, 2.78.

$[(CO)_2(CH_2CN)ReNH(CH_3)CH_2CH_2(\eta^5\text{-}C_5H_4)]^+Br^-$ (7g): yellow solid (53% yield). Mp: 145 °C dec. IR (CH_2Cl_2): 2219 (w), 2055 (s), 1986 (s) cm^{-1}. ^1H NMR (C_3D_6O, 300 MHz): δ 9.49−9.39 (1H, br s, N−H), 7.12−7.10 (1H, m, Cp H), 6.88−6.86 (1H, m, Cp H), 5.70−5.68 (1H, m, Cp H), 5.31−5.29 (1H, m, Cp H), 4.19−4.12 (1H, m, H_{1a}), 3.78−3.69 (1H, m, H_{1b}), 3.00−2.94 (1H, m, H_{2a}), 2.91 (3H, d, J = 5.7 Hz, N−CH_3), 2.45−2.33 (3H, m, H_{2b} and Re−CH_2CN). ^1H NMR (CD_3OD, 300 MHz): δ 6.77−6.75 (1H, m, Cp H), 6.61−6.59 (1H, m, Cp H), 5.43−5.41 (1H, m, Cp H), 5.36−5.34 (1H, m, Cp H), 4.04 (1H, ddd, J = 11.4, 4.7, 3.4 Hz, H_{1a}), 3.72−3.62 (1H, m, H_{1b}), 2.98

(3H, s, N−CH_3), 2.43−2.38 (2H, m), 2.35 (2H, s, Re−CH_2CN). ^{13}C NMR (CD_3OD, 75 MHz): δ 197.3 (CO), 196.2 (CO), 133.5 (CN), 127.9 (C, Cp), 94.0 (CH, Cp), 92.0 (CH, Cp), 91.1 (CH, Cp), 90.0 (CH, Cp), 79.0 (CH_2, C_1), 50.4 (CH_3, N−CH_3), 26.2 (CH_2, C_2), −37.7 (CH_2, Re−CH_2CN). Mass spectrum (FAB, ^{187}Re; *m*/*e* (relative intensity (%)): 405 (95, M^+), 377 (12, M^+ − CO), 154 (100). Anal. Calcd for $C_{12}H_{14}BrN_2O_2Re$: C, 29.76; H, 2.91; N, 5.78. Found: C, 30.04; H, 2.98; N, 5.93.

Reaction of 3 with Electrophiles: General Procedure for the Preparation of [(CO)$_2$(R)ReNH(CH$_3$)CH$_2$CH$_2$(η^5-C$_5$H$_4$)]$^+$X$^-$ (7a−g; R = CH$_3$, CH$_2$CH=CH$_2$, CH$_2$C$_6$H$_5$, CH$_2$C≡CH, CH$_2$CO$_2$CH$_3$, CH$_2$CO$_2$C$_2$H$_5$, CH$_2$CN; X = I for 7a and X = Br for 7b−g). For complexes **7a**, **7c**, and **7d**, a suspension of **3** (364 mg, 1 mmol) in 3 mL of electrophile (CH_3I, $BrCH_2C_6H_5$, or $BrCH_2C{\equiv}CH$) was stirred at room temperature. Solids were dissolved gradually during the course of the reaction. The progress of the reaction was monitored by checking the carbonyl absorptions in the infrared spectrum. After the reaction was complete (30 min to 2 h), ether was added to allow the product to precipitate. The precipitates were washed twice with ether to give **7a**, **7c**, and **7d**, respectively. For complexes **7b**, **7e**, **7f** and **7g**, the aminorhenium complex **3** (364 mg, 1 mmol) was dissolved in CH_2Cl_2 (2 mL). Three equivalents of electrophile ($BrCH_2CH{=}CH_2$, $BrCH_2CO_2CH_3$, $BrCH_2CO_2C_2H_5$, or $BrCH_2CN$) was then added. The solution was stirred at room temperature. After the carbonyl absorptions of **3** disappeared in the infrared spectrum (30 min to several hours), ether was added to allow the product to precipitate. The precipitates were washed twice with ether to give **7b**, **7e**, **7f**, and **7g**, respectively.

[(CO)$_2$(CH$_3$)ReNH(CH$_3$)CH$_2$CH$_2$(η^5-C$_5$H$_4$)]$^+$I$^-$ (7a): yellow solid (97% yield). Mp: 120−122 °C dec. IR (CH_2Cl_2): 2040 (s), 1971 (s) cm^{-1}. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 8.34 (1H, br s, N−H), 6.93−6.91 (1H, m, Cp H), 6.14−6.12 (1H, m, Cp H), 5.09−5.07 (1H, m, Cp H), 4.70−4.68 (1H, m, Cp H), 4.22−4.17 (1H, m), 3.38−3.15 (2H, m), 2.90 (3H, d, J = 5.8 Hz, N−CH_3), 2.23−2.16 (1H, m), 0.98 (3H, s, Re−CH_3). ^{1}H NMR (C_3D_6O, 300 MHz): δ 8.22 (1H, br s, N−H), 6.74−6.72 (1H, m, Cp H), 6.66−6.64 (1H, m, Cp H), 5.39−5.37 (1H, m, Cp H), 5.15−5.13 (1H, m, Cp H), 4.06−4.01 (1H, m, H_{1a}), 3.69−3.56 (1H, m, H_{1b}), 2.99−2.90 (1H, m, H_{2a}), 2.88 (3H, d, J = 5.8 Hz, N−CH_3), 2.39−2.33 (1H, ddd, J = 13.4, 6.0, 1.2 Hz, H_{2b}), 0.96 (3H, s, Re−CH_3). ^{1}H NMR (CD_3OD, 300 MHz): δ 7.39 (1H, br s, N−H), 6.58−6.56 (1H, m, Cp H), 6.43−6.41 (1H, m, Cp H), 5.18−5.15 (2H, m, Cp H), 4.01−3.94 (1H, m), 3.71−3.55 (1H, m), 2.99 (3H, d, J = 5.8 Hz, N−CH_3), 2.53−2.36 (2H, m), 0.98 (3H, s, Re−CH_3). ^{13}C NMR (CD_3OD, 75 MHz): δ 198.4 (CO), 197.4 (CO), 130.3 (C, Cp), 91.8 (CH, Cp), 90.4 (CH, Cp), 89.3 (CH, Cp), 88.1 (CH, Cp), 77.5 (CH_2), 50.7 (CH_3, N−CH_3), 26.4 (CH_2), −27.6 (CH_3, Re−CH_3). Mass spectrum (FAB, ^{187}Re; *m*/*e* (relative intensity (%)): 380 (100, M^+). Anal. Calcd for $C_{11}H_{15}INO_2Re$: C, 26.09; H, 2.99; N, 2.77. Found: C, 25.85; H, 3.06; N, 2.82.

[(CO)$_2$(CH$_2$CH=CH$_2$)ReNH(CH$_3$)CH$_2$CH$_2$(η^5-C$_5$H$_4$)]$^+$Br$^-$ (7b): unstable yellow solid (80% yield, about 90% purity). IR (CH_2Cl_2): 2034 (s), 1967 (s) cm^{-1}. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 8.74 (1H, br s, N−H), 6.90−6.88 (1H, m, Cp H), 6.36−6.34 (1H, m, Cp H), 6.02−5.85 (1H, m, internal olefinic H), 4.90−4.88 (1H, m, Cp H), 4.69 (1H, dd, J = 16.5, 1.2 Hz, terminal olefinic H_t), 4.64 (1H, dd, J = 9.8, 1.2 Hz, terminal olefinic H_c), 4.42−4.40 (1H, m, Cp H), 4.23−4.13 (1H, m, H_{1a}), 3.63−3.57 (1H, m, allylic H_a), 3.46−3.35 (1H, m, H_{1b}), 3.08−2.97 (1H, m, H_{2a}), 2.94 (3H, d, J = 5.6 Hz, N−CH_3), 2.78−2.73 (1H, m, allylic H_b), 2.28−2.21 (1H, m, H_{2b}). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 197.7 (CO), 195.6 (CO), 142.3 (CH, =CHR), 128.8 (C, Cp), 111.6 (CH_2, $=CH_2$), 94.0 (CH, Cp), 90.9 (CH, Cp), 88.9 (CH, Cp), 88.1 (CH, Cp), 78.0 (CH_2, C_1), 49.3 (CH_3, N−CH_3), 24.5 (CH_2, C_2), −2.0 (CH_2, Re−CH_2). Mass spectrum (FAB, ^{187}Re; *m*/*e* (relative intensity (%)): 406 (100, M^+), 365 (45, M^+ − C_3H_5).

[(CO)$_2$(CH$_2$C$_6$H$_5$)ReNH(CH$_3$)CH$_2$CH$_2$(η^5-C$_5$H$_4$)]$^+$Br$^-$ (7c): hygroscopic yellow solid (90% yield). IR (CH_2Cl_2): 2034 (s), 1966 (s) cm^{-1}. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 9.00 (1H, br s, N−H), 7.25−7.20 (2H, m, Ph), 7.09−7.04 (3H, m, Ph), 6.88−6.86 (1H, m, Cp H), 6.17−6.15 (1H, m, Cp H), 4.33−4.31 (1H, m, Cp H), 4.28−4.26 (1H, m, Cp H), 4.18−4.12 (1H, m, H_{1a}), 3.56 (1H, d, J = 10.5 Hz, benzylic H_a), 3.42 (1H, d, J = 10.5 Hz, benzylic H_b), 3.36−3.25 (1H, m, H_{1b}), 3.12 (1H, td, J = 13.1, 6.0 Hz, H_{2a}), 2.94 (3H, d, J = 5.7 Hz, N−CH_3), 2.12 (1H, dd, J = 13.5, 5.7 Hz, H_{2b}). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 198.2 (CO), 196.8 (CO), 147.2 (C, Ph), 130.1 (C, Cp), 127.8 (CH × 2, Ph), 127.2 (CH × 2, Ph), 125.2 (CH, Ph), 92.9 (CH, Cp), 90.7 (CH, Cp), 88.4 (CH, Cp), 88.2 (CH, Cp), 77.8 (CH_2, C_1), 48.8 (CH_3, N−CH_3), 24.3 (CH_2, C_2), −2.7 (CH_2, Re−CH_2Ph). Mass spectrum (FAB, ^{187}Re; *m*/*e* (relative intensity (%)): 456 (100, M^+), 428 (8, M^+ − CO), 365 (75, M^+ − $CH_2C_6H_5$). Anal. Calcd for $C_{17}H_{19}BrNO_2Re$: C, 38.13; H, 3.58; N, 2.62. Found: C, 37.94; H, 3.72; N, 2.68.

[(CO)$_2$(CH$_2$C≡CH)ReNH(CH$_3$)CH$_2$CH$_2$(η^5-C$_5$H$_4$)]$^+$Br$^-$ (7d): yellow solid (98% yield). Mp: 134−139 °C dec. IR (CH_2Cl_2): 2047(s), 1978(s) cm^{-1}. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 9.16 (1H, br s, N-H), 7.15−7.13 (1H, m, Cp H), 6.25−6.23 (1H, m, Cp H), 5.38−5.36 (1H, m, Cp H), 4.90−4.88 (1H, m, Cp H), 4.27−4.20 (1H, m, H_{1a}), 3.43−3.29 (1H, m, H_{1b}), 3.14 (1H, ddd, J = 13.4, 12.6, 6.1 Hz, H_{2a}), 2.94 (3H, d, J = 5.7 Hz, N−CH_3), 2.43 (1H, dd, J = 15.4, 2.8 Hz, acetylenic H_a), 2.35 (1H, dd, J = 15.4, 2.8 Hz, aceylenic H_b), 2.20 (1H, dd, J = 13.4, 6.1 Hz, H_{2b}), 2.09 (1H, t, J = 2.8 Hz, alkyne−H). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 197.1 (CO), 194.3 (CO),129.7 (C, Cp), 93.9 (CH, Cp), 90.9 (CH, Cp), 90.3 (C, RC≡), 89.5 (CH, Cp), 87.7 (CH, Cp), 78.5 (CH_2, C_1), 69.8 (CH, ≡CH), 49.3 (CH_3, N−CH_3), 24.6 (CH_2, C_2), −28.6 (CH_2, Re−CH_2). Mass spectrum (FAB, ^{187}Re; *m*/*e* (relative intensity (%)): 404 (4, M^+). Anal. Calcd for $C_{13}H_{15}BrNO_2Re$: C, 32.30; H, 3.13; N, 2.90. Found: C, 32.25; H, 3.28; N, 3.03.

[(CO)$_2$(CH$_2$CO$_2$CH$_3$)ReNH(CH$_3$)CH$_2$CH$_2$(η^5-C$_5$H$_4$)]$^+$Br$^-$ (7e): yellow crystal (90% yield).

[(CO)$_2$(CH$_2$CO$_2$C$_2$H$_5$)ReNH(CH$_3$)CH$_2$CH$_2$(η^5-C$_5$H$_4$)]$^+$Br$^-$ (7f): hygroscopic solid (83% yield).

[(CO)$_2$(CH$_2$CN)ReNH(CH$_3$)CH$_2$CH$_2$(η^5-C$_5$H$_4$)]$^+$Br$^-$ (7g): yellow solid (75% yield).

Preparation and crystal structure of [(CO)$_2$(CH$_2$C$_6$H$_5$)ReNH(CH$_3$)CH$_2$CH$_2$(η^5-C$_5$H$_4$)]$^+$BPh$_4^-$ (8). Sodium tetra-

Table 1. Crystallographic Data and Structure Refinements for 8

formula	$C_{41}H_{39}BNO_2Re$
fw	774.77
cryst size (mm)	0.13 × 0.16 × 0.44
cryst syst	monoclinic
space group	$P2_1/c$
a (Å)	10.163(3)
b (Å)	19.329(3)
c (Å)	17.145(3)
β (deg)	100.078(20)
V (Å^3)	3315.9(13)
Z	4
D_c (g cm^{-3})	1.552
F(000)	1547
λ(Mo Kα) (Å)	0.710 69
μ(Mo Kα) (cm^{-1})	37.491
transmissn	0.898; 1.000
scan speed (deg min^{-1})	2.06−8.24
$\theta/2\theta$ scan width (deg)	2(0.90 + 0.35 tan θ)
$2\theta_{max}$ (deg)	45.0
unit cell detn: no.; 2θ range (deg)	25; 15.84−32.72
hkl range	(−10 to +10), (0−20), (0−18)
no. of collected rflns	4606
no. of unique rflns	4320
no. of obsd rlfns ($I > 2.5\sigma(I)$)	3243
no. of refined params	415
R_F;[a] R_w[b]	0.026; 0.026
GOF	1.19
weight modifier k in kF_o^2	0.000 100
$(\Delta\rho)_{max,min}$ (e Å^{-3})	+0.660; −0.510

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

Table 2. Selected Bond Lengths (Å) and Bond Angles (deg) for 8

Re−N	2.223(5))	N−C(1)	1.493(9)
Re−C(9)	2.337(7))	C(16)−O(16)	1.114(8)
Re−C(16)	1.949(6)	C(17)−O(17)	1.139(8)
Re−C(17)	1.935(7)	C(2)−C(3)	1.491(10)
N−Re−C(9)	144.6(2)	C(16)−Re−C(17)	103.2(3)
N−Re−C(16)	84.5(2)	C(1)−C(2)−C(3)	107.6(6)
N−Re−C(17)	84.2(2)	Re−C(16)−O(16)	173.9(5)
C(9)−Re−C(16)	73.2(2)	Re−C(17)−O(17)	177.3(6)
C(9)−Re−C(17)	74.8(2)	Re−C(9)−C(10)	119.4(4)

phenylborate (140 mg, 0.4 mmol) was added to a yellow solution of complex **7c** (107 mg, 0.2 mmol) in methanol (4 mL) at room temperature. The mixture was shaken until $NaBPh_4$ dissolved. The solution was then cooled in a freezer (−20 °C) for 20 h. Orange solids were collected and washed twice with methanol to give 145 mg (94%) of **8**. Recrystallization of **8** from CH_2Cl_2/hexane gave yellow needles. Mp: 144−146 °C dec. IR (CH_2Cl_2): 2035 (s), 1964 (s) cm^{-1}. ^1H NMR (CD_2Cl_2, 300 MHz): δ 7.45−7.39 (8H, m), 7.27−7.22 (3H, m), 7.12−7.04 (10H, m), 6.94−6.89 (4H, m), 5.96−5.94 (1H, Cp H), 5.91−5.89 (1H, Cp H), 4.31−4.29 (1H, Cp H), 4.26−4.24 (1H, Cp H), 3.48 (1H, d, J = 10.4 Hz, benzylic H_a), 3.39 (1H, d, J = 10.4 Hz, benzylic H_b), 3.19−3.11 (1H, m, H_{1a}), 2.91−2.81 (1H, m, H_{1b}), 2.64 (3H, d, J = 5.8 Hz, N−CH_3), 1.77−1.72 (2H, m, H_2's). ^1H NMR (C_3D_6O, 300 MHz): δ 7.36−7.30 (8H, m), 7.25−7.18 (4H, m), 7.10−7.03 (1H, m), 6.92 (8H, t, J = 7.4 Hz), 6.79 (4H, t, J = 7.4 Hz), 6.69−6.67 (1H, Cp H), 6.47−6.45 (1H, Cp H), 4.90−4.88 (1H, Cp H), 4.78−4.76 (1H, Cp H), 4.16−4.08 (1H, m, H_{1a}), 3.83−3.70 (1H, m, H_{1b}), 3.53 (2H, s, benzylic H's), 3.12 (3H, d, J = 5.8 Hz, N−CH_3), 2.45−2.40 (2H, m, H_2's). Mass spectrum (FAB, ^{187}Re; m/e (relative intensity (%)): 456 (32, M^+), 365 (12, $M^+ - C_7H_7$). Anal. Calcd for $C_{41}H_{39}BNO_2Re$: C, 63.56; H, 5.07; N, 1.81. Found: C, 63.61; H, 5.12; N, 1.85.

A single crystal of **8** was obtained by slow diffusion of a CH_2Cl_2 solution of **8** into hexane at 5 °C for several days. Diffraction measurement was 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 cell was determined and refined using 25 randomly seleced 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 ($P2_1/n$) 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.[14] The structure was solved by direct methods and refined by a full-matrix least-squares routine[15] with anisotropic thermal parameters for all non-hydrogen atoms. The structure was 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 **8** (6 pages). Ordering information is given on any current masthead page.

OM960980P

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

(15) 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.