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Preparation and reactions of half-sandwich rhenium nitrosyl complexes containing a tethered amino ligand

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Abstract

The aminorhenium nitrosyl complex $[\eta^5:\eta^1\text{-}C_5H_4CH_2CH_2N(CH_3)_2Re(NO)(CO)]^+ BF_4^-$ (**5a**), in which the ligating amino group was connected to the cyclopentadienyl ring, was prepared by reacting the $\eta^5\text{-}C_5H_4CH_2CH_2N(CH_3)_2Re(NO)(CO)Br$ (**4**) with $AgBF_4$. Reaction of **5a** with alkylmetal reagents provided the acyl complex $\eta^5:\eta^1\text{-}C_5H_4CH_2CH_2N(CH_3)_2Re(NO)COR$ (**8**) (R = n-butyl, methyl, ethyl, isopropyl, benzyl). Solid state structures of **5b** ($X^- = BPh_4^-$) and the acetyl complex **8b** were characterized by single-crystal X-ray analyses.

Keywords: Rhenium; Cyclopentadienyl; Nitrosyl; Amine; Chelation; Acyl

1. Introduction

Phosphine ligands have been widely used in organometallic chemistry [1]. However, the isoelectronic species, amines, have received only slight attention [2]. For instance, in the area of half-sandwich rhenium complexes, a vast and rapidly expanding chemistry was based upon the chiral fragment $[ReCp(NO)(PPh_3)]^+$, which contains a triphenylphosphine ligand [3]. Complexation of this fragment with carbonyls [4] and hydrocarbyls [5] has been investigated extensively. Relatively little was known about the chemistry involving amino ligands [6].

Unlike the other members of Group 15, amine has no π-acceptor capability. Therefore, amine coordinates only weakly to low-valent transition metals and forms relatively labile complexes [2]. Through intramolecular chelation, we have prepared some stable amino group chelation complexes of manganese [2c] and molybdenum [2d]. It might be of interest to obtain some rhenium nitrosyl complexes containing an amino ligand and examine their properties and reactions. In this report, we would like to present some syntheses and reactions of complexes of the type $ReCp(NO)(NR_3)L$, in which the amino group links intramolecularly to the cyclopentadienyl ring.

2. Results and discussion

We have reported [7] that the lithium salt of the heterobifunctional compound $C_5H_4CH_2CH_2NMe_2$ reacts with rhenium pentacarbonyl bromide to provide the half-sandwich complex $(\eta^5\text{-}C_5H_4CH_2CH_2NMe_2)Re(CO)_3$ (**1**) in 62% yield (see Scheme 1). Having a pendent amino group on the cyclopentadienyl ring, complex **1** serves as our starting point for elaboration of amino group chelation complexes.

2.1. Preparation of rhenium bromide 4

The literature reported [8] transformation of Cp unsubstituted rhenium tricarbonyl $(\eta^5\text{-}C_5H_5)Re(CO)_3$ to rhenium bromide $(\eta^5\text{-}C_5H_5)Re(NO)(CO)Br$ was followed by some modifications. Reaction of **1** with nitrosyl tetrafluoroborate ($NOBF_4$) gave the rhenium nitrosyl complex **2** (Scheme 1). Two equivalents of $NOBF_4$ are required for this reaction. One equivalent of $NOBF_4$ reacted with the amino group to form presumably an N-nitrosonium adduct. The other equivalent of $NOBF_4$ then reacted with the rhenium center to give the desired nitrosyl complex. The actual form of the amino group

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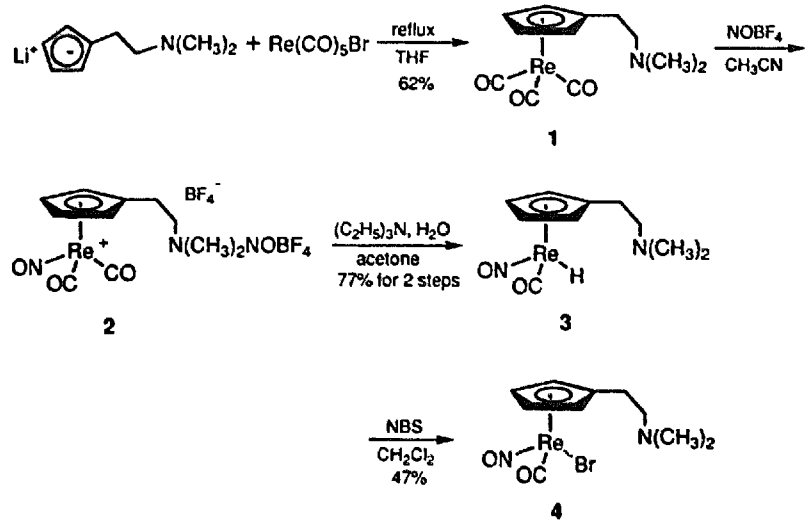


Scheme 1.

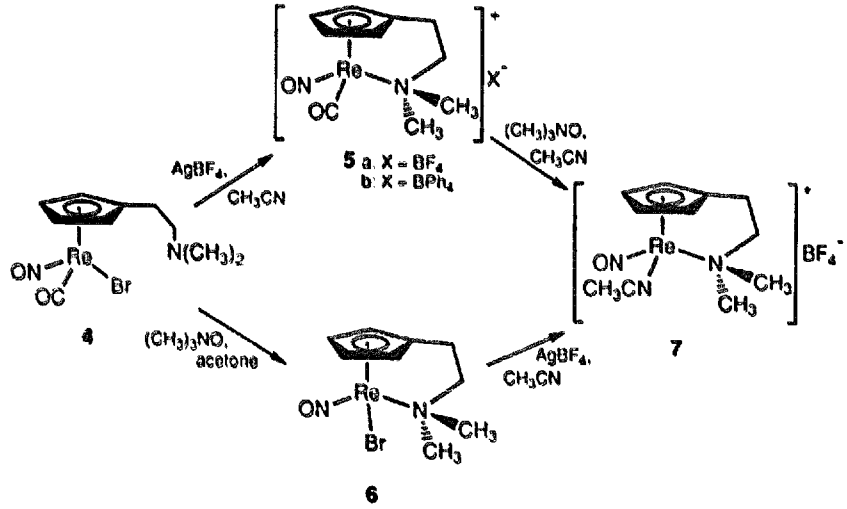
and the $NOBF_4$ adduct was not characterized. However, the amino group could be liberated in the next reaction. Treatment of **2** with a large excess of triethylamine in wet acetone provided rhenium hydride **3**. Use of a large quantity of triethylamine is essential for complete liberation of the amino group. Bromination of **3** with N-bromosuccinimide afforded rhenium bromide **4** in a total of 36% yield. Infrared spectra (ν_{NO} and ν_{CO}) of **2**, **3** and **4** are very similar to their corresponding Cp unsubstituted complexes. The rhenium center is chiral for **3** and **4**. Therefore, the Cp protons of both **3** and **4** split as a result of diastereotopism in the ^1H NMR spectra. Bromide **4** is a red liquid and can be handled under air for 1 h without noticeable decomposition.

2.2. Preparation of chelation complexes

Removal of the bromide ion from rhenium bromide **4** with $AgBF_4$ resulted in amino group coordination to give complex **5a** (Scheme 2). In contrast, removal of a carbon monoxide by treating the bromide **4** with one equivalent of $(CH_3)_3NO$ provided bromide **6**. Both **5a** and **6** were converted to the acetonitrile complex **7** by reaction of **5a** with $(CH_3)_3NO$ and **6** with $AgBF_4$ respectively in CH_3CN.

Upon chelation, the amino group donates electrons to the metal. This would cause reduction of the electron density on the methyl group. Therefore, in the ^1H NMR spectra the methyl groups would appear at lower field position than that of the non-chelate one. In addition, owing to the chirality in the metal center, the N,N-dimethyl groups become magnetically non-equivalent. Therefore, it is not difficult to know whether the amino group is ligated or not. For instance, the N,N-dimethyl groups of the chelation complexes appeared at δ 3.73 and 3.48 for **5a**; δ 3.25 and 3.04 for **6**; δ 3.32 and 3.11 for **7**, compared with the sole resonance at the higher field position (δ 2.26) of the N,N-dimethyl groups of the non-chelate complex **4**.

Complex **5a** was converted into the corresponding tetraphenylborate **5b**. The solid state structure of **5b** was then subjected to a single-crystal X-ray diffraction study.



Scheme 2.

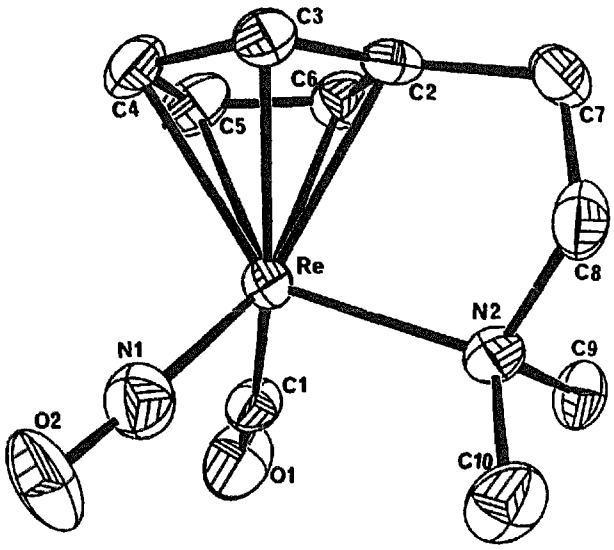
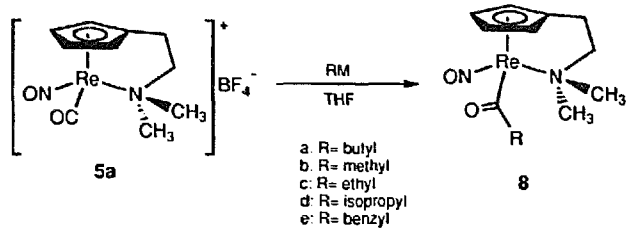


Fig. 1. ORTEP drawing of $[\eta^5:\eta^1\text{-}C_5H_4CH_2CH_2N(CH_3)_2Re(NO)(CO)]^+BPh_4^-$ (**5b**). The BPh_4 anion is omitted for simplicity.

Fig. 1 shows that the amino group is coordinated to the metal with a bond length of 2.177 Å (see Table 1). Both metal–carbonyl and metal–nitrosyl are in linear geometry, consistent with the bond angles Re–C(1)–O(1) (172.5°) and Re–N(1)–O(2) (177.0°). The torsion angles 165.8° for C(7)–C(2)–C(6)–C(5) and −166.8° for C(7)–C(2)–C(3)–C(4) suggest that the C(2)–C(7) bond of the side chain is bent about 13.7° away from the cyclopentadienyl plane. The torsion angle −3.0° for N(2)–Re–C(2)–C(7) indicates that the Re–N(2) and C(2)–C(7) bonds are coplanar.

2.3. Electrophilic reactions of 5a with alkylmetal reagents

Reaction of cationic rhenium carbonyl **5a** with alkyl nucleophiles occurred at the carbonyl carbon to provide



Scheme 3.

acyl complexes **8**. For instance, **5a** reacted with n-butyllithium to provide the rhenium valeryl complex **8a** (see Scheme 3). Reaction of **5a** with alkyl Grignards (methyl, ethyl, isopropyl and benzyl) also gave rhenium acyl complexes (**8b–8e**) in comparable yields (56–78%). Infrared spectroscopic study showed that the nitrosyl stretchings of **8** appeared at lower frequencies between 1618 and 1614 cm^{-1} relative to that of **5a** (1743 cm^{-1}). The stretching frequency of the acyl carbonyl appeared between 1524 and 1517 cm^{-1} for **8**, compared with 2006 cm^{-1} for the terminal carbonyl of **5a**. Being a neutral complex, the amino group of **8** donates fewer electrons to the metal relative to that of the cationic complex **5a**. Therefore, the chemical shifts of the dimethyl groups of **8** would appear at higher field than that of **5a**. Indeed, the N,N-dimethyl group displayed at δ 3.23 and 3.03 for **8a–8d** and δ 3.08 and 2.81 for **8e**, compared with δ 3.73 and 3.48 for **5a**.

The solid state structure of **8b** (Fig. 2) shows that an acyl ligand was bonded to the rhenium with a bond length of 2.073 Å (see Table 2). The amino group coordinated to the rhenium with a bond length of 2.198 Å, slight longer (0.021 Å) than that of **5b**. The torsion angles 163.8° for C(6)–C(1)–C(2)–C(3) and −163.4° for C(6)–C(1)–C(5)–C(4) suggest that the C(1)–C(6) bond of the side chain is bent about 16.4° away from the cyclopentadienyl plane. It is worth noting that the

Table 1
Selected bond lengths (Å), bond angles (°) and torsion angles (°) in complex **5b**

Re–N(1)	1.832(6)	N(2)–C(8)	1.501(8)
Re–N(2)	2.177(5)	N(2)–C(9)	1.510(7)
Re–C(1)	1.857(6)	N(2)–C(10)	1.492(8)
Re–C(2)	2.271(6)	O(1)–C(1)	1.141(8)
Re–C(4)	2.262(6)	C(2)–C(7)	1.530(9)
N(1)–O(2)	1.167(7)	C(7)–C(8)	1.498(11)
N(1)–Re–N(2)	98.54(20)	Re–C(1)–O(1)	172.5(6)
N(1)–Re–C(1)	93.6(3)	Re–N(2)–C(8)	108.6(3)
N(2)–Re–C(1)	97.94(22)	C(9)–N(2)–C(10)	104.6(5)
Re–N(1)–O(2)	177.1(6)	C(3)–C(2)–C(7)	123.1(6)
C(6)–Re–N(1)–O(2)	3.8(3)	C(4)–Re–N(2)–C(8)	2.1(3)
C(3)–Re–N(2)–C(8)	−2.9(3)	C(6)–Re–N(2)–C(10)	177.8(4)
C(5)–Re–N(2)–C(10)	173.9(4)	N(2)–Re–C(6)–C(5)	−175.3(5)
N(2)–Re–C(2)–C(7)	−3.0(3)	C(7)–C(2)–C(3)–C(4)	−166.8(8)
N(1)–Re–N(2)–C(10)	10.8(3)	C(7)–C(2)–C(6)–C(5)	165.8(8)

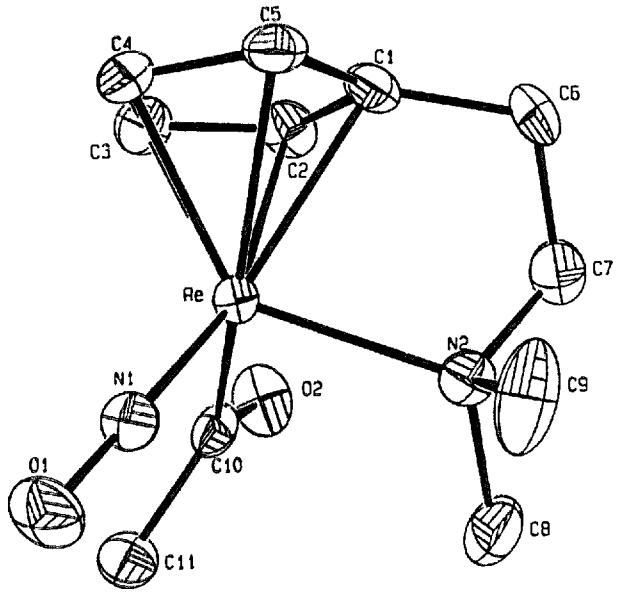


Fig. 2. ORTEP drawing of $\eta^5:\eta^1$-$C_5H_4CH_2CH_2N(CH_3)_2Re(NO)$-$COCH_3$ (**8b**).

carbonyl group and the Re–NO bond are coplanar (−179.2° for N(1)–Re–C(10)–O(2)). Similar to complex **5b**, the C(1)–C(6) and Re–N(2) bonds are also coplanar.

Complex **8** showed reasonable stability as it could be manipulated in solution under air for a short period of time without noticeable decomposition. Precipitations would appear if the solution was allowed to stay at room temperature under air for more than 1 h.

3. Conclusion

We have demonstrated that the amino group with a two carbon tether could easily be ligated to rhenium nitrosyl complexes. The resulting aminorhenium complex reacts with alkylmetal reagents to provide acyl complexes. The corresponding triphenylphosphine complex does not show this property. Complex **5a** reacted with $NaBH_4$ to provide **3** only. However, the terminal CO of the corresponding triphenylphosphine complex could be reduced to a methyl group [3] by treatment with $NaBH_4$. Obviously, the properties of aminorhenium and phosphinerhenium complexes may be quite different. Further exploration of the properties and reactions of the aminorhenium complexes is underway.

4. Experimental section

Reactions that required anhydrous conditions were performed under an argon atmosphere by use of Schlenk techniques. Tetrahydrofuran (THF) was distilled from sodium benzophenone ketyls; methylene chloride (CH_2Cl_2) and acetonitrile were distilled from CaH_2. The following chemicals were used as received: methylmagnesium chloride, ethylmagnesium bromide, isopropylmagnesium chloride and benzylmagnesium chloride (Aldrich); $NOBF_4$ (Strem); ^nBuLi, N-bromosuccinimide and $AgBF_4$ (Merck). Anhydrous $(CH_3)_3NO$ was obtained from $(CH_3)_3NO \cdot 2H_2O$ (Aldrich) by the literature procedure [9]. 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 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 a Bruker AC-200 FT or a Bruker AC-300 FT spectrophotometer. On the assignment of ^1H and ^{13}C NMR data, the carbon bound to the nitrogen was designated C_1 and the hydrogens on C_1 were designated H_{1a} and H_{1b}. The next carbon was designated C_2 and the hydrogens on C_2 were designated 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.

Table 2
Selected bond lengths (Å), bond angles (°) and torsion angles (°) in complex **8b**

Re–N(1)	1.763(9)	O(1)–N(1)	1.219(11)
Re–N(2)	2.198(9)	O(2)–C(10)	1.238(14)
Re–C(10)	2.073(11)	C(10)–C(11)	1.509(16)
N(1)–Re–N(2)	101.3(4)	Re–N(1)–O(1)	177.8(8)
N(1)–Re–C(10)	94.4(4)	Re–C(10)–O(2)	123.0(8)
N(2)–Re–C(10)	89.4(4)	Re–C(10)–C(11)	120.1(8)
N(1)–Re–C(10)–C(11)	5.2(5)	C(1)–Re–C(10)–O(2)	−3.0(5)
C(1)–Re–C(10)–C(11)	−178.6(8)	C(6)–C(1)–C(2)–C(3)	163.8(13)
N(2)–Re–C(1)–C(6)	−0.7(5)	C(6)–C(1)–C(5)–C(4)	−163.4(13)
N(1)–Re–C(10)–O(2)	−179.2(9)	C(2)–C(1)–C(5)–C(4)	2.7(6)

4.1. Preparation of η^5-$C_5H_4CH_2CH_2N(CH_3)_2Re(NO)(CO)H$ (3)

To an ice-water cooled, stirred, pale yellow solution of tricarbonyl **1** (10.38 g, 25.5 mmol) in acetonitrile (200 ml) was added white powders of $NOBF_4$ (6.2 g, 53.4 mmol) portionwise over 5 min. After stirring for another 15 min, acetonitrile was evaporated under reduced pressure. The residue was then dissolved with acetone (50 ml). THF (200 ml) was added to precipitate the desired nitrosyl complex. Powders were collected and washed twice with THF (100 ml × 2), giving 12.4 g of the complex **2** as brown powder. IR (CH_3CN): 2111s, 2056s, 1819s cm^{-1}. ^1H NMR (CD_3COCD_3, 300 MHz): δ 6.69 (2H, t, J = 2.3 Hz, Cp–Hs), 6.49 (2H, t, J = 2.3 Hz, Cp–Hs), 3.72–3.65 (2H, m), 3.40–3.34 (2H, m), 3.14 (6H, s). ^{13}C NMR (CD_3COCD_3, 75 MHz): δ 182.7 (CO × 2), 115.6 (C, Cp), 96.3 (CH × 2, Cp), 95.0 (CH × 2, Cp), 58.8 (CH_2), 44.2 (CH_3 × 2), 23.6 (CH_2).

Complex **2** was dissolved with wet acetone (250 ml, 1% water). Triethylamine (300 ml) was then added at room temperature. After stirring for 30 min, solvents were evaporated to dryness. The residue was flash chromatographed [10] on silica gel, using 30% followed by 50% then 80% of acetone in hexane as eluents. The first yellow–orange band was collected and evaporated to provide 7.6 g (78%) of hydride **3** as an orange liquid. TLC (silica gel): R_f = 0.30 (acetone). IR (CH_2Cl_2): 1969s, 1692s cm^{-1}. ^1H NMR ($CDCl_3$, 200 MHz): δ 5.60–5.56 (1H, m, Cp–H), 5.52–5.48 (1H, m, Cp–H), 5.45–5.41 (1H, m, Cp–H), 5.40–5.36 (1H, m, Cp–H), 2.69–2.61 (2H, m), 2.53–2.45 (2H, m), 2.32 (6H, s), −8.33 (1H, s, Re–H). ^1H NMR (CD_3COCD_3, 200 MHz): δ 5.86–5.84 (1H, m, Cp–H), 5.77–5.75 (1H, m, Cp–H), 5.63–5.57 (2H, m, Cp–Hs), 2.73–2.65 (2H, m), 2.59–2.51 (2H, m), 2.31 (6H, s), −8.28 (1H, s, Re–H). ^{13}C NMR (CD_3COCD_3, 50 MHz): δ 210.4 (CO), 112.6 (C, Cp), 89.1 (CH × 2, Cp), 87.1 (CH, Cp), 87.0 (CH, Cp), 61.4 (CH_2), 45.1 (CH_3 × 2), 26.3 (CH_2). Anal. Found: C, 31.22; H, 3.65; N, 7.58. $C_{10}H_{15}N_2O_2Re$ Calc.: C, 31.49; H, 3.96; N, 7.34%.

4.2. Preparation of η^5-$C_5H_4CH_2CH_2N(CH_3)_2Re(NO)(CO)Br$ (4)

A powder of N-bromosuccinimide (235 mg, 1.32 mmol) was added portionwise to a stirred orange solution of **3** (500 mg, 1.31 mmol) in CH_2Cl_2 (50 ml) at 0°C over 5 min. After stirring for an additional 20 min, the resulting red solution was concentrated and flash chromatographed on silica gel using acetone as an eluent. The first red band was collected and concentrated to provide 285 mg (47% yield) of bromide **4** as a red liquid. IR (CH_2Cl_2): 1995s, 1725s cm^{-1}. ^1H NMR ($CDCl_3$, 300 MHz): δ 5.86–83 (1H, m, Cp–H), 5.81–5.78 (1H, m, Cp–H), 5.54 (2H, t, J = 2.5 Hz, Cp–Hs), 2.66–2.60 (2H, m), 2.50–2.45 (2H, m), 2.26 (6H, s). ^{13}C NMR ($CDCl_3$, 50 MHz): δ 200.3 (CO), 118.8 (C, Cp), 91.4 (CH, Cp), 90.9 (CH, Cp), 90.2 (CH, Cp), 89.9 (CH, Cp), 58.9 (CH_2), 45.0 (CH_3 × 2), 25.8 (CH_2). Mass spectra (FAB, ^{187}Re), m/e (rel. int. (%)): 381 (M^+–Br, 100), 351 (M^+–Br–NO, 25). Anal. Found: C, 26.35; H, 2.95; N, 5.81. $C_{10}H_{14}BrN_2O_2Re$ Calc.: C, 26.09; H, 3.06; N, 6.08%.

4.3. Preparation of $[\eta^5:\eta^1$-$C_5H_4CH_2CH_2N(CH_3)_2Re(NO)(CO)]^+BF_4^-$ (5a)

Bromide **4** (285 mg, 0.62 mmol) was dissolved with CH_3CN (20 ml). A solution of silver tetrafluoroborate in CH_3CN (2.5 ml × 0.25 M, 0.62 mmol) was added at room temperature. After stirring for 30 min, the resulting cloudy solution was filtered through Celite. The yellow solids after concentration were recrystallized from acetone and THF, giving 215 mg (74% yield) of **5a** as a yellow–orange solid. M.p. 245°C (dec.): IR (CH_3CN): 2006s, 1743s cm^{-1}. ^1H NMR (CD_3COCD_3, 200 MHz): δ 6.87–6.84 (1H, m, Cp–H), 6.81–6.77 (1H, m, Cp–H), 6.29–6.26 (1H, m, Cp–H), 5.83–5.80 (1H, m, Cp–H), 3.98–3.91 (2H, m, H_1s), 3.73 (3H, s), 3.48 (3H, s), 3.06–2.91 (1H, m, H_{2a}), 2.73 (1H, dt, J = 14.7, 6.0 Hz, H_{2b}). ^1H NMR (CD_3CN, 200 MHz): δ 6.52–6.48 (2H, m, Cp–Hs), 5.93–5.89 (1H, m, Cp–H), 5.54–5.50 (1H, m, Cp–H), 3.69–3.62 (2H, m, H_1s), 3.50 (3H, s), 3.26 (3H, s), 2.74 (1H, dt, J = 14.8, 6.6 Hz, H_{2a}), 2.48 (1H, dt, J = 14.8, 6.0 Hz, H_{2b}). ^{13}C NMR (CD_3CN, 50 MHz): δ 197.9 (CO), 136.6 (C, Cp), 95.6 (CH, Cp), 92.0 (CH, Cp), 89.1 (CH, Cp), 88.0 (CH, Cp), 83.0 (CH_2), 65.2 (CH_3), 61.1 (CH_3), 25.6 (CH_2). Anal. Found: C, 25.93; H, 2.98; N, 5.85. $C_{10}H_{14}N_2O_2ReBF_4$ Calc.: C, 25.70; H, 3.02; N, 6.00%.

4.4. Preparation of $[\eta^5:\eta^1$-$C_5H_4CH_2CH_2N(CH_3)_2Re(NO)(CO)]^+BPh_4^-$ (5b)

White powders of sodium tetraphenylborate (120 mg, 0.35 mmol) were added to a yellow solution of complex **5a** (130 mg, 0.28 mmol) in methanol (10 ml) at room temperature. After stirring for 5 min, pale yellow powders were collected centrifugally and washed twice with methanol to give a quantitative yield of **5b**. Single crystals of **5b** were obtained by dissolving the pale yellow powders of **5b** in hot acetone and allowing it to stand in a refrigerator overnight. Orange crystals were obtained with the following properties. M.p. 190°C (dec.). ^1H NMR (CD_3COCD_3, 200 MHz): δ 7.37–7.28 (8H, m), 6.92 (8H, t, J = 7.2 Hz), 6.81–6.72 (6H, m, Ph and 2Cp–Hs), 6.24–6.20 (1H, m, Cp–H), 5.81–5.77 (1H, m, Cp–H), 3.96–3.89 (2H, m, H_1s), 3.72 (3H, s), 3.47 (3H, s), 2.95 (1H, dt, J = 14.7, 6.6 Hz, H_{2a}), 2.70 (1H, dt, J = 14.7, 6.0 Hz, H_{2b}).

4.5. Crystal structure of $[\eta^5:\eta^1\text{-}C_5H_4CH_2CH_2N(CH_3)_2Re(NO)(CO)]^+BPh_4^-$ (5b)

A single crystal of **5b** was obtained by cooling a hot acetone solution of **5b** in a refrigerator overnight. Diffraction measurements were made on an Enraf-Nonius CAD-4 diffractometer using graphite monochromated Mo Kα radiation ($\lambda = 0.71069$ Å) in the θ–2θ scan mode. Unit cell dimensions were obtained by least-squares refinement with 25 centered reflections for which $20.24° < 2\theta < 36.00°$. The highest peak of the last difference map (2.710 e Å^{-3}) is in the neighborhood of the rhenium atom (1.124 Å). Other crystal data and refinement details are listed in Table 3. Atomic coordinates are listed in Table 4.

4.6. Preparation of $\eta^5:\eta^1\text{-}C_5H_4CH_2CH_2N(CH_3)_2Re(NO)Br$ (6)

To a stirred red solution of bromide **4** (402 mg, 0.87 mmol) in acetone (15 ml) at 0°C was added anhydrous $(CH_3)_3NO$ (78 mg, 1.04 mmol) in several portions over 3 min. After stirring at 0°C for an additional 30 min, the resulting green solution was transferred to a short silica gel column (1.8 cm × 22 cm) and eluted with 5% followed by 20% acetone in CH_2Cl_2. A green band was collected and concentrated to give green powders of **6** (288 mg, 76% yield). The solubility of **6** in acetone is only moderate. Other physical properties are as follows. TLC: $R_f = 0.86$ (silica gel, 30% acetone in CH_2Cl_2). IR (CH_2Cl_2): 1637s cm^{-1}. ^{1}H NMR (CD_3COCD_3, 300 MHz): δ 6.59–6.58 (1H, m, Cp–H), 6.28–6.27 (1H, m, Cp–H), 5.03–5.01 (1H, m, Cp–H), 3.90–3.88 (1H, m, Cp–H), 3.65 (1H, ddd, $J = 11.8$, 7.2, 5.4 Hz, H_{1a}), 3.46 (1H, ddd, $J = 11.8$, 6.8, 5.3 Hz, H_{1b}), 3.25 (3H, s, N–CH_3), 3.04 (3H, s, N–CH_3), 2.54 (1H, ddd, $J =$ 14.3, 7.2, 5.3 Hz, H_{2a}), 2.21 (1H, ddd, $J = 14.3$, 6.8, 5.4 Hz, H_{2b}). Mass spectra (FAB, ^{187}Re), *m/e* (rel. int. (%)): 433 (M^+, 10). Anal. Found: C, 25.25; H, 3.22; N, 6.25. $C_9H_{14}BrN_2ORe$ Calc.: C, 25.00; H, 3.26; N, 6.48%.

4.7. Preparation of $[\eta^5:\eta^1\text{-}C_5H_4CH_2CH_2N(CH_3)_2Re(NO)(CH_3CN)]^+BF_4^-$ (7)

A solution of $(CH_3)_3NO$ (110 mg, 1.40 mmol) in CH_3CN (20 ml) was added dropwise to a stirred yellow solution of **5a** (650 mg, 1.39 mmol) at 0°C over 10 min. After stirring for an additional 10 min, CH_3CN was evaporated under reduced pressure to about 2 ml; CH_2Cl_2 (50 ml) was then added. Some precipitations were filtered off through Celite. Hexane (10 ml) was added and the resulting solution was allowed to stand in a refrigerator overnight. Red crystals were collected. Hexane was added to the mother liquid and allowed for more crystallization in a refrigerator. Crystals were

Table 3
Crystal data and details of the structure determination of complexes **5b** and **8b**

Complex	**5b**	**8b**
Formula	$C_{14}H_{14}BN_2O_2Re$	$C_{11}H_{17}N_2O_2Re$
Molecular weight	699.67	395.47
Crystal system	monoclinic	monoclinic
Space group	$P2_1/n$	$P2_1/n$
a (Å)	10.2654(10)	11.7268(13)
b (Å)	27.7013(10)	7.4297(7)
c (Å)	10.5097(10)	14.5777(21)
β (°)	90.554(5)	106.154(10)
Cell volume (Å^3)	2988.5(4)	1219.9(2)
Z; D_{calc} (g cm^{-3})	4; 1.555	4; 2.153
F(000)	1392	752
Crystal size (mm^3)	0.50 × 0.38 × 0.06	0.25 × 0.25 × 0.28
Scan range (°)	0.65 + 0.46 tan(θ)	0.70 + 0.35 tan(θ)
2θ range (°)	4–45	4–50
h, k, l range	(−12; 12), (0; 32), (0; 12)	(−13; 13), (0; 8), (0; 17)
μ (cm^{-1})	41.52	100.8
No. of collected reflections	5551	2258
No. of unique reflections	5245	2147
No. of reflections with $I > 2.5\sigma(I)$	3987	1786
No. of refined parameters	361	146
Weighting scheme	$1/\sigma^2(F)$	$1/\sigma^2(F)$
Final R, R_w	0.031, 0.039	0.030, 0.047
GOF	1.64	2.49
Maximum shift/σ ratio	0.0016	0.012
Min, max difference map (e Å^{-3})	−0.650, 2.710	−1.180, 2.510

Table 4
Atomic coordinates and B_{iso} of **5b**

Atom	x	y	z	B_{iso}
Re	0.79616(2)	0.11414(1)	0.05055(2)	3.28(1)
B	0.7622(6)	0.3674(2)	0.1047(6)	2.7(2)
N(1)	0.8274(6)	0.0562(2)	−0.0276(5)	5.3(3)
N(2)	0.8379(4)	0.0925(2)	0.2459(4)	3.3(2)
O(1)	1.0523(5)	0.1574(2)	−0.0209(5)	7.6(3)
O(2)	0.8428(6)	0.0198(2)	−0.0811(5)	7.4(3)
C(1)	0.9592(6)	0.1389(2)	0.0119(6)	4.1(3)
C(2)	0.6293(6)	0.1487(2)	0.1577(6)	4.2(3)
C(3)	0.5758(6)	0.1180(2)	0.0649(6)	4.3(3)
C(4)	0.6133(6)	0.1353(3)	−0.0576(6)	4.8(3)
C(5)	0.6908(7)	0.1772(2)	−0.0377(6)	5.3(3)
C(6)	0.6991(7)	0.1857(2)	0.0967(7)	4.7(3)
C(7)	0.6342(7)	0.1360(3)	0.2993(6)	5.2(3)
C(8)	0.7122(7)	0.0908(3)	0.3175(6)	4.8(3)
C(9)	0.9292(6)	0.1270(2)	0.3130(6)	4.1(3)
C(10)	0.9005(8)	0.0442(2)	0.2613(7)	5.7(4)
C(11)	0.6068(5)	0.3678(2)	0.1305(5)	3.0(2)
C(12)	0.5310(6)	0.3254(2)	0.1303(6)	4.0(3)
C(13)	0.3964(7)	0.3265(3)	0.1417(7)	5.3(3)
C(14)	0.3317(7)	0.3698(4)	0.1539(6)	5.7(4)
C(15)	0.3999(7)	0.4113(3)	0.1547(6)	5.1(3)
C(16)	0.5351(6)	0.4106(2)	0.1428(5)	3.9(3)
C(21)	0.7756(5)	0.3691(2)	−0.0514(5)	3.3(2)
C(22)	0.7847(6)	0.3283(2)	−0.1274(6)	4.5(3)
C(23)	0.7858(7)	0.3303(3)	−0.2604(7)	6.6(4)
C(24)	0.7774(8)	0.3747(4)	−0.3204(7)	7.3(5)
C(25)	0.7665(7)	0.4149(3)	−0.2500(8)	6.2(4)
C(26)	0.7660(6)	0.4128(2)	−0.1184(6)	4.5(3)
C(31)	0.8381(5)	0.3203(2)	0.1682(5)	3.1(2)
C(32)	0.9540(6)	0.3017(2)	0.1225(6)	4.2(3)
C(33)	1.0248(7)	0.2665(2)	0.1857(8)	5.7(4)
C(34)	0.9854(8)	0.2497(2)	0.3021(8)	5.6(4)
C(35)	0.8718(9)	0.2668(2)	0.3517(6)	5.4(4)
C(36)	0.7986(6)	0.3016(2)	0.2850(6)	4.1(3)
C(41)	0.8400(5)	0.4123(2)	0.1738(5)	3.1(2)
C(42)	0.9517(6)	0.4340(2)	0.1239(6)	4.0(3)
C(43)	1.0244(7)	0.4683(2)	0.1891(7)	5.3(3)
C(44)	0.9873(7)	0.4816(2)	0.3108(7)	5.2(3)
C(45)	0.8808(7)	0.4615(2)	0.3638(6)	4.5(3)
C(46)	0.8079(6)	0.4272(2)	0.2975(5)	3.8(3)

combined to give a total of 420 mg (62%) of complex **7**. M.p. 121–122°C. IR (CH_2Cl_2): 1677 cm^{-1}. ^1H NMR (CD_3COCD_3, 300 MHz): δ 6.84–6.82 (1H, m, Cp–H), 6.20–6.18 (1H, m, Cp–H), 5.69–5.67 (1H, m, Cp–H), 4.63–4.61 (1H, m, Cp–H), 3.80 (1H, dt, J = 12, 5.7 Hz, H_{1a}), 3.69 (1H, ddd, J = 12, 8.3, 5.7 Hz, H_{1b}), 3.32 (3H, s, N–CH_3), 3.24 (3H, s, CH_3CN), 3.11 (3H, s, N–CH_3), 2.62 (1H, dt, J = 14.5, 5.7 Hz, H_{2a}), 2.42 (1H, ddd, J = 14.5, 8.3, 5.7 Hz, H_{2b}). ^{13}C NMR (CD_3CN, 75 MHz): δ 141.4 (C, CN), 132.6 (C, Cp), 97.9 (CH, Cp), 86.0 (CH, Cp), 82.9 (CH, Cp), 81.6 (CH_2), 79.9 (CH, Cp), 60.8 (CH_3), 56.0 (CH_3), 25.8 (CH_2), 4.3 (CH_3, CH_3CN). Mass spectra (FAB, ^{187}Re), *m/e* (rel. int. (%)): 394 (M^+–BF_4, 100), 353 (M^+–BF_4–CH_3CN, 52). Anal. Found: C, 25.65; H, 3.45; N, 8.95. $C_{11}H_{17}N_3OReBF_4$ Calc.: C, 25.51; H, 3.57; N, 8.75%.

4.8. General procedure for the preparation of η^5:η^1-$C_5H_4CH_2CH_2N(CH_3)_2Re(NO)COR$ (8) (R = n-butyl, methyl, ethyl, isopropyl, benzyl)

Over a period of 3 min, a solution of alkylmetal reagent (n-butyllithium, methylmagnesium chloride, ethylmagnesium bromide, isopropylmagnesium chloride, benzylmagnesium chloride) (1.5 mmol) was added to a stirred suspension of **5a** (560 mg, 1.2 mmol) in THF (15 ml) at −78°C. After addition was complete, the cold bath was removed and the solution allowed to stir at room temperature for 20–30 min. The resulting orange solution was concentrated under reduced pressure. The residue was then dissolved with CH_2Cl_2 (2 ml) and flash column chromatographed on neutral alumina (activity V) upon elution with EtOAc. The first yellow or orange band was collected and concentrated to provide the desired product in 56–78% yield.

4.8.1. η^5:η^1-$C_5H_4CH_2CH_2N(CH_3)_2Re(NO)COCH_2CH_2CH_2CH_3$ (8a)

Orange liquid (65%). IR (CH_2Cl_2): 1618s, 1519m, 1456w cm^{-1}. ^1H NMR ($CDCl_3$, 300 MHz): δ 6.12–6.10 (1H, m, Cp–H), 5.56–5.54 (1H, m, Cp–H), 4.80–4.78 (1H, m, Cp–H), 4.56–4.54 (1H, m, Cp–H), 3.76–3.63 (1H, m, H_{1a}), 3.31–3.22 (1H, m, H_{2a}), 3.23 (3H, s, N–CH_3), 3.14–3.00 (2H, m, H_{1b} and H_{2b}), 3.03 (3H, s, N–CH_3), 2.54–2.44 (1H, m, $H_{2'a}$), 2.28–2.16 (1H, m, $H_{2'b}$), 1.61–1.51 (2H, m, $H_{3'}$), 1.43–1.29 (2H, m, $H_{4'}$), 0.91 (3H, t, J = 7.3 Hz, $H_{5'}$). ^{13}C ($CDCl_3$, 75 MHz): δ 263.0 (CO, $C_{1'}$), 127.9 (C, Cp), 98.1 (CH, Cp), 88.6 (CH, Cp), 81.7 (CH, Cp), 81.0 (CH, Cp), 78.7 (CH_2, C_1), 63.0 (CH_2, C_2), 61.8 (CH_3, N–CH_3), 58.6 (CH_3, N–CH_3), 28.3 (CH_2, $C_{3'}$), 25.1 (CH_2, $C_{2'}$), 22.6 (CH_2, $C_{4'}$), 14.1 (CH_3, $C_{5'}$). Mass spectra (FAB, ^{187}Re), *m/e* (rel. int. (%)): 439 (M^+ + 1, 20), 381 (M^+–C_4H_9, 100), 351 (M^+–C_4H_9–NO, 96). Anal. Found: C, 38.25; H, 5.35; N, 6.52. $C_{14}H_{23}N_2O_2Re$ Calc.: C, 38.43; H, 5.30; N, 6.40%.

4.8.2. η^5:η^1-$C_5H_4CH_2CH_2N(CH_3)_2Re(NO)COCH_3$ (8b)

Orange crystal (74%). M.p. 156°C (dec.). IR (CH_2Cl_2): 1616s, 1517m, 1455w cm^{-1}. ^1H NMR ($CDCl_3$, 300 MHz): δ 6.14–6.12 (1H, m, Cp–H), 5.56–5.54 (1H, m, Cp–H), 4.85–4.83 (1H, m, Cp–H), 4.59–4.57 (1H, m, Cp–H), 3.69 (1H, ddd, J = 11.8, 10.8, 5.3 Hz, H_{1a}), 3.23 (3H, s, N–CH_3), 3.13 (1H, ddd, J = 11.8, 5.1, 3.7 Hz, H_{1b}), 3.05 (3H, s, N–CH_3), 2.82 (3H, s, –$COCH_3$), 2.50 (1H, ddd, J = 14.5, 10.8, 5.1 Hz, H_{2a}), 2.21 (1H, ddd, J = 14.5, 5.3, 3.7 Hz, H_{2b}). ^{13}C ($CDCl_3$, 75 MH): δ 259.9 (CO, $C_{1'}$), 128.2 (C, Cp), 98.0 (CH, Cp), 88.8 (CH, Cp), 82.0 (CH, Cp), 81.6 (CH, Cp), 78.8 (CH_2, C_1), 61.6 (CH_3, N–CH_3), 58.4 (CH_3, N–CH_3), 50.1 (CH_3, $C_{2'}$), 25.0 (CH_2, C_2). Mass spectra (FAB, ^{187}Re), *m/e* (rel. int. (%)): 397 (M^+ + 1, 36), 381

(M^+–CH_3, 100), 351 (M^+–CH_3–NO, 40). Anal. Found: C, 33.35; H, 4.38; N, 7.15. $C_{11}H_{17}N_2O_2Re$ Calc.: C, 33.41; H, 4.33; N, 7.08%.

4.8.3. $\eta^5:\eta^1$-$C_5H_4CH_2CH_2N(CH_3)_2Re(NO)$-$COCH_2CH_3$ (8c)

Yellow powder (78%). IR (CH_2Cl_2): 1615s, 1521m, 1456w cm^{-1}. ^1H NMR ($CDCl_3$, 300 MHz): δ 6.14–6.12 (1H, m, Cp–H), 5.56–5.54 (1H, m Cp–H), 4.81–4.79 (1H, m, Cp–H), 4.57–4.55 (1H, m, Cp–H), 3.70 (1H, td, J = 11.3, 5.3 Hz, H_{1a}), 3.24 (3H, s, N–CH_3), 3.26–3.11 (2H, m, $H_{2'}$), 3.11 (1H, ddd, J = 11.8, 5.2, 3.7 Hz, H_{1b}), 3.03 (3H, s, N–CH_3), 2.49 (1H, ddd, J = 14.4, 10.8, 5.2 Hz, H_{2a}), 2.20 (1H, ddd, J = 14.4, 5.3, 3.7 Hz, H_{2b}), 1.03 (3H, t, J = 7.4 Hz, CH_3). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 263.2 (CO, $C_{1'}$), 128.0 (C, Cp), 98.1 (CH, Cp), 88.6 (CH, Cp), 81.8 (CH, Cp), 80.9 (CH, Cp), 78.7 (CH_2, C_1), 61.7 (CH_3, N–CH_3), 58.6 (CH_3, N–CH_3), 55.8 (CH_2, $C_{2'}$), 25.1 (CH_2, C_2), 10.3 (CH_3, $C_{3'}$). Mass spectra (FAB, ^{187}Re), m/e (rel. int. (%)): 411 (M^+ + 1, 34), 381 (M^+–C_2H_5, 100), 351 (M^+–C_2H_5–NO, 30). Anal. Found: C, 35.32; H, 4.65; N, 6.60. $C_{12}H_{19}N_2O_2Re$ Calc.: C, 35.20; H, 4.68; N, 6.84%.

4.8.4. $\eta^5:\eta^1$-$C_5H_4CH_2CH_2N(CH_3)_2Re(NO)COCH$-$(CH_3)_2$ (8d)

Orange-brown liquid (68%). IR (CH_2Cl_2): 1614s, 1522m, 1450w cm^{-1}. ^1H NMR ($CDCl_3$, 300 MHz): δ 6.14–6.12 (1H, m, Cp–H), 5.57–5.55 (1H, m, Cp–H), 4.77–4.75 (1H, m, Cp–H), 4.56–4.54 (1H, m, Cp–H), 3.71 (1H, td, J = 11.3, 5.4 Hz, H_{1a}), 3.69 (1H, heptet, J = 6.8 Hz, $H_{2'}$), 3.23 (3H, s, N–CH_3), 3.09 (1H, ddd, J = 11.8, 5.1, 3.6 Hz, H_{1b}), 3.03 (3H, s, N–CH_3), 2.49 (1H, ddd, J = 14.5, 11.0, 5.1 Hz, H_{2a}), 2.20 (1H, ddd, J = 14.5, 5.4, 3.6 Hz, H_{2b}), 1.05 (3H, d, J = 6.8 Hz, isopropyl–CH_3), 1.02 (3H, d, J = 6.8 Hz, isopropyl–CH_3). ^{13}C ($CDCl_3$, 75 MHz): δ 267.5 (CO, $C_{1'}$), 127.8 (C, Cp), 97.8 (CH, Cp), 88.6 (CH, Cp), 81.5 (CH, Cp), 80.4 (CH, Cp), 78.6 (CH_2, C_1), 61.8 (CH_3, N–CH_3), 59.1 (CH, $C_{2'}$), 58.9 (CH_3, N–CH_3), 25.1 (CH_2, C_2), 19.9 (CH_3, $C_{3'a}$), 18.8 (CH_3, $C_{3'b}$). Mass spectra (FAB, ^{187}Re), m/e (rel. int. (%)): 425 (M^+ + 1, 20), 381 (M^+–C_3H_7, 100), 351 (M^+–C_3H_7–NO, 25). Anal. Found: C, 37.12; H, 5.02; N, 6.44. $C_{13}H_{21}N_2O_2Re$ Calc.: C, 36.87; H, 5.00; N, 6.61%.

4.8.5. $\eta^5:\eta^1$-$C_5H_4CH_2CH_2N(CH_3)_2Re(NO)COCH_2Ph$ (8e)

Orange needles (56%). M.p. 154°C (dec.). IR (CH_2Cl_2): 1618s, 1524m, 1451w cm^{-1}. ^1H ($CDCl_3$, 300 MHz): δ 7.40–7.37 (2H, m, phenyl), 7.27–7.21 (2H, m, phenyl), 7.13 (1H, tt, J = 7.2, 2.1 Hz, $H_{6'}$), 5.88–5.68 (1H, m, Cp–H), 5.53 (1H, dd, J = 3.8, 2.4 Hz, Cp–H), 4.77 (1H, dd, J = 4.6, 2.2 Hz, Cp–H), 4.54 (1H, dd, J = 4.5, 2.6 Hz, Cp–H), 4.50 (1H, d, J = 11.9 Hz, benzylic–H_a), 4.33 (1H, d, J = 11.9 Hz, benzylic–H_b), 3.63 (1H, ddd, J = 11.8, 9.7, 5.3 Hz, H_{1a}), 3.10 (1H, dt, J = 11.8, 5.0 Hz, H_{1b}), 3.08 (3H, s, N–CH_3), 2.81 (3H, s, N–CH_3), 2.42 (1H, ddd, J = 14.5, 9.7, 5.1 Hz, H_{2a}), 2.17 (1H, dt, J = 14.5, 5.0 Hz, H_{2b}). ^{13}C ($CDCl_3$, 75 MHz): δ 257.6 (CO), 138.2 (C, phenyl), 129.9 (CH × 2, phenyl), 128.1 (C, Cp), 128.0 (CH × 2, phenyl), 125.3 (CH, phenyl), 98.1 (CH, Cp), 88.3 (CH, Cp), 82.4 (CH, Cp), 81.6 (CH, Cp), 79.5 (CH_2, C_1), 70.1 (CH_2, benzylic), 61.4 (CH_3, N–CH_3), 58.6 (CH_3, N–CH_3), 25.2 (CH_2, C_2). Mass spectra (FAB, ^{187}Re), m/e (rel. int. (%)): 473 (M^+ + 1, 8), 381 (M^+–benzyl, 100), 351 (M^+–benzyl–NO, 38). Anal. Found: C, 43.48; H, 4.55; N, 5.65. $C_{17}H_{21}N_2O_2Re$ Calc.: C, 43.30; H, 4.49; N, 5.94%.

Table 5
Atomic coordinates and B_{iso} of **8b**

Atom	x	y	z	B_{iso}
Re	0.50182(3)	0.04318(5)	0.24186(3)	2.36(2)
O(1)	0.6231(8)	−0.1656(13)	0.1217(6)	5.0(4)
O(2)	0.2432(7)	0.0782(12)	0.1658(7)	5.1(5)
N(1)	0.5721(8)	−0.0787(12)	0.1692(6)	3.1(4)
N(2)	0.5080(8)	0.3184(12)	0.1881(6)	3.1(4)
C(1)	0.5241(11)	0.2176(16)	0.3770(7)	3.7(5)
C(2)	0.4170(11)	0.1167(17)	0.3591(8)	3.8(6)
C(3)	0.4456(12)	−0.0731(17)	0.3625(9)	4.4(6)
C(4)	0.5719(12)	−0.0854(16)	0.3848(8)	4.0(6)
C(5)	0.6195(11)	0.0924(17)	0.3955(7)	3.9(5)
C(6)	0.5317(12)	0.4135(15)	0.3559(8)	4.0(6)
C(7)	0.4699(13)	0.4450(18)	0.2554(9)	5.0(7)
C(8)	0.4335(14)	0.3551(19)	0.0883(9)	5.9(8)
C(9)	0.6289(13)	0.3613(20)	0.1813(13)	6.8(9)
C(10)	0.3329(10)	0.0131(15)	0.1497(8)	3.2(5)
C(11)	0.3139(11)	−0.1030(17)	0.0618(8)	4.2(6)

4.9. Crystal structure of $\eta^5:\eta^1$-$C_5H_4CH_2CH_2N(CH_3)_2$-$Re(NO)COCH_3$ (8b)

A single crystal of **8b** was obtained by allowing a solution of **8b** in CH_2Cl_2/hexane (1 : 5) to stand in a refrigerator overnight. Diffraction measurements were made on an Enraf-Nonius CAD-4 diffractometer using graphite monochromated Mo Kα radiation (λ = 0.71069 Å) in the θ–2θ scan mode. Unit cell dimensions were obtained by least-squares refinement with 25 centered reflections for which 15.04° < 2θ < 31.94°. Other crystal data and refinement details are listed in Table 3. Atomic coordinates are listed in Table 5.

5. Supplementary material available

Tables of data collection parameters, bond lengths and bond angles, torsion angles, fractional atomic coordinates, and anisotropic thermal parameters for **5b** and **8b** are available from T.-F.W.

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