

Carbonyl ligand substitution of an aminerenium benzyl complex. Interconversion of η^1 - and η^3 -benzyl complexes

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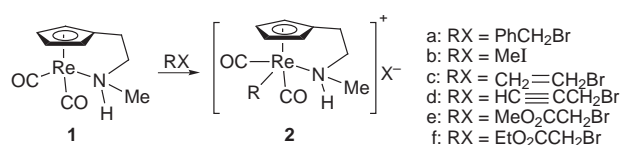
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Removal of a CO ligand from the η^1 -benzyl complex $[\text{Re}(\text{CO})_2(\eta^1\text{-CH}_2\text{Ph})\{\text{NH}(\text{Me})\text{CH}_2\text{CH}_2(\eta^5\text{-C}_5\text{H}_4)\}]^+\text{Br}^-$ yielded an η^3 -benzyl complex. The η^3 co-ordination mode was converted into η^1 when the compound was dissolved in acetonitrile. Evaporation of acetonitrile removed the labile acetonitrile ligand and regenerated the η^3 -benzyl complex. The η^3 -benzyl complex $[\text{Re}(\text{CO})(\eta^3\text{-CH}_2\text{Ph})\{\text{NH}(\text{Me})\text{CH}_2\text{CH}_2(\eta^5\text{-C}_5\text{H}_4)\}]^+\text{BF}_4^-$ is stable to air and moisture. The corresponding perrhenate salt has been characterized crystallographically. The tetrafluoroborate reacted with bromide, chloride and acetate anion to give the corresponding neutral η^1 -benzyl complexes in excellent yield. When treated with two-electron donor ligands, such as *tert*-butyl isocyanide and pyridine, it was converted into the corresponding (η^1 -benzyl)(isocyanide) and pyridine complexes.

Amines are the classic ligands of co-ordination chemistry, but they have not often been used with organotransition-metal compounds.¹ Unlike ligands containing the heavier Group 15 atoms, they show no π -acceptor ability. Therefore, they co-ordinate only weakly to the low-valent transition metals and form relatively labile complexes.² However, through intramolecular chelation, stable amine complexes of manganese,³ molybdenum⁴ and rhenium^{5,6} have been prepared. Strong σ donation of amine ligands to low-valent transition metals makes the metal centre much more electron-rich, thereby enhancing its ability to undergo nucleophilic reactions. We have reported such reactions of an aminerenium complex with various electrophiles.⁶ Complex **1** reacts with electrophiles to give exclusively the alkyl complexes **2** (see Scheme 1). Benzyl complex **2a** has been characterized by X-ray crystallography. The benzyl group and the amine ligand are mutually *trans* in a four-legged piano-stool structure. The carbonyl stretching bands of the aminerenium complex **1** appear at 1893 and 1816 cm^{-1} . Upon alkylation at Re to give cationic **2a** these bands shift to higher wavenumbers at 2034 and 1966 cm^{-1} , suggesting that the carbonyl ligands should be relatively labile. Ligand substitution of this type of labile carbonyl ligand is not uncommon.⁷ However, it is also of interest to see whether the η^1 -benzyl group forms the corresponding η^3 -benzyl complex when a carbonyl ligand is ejected.⁸ Here, we report the results of ligand substitution reactions of the benzyl complex **2a**, and the formation of a stable η^3 -benzyl complex.

Results and Discussion

The carbonyl groups of complex **2a** are tightly bonded to the metal and are not displaced by triphenylphosphine and isocyanides at ambient temperature through a dissociation-association mechanism.⁷ Extrusion of a carbonyl ligand by use of N-oxides was therefore investigated.⁹ Treatment of **2a** with either Me_3NO or PhIO in MeCN did cause extrusion of CO, only decomposition resulted. When 1 equivalent of the reagent was used similar decomposition was observed and some **2a** was recovered. These results suggest that the expected acetonitrile complex reacts much faster with the oxidizing agent than does **2a**. Nevertheless, when the reaction was carried out in acetone, the bromide **3** (66%) and the η^3 -benzyl complex **4** (5%) were obtained (see Scheme 2). The latter precipitated from the reaction mixture.



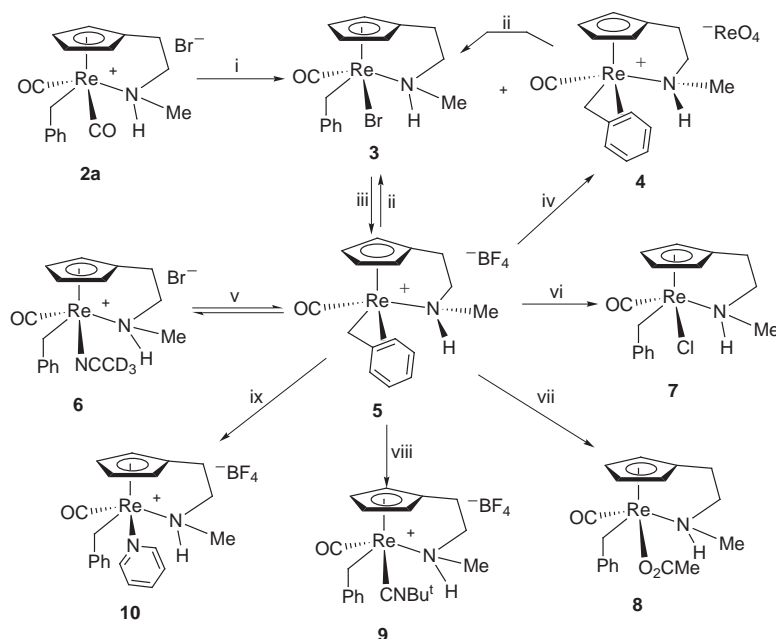
Scheme 1

The characterization of bromide **3** is based on spectroscopy. In the carbonyl stretching region of the infrared spectrum only one absorption at 1877 cm^{-1} was observed, indicating a terminal CO ligand. In the ¹H NMR spectrum the N-methyl group appeared at δ 3.12 as a doublet, suggesting that the Re–N bond is intact. The doublet signal of the methyl group, arising from the coupling with the N–H proton, is a general feature for amines ligated to rhenium.⁶ The diastereotopic benzylic protons appeared at δ 4.38 and 3.98. The four inequivalent C₅H₄ protons were observed at δ 5.79, 5.48, 4.91 and 3.47. These spectroscopic data and the presence of a molecular ion peak in the mass spectrum suggest the formulation shown. The relative stereochemistry of the N-methyl and the CO ligand is not defined.

The terminal carbonyl stretching of complex **4** appeared at 1927 cm^{-1} . The phenyl protons of **4** give rise to five distinctive signals in the ¹H NMR spectrum, suggesting that the benzene ring is not freely rotating. Definitive structural characterization of **4** was carried out by a single-crystal X-ray analysis. Fig. 1 shows that the benzyl group binds to the rhenium in an η^3 fashion with *exo* orientation. Bond distances (Table 1) from rhenium to the η^3 -carbons are 2.197 Å for Re–CH₂, 2.333 Å for Re–C_{ipso} and 2.535 Å for Re–C_{ortho}. The latter is 0.338 Å longer than the Re–CH₂ bond length, compatible with those reported for η^3 -benzyl complexes.¹¹ Being co-ordinated to the rhenium, C_{ipso}–C_{ortho} [C(11)–C(16)] is lengthened from the average value of 1.38 Å of benzene to 1.426 Å. Other carbon–carbon bonds of the six-membered ring show alternation in lengths, consistent with some localization of single and double bonds. Average distances are 1.426 Å for the ‘single bonds’ C(11)–C(12), C(13)–C(14) and C(15)–C(16) and 1.35 Å for the ‘double bonds’ C(12)–C(13) and C(14)–C(15). The N-methyl group and the CO ligand are mutually *syn*.

The perrhenate anion of the η^3 -benzyl complex **4** is apparently derived from over oxidation of some rhenium complexes by Me_3NO . The η^3 -benzyl complex **4** could be converted into the bromide **3** by excess of LiBr. Abstraction of the bromide anion from **3** with silver tetrafluoroborate in acetonitrile gave

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Scheme 2 (i) Me_3NO , acetone, room temperature (r.t.); (ii) LiBr , MeOH ; (iii) AgBF_4 , MeCN , 0°C ; (iv) KReO_4 , acetone; (v) CD_3CN ; (vi) LiCl , MeOH ; (vii) NaO_2CMe , MeOH ; (viii) Bu^nNC , CH_2Cl_2 ; (ix) pyridine, CH_2Cl_2

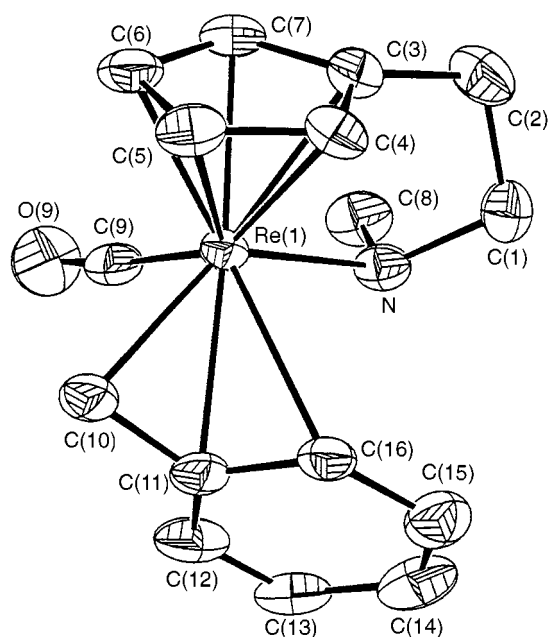


Fig. 1 An ORTEP¹⁰ drawing of $[\text{Re}(\text{CO})(\eta^3\text{-CH}_2\text{Ph})(\text{NH}(\text{Me})\text{-CH}_2\text{CH}_2(\eta^5\text{-C}_5\text{H}_4))]^+\text{ReO}_4^-$ **4**; ReO_4^- is omitted for simplicity

the corresponding acetonitrile complex, which showed a CO stretching band at 1908 cm^{-1} in the infrared spectrum. However, upon removal of acetonitrile and dissolving the residue in CH_2Cl_2 , the CO band shifts to 1927 cm^{-1} , which is the same frequency as that for the η^3 -benzyl complex **4**. The ^1H NMR spectrum also shows similarity with that of **4**. Therefore, the final product is believed to be the η^3 -benzyl complex **5**. Anion exchange of **5** with potassium perchlerate gave **4**, thus confirming the assignment. The *ipso*- and the co-ordinated *ortho*-carbons of the benzene ring of **5** resonate at δ 105.1 and 92.1 respectively in the ^{13}C NMR spectrum, consistent with the η^3 bonding mode. Solid **5** is stable at room temperature in air. In solution $[(\text{CD}_3)_2\text{CO}]$ there is no visible decomposition and the ^1H NMR spectrum remained unchanged after the solution was kept at room temperature in air overnight.

In the presence of acetonitrile the η^3 -benzyl complex **5** is in equilibrium with the corresponding (η^1 -benzyl)(acetonitrile)

Table 1 Selected bond lengths (\AA) and angles ($^\circ$) for complex **4**

$\text{Re}(1)\text{-Cp}^*$	1.918(1)	$\text{C}(11)\text{-C}(12)$	1.443(15)
$\text{Re}(1)\text{-N}$	2.189(8)	$\text{C}(11)\text{-C}(16)$	1.426(13)
$\text{Re}(1)\text{-C}(9)$	1.866(11)	$\text{C}(12)\text{-C}(13)$	1.339(18)
$\text{Re}(1)\text{-C}(10)$	2.197(10)	$\text{C}(13)\text{-C}(14)$	1.428(17)
$\text{Re}(1)\text{-C}(11)$	2.333(10)	$\text{C}(14)\text{-C}(15)$	1.369(17)
$\text{Re}(1)\text{-C}(16)$	2.535(10)	$\text{C}(15)\text{-C}(16)$	1.417(16)
$\text{C}(10)\text{-C}(11)$	1.454(15)		
$\text{Cp-}\text{Re}(1)\text{-N}$	107.2(2)	$\text{N-}\text{Re}(1)\text{-C}(16)$	82.1(3)
$\text{Cp-}\text{Re}(1)\text{-C}(9)$	123.3(3)	$\text{Re}(1)\text{-C}(9)\text{-O}(9)$	173.3(9)
$\text{Cp-}\text{Re}(1)\text{-C}(10)$	115.9(3)	$\text{C}(9)\text{-}\text{Re}(1)\text{-C}(10)$	82.5(4)
$\text{Cp-}\text{Re}(1)\text{-C}(11)$	138.9(3)	$\text{C}(9)\text{-}\text{Re}(1)\text{-C}(11)$	89.1(4)
$\text{Cp-}\text{Re}(1)\text{-C}(16)$	116.0(2)	$\text{C}(9)\text{-}\text{Re}(1)\text{-C}(16)$	119.7(4)
$\text{Cp-}\text{C}(3)\text{-C}(2)$	169.8(9)	$\text{C}(10)\text{-}\text{Re}(1)\text{-C}(11)$	37.3(4)
$\text{N-}\text{Re}(1)\text{-C}(9)$	90.4(4)	$\text{C}(10)\text{-}\text{Re}(1)\text{-C}(16)$	62.0(3)
$\text{N-}\text{Re}(1)\text{-C}(10)$	132.5(3)	$\text{C}(11)\text{-}\text{Re}(1)\text{-C}(16)$	33.7(3)
$\text{N-}\text{Re}(1)\text{-C}(11)$	96.0(3)	$\text{C}(10)\text{-}\text{C}(11)\text{-C}(16)$	116.9(3)

*Cp means the centre of the C_5H_4 ring.

complex **6**. The ^1H NMR spectrum of **5** in CD_3CN showed that **5** and **6** reach equilibrium in a ratio of 1:6 in less than 5 min. Evaporation of CD_3CN and dissolving the residue in $(\text{CD}_3)_2\text{CO}$ regenerates **5** completely, as shown by the ^1H NMR spectrum. The ease of formation of the η^3 -benzyl complex **5** over the acetonitrile complex **6** is interesting, because in the η^3 -binding mode the aromaticity of the six-membered ring is destroyed.

Although the η^3 -benzyl complex **5** is much more stable than the corresponding (η^1 -benzyl)(acetonitrile) complex, addition of ligands to the former proceeded smoothly to give the corresponding η^1 -benzyl complexes.¹² Treatment of **5** with an excess of lithium bromide provided bromide **3** in quantitative yield. Similarly, **5** reacts with an excess of lithium chloride and sodium acetate, to provide chloride **7** and acetate **8** respectively. Characterization of **7** and **8** was based upon their spectral data and elemental analyses. Complex **5** also reacts with two-electron donor ligands, such as *tert*-butyl isocyanide and pyridine, to give the cationic complexes **9** and **10** respectively. Isocyanide complex **9** shows characteristic isocyanide and carbonyl stretchings at 2176 and 1927 cm^{-1} respectively. The terminal CO stretching of the pyridine complex **10** appeared at 1893 cm^{-1} in the infrared spectrum. The pyridine is co-

ordinated in an η^1 -N mode, as suggested by the ^1H and ^{13}C NMR spectra.

In conclusion, a stable η^3 -benzyl complex has been prepared from the dicarbonyl **2a** in two steps. In acetonitrile solution, the η^3 -benzyl **5** and the η^1 -benzyl **6** are both observed, in a ratio of 1:6. Upon removal of acetonitrile the η^3 -benzyl **5** is regenerated. Preference for the η^3 -benzyl **5** over the η^1 -benzyl acetonitrile complex **6** has been testified by adding 1 equivalent of acetonitrile to a $(\text{CD}_3)_2\text{CO}$ solution of **5**. No resonances of the corresponding η^1 -benzyl acetonitrile complex were observed by ^1H NMR spectroscopy. The thermodynamic stability of **5** is noteworthy, because η^3 co-ordination of the benzyl group requires loss of aromaticity.

Experimental

Infrared solution spectra were recorded on a Perkin-Elmer 882 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. Proton (300 MHz) and ^{13}C NMR (75 MHz) spectra were obtained with a Bruker AC-300 FT spectrophotometer. For the assignments the carbon bound to the nitrogen is designated as C^1 and the hydrogens on it as H^{1a} and H^{1b} . The next carbon is designated as C^2 and the hydrogens on it as H^{2a} and H^{2b} . All chemical shifts are expressed in δ relative to SiMe_4 (δ 0.0). Elemental analyses were obtained on a Perkin-Elmer 2400 CHN elemental analyzer. Mass spectra were recorded on a VG 70-250S mass spectrometer.

Syntheses

[Re(CO)(η^1 -CH₂Ph)Br{NH(Me)CH₂CH₂(η^5 -C₅H₄)}] 3. To a stirred solution of complex **2a** (560 mg, 1.04 mmol) in acetone (30 cm³) was added trimethylamine *N*-oxide dihydrate (134 mg, 1.2 mmol) in one portion at room temperature. The progress of the reaction was monitored by infrared spectroscopy. After 30–60 min the CO bands associated with **2a** disappeared. The solvent was evaporated. To the residue was added CH_2Cl_2 (3 cm³). The resulting mixture was flashed through a column packed with silica gel (10 g), using ethyl acetate as eluent. The yellow band was collected and concentrated. The residue was dissolved in CHCl_3 (30 cm³). The resultant yellow solution was allowed to stand in a refrigerator at about 5 °C for 16 h. Some crystalline compound was collected and washed twice with CHCl_3 to give **4** (35 mg, 5% yield). The combined CHCl_3 solution was treated with LiBr (600 mg) at room temperature for 1 h. The resulting mixture was filtered through Celite. Filtrates were concentrated and dissolved in CH_2Cl_2 (5 cm³). The CH_2Cl_2 solution was added to hexane (50 cm³). The resultant orange powder was collected and washed twice with hexane to give **3** (350 mg, 66% yield). M.p. 123–129 °C (decomp.). IR (CH_2Cl_2): 1877s cm⁻¹. ^1H NMR (CDCl_3 , 300 MHz): δ 7.19–7.11 (4 H, m, Ph), 6.94–6.88 (1 H, m, Ph), 5.80–5.78 (1 H, m, C₅H₄), 5.49–5.47 (1 H, m, C₅H₄), 4.92–4.90 (1 H, m, C₅H₄), 4.74 (1 H, br, NH), 4.38 (1 H, d, J = 10.3, benzylic H^a), 3.98 (1 H, d, J = 10.3, benzylic H^b), 3.83–3.74 (1 H, m, H^{1a}), 3.48–3.46 (1 H, m, C₅H₄), 3.34–3.22 (1 H, m, H^{1b}), 3.12 (3 H, d, J = 6.1, NCH₃), 2.23 (1 H, ddd, J = 14.4, 10.3, 5.7, H^{2a}) and 2.07 (1 H, dt, J = 14.4, 4.9 Hz, H^{2b}). ^{13}C NMR (CDCl_3 , 75 MHz): δ 220.6 (CO), 152.4 (C, Ph), 128.0 (CH \times 2, Ph), 127.5 (CH \times 2, Ph), 123.3 (CH, Ph), 123.2 (C, C₅H₄), 99.5 (CH, C₅H₄), 97.9 (CH, C₅H₄), 78.9 (CH, C₅H₄), 73.1 (CH, C₅H₄), 69.2 (CH₂, C¹), 47.3 (NCH₃), 26.6 (CH₂, C²) and 7.1 (CH₂, benzylic CH₂). Mass spectrum (FAB, $^{187}\text{Re}^{81}\text{Br}$): m/z [relative intensity (%)] 509 (M^+ , 5), 428 (M^+ – Br, 100) (Found: C, 37.98; H, 3.69; N, 2.52). $\text{C}_{16}\text{H}_{19}\text{BrNORe}$ requires C, 37.87; H, 3.77; N, 2.76%.

[Re(CO)(η^3 -CH₂Ph){NH(Me)CH₂CH₂(η^5 -C₅H₄)}]⁺ReO₄⁻ 4. Orange crystals. M.p. 199–203 °C (decomp.). IR (CH_2Cl_2): 1927s cm⁻¹. ^1H NMR (CDCl_3 , 300 MHz): δ 8.19 (1 H, t,

J = 7.6), 7.85 (1 H, d, J = 8.6), 7.43 (1 H, t, J = 7.5), 7.18 (1 H, t, J = 8.2), 7.11 (1 H, d, J = 6.4), 6.65–6.63 (1 H, m, C₅H₄), 6.00–5.98 (1 H, m, C₅H₄), 5.28–5.26 (1 H, m, C₅H₄), 4.93–4.91 (1 H, m, C₅H₄), 3.87 (1 H, d, J = 3.7, H^{10a}), 3.69–3.60 (1 H, m, H^{1a}), 3.16 (1 H, d, J = 3.7, H^{10b}), 2.97–2.85 (1 H, m, H^{1b}), 2.77–2.67 (1 H, m, H^{2a}), 2.17–2.10 (1 H, m, H^{2b}) and 2.05 (3 H, d, J = 5.8 Hz, NCH₃). Mass spectrum (FAB, ^{187}Re): m/z [relative intensity (%)] 428 (M^+ , 100) (Found: C, 28.12; H, 2.95; N, 2.35). $\text{C}_{16}\text{H}_{19}\text{NO}_5\text{Re}_2$ requires C, 28.36; H, 2.82; N, 2.07%.

[Re(CO)(η^3 -CH₂Ph){NH(Me)CH₂CH₂(η^5 -C₅H₄)}]⁺BF₄⁻ 5. To a stirred solution of complex **3** (467 mg, 0.92 mmol) in MeCN (40 cm³) at 0 °C was added a MeCN solution of AgBF_4 (0.25 M, 3.7 cm³, 0.92 mmol) over 3 min. After stirring for 10 min, the reaction was complete as indicated by the infrared spectrum (1908 cm⁻¹). White precipitates were removed by filtering through Celite. The residue after concentration was dissolved in CH_2Cl_2 and filtered again through Celite. After removal of solvent **5** was obtained as an orange powder (471 mg, 99% yield). An analytically pure sample was obtained by recrystallization from acetone and hexane. M.p. 198–203 °C (decomp.). IR (CH_2Cl_2): 1926s cm⁻¹. ^1H NMR [(CD_3)₂CO, 300 MHz]: δ 8.09 (1 H, t, J = 7.5, H¹⁴), 7.97 (1 H, d, J = 8.4, H¹²), 7.27 (1 H, d, J = 5.6, H¹⁶), 7.18–7.13 (2 H, m, H¹³ and H¹⁵), 6.80–6.78 (1 H, m, C₅H₄), 6.48–6.46 (1 H, m, C₅H₄), 5.54–5.52 (1 H, m, C₅H₄), 5.36–5.34 (1 H, m, C₅H₄), 3.81 (1 H, d, J = 3.3, H^{10a}), 3.63–3.55 (1 H, m, H^{1a}), 3.40–3.30 (1 H, m, H^{1b}), 3.36 (1 H, d, J = 3.3 Hz, H^{10b}), 2.50–2.36 (2 H, m, H²) and 2.31 (3 H, br s, NCH₃). ^{13}C NMR [(CD_3)₂CO, 75 MHz]: δ 204.0 (CO), 138.7 (CH, C¹²), 134.5 (CH, C¹⁴), 132.6 (CH, C¹³ or C¹⁵), 129.9 (CH, C¹⁵ or C¹³), 126.2 (C, C₅H₄), 105.1 (C, C¹¹), 97.9 (CH, C₅H₄), 94.7 (CH, C₅H₄), 92.1 (CH, C¹⁶), 79.3 (CH, C₅H₄), 74.6 (CH, C₅H₄), 73.6 (CH₂, C¹), 50.1 (NCH₃), 26.1 (CH₂, C²) and 21.1 (CH₂, C¹⁰). Mass spectrum (FAB, ^{187}Re): m/z [relative intensity (%)] 428 (M^+ , 100) (Found: C, 37.10; H, 3.68; N, 2.57). $\text{C}_{16}\text{H}_{19}\text{BF}_4\text{NORe}$ requires C, 37.36; H, 3.72; N, 2.72%.

Interconversion of complexes 5 and 6. A 5 mm NMR tube was charged with complex **5** (3.1 mg), followed by CD_3CN (0.5 cm³). The resultant yellow solution was examined by NMR spectroscopy immediately. The ^1H NMR spectrum showed two complexes, **5** and **6**, in a ratio of 1:6. The ratio remained steady during a period of 24 h. The major resonances of **5** and **6** were well separated. Partial assignments: **5**, δ 8.09–8.04 (1 H, m), 7.92 (1 H, d, J = 8.7), 6.48–6.46 (1 H, m, C₅H₄), 6.20–6.18 (1 H, m, C₅H₄), 5.40–5.38 (1 H, m, C₅H₄) and 5.09–5.07 (1 H, m, C₅H₄); **6**, δ 7.21–7.12 (3 H, m, Ph), 7.02–6.95 (2 H, m, Ph), 6.11–6.09 (1 H, m, C₅H₄), 5.74–5.72 (1 H, m, C₅H₄), 5.01–4.99 (2 H, m, C₅H₄), 3.64–3.57 (1 H, m), 3.36–3.27 (1 H, m), 2.96 (3 H, d, J = 5.9 Hz, NCH₃) and 2.30–2.12 (2 H, m).

General procedure for [Re(CO)(η^1 -CH₂Ph)Cl{NH(Me)CH₂CH₂(η^5 -C₅H₄)}] 7 and [Re(CO)(η^1 -CH₂Ph)(MeCO)₂{NH(Me)CH₂CH₂(η^5 -C₅H₄)}] 8. To a stirred solution of complex **5** (120 mg, 0.23 mmol) in methanol (5 cm³) was added an excess of LiCl (200 mg) for the preparation of **7** or sodium acetate (300 mg) for **8**. The mixture was stirred at room temperature and the reaction monitored by IR spectroscopy. After reaction was complete (about 30 min) the solvent was evaporated. The product was taken up in CHCl_3 and filtered through Celite. Addition of the CHCl_3 solution to hexane gave a yellow precipitate, which was collected and washed with hexane. Analytically pure samples were obtained by recrystallization of the compounds from CH_2Cl_2 and hexane.

Complex 7. Yellow powder (107 mg, 99% yield). M.p. 181–183 °C. IR (CH_2Cl_2): 1872s cm⁻¹. ^1H NMR (CDCl_3 , 300 MHz): δ 7.23–7.13 (4 H, m, Ph), 6.93 (1 H, t, J = 7, Ph), 5.73–5.71 (1 H, m, C₅H₄), 5.49–5.47 (1 H, m, C₅H₄), 4.98–4.96 (1 H, m, C₅H₄), 4.63 (1 H, br, NH), 4.16 (1 H, d, J = 10.3, benzylic H^a), 3.91 (1 H, d, J = 10.3, benzylic H^b), 3.81–3.73 (1 H, m, H^{1a}), 3.56–

3.53 (1 H, m, C₅H₄), 3.37–3.24 (1 H, m, H^{1b}), 3.12 (3 H, d, $J = 6.1$ Hz, NCH₃), 2.25 (1 H, ddd, $J = 14.4, 10.3, 5.7$, H^{2a}) and 2.12 (1 H, dt, $J = 14.4, 4.9$ Hz, H^{2b}). ¹³C NMR (CDCl₃, 75 MHz): δ 220.5 (CO), 152.3 (C, Ph), 128.0 (CH \times 2, Ph), 127.6 (CH \times 2, Ph), 123.3 (CH, Ph), 123.3 (C, C₅H₄), 99.8 (CH, C₅H₄), 98.8 (CH, C₅H₄), 78.9 (CH, C₅H₄), 73.3 (CH, C₅H₄), 68.8 (CH₂, C¹), 47.1 (NCH₃), 26.6 (CH₂, C²) and 10.6 (CH₂, benzylic CH₂). Mass spectrum (FAB, ¹⁸⁷Re³⁵Cl): m/z [relative intensity (%)] 463 (M^+ , 35), 429 ($M^+ + 1 - \text{Cl}$, 100) (Found: C, 41.31; H, 3.97; N, 2.87. C₁₆H₁₉ClNORe requires C, 41.51; H, 4.14; N, 3.02%).

Complex **8**. Hygroscopic yellow powder (104 mg, 92% yield). IR (CH₂Cl₂): 1865s and 1595w cm⁻¹. ¹H NMR (CDCl₃, 300 MHz): δ 7.21–7.12 (4 H, m, Ph), 6.95–6.90 (1 H, m, Ph), 6.67 (1 H, br, NH), 6.11–6.09 (1 H, m, C₅H₄), 5.36–5.34 (1 H, m, C₅H₄), 4.89–4.87 (1 H, m, C₅H₄), 3.72 (1 H, d, $J = 10.1$, benzylic H^a), 3.62 (1 H, d, $J = 10.1$, benzylic H^b), 3.53–3.47 (1 H, m, H^{1a}), 3.46–3.44 (1 H, m, C₅H₄), 3.11–3.00 (1 H, m, H^{1b}), 2.95 (3 H, d, $J = 6.0$, NCH₃), 2.47 (1 H, ddd, $J = 14.0, 12.4, 5.6$, H^{2a}), 2.20 (3 H, s, O₂CCH₃) and 1.98 (1 H, ddd, $J = 14.0, 5.4, 2.0$ Hz, H^{2b}). ¹³C NMR (CDCl₃, 75 MHz): δ 215.7 (CO), 180.3 (C, O₂CCH₃), 152.0 (C, Ph), 127.8 (CH \times 2, Ph), 127.5 (CH \times 2, Ph), 123.0 (CH, Ph), 122.9 (C, C₅H₄), 99.6 (CH, C₅H₄), 96.8 (CH, C₅H₄), 78.7 (CH, C₅H₄), 73.1 (CH, C₅H₄), 67.5 (CH₂, C¹), 46.0 (NCH₃), 26.3 (CH₂, C²), 24.2 (CH₃, O₂CCH₃) and 17.4 (CH₂, benzylic CH₂). Mass spectrum (FAB, ¹⁸⁷Re): m/z [relative intensity (%)] 429 ($M^+ + 1 - \text{O}_2\text{CCH}_3$, 100) (Found: C, 44.62; H, 4.74; N, 2.59. C₁₈H₂₂NO₃Re requires C, 44.43; H, 4.56; N, 2.88%).

General procedure for [Re(CO)(η^1 -CH₂Ph)(Bu^tNC){NH(Me)-CH₂CH₂(η^5 -C₅H₄)}]⁺BF₄⁻ **9 and [Re(CO)(η^1 -CH₂Ph)(C₅H₅N){NH(Me)CH₂CH₂(η^5 -C₅H₄)}]⁺BF₄⁻ **10**.** To a stirred solution of complex **5** (120 mg, 0.23 mmol) in CH₂Cl₂ (15 cm³) was added Bu^tNC (0.15 cm³) for the preparation of **9** or pyridine (0.5 cm³) for **10**. The solution was stirred at room temperature and the reaction monitored by IR spectroscopy. After reaction was complete (0.5–4 h) the solvents were evaporated. The residue was dissolved in CH₂Cl₂ (3 cm³) and added to diethyl ether (30 cm³). Yellow precipitates were collected and washed twice with ether to give **9** and **10** respectively. Analytically pure samples were obtained by recrystallization of the compounds from CH₂Cl₂ and hexane.

Complex **9**. Yellow powder (135 mg, 97% yield). M.p. 139–141 °C. IR (CH₂Cl₂): 2176s and 1927s cm⁻¹. ¹H NMR (CDCl₃, 300 MHz): δ 7.21–7.15 (2 H, m, Ph), 7.05–6.97 (3 H, m, Ph), 6.26–6.24 (1 H, m, C₅H₄), 5.98 (1 H, br, NH), 5.81–5.79 (1 H, m, C₅H₄), 4.59–4.57 (1 H, m, C₅H₄), 3.94–3.88 (1 H, m, H^{1a}), 3.51–3.49 (1 H, m, C₅H₄), 3.45 (1 H, d, $J = 10.5$, benzylic H^a), 3.19 (1 H, d, $J = 10.5$, benzylic H^b), 3.15–3.00 (1 H, m, H^{1b}), 2.96 (3 H, d, $J = 5.8$, NCH₃), 2.67 (1 H, td, $J = 14.0, 5.7, \text{H}^{2a}$), 1.99 (1 H, dd, $J = 14.0, 5.4$ Hz, H^{2b}) and 1.67 (9 H, s, Bu^t). ¹³C NMR (CDCl₃, 75 MHz): δ 206.2 (CO), 150.1 (C, Ph), 136.9 (C, isocyanide), 127.8 (CH \times 2, Ph), 127.4 (CH \times 2, Ph), 127.1 (C, C₅H₄), 124.3 (CH, Ph), 91.6 (CH, C₅H₄), 90.4 (CH, C₅H₄), 86.7 (CH, C₅H₄), 83.4 (CH, C₅H₄), 74.4 (CH₂, C¹), 59.5 (C, Bu^t), 48.9 (CH₃, NCH₃), 30.1 (CH₃ \times 3, Bu^t), 25.2 (CH₂, C²) and -2.1 (CH₂, benzylic CH₂) (Found: C, 42.07; H, 4.49; N, 4.43. C₂₁H₂₈BF₄N₂ORe requires C, 42.22; H, 4.72; N, 4.69%).

Complex **10**. Yellow powder (133 mg, 96% yield). M.p. 106–110 °C (decomp.). IR (CH₂Cl₂): 1893s cm⁻¹. ¹H NMR (CDCl₃, 300 MHz): δ 9.19 (1 H, br, pyridine), 8.87 (1 H, br, pyridine), 8.01 (1 H, tt, $J = 7.7, 1.5$, pyridine), 7.67 (1 H, br, pyridine), 7.53 (1 H, br, pyridine), 7.18–7.12 (2 H, m, Ph), 7.01–6.95 (3 H, m, Ph), 6.27–6.25 (1 H, m, C₅H₄), 6.56–6.54 (1 H, m, C₅H₄), 5.06 (1 H, br, NH), 5.02–5.00 (1 H, m, C₅H₄), 3.88–3.81 (1 H, m, H^{1a}), 3.52–3.60 (1 H, m, C₅H₄), 3.44 (1 H, d, $J = 10.0$, benzylic H^a), 3.31 (1 H, d, $J = 10.0$, benzylic H^b), 3.27–3.13 (1 H, m, H^{1b}), 2.93 (1 H, td, $J = 13.7, 5.6, \text{H}^{2a}$), 2.76 (3 H, d, $J = 5.7, \text{NCH}_3$)

Table 2 Crystallographic data and structure refinements for complex **4**

Formula	C ₁₆ H ₁₉ NO ₃ Re ₂
<i>M</i>	677.74
Crystal size/mm	0.19 \times 0.28 \times 0.50
Crystal system	Monoclinic
Space group	<i>P</i> 2 ₁ / <i>n</i>
<i>a</i> /Å	7.842(2)
<i>b</i> /Å	22.687(3)
<i>c</i> /Å	10.110(3)
β /°	108.67(3)
<i>U</i> /Å ³	1703.9(7)
<i>Z</i>	4
<i>D</i> _c /g cm ⁻³	2.642
<i>F</i> (000)	1248
μ (Mo-K α)/cm ⁻¹	144.180
Transmission	0.329, 1.000
Scan speed/° min ⁻¹	1.37–8.24
θ –2 θ scan width/°	2(0.65 + 0.35 tan θ)
2 θ _{max} /°	50.0
<i>h, k, l</i> Ranges	–9 to 8, 0–26, 0–12
Collected reflections	3161
Unique reflections	2988
Observed reflections [<i>I</i> > 2.0 σ (<i>I</i>)]	2498
Refined parameters	218
<i>R, R'</i>	0.033, 0.039
Goodness of fit	1.95
Weight modifier <i>K</i> in KF_o^2	0.000 100
($\Delta\rho$) _{max,min} /e Å ⁻³	2.740, –1.630

$$R = \Sigma(F_o - F_c)/\Sigma(F_o), R' = [\Sigma w(F_o - F_c)^2/\Sigma wF_o^2]^{1/2}$$

and 2.08 (1 H, dd, $J = 13.7, 4.8$ Hz, H^{2b}). ¹³C NMR (CDCl₃, 75 MHz): δ 208.4 (CO), 160.5 (CH, pyridine), 157.6 (pyridine), 150.3 (C, Ph), 139.1 (CH \times 2, pyridine), 128.3 (CH, pyridine), 128.2 (C, C₅H₄), 127.8 (CH \times 2, Ph), 127.7 (CH \times 2, Ph), 124.1 (CH, Ph), 98.9 (CH, C₅H₄), 98.3 (CH, C₅H₄), 81.7 (CH, C₅H₄), 75.8 (CH, C₅H₄), 71.8 (CH₂, C¹), 47.2 (CH₃, NCH₃), 25.5 (CH₂, C²) and 15.9 (CH₂, benzylic CH₂). Mass spectrum (FAB, ¹⁸⁷Re): m/z [relative intensity (%)] 428 ($M^+ - \text{pyridine}$, 100) (Found: C, 42.67; H, 3.90; N, 4.43. C₂₁H₂₄BF₄N₂ORe requires C, 42.50; H, 4.08; N, 4.72%).

Crystallography

A single crystal of complex **4** was obtained by slow diffusion of a CH₂Cl₂ solution of **4** into hexane at 25 °C. Diffraction measurement was made on an Enraf-Nonius CAD-4 automated diffractometer by use of graphite-monochromated Mo-K α radiation ($\lambda = 0.710 69$ Å) with the θ –2 θ scan mode at 25 °C. The unit cell was determined and refined using 25 randomly selected reflections obtained with the automatic search, centre, index, and least-squares routines. Lorentz-polarization and empirical absorption corrections based on three azimuthal scans were applied to the data. The space group (*P*2₁/*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.¹³ The structure was solved by direct methods and refined by a full-matrix least-squares routine¹⁴ with anisotropic thermal parameters for all non-hydrogen atoms. The structure was refined by minimizing $\Sigma w|F_o - F_c|^2$, where $w = (1/\sigma^2)F_o$ was calculated from the counting statistics. Hydrogen atoms were included in the structure factor calculations in their expected positions based on idealized bonding geometry but not refined. The final cell parameters and data collection parameters are listed in Table 2.

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