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Cyrhetrenylimines and cyrhetrenylamines: Synthesis, characterization and X-ray crystal structure

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ABSTRACT

Cyrhetrenyl Schiff base derivatives of the form (η^5-C_5H_4CH=NAr)$Re(CO)_3$, [Ar = Ph (**1a**) C_6H_4OMe-*p* (**1b**) and $C_6H_4NO_2$-*p* (**1c**)] have been prepared from cyrhetrenylcarbaldehyde and the corresponding aromatic amines. ^1H and ^{13}C NMR indicates that these compounds have the *anti*-(*E*) conformation in solution and the X-ray crystal structure of **1b** confirms that it also adopts the *anti*-(*E*) form in the solid state. Further reaction of cyrhetrenylaldimines **1** with sodium borohydride in methanol produces quantitatively, the corresponding amine derivatives (η^5-$C_5H_4CH_2$–NHAr)$Re(CO)_3$ [Ar = Ph (**2a**) C_6H_4OMe-*p* (**2b**) and $C_6H_4NO_2$-*p* (**2c**)]. All these cyrhetrenylamines were characterized by IR, ^1H and ^{13}C NMR, MS. Additionally, **2b** has been characterized structurally.

1. Introduction

Ferrocenylimines (η^5-C_5H_5)Fe(η^5–C_5H_4CR=NAr) and ferrocenylamines (η^5-C_5H_5)Fe(η^5-$C_5H_4CHRNHAr$), R = H, Me, Ph; and Ar = a variety of substituted phenyl, have attracted a great deal of attention in the past two decade due to their wide application in molecular materials [1], bioorganometallic chemistry [2] and as ligands capable of coordinating transition metal ions giving complexes with potential applications in catalysis [3]. The above situation contrasts with the smaller number of analogous compounds bearing the cyrhetrenyl group (η^5-C_5H_4)$Re(CO)_3$, described in the literature. To our best knowledge the only known cyrhetrenylimine (η^5-C_5H_4CH=NPh)$Re(CO)_3$, was briefly described by Kolobova et al. [4,5]. More recently, complexes of these type have been used *in situ*, as intermediates for the preparation of some biological compounds containing the (η^5-C_5H_4)$Re(CO)_3$ group (see below) but details of their isolation and characterization remain unknown [6]. On the other hand, reduction of ferrocenylimines with sodium borohydride or lithium aluminium hydride has been shown to be an efficient procedure for the preparation of (*N*-aryl)-amino methylferrocenes. A similar approach have been used by Jaouen to prepare poly(amidoamine) dendrimers tethered with cyclopentadienyl rhenium tricarbonyl [6]. As part of our interest in comparing the properties of the cyrhetrenyl substituted systems with the well known analogous ferrocenyl [7], in this paper we would like to report the synthesis and characterization of the cyrhetrenylimine (Schiff base) complexes (η^5-C_5H_4CH=NAr)$Re(CO)_3$, and the cyrhetrenyl-amine derivatives (η^5-$C_5H_4CH_2$–NHAr)$Re(CO)_3$. The imine and amine complexes derived from *p*-anisidine were also studied X-ray crystallography.

2. Results and discussion

2.1. Cyrhetrenylimine complexes (η^5-C_5H_4CH=NAr)$Re(CO)_3$ (**1**)

The Schiff bases (η^5-C_5H_4CH=NAr)$Re(CO)_3$, Ar = Ph (**1a**) C_6H_4OMe-*p* (**1b**) and $C_6H_4NO_2$-*p* (**1c**) were synthesized following the same procedure to that described for analogous ferrocenylimines derivatives [8], that is by condensation of the corresponding aniline with formylcyrhetrene (η^5-C_5H_4COH)$Re(CO)_3$ [9] (Scheme 1).

The procedure consists of the reaction of equimolar amounts of formylcyrhetrene and the aromatic amine in refluxing toluene. A Dean–Stark apparatus was used to remove the toluene–water azeotrope formed during the reaction formation of **1c**. In all cases the products were isolated as white crystalline solids after crystallization from CH_2Cl_2-hexane mixture (1:5).

The IR spectra of these compounds showed the expected value of the $\nu_{C=N}$ stretch in the range 1625–1643 cm^{-1}, in CH_2Cl_2 solution. This absorption bands as well as the ν_{CO} of the carbonyls bound to rhenium are shifted to lower wavenumber when compared to the precursor formylcyrhetrene [9]. Similar $\nu_{C=N}$ frequency shifts have been reported for Schiff bases derived from

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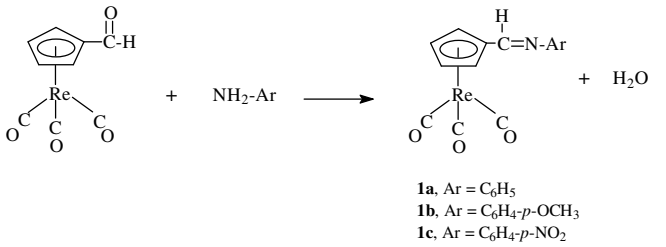


Scheme 1.

formylferrocene [8]. Each of **1a–c** showed a strong molecular ion and fragments corresponding to the successive lost of three CO, in their mass spectra.

The ^{1}H NMR spectra showed a singlet at about δ 8.0 due to the iminic proton and two apparent triplets between 5.42 and 6.07 ppm. The latter are ascribed to the monosubstituted cyclopentadienyl ring. In addition, resonances for the hydrogen atoms of the aryl ring and the methoxy substituent were also observed. ^{13}C NMR data were also in accordance with the existence of a single compound. Despite the fact that these type of compounds could adopt two different forms (*E*- or *Z*-) [1b,3c,10] their ^{1}H and ^{13}C NMR spectra, which agreed with those reported for related ferrocenyl Schiff bases [1b,3c,10], revealed that only one isomer (*E*-form) was present in solution. Further proof was provided by an X-ray crystal structure determination of **1b** (see below). The most important feature of these spectra is the presence of a low field resonance (δ 152–158) assigned to the iminyl carbon. This resonance occurs at almost the same δ as those reported for the ferrocene analogues [1,3c,10] and is indicative of some degree of conjugation of the C_5H_4 ring and the –HC=N entity.

With the aim to compare structural parameters of these compounds with the crystallographic data reported for several ferrocenylimines [1a,8c,10,11], we undertook a crystallographic study of complex **1b**. The structure of **1b** is shown in Fig. 1. Table 1 reports the crystal structure and refinement data and Table 2 shows selected bond lengths and angles. The structure confirms the *E* configuration assigned tentatively by NMR. Taking into account the internal and exocyclic C–C distances of the cyclopentadienyl ring and the classification done for substituted ferrocene derivatives [1a,10], a fulvenoid type of structure can be considered for **1b**, since it possesses alternated two short and three long C–C distances (C(2)–C(3) 1.403 Å; C(4)–C(5) 1.402 Å; C(1)–C(2) 1.446 Å; C(1)–C(5) 1.412 Å and C(3)–C(4) 1.433 Å), and the exocyclic C(1)–C(9) of 1.456 Å. Additional support for this assignment is to be found in the C=N bond length (1.265 Å), which is within the range to those measured in several ferrocenyl Schiff bases [1a,8c,10,11], and the C_5H_4CH=N part of the molecule are practically flat, the maxima deviation from the least-squares plane formed by the atoms of the C_5 ring and C(9), N(1) and C(10) atoms is only 0.1 Å. This is in agreement with the suggestion that some delocalization of electron density is found over the C_5H_4CH=N moiety. On the other hand, within the cyrhetrenyl group, the average Re–C(O) distance and the Re–C–O angle are concordant with related tricarbonyl cyclopentadienyl rhenium(I) complexes [7].

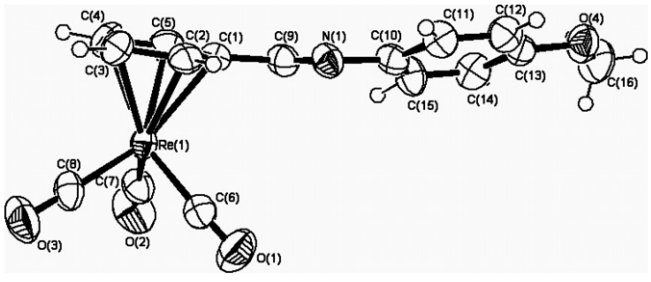


Fig. 1. Molecular structure of cyrhetrenylimine **1b**.

Table 1
Crystal data and structure refinement for **1b** and **2b**

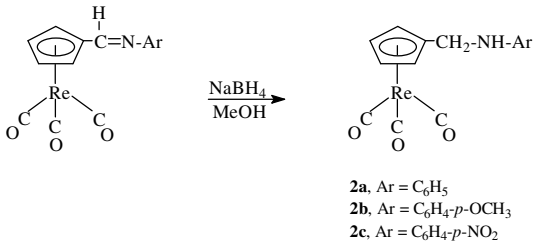
Compound	**1b**	**2b**
Empirical Formula	$C_{16}H_{12}NO_4Re$	$C_{16}H_{14}NO_4Re$
Formula weight	468.47	470.47
Temperature (K)	295(2)	295(2)
wavelength (Å)	0.71073	0.71073
Crystal system	monoclinic	triclinic
Space group	$P2(1)/n$	$P\bar{1}$
Unit cell dimensions		
a (Å)	11.2762(5)	7.4071(5)
b (Å)	8.3746(4)	7.9042(6)
c (Å)	16.1881(7)	13.8307(10)
α (°)	90	89.3360(10)
β (°)	93.2030(10)	86.6540(10)
γ (°)	90	78.6150(10)
Volume (Å^3)	1526.31(12)	792.46(10)
Z	4	2
D_{calc} (g/cm^3)	2.039	1.967
Absorption coefficient (mm^{-1})	7.978	7.683
F(000)	888	446
Crystal size (mm)	0.30 × 0.20 × 0.20	0.30 × 0.20 × 0.20
θ Range for data collection (°)	2.15–29.05	2.63–29.16
Index ranges	$-15 \leqslant h \leqslant 15$, $-11 \leqslant k \leqslant 11$, $-20 \leqslant l \leqslant 21$	$-9 \leqslant h \leqslant 9$, $-10 \leqslant k \leqslant 10$, $-18 \leqslant l \leqslant 18$
Reflections collected	13557	7576
Independent reflections (R_{int})	3786 (0.0377)	3776 (0.0269)
Completeness to theta = 29.05° (%)	92.7	88.6
Absorption correction	empirical	empirical
Refinement method	full-matrix least-squares on F^2	full-matrix least-squares on F^2
Data/restraints/parameters	3786/0/236	3776/0/251
Goodness-of-fit on F^2	1.127	1.053
Final R indices [$I > 2\sigma(I)$]	R_1 = 0.0373, wR_2 = 0.0622	R_1 = 0.0262, wR_2 = 0.0585
R indices (all data)	R_1 = 0.0550, wR_2 = 0.0659	R_1 = 0.0314, wR_2 = 0.0600
Largest difference in peak and hole (e Å^{-3})	0.983 and −1.233	0.769 and −0.905

2.2. Cyrhetrenylamine complexes (η^5-$C_5H_4CH_2NHAr$)$Re(CO)_3$ (**2**)

These compounds were prepared according to the general procedure described for most ferrocenylamines [3f,11] that is, by direct reduction of the corresponding cyrhetrenyl imine complex **1** with $NaBH_4$ in anhydrous methanol, at room temperature (Scheme 2).

Table 2
Select bond lengths (Å), bond angles and dihedral angles (°) for **1b** and **2b**

Compound	**1b**	**2b**
Bond lengths (Å)		
C(1)–C(9)	1.456(7)	1.511(5)
C(9)–N(1)	1.265(7)	1.454(5)
N(1)–C(10)	1.414(6)	1.414(5)
Cp(centroid)–Re(1)	1.961(6)	1.949(5)
Re–C(CO) av.	1.923	1.904
Bond angles (°)		
N(1)–C(9)–C(1)	121.8(5)	113.1(3)
C(9)–N(1)–C(10)	119.5(5)	119.9(3)
C(13)–O(4)–C(16)	116.3(5)	117.3(4)
OC–Re–CO av.	89.57	90.18



Scheme 2.

The products were purified by column chromatography and isolated in quantitative yields as white solids. The IR spectra, in CH_2Cl_2 solution, showed as expected, the presence of two ν_{CO} bands, which are slightly shifted to lower wavenumber compared to their parent complexes **1**. In addition to the resonances of the cyclopentadienyl and aryl groups, in all cases the ^1H NMR spectra, in C_6D_6 solution, clearly showed at $\delta \sim 3.4$, a doublet and a broad singlet for the CH_2 and NH groups, respectively. These assignments were confirmed by ^1H–^1H NMR COSY.

The main feature of the ^{13}C NMR spectrum of each compound, in $CDCl_3$ solution, is a resonance at about 41 ppm which has been assigned to the CH_2 group on the basis of the reported chemical shifts for the methylene group in analogous ferrocenylamines [12,13]. The resonances of CO groups (Re–CO) occurred to similar chemical shift to others tricarbonyl cyclopententadienyl functionalized complexes [7,9].

The mass spectra of **2a–c** exhibited the molecular ion, and the successive loss of three CO ligands. In all cases, the most intense peak corresponds to the elimination of the amine fragment (NHAr) to give cyrhetrenylmetylene cation (*m*/*z* 349, 100%). This fragmentation is similar to that observed for the complex (η^5-$C_5H_4CH_2NHC_6H_5$)Fe(η^5-C_5H_5) [12,13].

The elementals analyses are in a good agreement with the proposed structures.

The molecular structure of amine **2b** (Fig. 2) shows no significant differences in bond lengths and angles (Table 1) when compared to the structure of the ferrocene related compounds [12–14]. The torsion angle C(10)–N–C(9)–C(1) of 59.0° indicates a Syn-Clinal arrangement of the substituents at the N–C(9) bond. The angle 81.6° between the planes of the Cp ring with the aromatic ring is almost orthogonal. On the other hand, the rhenium-ring centroid distance 1.949 (5) Å, the average Re–C(O) distance and the Re–C–O angles are concordant with the corresponding values reported for substituted-cyclopentadienyl tricarbonyl rhenium(I) complexes [7,15].

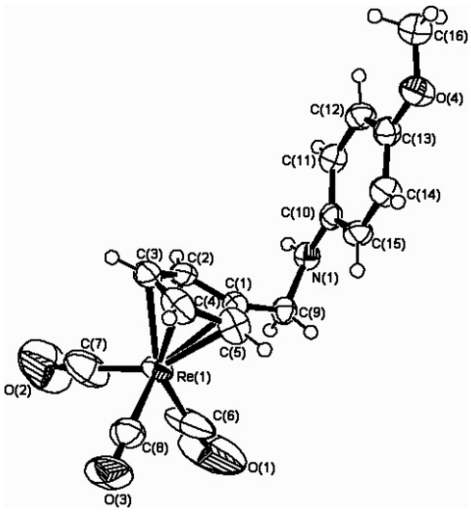


Fig. 2. Molecular structure of cyrhetrenylamine **2b**.

3. Experimental

(η^5-C_5H_4CHO)$Re(CO)_3$ was prepared according to the literature method [9]. Anilines and $NaBH_4$ were obtained commercially (Aldrich). All the solvents were purified according standard methods prior to use. Infrared spectra were recorded in solution (NaCl cell) on a Perkin–Elmer FT-1605 spectrophotometer, and the ^1H and ^{13}C NMR spectra were measured on a Bruker AVANCE 400 spectrometer. ^1H NMR chemical shifts were referenced using the chemicals shifts of residual solvent resonances, and ^{13}C chemical shifts to solvent peaks. Mass spectra were obtained on a Thermo-Finnigan MAT 900XP, at the Facultad de Ciencias Químicas y Farmacéuticas, Universidad de Chile.

3.1. (η^5-C_5H_4CH=NC_6H_5)$Re(CO)_3$ (**1a**)

To a solution of (η^5-C_5H_4CHO)$Re(CO)_3$ (50.0 mg, 0.138 mmol) in toluene (15 mL) was added 1.25 mL (0.138 mmol) of a 0.110 M aniline solution in toluene. The mixture was refluxed for 15 h. After this time, an IR spectrum of the solution showed the complete disappearance of the cyrhetrenylcarboxaldehyde complex (2033s; 1940s and 1694 cm^{-1}) and the presence of the new CO absorptions due to **1a**. The solvent was pumped off and the solid crystallized from CH_2Cl_2/hexane at −18 °C to give white crystals of **1a** (yield: 58.0 mg, 0.132 mmol, 95.7%). IR (CH_2Cl_2, cm^{-1}) 2026s, (νCO); 1934s, (νCO); 1630w, (νC=N). ^1H NMR ($CDCl_3$) δ: 5.44 (t, J = 2.4 Hz, 2H,C_5H_4); 6.00 (t, J = 2.4 Hz, 2H, C_5H_5); 7.09 (m, 2H, C_6H_5); 7.23 (t, J = 7.4, 1H, C_6H_5); 7.37 (t, J = 7.8, 2H, C_6H_5); 8.07 (s, 1H, *CH*=N). ^{13}C NMR ($CDCl_3$) δ: 84.9 (C_5H_4); 86.0 (C_5H_4); 99.5 (s, C_{ipso}, C_5H_4); 120.6 (s, C_6H_4); 126.3 (s, C_6H_4); 129.2 (s, C_6H_4); 151.0 (s, C_6H_4); 152.1 (*C*H=N); 192.7 (*C*O). Mass spectrum (based on ^{187}Re) *m*/*z* 439 [M^+], 411 [M^+−CO], 383 [M^+−2CO], 355 [M^+−3CO]. *Anal.* Calc. for $C_{15}H_{10}O_3NRe$: C, 41.09; H, 2.28. Found: C, 42.02; H, 2.31%.

3.2. (η^5-C_5H_4CH=$NC_6H_4OCH_3$-*p*)$Re(CO)_3$ (**1b**)

To a solution of (η^5-C_5H_4CHO)$Re(CO)_3$ 50.0 mg (0.138 mmol) in toluene (10 mL) was added *p*-anisidine 17.0 mg (0.138 mmol). The mixture was refluxed under nitrogen atmosphere for 5 h. After this time, the solution changed color from yellow to brown. The IR spectrum showed the complete disappearance of the starting complex and three new absorption bands. The solvent was removed under vacuum and a gray oil was obtained. Crystallization from CH_2Cl_2/hexane (1:5) at −18 °C to give off-white microcrystals of **1b** (Yield: 61 mg, 0.130 mmol, 94.4%). IR (CH_2Cl_2, cm^{-1}): 2026s, (νCO), 1932s, (νCO), 1627w, (νC=N). ^1H NMR ($CDCl_3$): δ: 3.81 (s, 3H, O*CH*$_3$); 5.42 (t, J = 2.4 Hz, 2H, C_5H_4); 5.96 (t, J = 2.4 Hz, 2H, C_5H_4); 6.90 (pseudo-dt, 2H, C_6H_4); 7.11 (pseudo-dt, 2H, C_6H_4); 8.08 (s,1H, *CH*=N). ^{13}C NMR ($CDCl_3$): δ: 55.5 (s, OCH_3); 84.8 (C_5H_4); 85.7 (C_5H_4); 100.2 (s, C_5H_4); 114.4 (s, C_6H_4); 122.0 (s, C_6H_4); 143.8 (s, C_6H_4); 150.0 (s, C_6H_4); 158.54 (*C*H=N), 192.86 (*C*O). Mass spectrum (based on ^{187}Re) *m*/*z*: 469 [M^+], 441 [M^+−CO], 413 [M^+−2CO], 385 [M^+−3CO]. *Anal.* Calc. for $C_{16}H_{12}O_4NRe$: C, 41.02; H, 2.58. Found: C, 42.13; H, 2.64%.

3.3. (η^5-C_5H_4CH=$NC_6H_4NO_2$-*p*)$Re(CO)_3$ (**1c**)

The synthesis of the complex **1c** was carried out in a similar manner to that described for complex **1b** using (η^5-C_5H_4CHO)$Re(CO)_3$ (50.0 mg, 0.138 mmol) and *p*-nitroaniline (19.0 mg, 0.138 mmol) but refluxing for 48 h using a Dean–Stark apparatus. **1c** was

obtained as white-yellow crystals (Yield: 61, 0.126 mmol, mg, 91.3%). IR (CH_2Cl_2, cm^{-1}) 2028s (νCO), 1936s (νCO), 1625w (νC=N). ^1H NMR ($CDCl_3$) δ: 5.49 (t, J = 2.0 Hz, 2H,C_5H_4), 6.03 (t, J = 2.0 Hz, 2H, C_5H_4), 7.13 (pseudo-dt, 2H, C_6H_4); 8.08 (s, 1H, CH=N); 8.24 (pseudo-dt, 2H, C_6H_4); ^{13}C NMR ($CDCl_3$): δ 85.4 (C_5H_4); 86.8 (C_5H_4); 97.5 (s, C_5H_4); 111.3 (s, C_6H_4); 121.1 (s, C_6H_4); 125.0 (s, C_6H_4); 126.3 (s, C_6H_4); 156.7 (CH=N), 192.86 (CO). Mass spectrum (based on ^{187}Re) m/z: 484 [M^+], 456 [M^+−CO], 428 [M^+−2CO], 400 [M^+−3CO]. *Anal.* Calc. for $C_{15}H_9O_5N_2Re$: C, 37.19; H, 1.86. Found: C, 37.79; H, 1.97%.

3.4. (η^5-$C_5H_4CH_2NHC_6H_5$)Re(CO)$_3$ (**2a**)

Complex **1a** (50.0 mg, 0.114 mmol) was dissolved in anhydrous methanol (10 ml) followed by addition an excess of solid $NaBH_4$ (16.0 mg, 0.423 mmol). The mixture was stirred under nitrogen atmosphere for 2 h. After this time, the IR spectrum showed the complete disappearance of the imine complex **1a**, and the presence of two new absorption bands shifted to low energy (2020, 1924 cm^{-1}). The white solid obtained after evaporation of methanol was chromatographed on a silica gel column; elution with CH_2Cl_2 moved the amine complex. The complex **2a** was isolated quantitatively as white solid, after crystallization from CH_2Cl_2/hexane (1:5) at −18 °C. (Yield: 50.0 mg, 0.114, 100%). IR (CH_2Cl_2, νCO, cm^{-1}): 2024s, 1929s. ^1H NMR ($CDCl_3$) δ: 4.14 (s, 2H, CH_2); 5.28 (t, J = 2.4 Hz, 2H, C_5H_4); 5.43 (t, J = 2.4 Hz, 2H, C_5H_4); 6.66 (d, J = 7.8 Hz, 2H, C_6H_5); 6.78 (d, J = 7.3 Hz, 1H, C_6H_5); 7.22 (pseudo-dt, 2H, C_6H_5). ^1H NMR (C_6D_6) δ: 3.19 (s, broad, 1H, NH); 3.48 (d, J = 6.6 Hz, 2H, CH_2); 4.38 (pseudo- t, 2H, C_5H_4); 4.58 (pseudo-t, 2H, C_5H_4); 6.37 (d, J = 7.7 Hz, 2H, C_6H_5); 6.79 (d, J = 7.3 Hz, 1H, C_6H_5); 7.15 (t, J = 7.7 Hz, 2H, C_6H_5). ^{13}C NMR ($CDCl_3$) δ: 41.4 (s, CH_2); 83.5 (s, C_5H_4); 83.7 (s, C_5H_4); 108.7 (s, C_5H_4); 113.1 (s, C_6H_5); 118.5 (s, C_6H_5); 129.5 (s, C_6H_5); 147.3 (s, C_6H_5); 193.9 (CO). Mass spectrum (based on ^{187}Re) m/z: 441 [M^+]; 413 [M^+−CO]; 385 [M^+−2CO]; 357 [M^+−3CO]; 349 [M^+−NHC_6H_5]. *Anal.* Calc. for $C_{15}H_{12}O_3NRe$: C, 40.81; H, 2.72. Found: C, 40.94; H, 2.86%.

3.5. (η^5-$C_5H_4CH_2NHC_6H_4OCH_3$-p)Re(CO)$_3$ (**2b**)

Complex **2b** was obtained following the same procedure described for **2a**. It was isolated as white crystals. (Yield: 50.0 mg, 0.106 mmol, 100%). IR (CH_2Cl_2, νCO, cm^{-1}): 2022 s, 1926 s. ^1H NMR ($CDCl_3$): δ 3.76 (s, 3H, OCH_3); 4.08 (s, 2H, CH_2); 5.27 (t, J = 2.4 Hz, 2H, C_5H_4); 5.41 (t, J = 2.4 Hz, 2H, C_5H_4); 6.63 (pseudo-dt, 2H, C_6H_4); 6.80 (pseudo-dt, 2H, C_6H_4). ^1H NMR (C_6D_6): δ 2.98 (s, broad, 1H, NH); 3.44 (s, 3H, OCH_3); 3.50 (d, J = 6.6 Hz, 2H, CH_2); 4.35 (t, J = 2.0 Hz, 2H, C_5H_4); 4.66 (t, J = 2.0 Hz, 2H, C_5H_4); 6.36 (pseudo-dt, 2H, C_6H_4); 6.81 (pseudo-dt, 2H, C_6H_4). ^{13}C NMR ($CDCl_3$) δ: 42.5(CH_2); 55.6 (s, OCH_3); 83.5 (s, C_5H_4); 83.6 (s, C_5H_4); 108.8 (s, C_5H_4); 114.7 (s, C_6H_4); 115.5 (s, C_6H_4); 141.3 (s, C_6H_4); 152.9 (s, C_6H_4); 193.94(CO). Mass spectrum (based on ^{187}Re) m/z: 471 [M^+]; 443 [M^+−CO]; 415 [M^+−2CO]; 387 [M^+−3CO]; 349 [M^+−NHC_6H_4-p-OCH_3]. *Anal.* Calc. for $C_{16}H_{14}O_4NRe$: C, 40.85; H, 3.00. Found: C, 40.98; H, 3.05%.

3.6. (η^5-$C_5H_4CH_2NHC_6H_4NO_2$-p)Re(CO)$_3$ (**2c**)

Complex **2b** was obtained following the same procedure described for **2a**. It was isolated as white crystals. (Yield: 50.0 mg, 0.103 mmol, 100%). IR (CH_2Cl_2, νCO, cm^{-1}): 2024 s, 1929 s. ^1H NMR ($CDCl_3$) δ: 4.24 (d, J = 5.9 Hz, 2H, CH_2); 4.54 (pseudo-t, 1H, NH); 5.33 (t, J = 2.4 Hz, 2H, C_5H_4); 5.43 (t, J = 2.4 Hz, 2H, C_5H_4); 6.63 (pseudo-dt, 2H, C_6H_4); 8.13 (pseudo-dt, 2H, C_6H_4). ^1H NMR (C_6D_6) δ: 3.21 (d, J = 6.1 Hz, 2H, CH_2); 3.48 (pseudo-t, 1H, NH); 4.37 (pseudo-t, 2H, C_5H_4); 4.48 (pseudo-t, 2H, C_5H_4); 5.80 (d, J = 9.0 Hz, 2H, C_6H_4); 8.04 (d,J = 9.0 Hz, 2H, C_6H_4). ^{13}C NMR ($CDCl_3$): δ 40.7 (s, CH_2); 83.7 (s, C_5H_4); 84.1 (s, C_5H_4); 106.2 (s, C_5H_4); 111.4 (s, C_6H_4); 126.4 (s, C_6H_4); 139.1 (s, C_6H_4); 152.2 (s, C_6H_4); 193.4 (s, CO). Mass spectrum (based on ^{187}Re) m/z: 486 [M^+]; 458 [M^+−CO]; 430 [M^+−2CO]; 402 [M^+−3CO]; 349 [M^+−NHC_6H_4-p-NO_2]. *Anal.* Calc. for $C_{15}H_{11}O_5N_2Re$: C, 37.04; H, 2.26. Found: C, 37.61; H, 2.37%.

4. Crystal structure determination

A summary of the fundamental crystal and refinement data for **1a** and **1b** are given in Table 1. Crystals of **1b** and **2b** were mounted on a Brucker-Siemens Smart CCD diffractometer equipped with a normal focus, 2.4 kW sealed tube X-ray source (Molybdenum radiation, λ = 0.71073 Å) operating at 50 kV and 20 mA. Data were collected over a hemisphere of the reciprocal space by a combination of three frame sets. The cell parameters were determined and refined by least-squares fit of all reflection collected. Each frame exposure time was of 20 s. covering 0.3° in ω. The crystal to detector distance was 5.08 cm. The first 100 frames were recollected at the end of the data collection to monitor crystal decay. Empirical absorption corrections were made using SADABS program [16]. The structure solution by direct methods, Fourier methods, and full matrix least-square refinement was carried out using SHELXTL [17] minimizing $w(F_o^2 - F_c^2)^2$. Hydrogen atoms have been located y refined isotropically except the hydrogen atoms of the methyl group of the compound **1b**. Weighted R factors (Rw) and all goodness of fit$S$ are based on F^2, conventional R factors (R) are based on F.

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Appendix A. Supplementary data

CCDC 668276 and 668277 contain the supplementary crystallographic data for **1b** and **2b**. These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.poly.2008.04.021.

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