

Note

A picolinate- N_2 complex of rhenium, the first dinitrogen complex bearing a carboxylate or a N,O -ligand

Alexander M. Kirillov^a, Matti Haukka^b, M. Fátima C. Guedes da Silva^{a,c},
João J.R. Fraústo da Silva^a, Armando J.L. Pombeiro^{a,*}

^a Centro de Química Estrutural, Complexo I, Instituto Superior Técnico, Av. Rovisco Pais, 1049-001 Lisbon, Portugal

^b University of Joensuu, Department of Chemistry, P.O. Box 111, FIN-80101, Joensuu, Finland

^c Universidade Lusófona de Humanidades e Tecnologias, Campo Grande 376, 1749-024 Lisbon, Portugal

Received 9 May 2006; accepted 8 June 2006

Available online 21 June 2006

Abstract

A new dinitrogen rhenium(I) complex with a picolinate ligand has been prepared and fully characterized, providing the first example of a genuine $N\equiv N$ complex bearing a carboxylate or a N,O -coligand. The Lever electrochemical E_L ligand parameter was estimated for the first time for the picolinate ligand and shows that its carboxylate arm has a net electron-donor character similar to that of chloride, thus stabilizing the *trans* $Re-N_2$ bond.

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Keywords: Rhenium complexes; Dinitrogen complexes; N,O -ligands; Picolinic acid; Crystal structures; Electrochemistry

1. Introduction

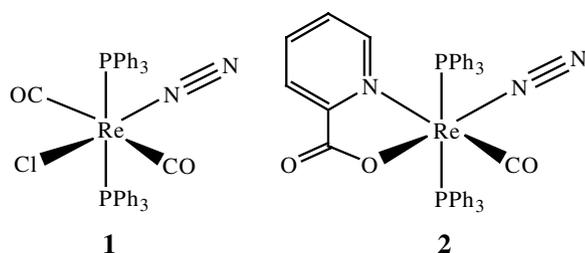
The chemistry of metal dinitrogen complexes has been widely developed for several decades, mostly in view of their high interest in coordination chemistry and significance in the field of nitrogen fixation [1]. Hundreds of dinitrogen complexes with a variety of coligands and with nearly all transition metals have already been synthesized and ca. 310 have been structurally characterized [2]. However, to our knowledge, no $N\equiv N$ complex with a carboxylate or any N,O -coligand has been reported, although the bimetallic complex [$\{(i\text{-PrNPh})_2\text{OTi}(\text{PMe}_3)_2\}_2(\mu\text{-N}_2)$] [3], with the rare η^3 -di(amidophenyl)ether(2⁻) ligand, and with a bridging N_2 in the reduced $N_2(4\text{-})$ hydrazido form, $[\text{Ti}=\text{N}-\text{N}=\text{Ti}]$, is known. These observations suggest that carboxylate and N,O -ligands promote the lability of the metal- N_2 bond what, however, has not yet been established and would disfavour the hypothesis of N_2 -binding at the Mo centre of FeMoco of nitrogenase which presents an

imidazole and a η^1 -carboxylate bound bidentate homocitrate ligands [4]. Moreover, the significance of N,O -ligands has also been recognized in catalytic and pharmacological systems [5]. Hence, a primary objective of the current study was to synthesize a stable mononuclear dinitrogen complex with a N,O -coligand bearing an O -bonded carboxylate arm, thus showing that these ligands can co-exist at a common metal centre.

As a metal, we have chosen rhenium as it can form considerably stable N_2 complexes, is (in the periodic table) in the common diagonal line with Mo and we have recently found [6] that some Re complexes with aminocarboxylate ligands can be active in catalysis (functionalization of alkanes under mild conditions). Besides, rhenium complexes attract a high interest in the field of nuclear medicine to design Re-labeled biomolecules [5c,7].

In addition, some polyaminocarboxylate N,O -ligands are prominent chelating agents in radiopharmaceuticals [5c], and we have chosen a simple carboxylate N,O -ligand, i.e. picolinate (2-pyridinecarboxylate) which is a prime natural chelating agent in the body [8], and has important dietary [9] and pharmacological [10] applications. The

* Corresponding author. Tel.: +351 21 841 9237; fax: +351 21 846 4455.
E-mail address: pombeiro@ist.utl.pt (A.J.L. Pombeiro).



Scheme 1.

combination of picolinate with a relatively labile ligand (N_2 , which can be replaced, e.g. by a donor group of a protein or peptide) [5c,11] at a Re centre could possibly provide a new compound with potential significance in nuclear medicine and in therapy.

Herein we report the synthesis, characterization and redox properties of $[Re(pic)(N_2)(CO)(PPh_3)_2]$ (**2**) (pic = picolinate) (Scheme 1), which constitutes, to our knowledge, the first example of a genuine dinitrogen (neutral $N\equiv N$ ligand) complex with a carboxylate or a N,O -coligand. For comparative purposes, we also report the X-ray crystal structure of the dinitrogen complex precursor $[ReCl(N_2)(CO)_2(PPh_3)_2]$ (**1**).

2. Results and discussion

2.1. Synthesis and characterization

Refluxing a mixture of **1** with an excess of picolinic acid (Hpic) in MeOH/ C_6H_6 led to the displacement of the chloride and one carbonyl ligands by picolinate with formation of the neutral dinitrogen rhenium(I) complex **2**, which was isolated in 65% yield as an orange microcrystalline solid and characterized by IR, 1H , $^{31}P\{^1H\}$ and $^{13}C\{^1H\}$ NMR spectroscopies, cyclic voltammetry, FAB⁺-MS, elemental and single crystal X-ray diffraction structural analyses. Complex **2** is rather stable in air, either in the solid state or in C_6H_6 , CH_2Cl_2 , $CHCl_3$ or Me_2CO solutions.

The IR spectrum of **2** exhibits a sharp $\nu(N_2)$ band (with a medium intensity) at 2040 cm^{-1} , which is below that observed for **1** (2116 cm^{-1}), in accord with a more effective π -electron release from the metal to $\pi^*(N_2)$ orbitals in the former complex (see also below) which presents a lower number of CO ligands (CO, as a very strong π -electron acceptor, competes with N_2 for the available metal d_π electrons). Additional bands at 1926, 1855, 1659 and 1599 cm^{-1} are assigned to $\nu(CO)$, ν_{as} and ν_s of the carboxylate group. The monoprotonated molecular ion is clearly observed at $m/z = 890$ with the expected isotopic pattern in the FAB⁺-MS spectrum. Other peaks correspond to the stepwise fragmentations by loss of N_2 , picolinate, CO and PPh_3 ligands or their combinations. The 1H , $^{31}P\{^1H\}$ and $^{13}C\{^1H\}$ NMR spectra show the expected resonances at usual chemical shifts for the corresponding ligands.

2.2. X-ray crystal structures

The molecular structures of both dinitrogen complexes **1** and **2** (Figs. 1 and 2, respectively) present a distorted octahedral geometry with mutually *trans* triphenylphosphines (thus minimizing their steric repulsion) and the other ligands in equatorial sites. The ligated N_2 has the anionic ligand in *trans* position, i.e. chloride in **1** and the carboxylate arm of picolinate in **2**, whereas the two CO ligands in **1** are mutually *trans* and the CO ligand in **2** has the pyridine nitrogen (N3) of picolinate in *trans* position. The strong electron-donor character of the anionic ligand conceivably has a stabilizing effect on the *trans* Re– N_2 bond, promoting the π -electron release from the metal to this ligand thus compensating for the known [1] rather weak σ -electron-donor ability of N_2 to the metal. The Re– N_2 (Re–N1) and Re–CO (Re–C1) bond lengths in **2** [1.911(3) and 1.896(3) Å, respectively] are shorter than the corresponding distances in **1** [1.981(10) and avg. 1.991(13) Å], whereas the $N\equiv N$ (N1–N2) and $C\equiv O$ (C1–O1) bonds [1.144(3) and 1.169(4) Å, respectively] in **2** are slightly lengthened relatively to those of **1** [1.080(16) and avg. 1.024(17) Å]. Although in **1** the N1–N2 distance [1.080(16) Å] is identical

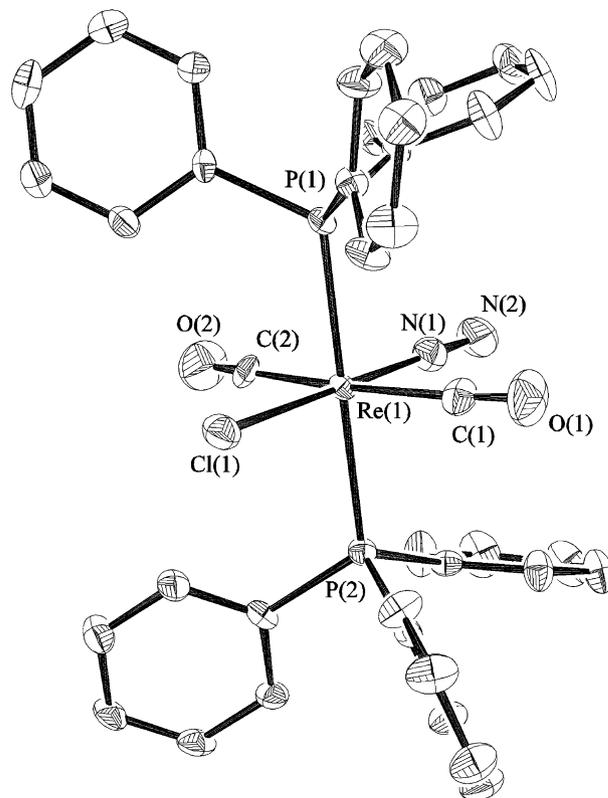


Fig. 1. An ORTEP representation of **1**. Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and bond angles ($^\circ$): Re(1)–Cl(1) 2.476(3), Re(1)–P(1) 2.431(3), Re(1)–P(2) 2.427(3), Re(1)–N(1) 1.981(10), Re(1)–C(1) 1.978(12), Re(1)–C(2) 2.003(13), O(1)–C(1) 1.046(16), O(2)–C(2) 1.001(17), N(1)–N(2) 1.080(16); Re(1)–C(1)–O(1) 173.5(12), Re(1)–C(2)–O(2) 176.5(12), Cl(1)–Re(1)–N(1) 178.5(3), Cl(1)–Re(1)–C(1) 97.2(3), Cl(1)–Re(1)–C(2) 93.4(3), P(1)–Re(1)–P(2) 174.97(8), N(1)–Re(1)–C(1) 84.1(4), N(1)–Re(1)–C(2) 85.2(4), Re(1)–N(1)–N(2) 177.7(10).

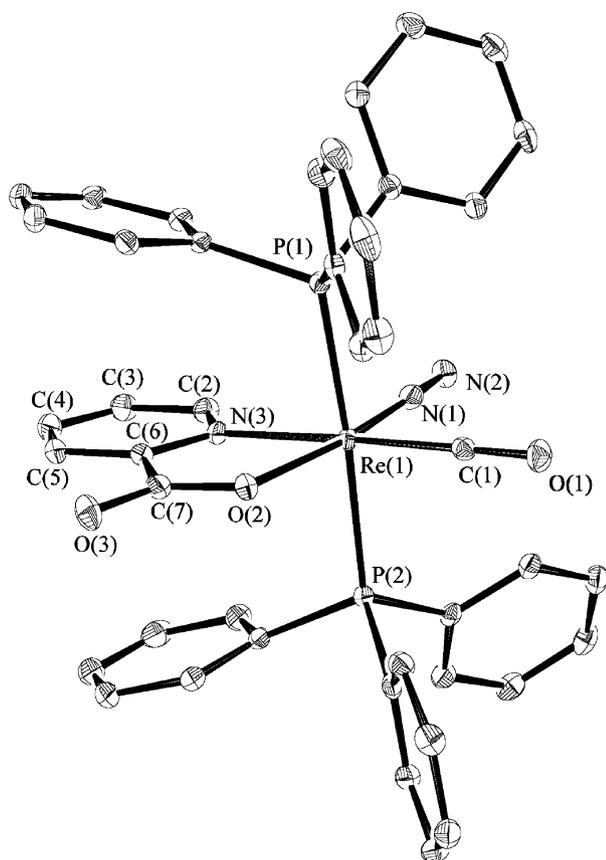
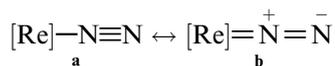


Fig. 2. An ORTEP representation of **2**. Hydrogen atoms and solvent molecules are omitted for clarity. Selected bond lengths (Å) and bond angles (°): Re(1)–C(1) 1.896(3), Re(1)–N(1) 1.911(3), Re(1)–O(2) 2.152(2), Re(1)–N(3) 2.178(2), Re(1)–P(2) 2.4185(7), Re(1)–P(1) 2.4315(7), O(1)–C(1) 1.169(4), N(1)–N(2) 1.144(3); C(1)–Re(1)–N(1) 89.57(12), N(1)–Re(1)–O(2) 168.21(10), C(1)–Re(1)–N(3) 177.29(11), N(1)–Re(1)–N(3) 92.93(10), O(2)–Re(1)–N(3) 75.27(8), P(2)–Re(1)–P(1) 173.20(3), N(2)–N(1)–Re(1) 177.6(3), O(1)–C(1)–Re(1) 177.8(3).

to that of free N₂ [1.0976 Å] [1], in **2** that bond length [1.144(3) Å] is significantly longer. These features possibly reflect the stronger π-electron releasing ability of the {Re(pic)(PPh₃)₂} centre in **2** than that of {ReCl(CO)(PPh₃)₂} (with an effective π-acceptor CO ligand) in **1**. Hence, in complex **2**, the canonical form **b** in the VB representation of the Re–N1–N2 moiety has a higher weight than in **1**



Nevertheless, the Re–N and N–N bond lengths of complexes **1** and **2** are within the overall ranges of values encountered in other mononuclear Re complexes [12]. In **2**, the Re–N3 and Re–O2 coordination bond distances of picolinate, 2.178(2) and 2.1517(19) Å, respectively, are comparable to those at the related benzyldiazenido [ReCl(pic){N=NC(O)Ph}(PPh₃)₂] [6a] and oxorhenium [ReOCl₂(pic)(PPh₃)] [6b] complexes. The metal ligated picolinate forms a Re–N3–C6–C7–O2 chelating ring with a O2–Re–N3 bite angle of 75.27(8)°, which is reduced sig-

nificantly from the octahedral 90° value. Other bond lengths and angles in **1** and **2** do not differ significantly from the expected values found for related octahedral-type rhenium complexes comprising N₂, CO, PPh₃ or N,O-ligands [6,12a,12b].

2.3. Electrochemical studies

Complex **2** exhibits, by cyclic voltammetry at a Pt electrode in 0.2 M CH₂Cl₂/[Bu₄N][BF₄] solution, a first single-electron reversible oxidation at ^IE_{1/2}^{ox} = 0.69 V *vs.* SCE, assigned to the Re^I → Re^{II} oxidation, followed by a second irreversible one at ^{II}E_p^{ox} = 1.17 V *vs.* SCE, due to the Re^{II} → Re^{III} oxidation with loss of N₂ ligand, following a behaviour that is similar to that of other dinitrogen Re^I complexes [13]. These oxidation potentials are lower than the corresponding ones for complex **1** (^IE_{1/2}^{ox} = 0.94, ^{II}E_p^{ox} = 1.79 V *vs.* SCE, measured in this work under identical experimental conditions, or 1.01 and ca. 1.9 V, respectively, as reported by others [13a] in 0.2 M THF/[Bu₄N][BF₄] solution), thus confirming the stronger electron donor character of the picolinate ligand in **2** relatively to ligated Cl[−] + CO in **1**. The first oxidation potential of complex **2** and the corresponding IR ν(N₂) value fit the previously recognized [12a,13a] linear relationship between these parameters for other Re^I–N₂ complexes.

Based on the measured first oxidation potential of complex **2** and of the related picolinate-benzyldiazenido complex [ReCl(pic){N=NC(O)Ph}(PPh₃)₂] [6a] and applying the Lever's equation [14] $E = S_M(\sum E_L) + I_M$ (in V *vs.* NHE, where $\sum E_L$ is the sum of the values for all the ligands of the ligand E_L parameter, S_M and I_M are standard parameters dependent on the redox metal couple, spin state and stereochemistry), we have estimated (see the [Supplementary material](#) for full calculation details of electrochemical parameters), for the first time, the value of the electrochemical Lever ligand parameter, $E_L = 0.05 \pm 0.02$ V *vs.* NHE, for the bidentate picolinate ligand, as the average of the values obtained from these two complexes. This E_L value was confirmed by applying it in the above equation to the prediction of the oxidation potential of the dipicolinate complex [Ru(pic)₂(PPh₃)₂]. The estimated value of 0.89 V *vs.* NHE is equal to that measured experimentally [15].

The estimated E_L value (0.05 ± 0.02 V) for the bidentate picolinate ligand is identical or similar to the sum of E_L values for Cl[−] plus pyridine-4-carboxylic acid ligands (the latter being coordinated by the pyridine group) (−0.24 [14] + 0.29 [14] = +0.05 V) or for Cl[−] plus pyridine itself (−0.24 [14] + 0.25 [14] = +0.01 V). In view of the usual additive character of E_L and of the meaning of this parameter (a measure of the electron donor character of the ligand) [14], this indicates that the ligated carboxylate arm of picolinate, i.e. the O-bound 2-pyridylcarboxylate ligand (2-pyCOO[−]), exhibits an electron donor character similar to that of chloride, i.e. $E_L(2\text{-pyCOO}^-)$ ca. −0.24 V *vs.* NHE, what accounts for its stabilizing effect

(as known [1,4] for Cl^-) on the ligation of N_2 . Moreover, its E_L value is also comparable to those of some alkynyl ligands, e.g. $\text{C}\equiv\text{CPh}^-$ at $\text{trans}\{-\text{OsCl}(\text{dppm})_2\}^+$ ($\text{dppm} = \text{Ph}_2\text{PCH}_2\text{PPh}_2$) [16].

3. Conclusions

We have shown that N_2 and a bound carboxylate N,O -ligand can be compatible at a single metal centre, and have prepared, by a convenient route, the first example of such a type of complex with a genuine neutral $\text{N}\equiv\text{N}$ ligand. The complex is stable in air, either as a solid or in solution, and the carboxylate arm of the picolinate ligand is shown to be an electron-donor similar to chloride, presenting, as Cl^- , a noteworthy stabilizing effect on the trans Re-N_2 bond. Hence, carboxylate groups of biological molecules can co-exist with N_2 at a common binding metal centre, what is in accord with the hypothesis [4] of coordination of dinitrogen at the Mo centre (which has a homocitrate ligand) of FeMoco of nitrogenase.

Preliminary studies on the reactivity of the dinitrogen complex **2** show that N_2 can be displaced by imidazole ($\text{C}_3\text{H}_4\text{N}_2$) to give $[\text{Re}(\text{pic})(\text{C}_3\text{H}_4\text{N}_2)(\text{CO})(\text{PPh}_3)_2]$. The combination, at a single metal centre, of different ligands with recognized biological significance and the possibility to replace N_2 by imidazole and potential biological carriers at a Re-picolinate centre (bearing a metal and a N,O -ligand, both with pharmacological applications) are also interesting features of the obtained complex, although the lack of solubility in water is a drawback. They deserve further exploration and encourage the search for the synthesis of more N,O and carboxylate dinitrogen complexes and, for those soluble in water, with a potential application in medicinal chemistry.

4. Experimental

4.1. General materials and experimental procedures

All synthetic and electrochemical work was performed under dinitrogen using standard Schlenk techniques. The solvents were dried and degassed by standard methods. Potassium perrhenate (Merck), triphenylphosphine (Aldrich), benzoylhydrazine (Aldrich), carbon monoxide (Air Products) and picolinic acid (Aldrich) were obtained from commercial sources and used as received. C, H and N elemental analyses were carried out by the Microanalytical Service of the Instituto Superior Técnico. Positive-ion FAB mass spectra were obtained on a Trio 2000 instrument by bombarding 3-nitrobenzyl alcohol (m -NBA) matrices of the samples with 8 keV (ca. 1.18×10^{15} J) Xe atoms. Mass calibration for data system acquisition was achieved using CsI. Infrared spectra ($4000\text{--}400\text{ cm}^{-1}$) were recorded on a Jasco FT/IR-430 instrument in KBr pellets. For TLC, Merck UV 254 SiO_2 plates have been used. ^1H , $^{31}\text{P}\{^1\text{H}\}$ and $^{13}\text{C}\{^1\text{H}\}$ NMR spectra were measured on a Varian UNITY 300 spectrometer at ambient temperature.

The electrochemical experiments were carried out on an EG&G PAR 273A potentiostat/galvanostat connected to a personal computer through a GPIB interface. Cyclic voltammetry (CV) studies were undertaken in a two-compartment three-electrode cell, at platinum wire working ($d = 0.5\text{ mm}$) and counter electrodes. A Luggin capillary connected to a silver-wire pseudo-reference electrode was used to control the working electrode potential. The solutions were saturated with N_2 by bubbling this gas before each run, and the oxidation potentials of the complexes were measured by CV, in the presence of ferrocene as the internal standard, and the redox potential values are quoted relative to the SCE by using the $[\text{Fe}(\eta^5\text{-C}_5\text{H}_5)_2]^{0/+}$ ($E_{1/2}^{\text{ox}} = 0.525\text{ vs. SCE}$) redox couple in 0.2 M CH_2Cl_2 /[$\text{Bu}_4\text{N}][\text{BF}_4]$ solution [17]. The obtained potentials vs. SCE were converted to the NHE scale by addition of 0.245 V.

4.2. Synthesis of $[\text{ReCl}(\text{N}_2)(\text{CO})_2(\text{PPh}_3)_2]$ (**1**)

Complex **1** was prepared by a published method [18]. CV (CH_2Cl_2 , [$\text{Bu}_4\text{N}][\text{BF}_4]$, $v = 0.2\text{ V s}^{-1}$, vs. SCE): $E_{1/2}^{\text{ox}} = 0.94\text{ V}$, $E_p^{\text{ox}} = 1.79\text{ V}$. X-ray quality crystals were grown by slow evaporation at 5°C of $\text{C}_6\text{H}_6/\text{MeOH}$ or $\text{C}_6\text{H}_6/\text{EtOH}$ solutions.

4.3. Synthesis of $[\text{Re}(\text{pic})(\text{N}_2)(\text{CO})(\text{PPh}_3)_2]$ (**2**)

To a cloudy solution of **1** (100 mg, 0.12 mmol) in MeOH (20 mL)/ C_6H_6 (20 mL) an excess of picolinic acid (148 mg, 1.20 mmol) was added and the reaction mixture was refluxed for 15 h under dinitrogen. The resulting orange clear solution was concentrated under reduced pressure to give an orange oily solid which was treated with 10 mL MeOH to produce a suspension. The solid was then filtered off (see below for the use of filtrate), washed with MeOH ($3 \times 5\text{ mL}$) and Et_2O ($3 \times 5\text{ mL}$), whereafter it was dissolved in CH_2Cl_2 (5 mL) to form a clear solution which was taken to dryness under reduced pressure yielding an orange oil. The addition of Et_2O (40 mL) followed by freezing the obtained mixture in liquid nitrogen (freeze-thaw method) led to the precipitation of a solid which was isolated by filtration, washed with Et_2O ($3 \times 5\text{ mL}$) and dried in vacuo to yield complex **2** as an orange microcrystalline solid (55 mg, 51%). The filtrate from the first filtration (see above) was left to evaporate in air for 2 d. During this time, orange crystals were separated out from the solution. They were collected, washed with MeOH ($3 \times 3\text{ mL}$), Et_2O ($3 \times 3\text{ mL}$) and dried in vacuo to give a second crop of **2** (15 mg, 14%; i.e. total isolated yield of 65%). Further purification of **2** can be achieved by recrystallization from $\text{C}_6\text{H}_6/\text{MeOH}(\text{EtOH})$, $\text{C}_6\text{H}_6/n\text{-C}_5\text{H}_{12}$ or $\text{CH}_2\text{Cl}_2/n\text{-C}_5\text{H}_{12}$ mixtures. Anal. Calc. for $\text{C}_{43}\text{H}_{34}\text{N}_3\text{O}_3\text{-P}_2\text{Re}$: C, 58.10; H, 3.86; N, 4.73. Found: C, 58.19; H, 4.01; N, 4.40. IR (KBr $\nu_{\text{max}}/\text{cm}^{-1}$): 3054w $\nu(\text{CH})$, 2040m $\nu(\text{N}_2)$, 1926m and 1855s $\nu(\text{CO})$, 1659m $\nu_{\text{as}}(\text{COO})$, 1599m $\nu_{\text{s}}(\text{COO})$, 747m and 695s $\nu(\text{PPh})$; ^1H NMR (300 MHz,

CDCl₃, Me₄Si, δ): 7.95 (1H, t, *J* = 5.2 Hz, py), 7.46–7.38 (12H, m, PPh₃), 7.31–7.25 (18H, m, PPh₃), 7.16–7.10 (2H, m, py), 6.73 (1H, t, *J* = 5.5 Hz, py). ¹³C{¹H} NMR (75.4 MHz, CDCl₃, Me₄Si, δ): 189.71 (CO), 151.22 (COO), 136.54, 132.82, 132.05 and 127.34 (py), 134.44–134.29 and 129.07–128.97 (m, PPh₃), 130.28 and 130.17 (PPh₃). ³¹P{¹H} NMR (121.4 MHz, CDCl₃, H₃PO₄, δ): 24.53 (s) (a lower intensity singlet is also observed at δ 23.20, even after repeated recrystallization of the samples by using different combinations of solvents, although only one compound is revealed by TLC (Et₂O:Me₂CO = 5:1, v/v, *R_f* = 0.5)). FAB⁺-MS (*m*-NBA, *m/z*): 890 (M⁺ + H), 861 (M⁺ – N₂), 784 (M⁺ – pic + OH), 767 (M⁺ – pic), 739 (M⁺ – N₂ – pic), 709 (Re(PPh₃)₂ – 2H), 627 (M⁺ – PPh₃), 571 (M⁺ – PPh₃ – N₂ – CO), 448 (Re(PPh₃) – H). CV (CH₂Cl₂, [Bu₄N][BF₄], *v* = 0.2 V · s⁻¹, vs. SCE): ^I*E*_{1/2}^{ox} = 0.69 V, ^{II}*E*_p^{ox} = 1.17 V. X-ray quality crystals of a 2 · C₆H₆ · MeOH were grown by slow evaporation at 5 °C of a C₆H₆/MeOH solution.

4.4. Refinement details for the X-ray crystal structure analysis of compounds 1 and 2

X-ray data were collected on a Nonius-Kappa CCD diffractometer (complex 2) or an Enraf-Nonius CAD4 diffractometer (complex 1), equipped with a graphite monochromator and using Mo-Kα radiation (*λ* = 0.71073 Å) and the COLLECT [19] data collection program. The Denzo-Scalepack [20] or EvalCCD [21] program packages were used for cell refinements and data reduction for 2. The structures were solved by direct methods using the SHELXS-97 [22] or SHELXL-97 program [23]. An empirical

absorption correction based on equivalent reflections was applied [24,25]. Structures were refined with the SHELXL-97 program [23] and the WINGX graphical user interface [25]. In 2 the OH hydrogen of MeOH solvent was located from the difference Fourier map but not refined. All other hydrogens were placed in idealized positions and constrained to ride on their parent atom. The crystallographic data are summarized in Table 1.

Acknowledgements

This work has been partially supported by the Fundação para a Ciência e a Tecnologia (FCT), Portugal and its POCI 2010 programme (FEDER funded). A.M.K. is grateful to the FCT and the POCTI programme for a fellowship (BD/6287/01).

Appendix A. Supplementary material

Crystallographic data for 1 and 2 have been deposited with the Cambridge Crystallographic Data Centre (CCDC Nos. 601690 (1) and 601691 (2)). Copies of these data may be obtained free of charge from the Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (fax: +44 1223 336 033; email: deposit@ccdc.cam.ac.uk or <http://www.ccdc.cam.ac.uk>). Supplementary data (calculation details of electrochemical parameters) associated with this article can be found, in the online version, at doi:10.1016/j.jorganchem.2006.06.015.

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Table 1
Crystal data and structure refinement details for complexes 1 and 2

	1	2 · C ₆ H ₆ · MeOH
Empirical formula	C ₃₈ H ₃₀ ClN ₂ O ₂ P ₂ Re	C ₅₀ H ₄₄ N ₃ O ₄ P ₂ Re
Formula weight	830.23	999.02
Temperature (K)	293(2)	120(2)
Wavelength (Å)	0.71069	0.71073
Crystal system	Triclinic	Monoclinic
Space group	<i>P</i> $\bar{1}$	<i>P</i> 2 ₁ / <i>c</i>
<i>a</i> (Å)	10.2524(10)	10.8965(2)
<i>b</i> (Å)	12.714(3)	21.9095(3)
<i>c</i> (Å)	14.1035(11)	17.8008(3)
α (°)	69.214(14)	90
β (°)	75.237(8)	95.9870(10)
γ (°)	81.5380(10)	90
<i>V</i> (Å ³)	1658.6(4)	4226.53(12)
<i>Z</i>	2	4
<i>D</i> _{calc} (Mg/m ³)	1.662	1.570
μ (Mo Kα) (mm ⁻¹)	3.878	3.001
Number of reflections	7602	45,187
Number of unique data	7300	9675
<i>R</i> _{int}	0.0562	0.0646
Final <i>R</i> ₁ ^a , <i>wR</i> ₂ ^b (<i>I</i> ≥ 2σ)	0.0635, 0.1442	0.0283, 0.0550
Goodness-of-fit on <i>F</i> ²	1.038	1.032

^a $R_1 = \sum |F_o| - |F_c| / \sum |F_o|$.

^b $wR_2 = [\sum [w(F_o^2 - F_c^2)] / \sum [w(F_o^2)^2]]^{1/2}$.

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