

Syntheses and properties of Re(III) complexes derived from hydrotris(1-pyrazolyl)methanes: molecular structure of $[\text{ReCl}_2(\text{HCpz}_3)(\text{PPh}_3)][\text{BF}_4]$

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Conference on nitrogen ligands organised by Prof. Pettinari

Abstract

The complexes $[\text{ReCl}_2\{\text{N}_2\text{C}(\text{O})\text{Ph}\}(\text{Hpz})(\text{PPh}_3)_2]$ (**1**) (Hpz = pyrazole), $[\text{ReCl}_2\{\text{N}_2\text{C}(\text{O})\text{Ph}\}(\text{Hpz})_2(\text{PPh}_3)]$ (**2**), $[\text{ReCl}_2(\text{HCpz}_3)(\text{PPh}_3)][\text{BF}_4]$ (**3**) and $[\text{ReCl}_2(3,5\text{-Me}_2\text{Hpz})_3(\text{PPh}_3)]\text{Cl}$ (**4**) were obtained by treatment of the chelate $[\text{ReCl}_2\{\eta^2\text{-N,O-N}_2\text{C}(\text{O})\text{Ph}\}(\text{PPh}_3)_2]$ (**0**) with hydrotris(1-pyrazolyl)methane HCpz_3 (**1,3**), pyrazole Hpz (**1,2**), hydrotris(3,5-dimethyl-1-pyrazolyl)methane $\text{HC}(3,5\text{-Me}_2\text{pz})_3$ (**4**) or dimethylpyrazole 3,5- Me_2Hpz (**4**). Rupture of a $\text{C}(\text{sp}^3)\text{-N}$ bond in HCpz_3 or $\text{HC}(3,5\text{-Me}_2\text{pz})_3$, promoted by the Re centre, has occurred in the formation of **1** or **4**, respectively. All compounds have been characterized by elemental analyses, IR and NMR spectroscopy, FAB-MS spectrometry, cyclic voltammetry and, for **1** · CH_2Cl_2 and **3**, also by single crystal X-ray analysis. The electrochemical E_L Lever parameter has been estimated, for the first time, for the HCpz_3 and the benzyldiazene $\text{NNC}(\text{O})\text{Ph}$ ligands.

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1. Introduction

The current growth of interest in the coordination chemistry of N_3 tripodal neutral tris(1-pyrazolyl)alkanes, isoelectronic with the tris(1-pyrazolyl)borates anionic ligands, is related to their applications in catalysis and synthetic inorganic, bioinorganic and organometallic chemistries [1–4]. However, in spite of their importance, the coordination chemistry of hydrotris(1-pyrazolyl)methanes [3,5–9], HCpz_3 and substi-

tuted ones, in particular at Re centres, and in contrast with the tris(1-pyrazolyl)borate chemistry [10], has so far been reported only rarely [3,8,9]. The underdevelopment of this chemistry results from the relatively small number of such ligands currently available, the difficulties associated with their synthesis and the usually low yields. The rhenium(V) tris(pyrazolyl)methane complex $[\text{ReOCl}_2(\text{HCpz}_3)]^+$, analogous to the tris(pyrazolyl)borate compound $[\text{ReOCl}_2(\text{HBpz}_3)]$, was prepared and shown [8] to add PPh_3 to give the phosphine oxide complex $[\text{ReCl}_2(\text{HCpz}_3)(\text{OPPh}_3)]^+$, whereas rhenium(I) tricarbonyl complexes of tris(pyrazolyl)methane ligands have also been reported [9].

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Within the search for a suitable starting material for the synthesis of Re complexes with such a class of ligands, we have chosen the benzoylhydrazido-Re(V) chelate $[\text{ReCl}_2\{\eta^2\text{-}N,O\text{-}N_2\text{C}(\text{O})\text{Ph}\}(\text{PPh}_3)_2]$ (**0**) which is a very useful precursor for a variety of organodiazenide and dinitrogen complexes in lower metal oxidation states, containing usually phosphines [11], phosphites or phosphonites [12,13] and, to a smaller extent, amine-based [14] ligands. From the study of the reaction of $[\text{ReCl}_2\{\eta^2\text{-}N,O\text{-}N_2\text{C}(\text{O})\text{Ph}\}(\text{PPh}_3)_2]$ (**0**) with hydrotris(1-pyrazolyl)methanes, i.e. HCpZ_3 and $\text{HC}(3,5\text{-Me}_2\text{pz})_3$, we should be able to investigate not only the coordination chemistry of these species at rhenium centres with an organodiazenide or a derived ligand, but also to prepare novel types of complexes with such classes of ligands and/or derived ones. We have thus prepared new Re(III) complexes with hydrotris(1-pyrazolyl)methane or benzoylhydrazide ligands and, since in some cases we have observed the conversion of the tris(pyrazolyl)methane into the corresponding pyrazole, i.e. Hpz or $3,5\text{-Me}_2\text{Hpz}$, we have also performed some reactions with the latter species for comparative purposes.

Moreover, by investigating the redox behaviour of the obtained products, we have got an insight into the net electron donor/acceptor ability of such ligands, in particular the hydrotris(1-pyrazolyl)methane and the benzoyldiazenide, and succeeded in the estimate, for the first time, of the values of the electrochemical E_L Lever ligand parameter [15–17], a measure of that character.

2. Results and discussion

2.1. Synthesis and characterization

The attempt to synthesise a rhenium complex with an hydrotris(1-pyrazolyl)methane ligand i.e. hydrotris(1-pyrazolyl)methane HCpZ_3 or the corresponding disubstituted $\text{HC}(3,5\text{-Me}_2\text{pz})_3$, from the reaction with the benzoylhydrazido rhenium(V) chelate $[\text{ReCl}_2\{\eta^2\text{-}N,O\text{-}N_2\text{C}(\text{O})\text{Ph}\}(\text{PPh}_3)_2]$ (**0**) (in stoichiometric amount) in refluxing methanol, led to the formation of the corresponding pyrazole derivatives $[\text{ReCl}_2\{N_2\text{C}(\text{O})\text{Ph}\}(\text{Hpz})\text{-}(\text{PPh}_3)_2]$ (**1**) or $[\text{ReCl}_2\{3,5\text{-Me}_2\text{Hpz}\}_3(\text{PPh}_3)]\text{Cl}$ (**4**) [Scheme 1, reactions (a) and (f)]. In the formation of **1**, the benzoylhydrazido behaves as a hemilabile ligand with opening of the chelating ring leading to a monodentate benzoyldiazenide, $\eta^1\text{-NNC}(\text{O})\text{Ph}$, the vacant coordination position being occupied by a pyrazole. This ligand, as well as its 3,5-dimethyl derivative in the case of the formation of **4**, are derived from the rupture of a $\text{C}(\text{sp}^3)\text{-N}$ bond in the corresponding hydrotris(1-pyrazolyl)methane compound. Other cases of rupture of a carbon–nitrogen or boron–nitrogen bond by a me-

tal ion have been reported, namely the C–N bond cleavage in bis(pyrazolyl)propane $(\text{CH}_3)_2\text{CpZ}_2$ by Pt(II) complexes [18] such as PtCl_2 , $[\text{PtCl}_2(\text{RCN})_2]$ (R = Me or Ph) or $\text{K}_2[\text{PtCl}_4]$, observed also in the reaction of Ru(II) species with 1-hydroxymethyl-3,5-dimethylpyrazole resulting in 3,5-dimethylpyrazole complexes [19], and the B–N bond rupture in $\text{K}[\text{HB}(3,5\text{-Me}_2\text{pz})_3]$ by Ru(II) complexes [20] such as $[\text{Ru}(\eta^6\text{-C}_6\text{H}_6)\text{Cl}_2]_2$. Such a behaviour, to our knowledge, has not been previously shown for rhenium. In all the reported cases, the way the cleavage reaction occurs has not been established.

Complexes **1** and **4** are also obtained upon reaction of $[\text{ReCl}_2\{\eta^2\text{-}N,O\text{-}N_2\text{C}(\text{O})\text{Ph}\}(\text{PPh}_3)_2]$ (**0**) with pyrazole or 3,5-dimethylpyrazole [Scheme 1, reactions (c) and (g), respectively]. The former product **1** has previously been obtained by others [21] by refluxing for 2 days a methanol mixture or stirring at room temperature an acetone suspension of the starting benzoylhydrazido chelate and an excess (ca. 7:1) of pyrazole. In our case, **1** has been prepared [reaction(c)] by using a benzene solution, at room temperature for 20 h, with stoichiometric amounts of reagents, whereas **4** was prepared by refluxing a methanol solution for 28 h.

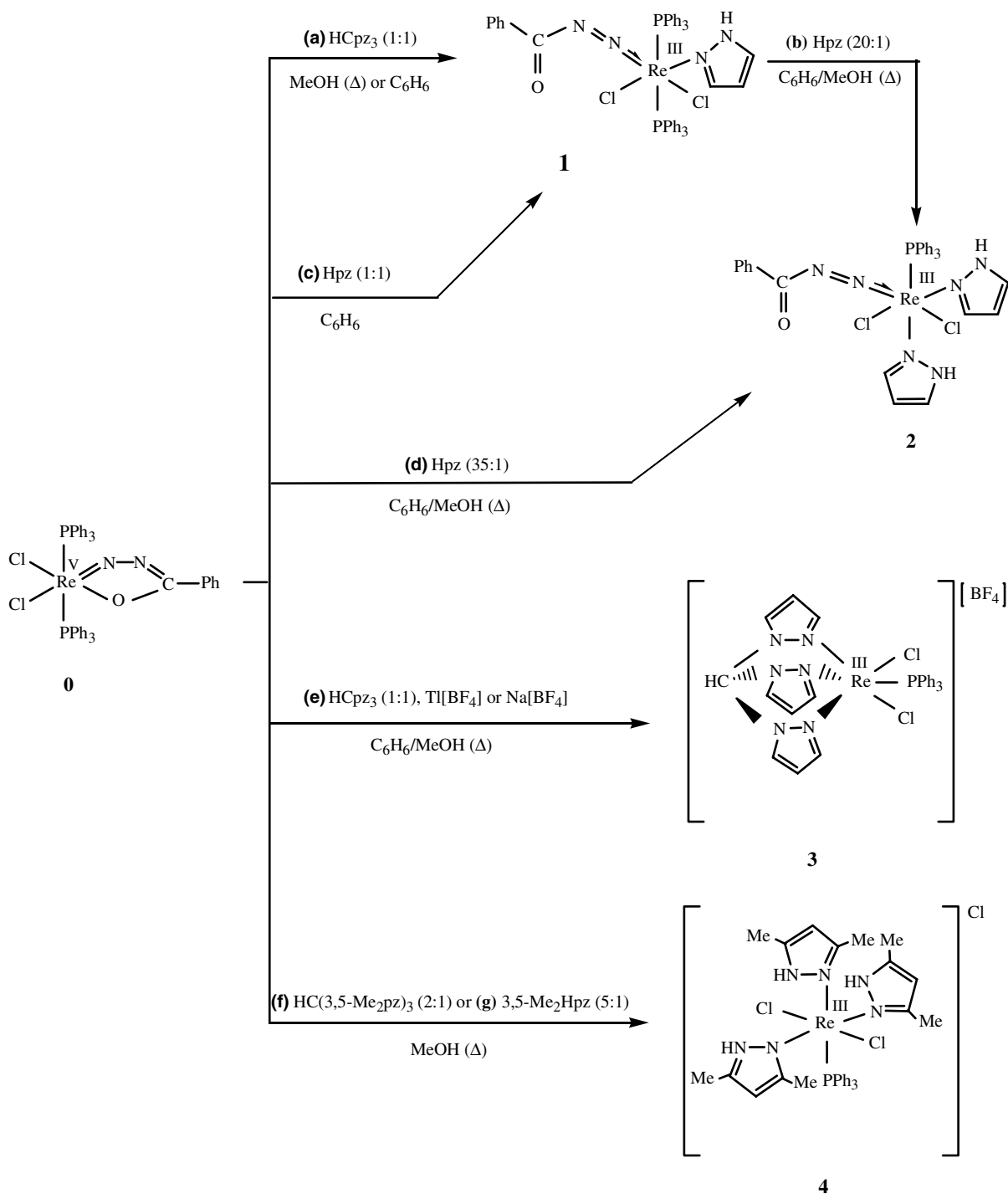
If the reaction of the benzoylhydrazido chelate is performed in the presence of a high excess of pyrazole (35:1 molar ratio), the bispyrazole complex $[\text{ReCl}_2\{N_2\text{C}(\text{O})\text{Ph}\}(\text{Hpz})_2(\text{PPh}_3)]$ (**2**) is the obtained product [Scheme 1, reaction (d)] which is also formed by further reaction of the monopyrazole complex **1** with an excess of pyrazole [Scheme 1, reaction (b)].

Complex **2**, similarly to **1**, is obtained either in a refluxing methanol suspension of the starting benzoylhydrazido chelate or in a benzene solution of this complex (it is soluble in this solvent) at room temperature.

When the reaction of the starting chelate **0** with HCpZ_3 (1:1) is carried out in the presence of $\text{Ti}[\text{BF}_4]$ or $\text{Na}[\text{BF}_4]$, in $\text{C}_6\text{H}_6/\text{MeOH}$ under reflux, one obtains the hydrotris(1-pyrazolyl)methane dichloro complex $[\text{ReCl}_2(\text{HCpZ}_3)(\text{PPh}_3)][\text{BF}_4]$ (**3**) [Scheme 1, reaction (e)]. The formation of this product, with preservation of the two chloride ligands, is surprising in view of the well known ability of Ti^+ to abstract such ligands. In contrast, the formation of compound **3** involves the formal replacement of the chelating benzoylhydrazide and one of the phosphine ligands by the tri-hapto HCpZ_3 .

All the above reactions involve a formal two-electron reduction of Re(V) to Re(III). This is believed to result from an intra-molecular redox process on account of the involvement of the expected conversion of the dihapto benzoylhydrazido(3–) ligand, $\eta^2\text{-NNC}(\text{O})\text{Ph}(3\text{-})$, into the monohapto benzoyldiazenido(1–), $\eta^1\text{-NNC}(\text{O})\text{Ph}(1\text{-})$.

However, in spite of the latter ligand being a good precursor for a ligated dinitrogen at related rhenium centres [11–14], in our reactions we have failed to isolate



Scheme 1.

any N₂ complex. The N₂ ligand could be formed from a ligated NNC(O)Ph upon nucleophilic attack of methanol on the carbonyl carbon, leading also to the elimination of methylbenzoate PhCOOMe upon N–C bond cleavage [11]. This cleavage can also be homolytic upon heating [11].

Neither NaOTf nor TlOTf promote the conversion of the benzoylhydrazido ligand into N₂, in our cases,

since a mixture of the products **1** and **2** was obtained from the reaction of the benzoylhydrazido complex with Hpz, in refluxing C₆H₆/MeOH, in the presence of the triflate salt. This contrasts with the reported [14] formation of various amine dinitrogen complexes of rhenium derived from the reaction of the same benzoylhydrazido complex with an amine in the presence of NaOTf, under experimental conditions similar to ours.

All the complex products have been characterized by elemental analyses, IR and NMR spectroscopy, FAB-MS spectrometry, electrochemical methods and, in the case of **1**·CH₂Cl₂ and **3**, also by X-ray diffraction analysis.

In the IR spectra, the pyrazole complexes **1**, **2** and **4** exhibit a medium band at 3076, 3286 and 3118 cm⁻¹, respectively, assigned to the ν(NH) stretching mode of the pyrazole ring(s). Moreover, complexes **1** and **2** exhibit strong bands at 1593 and 1588 cm⁻¹, respectively, assigned to ν(C=O) of the benzoyldiazenido ligand and to ν(C=C) of the ligating pyrazole, and in the 1565–1549 cm⁻¹ range, attributed to ν(N=N) of the organodiazenido moiety and to ν(N=C) of the pyrazole ring. In other rhenium complexes, such IR bands for η¹-N–NNC(O)Ph complexes appear at comparable values, e.g. [ReCl₂{N₂C(O)Ph}(PPh₃)(L₁)(L₂)] [11] [L₁ = PPh₃, L₂ = MeCN, py or L₁ = Ph₂PCH₂CH₂PPh₂, Ph₂AsCH₂CH₂AsPh₂; ν(C=O) 1640–1700; ν(N=N) 1530–1580 cm⁻¹] and [ReCl₂{N₂C(O)Ph}{=C(CH₂)_n-CH(R)O}-(PPh₃)₂] [11] [n = 1, R = H, Me; n = 2, R = H, Me; ν(C=O) 1648–1663; (N=N) 1537–1551 cm⁻¹]. Complex **3** exhibits a broad band at ca. 1532 cm⁻¹ attributed to (N=C) of the pyrazole rings.

The *trans* geometry of complex **1** is assigned on the basis of the singlet observed in the ³¹P–{¹H} NMR spectrum and confirmed by the X-ray analysis.

In the ¹H NMR spectrum, the methine hydrogen of compound **3** appears at δ 9.66, i.e. slightly deshielded from that observed for the uncomplexed ligand by 1.26, in accord with the reported observations for the complexes [ReOCl₂(HCp₃)] [BF₄] [8] and [Re(HCp₃)(CO)₃][BF₄] [9], suggesting a weak hydrogen-bonding interaction with the [BF₄]⁻ counterion in solution. In the ¹³C–{¹H} NMR spectra, the three carbon atoms from the pyrazole ring in all complexes appear as singlets. Their resonances are very similar to those observed [18] for Pt complexes such as *cis* or *trans*-[PtX₂(Hpz)₂] X (X = I or Cl) or [Pt{NH=C(Ph)pz}]Cl₂. All the other resonances of the benzoylhydrazido and triphenylphosphine ligands have also been assigned (see Section 3) in the ¹H, ¹³C–{¹H} and ¹³C NMR spectra, including those of the *ipso*-, *ortho*-, *meta*- and *para*-atoms of the phenyl rings.

The FAB⁺-MS spectra of the complexes exhibit the molecular ion [M⁺ and the fragmentation pathways occur by cleavage of the metal–ligand bonds and rupture of bonds within the PPh₃ and HCp₃ (complex **3**) ligands. Hence for **3** the fragments [M – Cl]⁺, [M – Cl – pz]⁺, and those derived upon further loss of pyrazolyl and phenyl groups are detected. Coupling of pyrazolyl with metal fragments has also been observed, e.g. [M – Cl + pz]⁺ and derivatives. In the chemical reactions (see above), the pyrazole derived from HCp₃ can also bind the metal centre. In the case of **1** and **2**, the fragments [M – Hpz]⁺, [M – Cl]⁺, [M – Hpz–Cl]⁺ and, to a less extent,

[M – N₂COPh]⁺ are observed. In all the complexes, the elimination of PPh₃ from any of the starting complexes is less favoured relatively to the loss of the other ligands since the fragment [M – PPh₃]⁺ is not visible.

2.2. Electrochemical studies

Complexes **1–4** exhibit by cyclic voltammetry, at a platinum electrode at 25 °C in a 0.2 M [t⁺Bu₄N][BF₄]/CH₂Cl₂ solution, a first single-electron partially reversible **1–3** or irreversible **4** oxidation wave (wave I^{ox}) at ^IE_{1/2}^{ox} = 0.73 (**1**), 0.68 (**2**) and 0.54 (**3**) V versus SCE (Fig. 1 for **2**) or ^IE_p^{ox} = 0.86 **4** V versus SCE, assigned to the Re^{III} → Re^{IV} oxidation, which is followed, at a higher potential, by a second one (II^{ox}), irreversible for **1**, **2** and **4** (^{II}E_p^{ox} = 1.65, 1.64 and 1.42 V, respectively), but reversible for **3** (^{II}E_{1/2}^{ox} = 1.42 V), assigned to the Re^{IV} → Re^V oxidation. In the first oxidation process (wave I^{ox}) a new, yet unidentified, species is formed to a certain extent as shown by the reduction wave at E_p ca. 0.3 V detected upon scan reversal following the anodic scan beyond wave I^{ox}.

The complexes also exhibit one reduction wave (wave I^{red}) (irreversible for **1** and **2** at ^IE_p^{red} = -1.56 or -1.51 V, respectively; reversible for **3** and **4**, at ^IE_{1/2}^{red} = -0.74 or -0.36 V, respectively) whereas complex **3** displays also a second irreversible one (II^{red}) at a lower potential, ^{II}E_p^{red} = -1.53 V.

The starting chelate **0** was also investigated and shown to exhibit, by cyclic voltammetry, three irreversible oxidation waves at 0.93, 1.42 and 1.80 V. The values of the first oxidation potential of the complexes **1–4** are less anodic than that of complex **0**, in accord with the lower metal oxidation state of the former (III) in comparison with the latter (V).

The slightly lower first oxidation potential of **2** in comparison with **1** is indicative of a slightly stronger

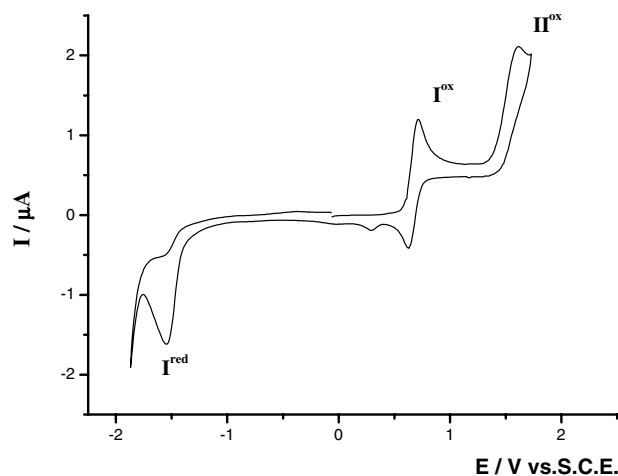


Fig. 1. Cyclic voltammogram of [ReCl₂{N₂C(O)Ph}(Hpz)₂(PPh₃)] (**2**), initiated by the anodic sweep, at a Pt electrode, in 0.2 M [t⁺Bu₄N][BF₄]/CH₂Cl₂ solution (ν = 200 mV/s). Complex concentration: 1.6 mM.

electron-donor character of the pyrazole relatively to the PPh_3 ligand in accordance with the values [15–17] of the electrochemical Lever E_L parameter (the stronger that character, the lower E_L) for these ligands (0.20 and 0.39 V versus NHE, respectively). The considerable lower first oxidation potential of complex **3** compared to **1** and **2** suggests that the tri-hapto HCpZ_3 ligand behaves as a stronger electron-donor than $\text{NNC}(\text{O})\text{Ph}^- + \text{Hpz} + \text{PPh}_3$ (in **1**) and than $\text{NNC}(\text{O})\text{Ph}^- + 2\text{Hpz}$ (in **2**). The higher first oxidation potential of **4**, relatively to **3**, is indicative of a stronger overall electron-donor ability of HCpZ_3 , in the latter, in comparison with the three 3,5- Me_2pz ligands in the former complex (see Table 1).

2.2.1. Estimate of electrochemical ligand parameters

The measured first oxidation potential ($E_{1/2}^{\text{ox}}$ for the $\text{Re}^{\text{III}} \rightarrow \text{Re}^{\text{IV}}$ oxidation) of the complexes allows us to estimate, for the first time, the electrochemical E_L Lever parameter for the benzyldiazene and the hydrotris(1-pyrazolyl)methane HCpZ_3 ligands, by applying the linear relationship (1), valid for octahedral complexes, that relates their redox potential (V versus NHE) with the sum of the E_L values for all the ligands ($\sum E_L$). The slope (S_M) and intercept (I_M) are dependent upon the metal, redox couple, spin state and stereochemistry [15,16].

$$E_{1/2}^{\text{ox}} = S_M(\sum E_L) + I_M \text{ V versus NHE.} \quad (1)$$

Hence, by using the reported [16] S_M and I_M values for the $\text{Re}^{\text{III/IV}}$ redox couple (0.86 and 0.51 V versus NHE, respectively), the known [16,17] ligand E_L values for the PPh_3 , Hpz and Cl^- ligands (0.39, 0.20 and -0.24 V versus NHE, respectively), and $E_{1/2}^{\text{ox}}$ values of our complexes (referred to the NHE, see Section 3), we have estimated the following E_L values. For the benzyldiazene ligand, $E_L = 0.11$ V versus NHE, as the average of the values obtained from complexes **1** and **2**; for each coordinated pyrazole group in the hydrotris(1-pyrazolyl)methane ligand, $E_L = 0.14$ V versus NHE, obtained from complex **3**.

olyl)methane ligand, $E_L = 0.14$ V versus NHE, obtained from complex **3**.

The latter E_L value was confirmed by applying Eq. (1) to the first reduction process ($\text{Re}^{\text{III}}/\text{Re}^{\text{II}}$) of complex **3**, i.e. by considering the corresponding S_M and I_M values [16] of 1.17 and -0.88 V versus NHE.

Since the E_L parameter is a measure of the electron donor character of a ligand (the lower the parameter, the stronger is that character), one can conclude that the $\text{NNC}(\text{O})\text{Ph}^-$ ligand ($E_L = 0.11$ V) is a slightly stronger electron donor than each pyrazole ligand in HCpZ_3 ($E_L = 0.14$ V) and the latter is comparable to benzylamine ($E_L = 0.14$ V) [16,17], di-R-alkyl-diazabutadienes ($E_L = 0.14$ V) [16,17], biimidazol ($E_L = 0.13$ V) [16,17] and imidazole ($E_L = 0.12$ V) [16,17]. Interestingly, the pyrazole ring ($E_L = 0.14$ V) in HCpZ_3 presents a stronger electron-donor ability than the Hpz ligand ($E_L = 0.20$ V) [16,17], suggesting an electron-donor character for the methine HC group. Nevertheless, both are weaker electron-donors than e.g. ammonia ($E_L = 0.07$ V) [16,17], water ($E_L = 0.04$ V) [16,17] or N-methylimidazole ($E_L = 0.08$) [16,17]. That is consistent with the reported [3,22,23] moderately strong σ -donor and weak π -donor capacity of HCpZ_3 .

2.3. Solid state structures

The molecular structures of the pyrazole complex **1** with dichloromethane of crystallization, $\mathbf{1} \cdot \text{CH}_2\text{Cl}_2$, and of the hydrotris(1-pyrazolyl)methane complex **3** were determined by single-crystal X-ray diffraction analysis. They are depicted in Figs. 2 and 3. Crystallographic details are given in Table 2 and selected bond distances and angles in Table 3.

Although the molecular structure of $[\text{ReCl}_2\{\text{N}_2\text{C}(\text{O})\text{C}_6\text{H}_5\}(\text{Hpz})(\text{PPh}_3)_2]$ (**1**) is already known [21] we present here the crystal structure of $[\text{ReCl}_2\{\text{N}_2\text{C}(\text{O})\text{C}_6\text{H}_5\}(\text{Hpz})(\text{PPh}_3)_2] \cdot \text{CH}_2\text{Cl}_2$, i.e. **1** crystallized with a CH_2Cl_2 solvent molecule. Cell parameters reflect the different crystal packing.

In both molecules of $\mathbf{1} \cdot \text{CH}_2\text{Cl}_2$ and **3**, the coordination around the rhenium atom assumes an octahedral geometry. The least-square plane of the two chlorine and the two nitrogen atoms in **1** are within a standard deviation of 0.0171 Å with the Re atom lying in it. In **3** the standard deviation of an equivalent plane is of 0.0095 Å with the rhenium atom lying 0.1866(45) Å above it. The slight distortion in **3** with short N–Re–N bond angles [ranging from 81.1(4)° to 85.4(4)°] is common [8,9], and is probably a consequence of the tridentate feature of the HCpZ_3 .

The Re–N(pz) bond distances in both structures range from 2.094(11) to 2.163(11) Å and are within the usual one found [24,25] in pyrazole or pyrazolyl coordination compounds independently from the fact that the pz ring is monodentate (as in **1**) or is part

Table 1
Cyclic voltammetric data^a for $[\text{ReCl}_2\{\eta^2\text{-}N,O\text{-}N_2\text{C}(\text{O})\text{Ph}\}(\text{PPh}_3)_2]$ (**0**), $[\text{ReCl}_2\{\text{N}_2\text{C}(\text{O})\text{Ph}\}(\text{Hpz})(\text{PPh}_3)_2]$ (**1**), $[\text{ReCl}_2\{\text{N}_2\text{C}(\text{O})\text{Ph}\}(\text{Hpz})_2(\text{PPh}_3)]$ (**2**), $[\text{ReCl}_2(\text{HCpZ}_3)(\text{PPh}_3)_2]$ (**3**) and $[\text{ReCl}_2(3,5\text{-Me}_2\text{Hpz})_3(\text{PPh}_3)]\text{Cl}$ (**4**)

Complex	$E_{1/2}^{\text{ox}}$ ($E_{1/2}^{\text{ox}}$)($E_{1/2}^{\text{ox}}$)	$E_{1/2}^{\text{ox}}$ ($E_{1/2}^{\text{ox}}$)($E_{1/2}^{\text{ox}}$)	$E_{1/2}^{\text{red}}$ ($E_{1/2}^{\text{red}}$)($E_{1/2}^{\text{red}}$)
0 ^b	0.93	1.42	−1.41
1 ^c	(0.73)	1.65	−1.46
2	(0.68)	1.64	−1.51
3 ^d	(0.54)	(1.42)	(−0.74)
4	0.86	1.42	(−0.36)

^a Values in V \pm 0.02 relative to SCE (see Section 3); scan rate of 200 mV s^{-1} . Values for reversible waves are given in brackets.

^b A third irreversible oxidation wave is observed at $E_{1/2}^{\text{ox}} = 1.80$ V.

^c A third irreversible oxidation wave is observed at $E_{1/2}^{\text{ox}} = 1.99$ V.

^d A second irreversible reduction wave is observed at $E_{1/2}^{\text{red}} = -1.53$ V.

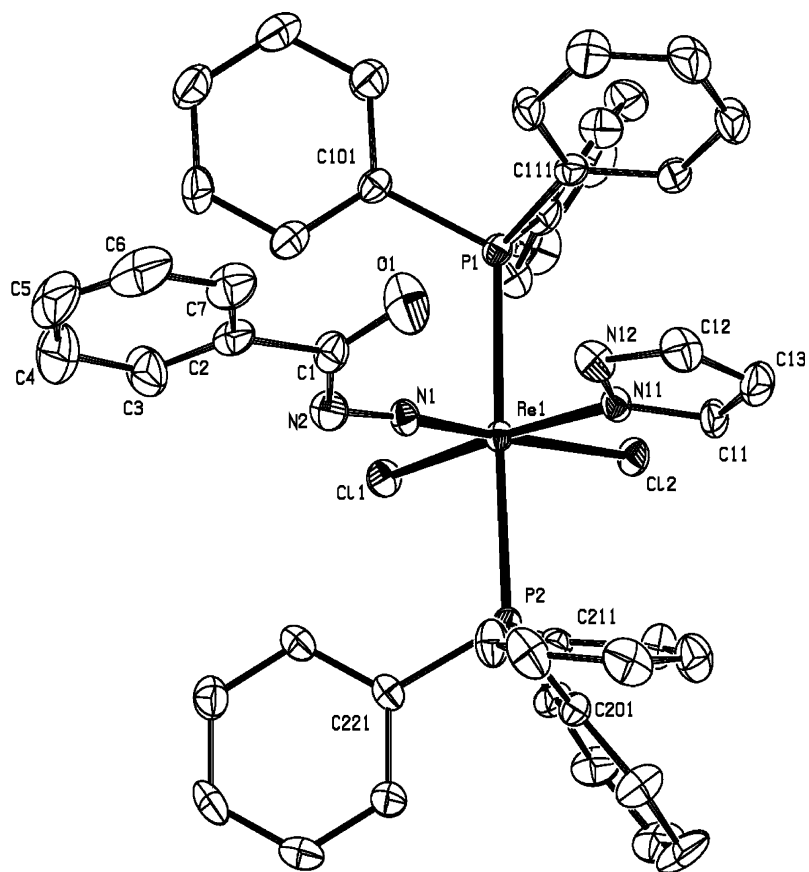


Fig. 2. Molecular structure of the neutral complex of $[\text{ReCl}_2\{\text{N}_2\text{C}(\text{O})\text{Ph}\}(\text{Hpz})(\text{PPh}_3)_2] \cdot \text{CH}_2\text{Cl}_2 \cdot \text{CH}_2\text{Cl}_2$, indicating the atom numbering scheme.

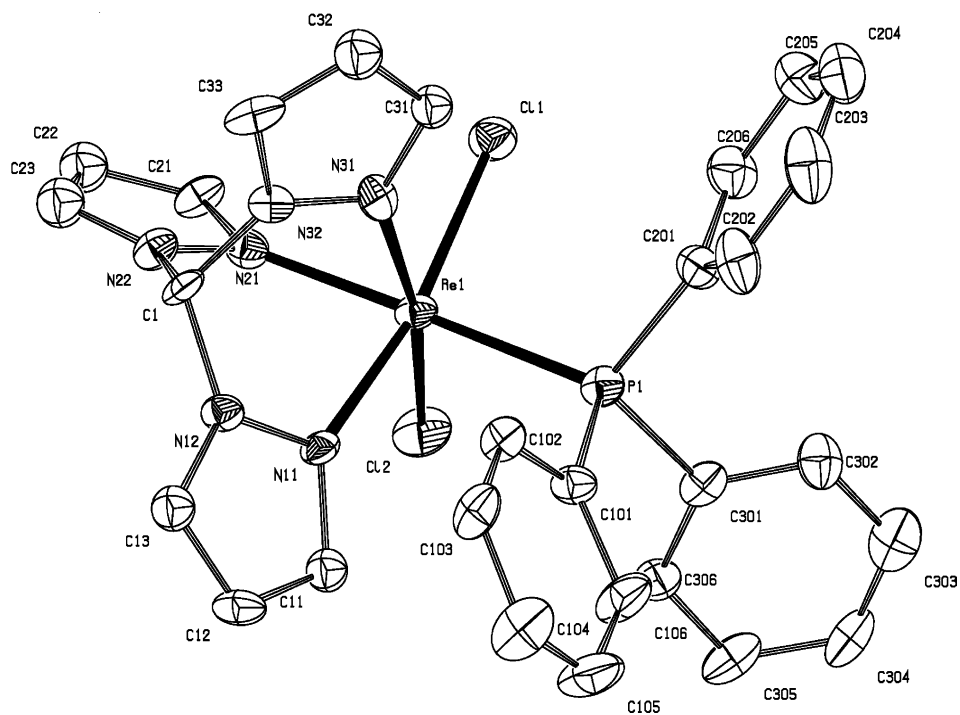


Fig. 3. Molecular structure of the cationic complex of $[\text{ReCl}_2(\text{HCpz}_3)(\text{PPh}_3)][\text{BF}_4]$ (3), indicating the atom numbering scheme.

Table 2

Crystal data and structure for $[\text{ReCl}_2\{\text{NNC}(\text{O})\text{C}_6\text{H}_5\}(\text{Hpz})(\text{PPh}_3)_2] \cdot \text{CH}_2\text{Cl}_2$ (**1** · CH_2Cl_2) and $\text{ReCl}_2(\text{HCpz}_3)(\text{PPh}_3)[\text{BF}_4]$ (**3**)

	1 · CH_2Cl_2	3
Empirical formula	$\text{C}_{47}\text{H}_{41}\text{Cl}_4\text{N}_4\text{O}_2\text{Re}$	$\text{C}_{28}\text{H}_{25}\text{BCl}_2\text{F}_4\text{N}_6\text{PRe}$
Formula weight	1067.78	820.42
Crystal system	Monoclinic	Monoclinic
Space group	$P2_1/c$	$P2_1/c$
a (Å)	12.708(5)	16.376(3)
b (Å)	18.081(5)	10.0460(8)
c (Å)	19.877(5)	19.337(3)
α (°)	90.000(5)	90.000(5)
β (°)	100.747(5)	104.469(12)
γ (°)	90.000(5)	90.000(5)
V (Å ³)	4487(2)	3080.3(7)
T (K)	293(2)	293(2)
Z	4	4
Density (calculated) (g cm ⁻³)	1.581	1.769
Absorption coefficient (mm ⁻¹)	3.058	4.225
$F(000)$	2128	1600
θ range for data collection (°)	1.53–27.02	2.18–25.99
Index ranges	$-16 \leq h \leq 15, -23 \leq k \leq 0, 0 \leq l \leq 25$	$-19 \leq h \leq 19, 0 \leq k \leq 11, -23 \leq l \leq 0$
Reflections collected/unique	10062/9779 [$R_{\text{int}} = 0.0387$]	6166/5978 [$R_{\text{int}} = 0.1080$]
Completeness to $\theta = 27.02$	99.6%	98.8%
Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
Data/restraints/parameters	9779/0/677	5978/0/359
Goodness-of-fit on F^2	0.944	0.948
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0505, wR_2 = 0.0748$	$R_1 = 0.0766, wR_2 = 0.1527$
R indices (all data)	$R_1 = 0.1111, wR_2 = 0.0852$	$R_1 = 0.1629, wR_2 = 0.1780$

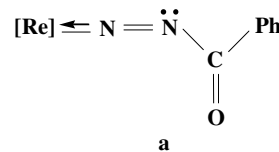
Table 3

Selected bond distances (Å) and angles (°) for the complexes $[\text{ReCl}_2(\text{PPh}_3)_2\{\text{NNC}(\text{O})\text{C}_6\text{H}_5\}(\text{Hpz}) \cdot \text{CH}_2\text{Cl}_2$ (**1** · CH_2Cl_2) and $\text{ReCl}_2(\text{HCpz}_3)(\text{PPh}_3)[\text{BF}_4]$ (**3**)

1		3	
<i>Bond lengths</i>			
Re–N1	1.762(5)	Re–N11	2.094(11)
Re–N11	2.149(6)	Re–N21	2.121(12)
Re–Cl1	2.4410(19)	Re–N31	2.163(11)
Re–Cl2	2.4006(18)	Re–P1	2.467(5)
Re–P1	2.4773(19)	Re–Cl1	2.347(4)
Re–P2	2.4660(19)	Re–Cl2	2.357(4)
N1–N2	1.252(7)		
N2–C1	1.307(8)		
C1–O1	1.254(9)		
C1–C2	1.499(9)		
<i>Bond angles</i>			
Cl(1)–Re–Cl(2)	88.31(6)	Cl(1)–Re–Cl(2)	92.52(14)
Cl(1)–Re–P(1)	90.29(5)	Cl(1)–Re–P(1)	97.21(15)
Cl(1)–Re–P(2)	89.45(5)	Cl(1)–Re–N(11)	169.8(3)
Cl(1)–Re–N(1)	94.49(14)	Cl(1)–Re–N(21)	87.1(3)
Cl(1)–Re–N(11)	172.18(15)	Cl(1)–Re–N(31)	89.2(3)
Cl(2)–Re–P(1)	86.36(6)	Cl(2)–Re–P(1)	96.84(14)
Cl(2)–Re–P(2)	90.91(6)	Cl(2)–Re–N(11)	91.3(3)
Cl(2)–Re–N(1)	177.06(16)	Cl(2)–Re–N(21)	88.8(3)
Cl(2)–Re–N(11)	83.93(15)	Cl(2)–Re–N(31)	169.7(3)
P(1)–Re–P(2)	177.27(5)	P(1)–Re–N(11)	91.8(3)
P(1)–Re–N(1)	92.71(18)	P(1)–Re–N(21)	172.7(3)
P(1)–Re–N(11)	90.19(15)	P(1)–Re–N(31)	93.0(3)
P(2)–Re–N(1)	90.03(18)	N(11)–Re–N(21)	83.4(4)
P(2)–Re–N(11)	89.69(15)	N(11)–Re–N(31)	85.4(4)
N(1)–Re–N(11)	93.3(2)	N(21)–Re–N(31)	81.1(4)
Re–N(1)–N(2)	171.24(4)		
N(1)–N(2)–C(1)	119.8(6)		

of a chelating hydrotris(1-pyrazolyl)methane moiety (as in **3**). Moreover, the bond lengths within the pyrazole groups of the HCpz₃ ligand in complex **3** are identical to those observed for the pyrazole ligand in complex **1**. Such a type of similarity has been recognized in other cases like $[\text{M}(\text{HCpz}_3)_2]^{2+}$ (M=Ni, Co or Zn) [23]. It has also previously been observed that complexes of tris(1-pyrazolyl)methane or tris(1-pyrazolyl)borane have quite similar structural parameters [8,9].

For the benzyldiazene ligand in **1**, the Re–N bond distance [1.762(5) Å] is much shorter than that of Re–N(pz), being indicative of a double bond character, and the coordination is essentially linear [Re–N(1)–N(2) angle of 171.2(4)°]. The ligand is bent at N(2) with the N(1)–N(2)–C(1) angle of 119.8(6)°. Hence, the benzyldiazene ligand acts as a 3-electron donor (if considered in the neutral form **a**) or as a 4-electron donor (negatively charged form) [26], thus giving an 18-electron configuration to the complex. A similar coordination mode is known for a variety of organodiazene rhenium complexes [11c,27–30].



The average Re–Cl bond distance in compound **1** [2.4208(19) Å] is longer than that found in complex **3**

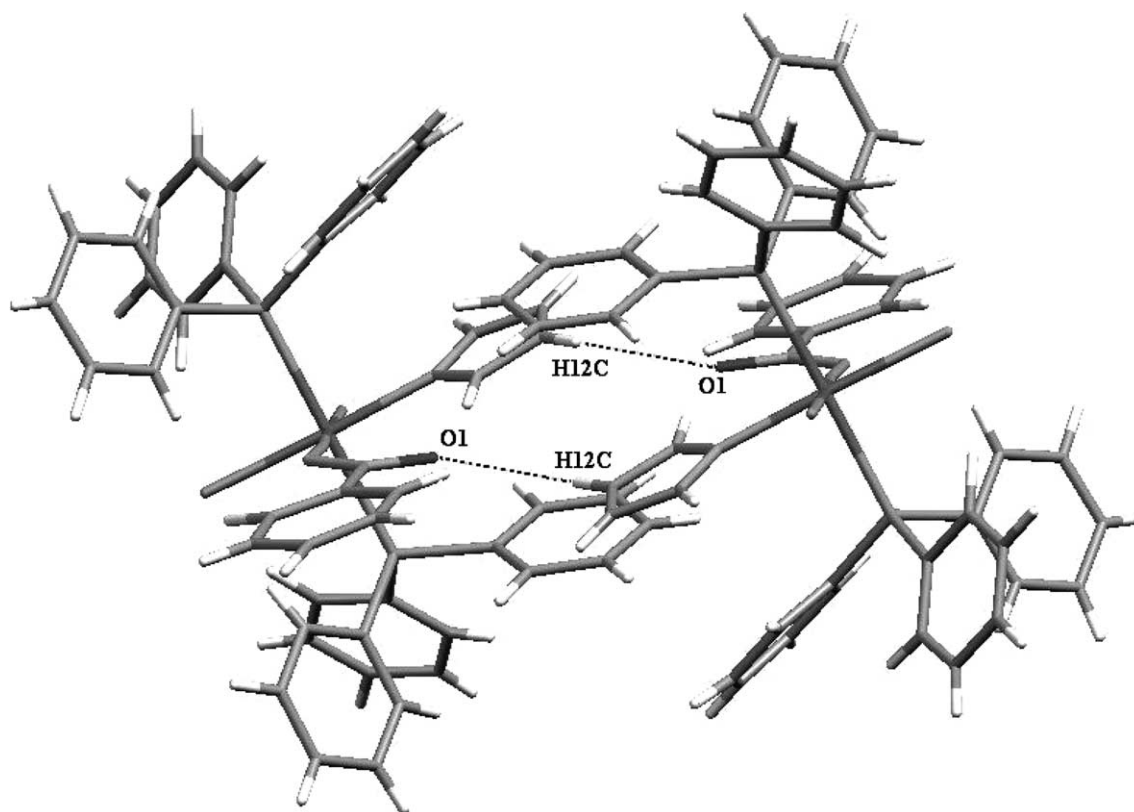


Fig. 4. View of the intermolecular (dotted line) interaction in **1**.

[2.352(4) Å] what probably reflects the neutral and cationic nature of the compounds, respectively. Such an effect is not evident in the Re–P bond distances which are essentially equivalent in both compounds.

There is an intramolecular H bond N12–H12···O1 (H12···O1, 1.938 Å) in **1** which implies the coplanarity of both the pyrazolyl and the organodiazenide groups. Due to the weak intermolecular hydrogen bond C12–H12C···O1 (C12–O1, 3.470 Å) the molecules form pseudo dimers as can be seen in Fig. 4. The CH₂Cl₂ moieties occupy the voids between the phenyl rings of the molecule without any short contact. A few weak hydrogen-bonding interactions between the chlorine ligands and the phenyl hydrogens of the phosphines could be found in both **1** and **3** structures. Moreover, short contact distances between the rhenium atom and some phenyl hydrogens of the phosphines (H102, H126, H202, H226) could be found in structure **1** with the obtained distances ranging from 3.26(6) to 3.43(8) Å.

3. Experimental

All manipulations and reactions were performed under an atmosphere of dinitrogen using standard vacuum and inert-gas flow techniques. Solvents were purified by

standard procedures and freshly distilled immediately prior to use.

The hydrotris(1-pyrazolyl)methane and hydrotris(3,5-dimethyl-1-pyrazolyl)methane were prepared in accord with published procedures [31]. The first one was further recrystallized from warm diethyl ether. Infrared spectra (4000–400 cm⁻¹) were recorded on a Nicolet Impact 400D spectrophotometer instrument in KBr pellets; wavenumbers are in cm⁻¹; abbreviations: vs, very strong; s, strong; m, medium; w, weak; br, broad. ¹H, ³¹P and ¹³C NMR spectra were recorded on a Varian Unity 300 spectrometer at ambient temperature; δ values are in ppm relative to SiMe₄ (¹H or ¹³C) or H₃PO₄ (³¹P). In the ¹³C NMR data, assignments and coupling constants common to the ¹³C–{¹H} NMR spectra are not repeated. Coupling constants are in Hz; abbreviations: s, singlet; d, doublet; t, triplet; q, quartet; qt, quintet; m, complex multiplet; br, broad; dd, doublet or doublets; dt, doublet of triplets, tm, triplet of complex multiplets. Atom labeling for the Hpz ligand: HN(1)N(2)C(3)HC(4)HC(5)H. Positive-ion FAB mass spectra were obtained on a Trio 2000 spectrometer by bombarding 3-nitrobenzyl alcohol (NBA) matrices of the samples with 8 keV (ca. 1.28 × 10¹⁵ J) Xe atoms. Mass calibration for data system acquisition was achieved using CsI. The C, H, N elemental analyses were carried out by the

Microanalytical Service of the Instituto Superior Técnico.

The electrochemical experiments were performed on an EG&G PAR 273A potentiostat/galvanostat connected to personal computer through a GPIB interface. Cyclic voltammograms were obtained in 0.2 M [$^{18}\text{Bu}_4\text{N}$][BF_4]/ CH_2Cl_2 , at a platinum disc working electrode ($d = 1$ mm). Controlled-potential electrolyses (CPE) were carried out in electrolyte solutions with the above-mentioned composition, in a three-electrode H-type cell. The compartments were separated by a sintered glass frit and equipped with platinum gauze working and counter electrodes. For both CV and CPE experiments, a Luggin capillary connected to a silver wire pseudo-reference electrode was used to control the working electrode potential. The CPE experiments were monitored regularly by cyclic voltammetry (CV), thus assuring no significant potential drift occurred along the electrolyses. The oxidation potentials of the complexes were measured by CV (see above) in the presence of ferrocene as the internal standard, and the redox potential values are quoted relative to the SCE by using the $[\text{Fe}(\eta^5\text{-C}_5\text{H}_5)_2]^{0/+}$ ($E_{1/2}^{\text{ox}} = 0.55$ V versus SCE) redox couple in 0.2 M [$^{18}\text{Bu}_4\text{N}$][BF_4]/ CH_2Cl_2 . They are converted to the NHE scale by addition of 0.245 V [15,16]

Intensity data for $[\text{ReCl}_2\{\text{NNC}(\text{O})\text{C}_6\text{H}_5\}(\text{Hpz})(\text{PPh}_3)_2] \cdot \text{CH}_2\text{Cl}_2 \cdot \text{CH}_2\text{Cl}_2$ and $[\text{ReCl}_2(\text{HCpz}_3)(\text{PPh}_3)_2][\text{BF}_4]$ **3** were collected using a Enraf-Nonius CAD4 diffractometer and structures were solved by direct methods by using the SHELXS-97 package [32]. The structure refinements were carried out with SHELXL-97 [33]. All hydrogens, except H12 in the pyrazolyl ring of structure **1** · CH_2Cl_2 , were inserted in calculated positions. The maximum and minimum peaks in the final difference electron density map were of -0.845 and $0.864 \text{ e } \text{Å}^{-3}$ for structure **1** · CH_2Cl_2 and of -2.198 and $2.755 \text{ e } \text{Å}^{-3}$ (close to the rhenium atom) for structure **3**.

3.1. Synthesis of

$[\text{ReCl}_2\{\text{NNC}(\text{O})\text{C}_6\text{H}_5\}(\text{Hpz})(\text{PPh}_3)_2] \mathbf{1}$

To a light green suspension of $[\text{Re}\{\text{N}-\text{O}-\text{N}_2\text{C}(\text{O})\text{Ph}\}(\text{PPh}_3)_2]$ (**0**) (green chelate) (156 mg, 0.171 mmol) in methanol (20 cm^3), HCpz_3 was added (44 mg, 0.206 mmol) and the mixture was heated under reflux during ca. 28 h. The obtained dark green powder of complex **1** was filtered off, washed with Et_2O and dried in vacuo (0.11 g, 66% yield). Complex **1** was also obtained by treatment of a benzene solution (15 cm^3) of the chelate complex (68 mg, 0.075 mmol) with HCpz_3 (0.016 g, 0.075 mmol) at room temperature during ca. 8–10 h. Concentration in vacuo, followed by slow addition of Et_2O , led to the precipitation of **1** as a green solid which was washed with Et_2O and dried in vacuo (0.042 g, 57% yield). Complex **1** is insoluble in methanol and diethyl ether but very soluble in CH_2Cl_2 , acetone or

C_6H_6 . The crystal of complex **1** analysed by X-rays was obtained by slow addition of Et_2O to a dichloromethane solution of **1**.

IR (KBr pellet): 3076 [s, $\nu(\text{NH})$], 1592.5 [vs, $\nu(\text{C}=\text{O})$], 1564.5, 1554.8 [vs, $\nu(\text{N}=\text{N})$ $\text{N}_2\text{C}(\text{O})\text{Ph}$ and/or $\nu(\text{N}=\text{C})$ Hpz]. NMR: ^1H (CD_2Cl_2), δ 13.94 [s, 1H, H(1) Hpz], 7.75 [d, 2H, $^3J_{\text{HH}} = 8.3$, $o\text{-C}(\text{O})\text{Ph}$], 7.59–7.53 [m, 12H, (o or m)- PPh_3], 7.35 [m, 1H, $p\text{-C}(\text{O})\text{Ph}$], 7.31 [m, 2H, $m\text{-C}(\text{O})\text{Ph}$], 7.27–7.19 m, 18H, $\{(m \text{ or } o) + p\}\text{-PPh}_3$], 6.97 dd, 1H, $J_{\text{H,H}} = 2.4$, H(3) or H(5) Hpz], 6.90 [dd, 1H, $J_{\text{H,H}} = 1.95$, H(3) or H(5) Hpz], 5.63 [q, 1H, $J_{\text{H,H}} = 2.3$, H(4) Hpz]. $^{31}\text{P}\{-^1\text{H}\}(\text{CD}_2\text{Cl}_2)$, δ -6.8 s. $^{13}\text{C}\{-^1\text{H}\}(\text{CD}_2\text{Cl}_2)$, δ 167.50 [s, $\text{C}=\text{O}$], 140.53 [s, C(3) Hpz], 134.76 [s, C_p (COPh)], 134.57 [t, $J_{\text{CP}} = 5.3$, C_o (PPh_3)], 133.04 [s, C(5) Hpz], 131.57 [s, C_o or C_m (COPh)], 130.73 [s, C_m or C_o (COPh)], 130.04 [s, C_p (PPh_3)], 128.52 [t, $J_{\text{CP}} = 8.0$, C_i (PPh_3)], 128.23 [t, $J_{\text{CP}} = 4.6$, C_m (PPh_3)], 127.46 [s, C_i (COPh)], 106.77 [s, C(4) Hpz]. ^{13}C (CD_2Cl_2), 167.50, 140.53 [d, $J_{\text{CH}} = 187.3$, C(3) Hpz], 134.76 [d, $J_{\text{CH}} = 158.1$, C_p (COPh)], 134.57 [dt, $J_{\text{CH}} = 161.2$, C_o (PPh_3)], 133.04 [d, $J_{\text{CH}} = 160.2$, C(5) Hpz], 131.57 [d, $J_{\text{CH}} = 165.4$, C_o or C_m (COPh)], 130.73 [d, $J_{\text{CH}} = 171.2$, C_m or C_o (COPh)], 130.04 [d, $J_{\text{CH}} = 160.05$, C_p (PPh_3)], 128.52, 128.23 [dt, $J_{\text{CH}} = 158.2$, C_m (PPh_3)], 127.46, 106.77 [d, $J_{\text{CH}} = 185.3$, C(4) Hpz]. FAB $^+$ -MS: m/z 982 ($[\text{M}]^+$), 915 ($[\text{M} - \text{Hpz}]^+$), 880 ($[\text{M} - \text{Hpz} - \text{Cl}]^+$), 877 ($[\text{M} - \text{COPh}]^+$), 849 ($[\text{M} - \text{N}_2\text{C}(\text{O})\text{Ph}]^+$). Found: C, 56.5; H, 4.0; N, 5.6%. $\text{ReC}_{46}\text{H}_{39}\text{N}_4\text{P}_2\text{OCl}_2$ requires C, 56.2; H, 4.0; N, 5.7.

3.2. Synthesis of

$[\text{ReCl}_2\{\text{NNC}(\text{O})\text{C}_6\text{H}_5\}(\text{Hpz})_2(\text{PPh}_3)] \mathbf{2}$

To a solution of compound **1** (101 mg, 0.103 mmol) in benzene (15 cm^3) was added a methanol (15 cm^3) solution of pyrazole (140 mg, 2.06 mmol) and the mixture was stirred under reflux for ca. 29 h. Concentration in vacuo of the dark green solution followed by slow addition of Et_2O resulted in the precipitation of compound **2** as a dark green solid which was filtered-off, washed with Et_2O and dried in vacuo (0.047 g, 58% yield). Complex **2** can also be obtained by treatment of a benzene solution (20 cm^3) of the green chelate (127.9 mg, 0.14 mmol) with a methanol solution (20 cm^3) of pyrazole (334 mg, 4.92 mmol) under reflux for ca. 35 h. Concentration and addition of Et_2O leads to the precipitation of compound **2** (0.053 g, 48% yield). IR (KBr pellet): 3286 [s, $\nu(\text{NH})$], 1588 [s, $\nu(\text{C}=\text{O})$], 1549 [vs, $\nu(\text{N}=\text{N})$ N_2COPh and/or $\nu(\text{N}=\text{C})$ Hpz]. NMR: ^1H (CD_2Cl_2), δ 14.31 and 12.61 [s, 1H+1H, H(1) Hpz], 7.86 [dd, 2H, $^3J_{\text{HH}} = 8.1$, $^4J_{\text{HH}} = 1.2$, $o\text{-COPh}$], 7.72 [m, 1H, H(3) or H(5) Hpz], 7.66 [m, 1H, H(3) or H(5) Hpz], 7.63–7.51 [m, 6H, (o or $m\text{-PPh}_3$)], 7.36 [m, 1H, $p\text{-COPh}$], 7.33 [m, 2H, $m\text{-COPh}$], 7.30 [s, 1H, H(3) or H(5) Hpz], 7.28–7.26 [m, 9H, $\{(o \text{ or } m\text{-PPh}_3)\}$]

m)+*p*}-PPh₃, 6.80 [m, 1H, H(3) or H(5) Hpz], 6.36 [m, 1H, H(4) Hpz], 6.14 [m, 1H, H(4) Hpz]. ³¹P-¹H}(CD₂Cl₂), δ -0.25 s. ¹³C-¹H}(CD₂Cl₂), δ 169.92 [s, C=O], 141.49 and 140.80 [s, C(3) Hpz], 134.49 [d, *J*_{CP} = 9.3, C_o or C_m (PPh₃)], 134.03 [s, C_p (COPh)], 133.20 and 132.79 [s, C(5) Hpz], 130.94 [s, C_o or C_m (COPh)], 130.34 [d, *J*_{CP} = 2.5, C_p (PPh₃)], 128.89 [d, *J*_{CP} = 9.4, C_i (PPh₃)], 128.83 [s, C_i (COPh)], 128.78 [m, C_o or C_m (COPh)], 128.45 [d, *J*_{CP} = 10.6, C_o or C_m (PPh₃)], 107.62 and 107.19 [s, C(4) Hpz]. ¹³C (CD₂Cl₂) 169.92, 141.49 and 140.80 [d, *J*_{CH} = 185.3 and 189.2, C(3) Hpz], 134.49 [dd, *J*_{CH} = 160.8, C_o or C_m (PPh₃)], 134.03 [d, *J*_{CH} = 142.7, C_p (COPh)], 133.20 and 132.79 [d, *J*_{CH} = 157.6 and 163.7, C(5) Hpz], 130.94 [d, *J*_{CH} = 173.5, C_o or C_m (COPh)], 130.34 [dd, *J*_{CH} = 159.1, C_p (PPh₃)], 128.89, 128.83, 128.78 [dm, *J*_{CH} = 150.8, C_o or C_m (COPh)], 128.45 [dd, *J*_{CH} = 162.5, C_o or C_m (PPh₃)], 107.62 and 107.19 [d, *J*_{CH} = 184.6 and 187.4, C(4) Hpz]. FAB⁺-MS: *m/z* 787 ([M]⁺), 719 ([M - Hpz]⁺), 683 ([M - Hpz - Cl]⁺), 654 ([M - N₂COPh]⁺). Found: C, 42.6; H, 3.3; N, 9.4%. Re-C₃₁H₂₆N₆POCl₂ · 3/2CH₂Cl₂ requires C, 42.8; H, 3.2; N, 9.2.

3.3. Synthesis of [ReCl₂(HCpz₃)(PPh₃)] [BF₄] 3

A benzene solution (20 cm³) of the green chelate **0** (71.5 mg, 0.0785 mmol) was treated with a methanol solution (ca. 10 cm³) of Ti[BF₄] (34.3 mg, 0.118 mmol) and stirred at room temperature for ca. 15–20 min. where after HCpz₃ (22.9 mg, 0.0785 mmol) was added. The resulting solution was stirred and heated at reflux for 5–6 h. During this time, the solution colour changed from green to brown. The mixture was filtered through celite and the reddish brown filtered solution was concentrated in vacuo and Et₂O was added slowly. Cooling overnight at -18 °C yielded complex **3** as a reddish brown crystalline solid which was filtered-off, washed with Et₂O and dried in vacuo (31.5 mg, 49% yield). Complex **3** is soluble in ethanol, CH₂Cl₂ and acetone. The crystal of this complex analysed by X-rays was obtained by slow addition of Et₂O to a dichloromethane solution of **3**. Complex **3** could also be obtained by reaction of a benzene (10 cm³) solution of the green chelate **0** (73.0 mg, 0.082 mmol) with a methanol (10 cm³) solution of NaBF₄ (13.2 mg, 0.123 mmol) and HCpz₃ (20.6 mg, 0.098 mmol). The mixture was stirred under reflux for ca. 27 h. The brown solution was filtered and concentrated. Et₂O was then added and the solution was taken to dryness. Dissolution in THF followed by addition of *n*-pentane resulted in the precipitation of complex **3** which was filtered-off, washed with *n*-pentane and dried in vacuo (38 mg, 56% yield).

IR (KBr pellet): 3133 [s, ν(CH)], 1532 [vs, ν(N=C)], HCpz₃], 1064 [vs, ν(B-F), BF₄] NMR: ¹H (CD₂Cl₂), 9.66 [s, 1H, H Cpz₃], 8.41 [d, 1H, ³*J*_{HH} = 2.7, H(3) or

H(5)], 8.36 [d, 1H, ³*J*_{HH} = 2.8, H(3) or H(5)], 8.10 [d, 1H, ³*J*_{HH} = 2.7, H(3) or H(5)], 7.95 [d, 1H, ³*J*_{HH} = 2.1, H(3) or H(5)], 7.61–7.55 [m, 6H, *o* or *m*-PPh₃], 7.44–7.33 [m, 9H, (*o* or *m*)+*p*-PPh₃], 6.80 [d, 1H, ³*J*_{HH} = 2.1, H(3) or H(5)], 6.55 [dd, 1H, ³*J*_{HH} = 2.4, H(4)], 6.49 [d, 1H, ³*J*_{HH} = 2.7, H(3) or H(5)], 6.31 [dd, 1H, ³*J*_{HH} = 2.6, H(4)], 6.10 [dd, 1H, ³*J*_{HH} = 2.4, H(4)]. ³¹P-¹H}(CD₂Cl₂), δ 4.66 s. ¹³C-¹H}(CD₂Cl₂), δ 149.71, 147.66 and 146.84 [s, C(3), HCpz₃], 134.56 [d, *J*_{CP} = 9.4, C_o or C_m (PPh₃)], 133.90, 132.96 and 132.29 [s, C(5), HCpz₃], 131.30 [d, *J*_{CP} = 2.2, C_p (PPh₃)], 129.28 [d, *J*_{CP} = 9.4, C_o or C_m (PPh₃)], 129.00 [d, *J*_{CP} = 11.2, C_i (PPh₃)], 109.77, 109.41 and 108.79 [s, C(4), HCpz₃], 75.81 [s, HCpz₃]. ¹³C (CD₂Cl₂), δ 149.71, 147.66 and 146.84 [d, *J*_{CH} = 172.7, 162.2 and 171.0, C(3) HCpz₃], 134.56 [dd, *J*_{CH} = 162.5, C_o or C_m (PPh₃)], 133.90, 132.96 and 132.29 [d, *J*_{CH} = 168.2, 170.5 and 173.4, C(5), HCpz₃], 131.30 [dd, *J*_{CH} = 160.7, C_p (PPh₃)], 129.28 [dd, *J*_{CH} = 155.1, C_o or C_m (PPh₃)], 129.00, 109.77, 109.41 and 108.79 [d, *J*_{CH} = 179.5, 168.2 and 183.3, C(4), HCpz₃], 75.81 [d, *J*_{CH} = 152.5, HC pz₃]. FAB⁺-MS: *m/z* 733 ([M]⁺), 698 ([M - Cl]⁺), 630 ([M - Hpz]⁺), 766 ([M + Hpz]⁺). FAB⁻-MS: *m/z* 87 ([BF₄]⁻). Found: C, 39.6; H, 3.1; N, 9.7%. ReC₂₈H₂₅N₆PCl₂BF₄ · 1/2CH₂Cl₂ requires C, 39.7; H, 3.0; N, 9.8.

3.4. Synthesis of [ReCl₂(3,5-MeHpz)₃(PPh₃)] Cl 4

Refluxing a suspension of the green chelate **0** (107 mg, 0.118 mmol) in methanol (20 cm³) with hydrotris(3,5-dimethyl-1-pyrazolyl)methane (70.0 mg, 0.236 mmol) during 28 h resulted in a dark brown solution which was concentrated and Et₂O added. The solution was taken to dryness and the residue was dissolved in THF. Addition of *n*-pentane lead to the precipitation of a brown compound which was filtered-off, washed with *n*-pentane and dried in vacuo (0.06 g, 59% yield). Complex **4** can also be formed by refluxing a suspension of the green chelate (134 mg, 0.147 mmol) in methanol (20 cm³) with 3,5-dimethylpyrazole (70.7 mg, 0.735 mmol) during 29 h what leads to a dark brown solution. This solution was concentrated almost to dryness in vacuo and Et₂O was slowly added. The reddish-brown compound **4** was filtered-off and dried in vacuo (0.08 g, 65% yield).

IR (KBr pellet): 3118 [s, ν(NH)], 1572 [vs, ν(N=C), (3,5-Me₂Hpz)]. NMR: ¹H (CDCl₃), δ 15.67 [s, br, 3H, H(1), (3,5-Me₂Hpz)], 7.77–7.75 [m, 6H, (*o* or *m*)-PPh₃], 7.44–7.42 [m, 9H, {(*o* or *m*)+*p*}-PPh₃], 6.10 [s, 3H, H(4) (3,5-Me₂Hpz)], 2.53 [s, 18H, CH₃ (3,5-Me₂Hpz)]. ³¹P-¹H}(CDCl₃), δ 21.27 s. ¹³C-¹H}(CDCl₃), δ 144.71 [s, C(3), 3,5-Me₂pz], 134.68 [s, C(5), 3,5-Me₂pz], 132.13 [d, *J*_{CP} = 9.8, C_o or C_m (PPh₃)], 130.74 [d, *J*_{CP} = 14.3, C_i (PPh₃)], 128.60 [s, C_p (PPh₃)], 128.51 [d, *J*_{CP} = 13.2, C_o or C_m (PPh₃)], 106.22 [s, C(4), 3,5-

Me₂pz], 11.10 [s, CH₃, 3,5-Me₂pz]. ¹³C (CDCl₃), δ 144.71, 134.68, 132.13 [dd, *J*_{CH} = 188.68, C_o or C_m (PPh₃)], 130.74, 128.60 [d, *J*_{CH} = 169.7, C_p (PPh₃)], 128.51 [dd, *J*_{CH} = 176.3, C_o or C_m (PPh₃)], 106.22 [d, *J*_{CH} = 179.9, C(4), 3,5-Me₂pz], 11.10 [q, *J*_{CH} = 130.3, CH₃, 3,5-Me₂pz]. FAB⁺-MS: *m/z* 807 ([M]⁺), 711 ([M - 3,5-Me₂Hpz]⁺), 674 {[M - (3,5-Me₂Hpz-Cl)]⁺}, 521 (M - 2(3,5-Me₂Hpz-Cl)]⁺). FAB⁻-MS: *m/z* 35 (Cl⁻). Found: C, 46.52; H, 4.67; N, 9.92%. ReC₃₃H₃₉N₆PCl₃ requires C, 47.0; H, 4.63; N, 9.97.

4. Supplementary material

Crystallographic data for the structural analysis has been deposited with the Cambridge Crystallographic Data Centre, CCDC No. 253079 for compound **1**·CH₂Cl₂ and CCDC No. 253080 for compound **3**. Copies of this information may be obtained free charge from The Director, CCDC, 12, Union Road, Cambridge CB2 1EZ (fax: +44 1223 336 033) or e-mail: deposit@ccdc.cam.ac.uk or <http://www.ccdc.cam.ac.uk>.

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