# Pyrazolato Metal Complexes: Synthesis, Characterization and X-ray Crystal Structures of Rhenium(I) Derivatives

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The mononuclear complexes [Re(CO)$_3$(Hpz)$_2$Br] (**1**) and [Re(CO)$_3$(Hdmpz)$_2$Br] (**2**) were obtained by treating [Re(CO)$_5$Br] with pyrazole (Hpz) or 3,5-dimethylpyrazole (Hdmpz). Complex **1** reacted with triethylamine affording a mixture of the ionic dinuclear derivative (Et$_3$NH)[Re$_2$(CO)$_6$(pz)$_2$Br] (**3**) and of the mononuclear species [Re(CO)$_3$(Hpz)$_2$(pz)] (**4**). Complex **4** was obtained in a pure form by carrying out the reaction in the presence of excess free pyrazole. Treatment of **4** with pyridine afforded the [Re(CO)$_3$(py)(Hpz)(pz)] species (**6**). The analogues of **4** and **6** with Hdmpz, i.e. [Re(CO)$_3$(Hdmpz)$_2$(dmpz)] (**7**) and [Re(CO)$_3$(py)(Hdmpz)(dmpz)] (**8**) were also synthesized. All species were characterized in solution by $^1$H-NMR spectroscopy, while the crystal structures of complexes **1**, **3**, **4** and **6** were determined by single-crystal X-ray diffraction analysis. The [(CO)$_3$Re(μ-pz)$_2$(μ-Br)Re(CO)$_3$]$^-$ anion represents the first structurally characterized species containing rhenium(I) atoms bridged by μ-pyrazolate ligands.

## Introduction

The rapid development of the coordination and organometallic chemistry of the pyrazolate anion and its derivatives has been witnessed in recent years[1]. Thanks to the possibility of modifying the steric and electronic properties of the pyrazole ligand by the action of the substituents of the heterocyclic ring, pyrazolates, which possess two adjacent nucleophilic sites, give rise to a versatile and varied chemistry. For example, it is well known that pyrazolates (i) can act as monodentate, *exo*- or even *endo*-bidentate anionic ligands[1], (ii) can afford, for the same stoichiometry, oligomers of different nuclearities (and polymers) depending on the synthetic methods used[2] and (iii) have been shown to possess a rather wide conformational variability,[2c][3] despite possessing a stiff heterocyclic ring.

In the recent past we have been active in the field of metal pyrazolates and have reported extensively on copper, silver and palladium species, demonstrating the structural versatility caused by the pyrazolate ligand and the catalytic activity of some of its complexes[2c][4]. Our continual interest in evaluating the coordination properties of this class of ligands led us to explore the synthesis and reactivity of rhenium(I) pyrazolate derivatives, a field so far scarcely investigated.

The easily accessible mononuclear carbonylrhenium(I) complex [Re(CO)$_5$Br] was found to be an excellent starting material for the synthesis of pyrazole- and pyrazolatorhenium(I) derivatives. In this paper we report the synthesis, spectroscopic and structural characterization of a series of rhenium(I) species derived by direct reaction of [Re(CO)$_5$Br] with pyrazole (Hpz) and 3,5-dimethylpyrazole (Hdmpz).

## Results and Discussion

The reaction of [Re(CO)$_5$Br] with pyrazole in toluene at 80°C afforded quantitatively a white product, revealed by analysis as [Re(CO)$_3$(Hpz)$_2$Br] (**1**), produced by the substitution of two carbonyl groups with two pyrazole molecules (eq. 1).

$$[\mathrm{Re(CO)_5Br}] + 2\ \mathrm{Hpz} \rightarrow [\mathrm{Re(CO)_3(Hpz)_2Br}]\ (\mathbf{1}) + 2\ \mathrm{CO} \qquad (1)$$

The IR spectrum of **1**, recorded in toluene, shows three strong $\tilde{\nu}$(CO) bands at 2031, 1929 and 1897 cm$^{-1}$ typical for a *fac* structure [the spectrum of the alternative *mer* geometry would show two strong and one weak $\tilde{\nu}$(CO) bands][5]. Evidence for a similar geometry, the most plausible taking in account the *trans* effect of the carbonyl groups, was also found in earlier substitution studies on [Re(CO)$_5$Br] with nitrogen[6] or phosphorous[7] ligands. An X-ray crystal-structure determination provided an unambiguous confirmation of the assigned geometry (see later).

It is noteworthy that the monosubstituted product, i.e. [Re(CO)$_4$(Hpz)Br], could not be isolated (even by carrying out the reaction with a Hpz/Re ratio < 2 and employing a decarbonylating agent such as Me$_3$NO), nor did the IR spectra of the reaction mixture show any indication of a spectroscopically detectable monosubstituted intermediate. On the contrary, in earlier studies on the substitution of CO with PPh$_3$ in [Re(CO)$_5$Br], the intermediate formation of

1434–1948/98/1010–1503 $ 17.50+.50/0

monosubstitution derivatives was proved by means of IR spectroscopy[7a].

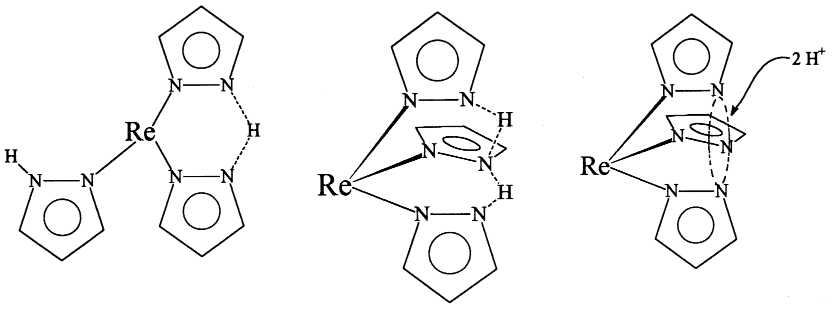
The $^1$H-NMR spectrum of **1** recorded in $CD_2Cl_2$ at 20°C shows three sharp signals at $\delta$ = 6.29 [C(4)−*H*], 7.53 [C(3)−*H*] and 7.66 [C(5)−*H*][8], and a broader signal at $\delta$ = 11.7 assignable to N−*H* protons. The presence of only one set of signals for each pyrazole hydrogen atom reveals the equivalence of the two pyrazole molecules coordinated to the rhenium centre. The scrambling process which equalizes the 3 and 5 sites, frequently found in complexes containing anionic *mono*dentate pyrazolate ligands[9], is in this case absent. Indeed, in complexes containing neutral pyrazoles, the interchange of the nitrogen sites requires simultaneous proton transfer and metal hopping, and is, therefore, expected to be more difficult. Accordingly, the dynamic behaviour observed for $[Ir(CO)(PPh_3)(dmpz)]$ disappears upon protonation to the corresponding Hdmpz derivative[9a]. The NMR characterization of various pyrazole complexes revealed both static[10] and dynamic[11] behaviour. On lowering the temperature to −80°C, all signals split as a result of the coupling C(3)−*H*/C(4)−*H*, C(5)−*H*/C(4)−*H* and of N−*H* with the three heterocyclic C−*H* protons, leading to a very complex spectrum because of partial overlapping of the signals. N−*H* irradiation allows a simplification of the $^1$H-NMR spectrum of **1** to three resonances, a doublet [$\delta$ = 7.65, $J_{5,4}$ = 2.2 Hz, C(5)−*H*], a second doublet [$\delta$ = 7.53, $J_{3,4}$ = 1.8 Hz, C(3)−*H*] and a pseudotriplet centred at $\delta$ = 6.29 [C(4)−*H*]. Similar features were previously reported for the pyrazoleplatinum(II) derivative $[(C_6Cl_5)_2Pt(Hpz)_2]$[10a].

Table 1. IR (toluene) and $^1$H-NMR ($CD_2Cl_2$, 198 K) data for complexes **1−8**

| | Complex | IR [cm$^{-1}$] $\tilde{\nu}$(CO) | $^1$H NMR $\delta$ C(4)−*H*[a] | C(3)−*H*[b] | C(5)−*H*[b] | **N−**H | $J_{3,4}$ [Hz] | $J_{5,4}$ [Hz] |
|---|---|---|---|---|---|---|---|---|
| **1** | $[Re(CO)_3(Hpz)_2Br]$ | 2031, 1929, 1897 | 6.29 | 7.53 | 7.65 | 11.2 | 1.80 | 2.20 |
| **2** | $[Re(CO)_3(Hdmpz)_2Br]$ | 2028, 1925, 1893 | 5.96 | 2.20[c] | 2.27[c] | 10.7 | − | − |
| **3** | $[Re_2(CO)_6(pz)_2Br](Et_3NH)$ | 2008, 1899 (br.) | 6.11 | 7.77 | 7.77 | 1.73[d] | 2.05 | 2.05 |
| | | | 6.17 | 7.80 | 7.80 | | 1.99 | 1.99 |
| **4** | $[Re(CO)_3(Hpz)_2(pz)]$ | 2024, 1916, 1902 | 6.35 | 7.67 | 7.80 | 14.6 | 1.75 | 2.37 |
| **6** | $[Re(CO)_3(Hpz)(pz)(py)]$ | 2023, 1915, 1898 | 6.28 | 7.55 | 7.85 | 18.2 | 1.95 | 2.15 |
| **7** | $[Re(CO)_3(Hdmpz)_2(dmpz)]$ | 2018, 1907, 1893 | 5.79 | 2.02[c] | 2.13[c] | 13.1 | − | − |
| **8** | $[Re(CO)_3(Hdmpz)(dmpz)(py)]$ | 2017, 1906, 1893 | 5.76 | 2.04[c] | 2.15[c] | 17.8 | − | − |

[a] Triplets or pseudo-triplets − [b] Doublets − [c] $CH_3$ signals − [d] $Et_3NH^+$, other signals at 1.22 (t, $CH_2$) and 3.04 (d, $CH_3$).

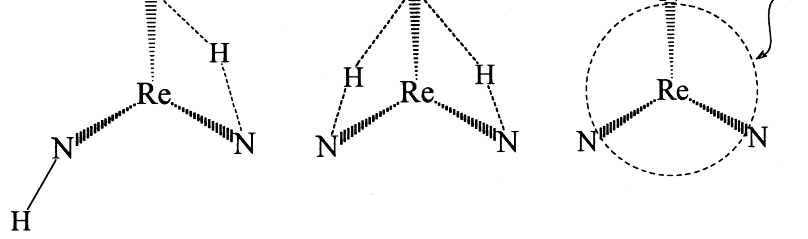
Scheme 1



similar to:
$[(Cp^*)Ir(Hdmpz)_2(Hdmpz)]^+$
$[(p\text{-cymene})Ru(Hpz)_2(pz)]^+$

**4** and **7** (solid state)

**4** and **7** (solution)



**A** (static or dynamic)

**B** (static)

**C** (dynamic)

When $[Re(CO)_5Br]$ was treated with Hdmpz, the $[Re(CO)_3(Hdmpz)_2Br]$ species (**2**) was similarly obtained. Its IR spectrum (toluene solution) shows three strong $\tilde{\nu}(CO)$ bands at 2028, 1925, and 1893 $cm^{-1}$. On the basis of a comparison between the IR and $^1H$-NMR spectra of **1** and **2** (see Table 1) we assign to the latter species a structure identical to **1**. Note, however, the significant red-shift of all resonances, ca. 4 $cm^{-1}$, caused by the higher basicity of Hdmpz compared to Hpz.

A closely related rhenium(I) species, $[Re(CO)_3(Hdmpz)_2Cl]$, derived by the breakdown of the tridentate pyrazolylborate ligand into pyrazole fragments, was fortuitously obtained by reaction of $[Re(CO)_4Cl]_2$ with $K[HB(dmpz)_3]$[12].

### Reaction of 1 with Triethylamine

When monitoring the treatment of $[Re(CO)_3(Hpz)_2Br]$ with $Et_3N$ in toluene at 60°C using IR spectroscopy, the $\tilde{\nu}(CO)$ absorptions of the starting complex were observed to disappear along with the simultaneous appearance of a complex pattern of CO bands. The changes in the IR spectrum were accompanied by the formation of a white precipitate. The work-up of the reaction mixture (see Experimental Section) led to the isolation of two rhenium(I) complexes, both exhibiting $\tilde{\nu}(CO)$ bands in their IR spectra (eq. 2).

$$[Re(CO)_3(Hpz)_2Br] + Et_3N \rightarrow \mathbf{3} + \mathbf{4} + (Et_3NH)Br \qquad (2)$$

Complex **3**, sparingly soluble in toluene, was isolated in an analytically pure form, whereas the second species, **4**, soluble in the reaction medium, was always recovered contaminated by variable amounts of **3**; only by employing an alternative synthetic route was it possible to isolate **4** in a pure form (see later).

Complex **3** shows two strong bands at 2008 and 1899 $cm^{-1}$, the latter, broader, is probably due to the superposition of two different bands. Additionally, a broad absorption attributable to the $\tilde{\nu}(N-H)$ of the triethylammonium cation is also observed. On the basis of elemental analysis and spectroscopic data, the ionic dinuclear formulation $(Et_3NH)[Re_2(CO)_6(pz)_2Br]$ was assigned to complex **3**. As later shown by an X-ray crystal structure analysis, the two rhenium centres are held together by one bromide and two pyrazolate bridges.

Care must be paid in order to exclude moisture from the reaction medium because the presence of adventitious water in solvents or reactants caused the formation of the hydroxo-bridged $(Et_3NH)[Re_2(CO)_6(pz)_2(OH)]$ species (**5**), formally derived by hydrolysis of the bromide bridge in complex **3**, and characterized by an ancillary X-ray diffraction study[13].

### Reaction of 1 with Triethylamine in the Presence of Pyrazole

When reaction 2 was carried out in the presence of excess pyrazole, complex **4** could be obtained in analytically pure form as the unique reaction product. On the basis of elemental analysis and spectroscopic data, it was formulated as monomeric $[Re(CO)_3(Hpz)_2(pz)]$ species (**4**) (eq. 3).

$$[Re(CO)_3(Hpz)_2Br] + Et_3N + Hpz \rightarrow [Re(CO)_3(Hpz)_2(pz)]\ (\mathbf{4}) + (Et_3NH)Br \qquad (3)$$

The IR spectrum of **4**, recorded in toluene, shows three strong $\tilde{\nu}(CO)$ bands at 2024, 1916, and 1902 $cm^{-1}$, suggesting a *fac* geometry in this case too. An additional broad band centred at about 2850 $cm^{-1}$ (nujol mull) indicates the presence of hydrogen bonds between the pyrazole and pyrazolate groups. The proposed formulation was confirmed by an X-ray diffraction study (see later).

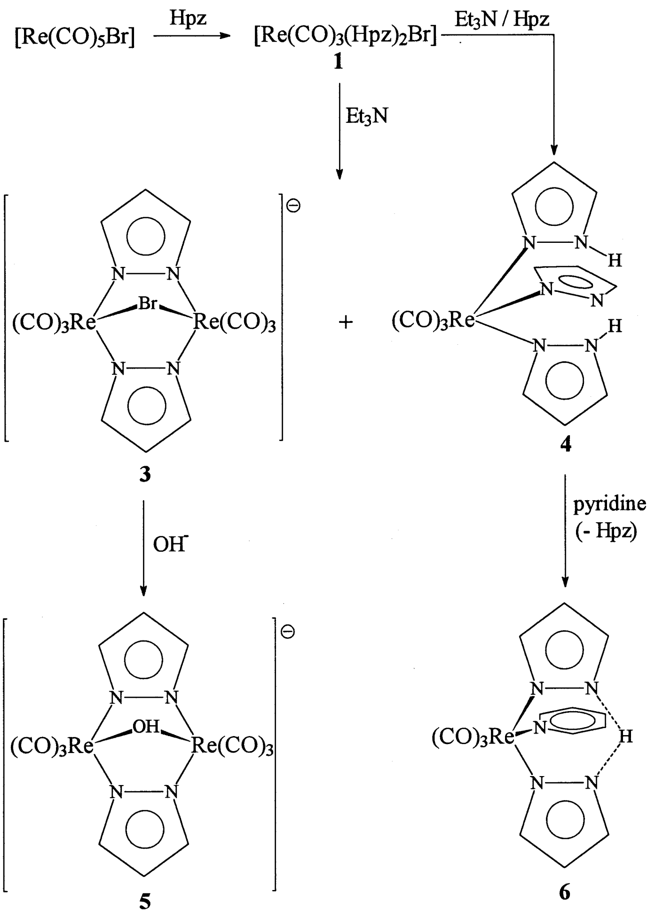
The simultaneous formation of complexes **3** and **4** in reaction 2 can therefore be rationalized by taking into account the stoichiometries of formation of **3** and **4** (eq. 4a and b).

$$2\,[Re(CO)_3(Hpz)_2Br] + 2\,Et_3N \rightarrow (Et_3NH)[Re_2(CO)_6(pz)_2Br]\ (\mathbf{3}) + 2\,Hpz + (Et_3NH)Br \qquad (4a)$$

$$[Re(CO)_3(Hpz)_2Br] + Hpz + Et_3N \rightarrow [Re(CO)_3(Hpz)_2(pz)]\ (\mathbf{4}) + (Et_3NH)Br \qquad (4b)$$

The pyrazole released in eq. 4a, as a result of the presence of $Et_3N$, is deprotonated to the pyrazolate anion, which is

Scheme 2



responsible for the nucleophilic substitution of the bromide anion on the starting [Re(CO)$_3$(Hpz)$_2$Br] derivative. In the light of these observations, it is reasonable to exclude the intermediacy of **3** in the formation of complex **4** in eq. 3, the more probable reaction pathway being a direct substitution of the terminal bromide anion by the pyrazolate anion generated in situ in the reaction medium.

The $^1$H-NMR spectrum of **4**, recorded in $CD_2Cl_2$ at 298 K, shows three resonances: a doublet centred at $\delta = 7.80$ ($J_{4,5} = 2.37$ Hz), a second doublet centred at $\delta = 7.67$ ($J_{3,4} = 1.75$ Hz) and a pseudotriplet (due to partial overlapping of two doublets) at $\delta = 6.35$. In addition, a broad peak at $\delta \approx 13$, due to N$-$*H*, is found. The spectral features do not change appreciably on lowering the temperature down to 198 K. The first two doublets can easily be assigned to the 3,5 protons of the heterocyclic ring, and, taking into account that $J_{4,5}$ is usually larger than $J_{3,4}$[14], the doublet downfield can likely be assigned to the C(5)$-$*H* protons. The pseudotriplet is due to the C(4)$-$*H* coupled to the 3 and 5 protons. As a matter of fact, the $^1$H-NMR spectrum of **4** clearly shows that both (neutral) pyrazoles and the pyrazolate ligand appear identical on the NMR time scale. Although a static conformation with the two pyrazole *N*-hydrogen atoms sharing the same uncoordinated pyrazolate nitrogen atom cannot be completely ruled out, an (N)$-$H intramolecular exchange, producing a dynamic hydrogen bonding between the three pyrazole/pyrazolate ligands is probably more realistic. Indeed, of the three conformations which can be envisaged for a (CO)$_3$Re(Hpz)$_2$(pz) molecule (see Scheme 1), only a dynamic proton exchange as depicted in C is in full agreement with our spectroscopic observations. It is useful to compare the chemical shift of the N$-$*H* protons for complex **4** [$\delta = 12.8$ (298 K); 14.6 (198 K)] to that found in the palladium(II) derivative [Pd(dmpz)$_2$(Hdmpz)$_2$]$_2$[15] ($\delta = 18.1$, 198 K). In the latter, the presence of very strong hydrogen bonds, shown also by IR bands at 2400 and 1900 cm$^{-1}$, caused the dramatic downfield shift of the N$-$*H* signals [free Hdmpz: $\delta = 13.1$ ($CD_2Cl_2$, 0.5 M)], and the total rigidity of the molecular framework. In contrast, the chemical shift of the N$-$*H* protons in **4** is close to that of free pyrazole [$\delta = 12.6$ ($CD_2Cl_2$, 0.5 M)], thus suggesting a rather flexible (Hpz)$_2$(pz) system with dynamic exchange of the H atoms.

When complex **4** is treated with pyridine, the substitution of only one pyrazole molecule takes place, giving the mononuclear [Re(CO)$_3$(py)(Hpz)(pz)] (**6**) derivative, (eq. 5).

$$[\mathrm{Re(CO)_3(Hpz)_2(pz)}] + \mathrm{py} \rightarrow [\mathrm{Re(CO)_3(Hpz)(pz)(py)}]\ (\mathbf{6}) + \mathrm{Hpz} \quad (5)$$

The IR spectrum of **6** shows, in the carbonyl region, three strong bands at 2023, 1915 and 1898 cm$^{-1}$. Furthermore, a broad band in the region 3300$-$3400 cm$^{-1}$, attributable to hydrogen bonds, is also observed. Significantly, the $^1$H-NMR spectrum of **6** (toluene, 298 K) shows the N$-$*H* resonance as a very sharp peak at $\delta = 18.2$, indicating the presence of a strong hydrogen bond equalizing the pyrazole and pyrazolate ligands (as revealed by the signals of the carbon protons of the heterocyclic rings, see Table 1), stabilizing the complex and hampering, in our opinion, the substitution of the second pyrazole molecule, even when reaction 5 is performed with excess pyridine.

*Intra*molecular hydrogen bonds between pyrazole and pyrazolate ligands have been previously observed by $^1$H-NMR spectroscopy in rhenium(V)[16], iridium(III)[17], palladium(II)[10] and platinum(II)[10] derivatives, and confirmed by means of X-ray crystallography[10][17], but in no case was the chemical shift of the N$-$*H* protons found so downfield shifted as in **6**.

Employing 3,5-dimethylpyrazole in place of pyrazole, the related [Re(CO)$_3$(Hdmpz)$_2$(dmpz)] (**7**) and [Re(CO)$_3$(py)(Hdmpz)(dmpz)] (**8**) derivatives have been obtained. As revealed by $^1$H-NMR spectroscopy (see Table 1), the solution behaviour of complexes **7** and **8** is quite similar to that of the related derivatives **4** and **6**, indicating that the steric hindrance of the methyl substituents on the pyrazole ring plays a minor role. A different situation was found for the iridium(III) couple [(Cp*)Ir(Hpz)(pz)$_2$] and [(Cp*)Ir(Hdmpz)(dmpz)$_2$], where the presence of the more sterically demanding Hdmpz ligand prevented the formation of a (dynamic) *bifurcated* hydrogen bond, such as that observed in the Hpz analogue[17a]. The larger ionic radius is probably responsible for these differences.

A synopsis of the spectroscopic data for complexes **1**$-$**8** is collected in Table 1, and Scheme 2 summarizes the reactions discussed above.

## Crystal Structures of 1, 4 and 6

All these compounds are mononuclear species, packed in space by normal van der Waals contacts. Their ORTEP drawings are shown in Figures 1$-$3, together with a partial labelling scheme.

Table 2 reports the significant bond lengths and angles for **1**, **4** and **6**. These three compounds belong to the class of octahedral rhenium(I) species, bearing three carbonyl ligands in a *fac* disposition. The remaining coordination sites are occupied by one negatively charged ligand (pyrazolate or bromide) and two neutral fragments, such as pyrazole and/or pyridine. Despite this formal distinction, when both Hpz and pz fragments are present in the same molecule, such as in **4** and **6**, one might suspect that assignment of the Hpz/pz nature could be dubious. This is indeed the case for the hydrogen-bonded ligands of **6**, which, sharing a common H atom [N2$-$H 1.36(5) and N4$-$H 1.28(4) Å], show a very short N···N distance of 2.561(8) Å {in agreement with the $^1$H-NMR spectrum and with other pyrazole/pyrazolato complexes such as [M(C$_6$F$_5$)(Hpz)(pz)], (M = Pd, Pt)[10a], [Zn$_2$(Hdmpz)$_2$(dmpz)$_4$][18], [Co(Hdmpz)$_2$(dmpz)$_4$][19], [($\eta^5$-C$_5$Me$_5$)Ir(dmpz)$_2$(Hdmpz)][17a] and [($\eta^6$-p-cymene)Ru(Hpz)$_2$(pz)]$^{+}$[20]}.

In contrast, the situation in **4** is much clearer: Two H atoms are bound to two (different) neutral ligands, with both N$-$H vectors pointing toward the bare nitrogen atom of the

Figure 1. ORTEP drawing of the $[Re(CO)_3(Hpz)_2Br]$ species with partial labelling scheme; thermal ellipsoids drawn at the 30% probability level; hydrogen atoms are omitted for clarity; primed atoms are generated by the $-x, y, -z - 1/2$ symmetry operation

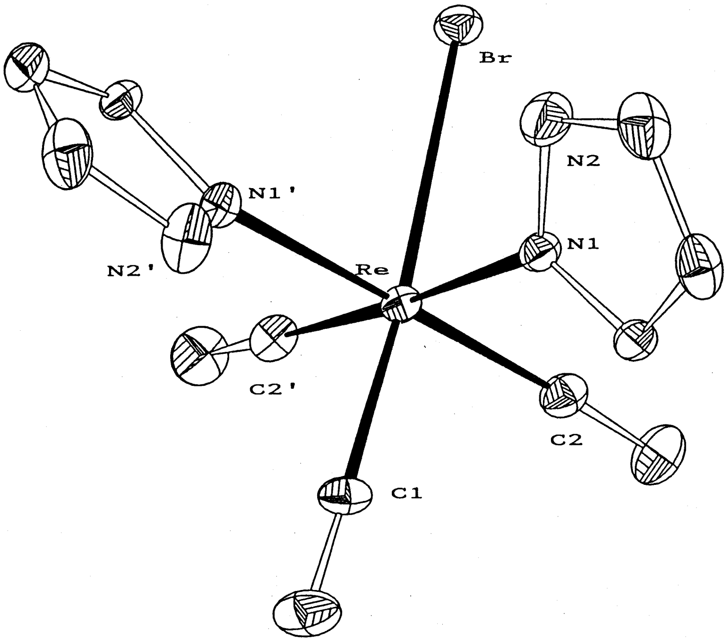


Figure 2. ORTEP drawing of the $[Re(CO)_3(Hpz)_2(pz)]$ species with partial labelling scheme; thermal ellipsoids drawn at the 30% probability level; hydrogen atoms connected to carbon vatoms are omitted for clarity; at the drawing resolution, the other independent molecule looks similar

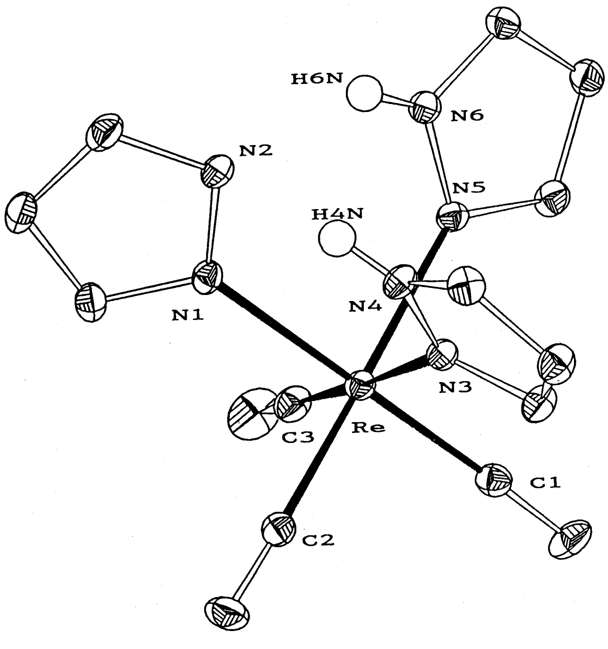
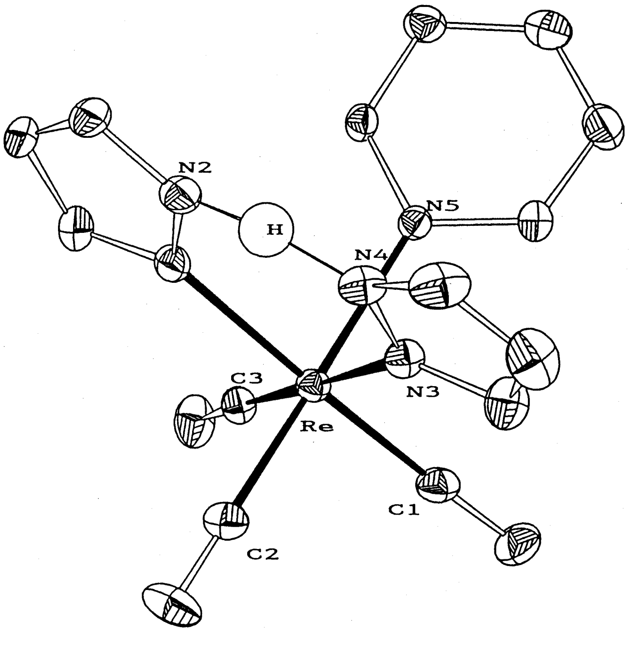


Figure 3. ORTEP drawing of the $[Re(CO)_3(Hpz)(pz)(py)]$ species with partial labelling scheme; thermal ellipsoids drawn at the 30% probability level; hydrogen atoms connected to carbon atoms are omitted for clarity



remaining pz fragment [four N−H···N interactions in the range 2.749(7)−2.883(6) Å]. This is indeed observed in both crystallographically independent molecules and confirmed by an ancillary successful crystal-structure determination of **7**[21], with a (crystallographically unique) N−H···N contact of 2.751 Å, clearly demonstrating the N−H···N···H−N nature of this interaction. Therefore, *in the solid state*, molecules of **4** and **7** are better represented by the static picture B (see Scheme 1). When no pyrazolates are present, such as in **1**, the nitrogen atoms of the neutral Hpz ligands in A are found to lie far apart from each other (ca. 5.27 Å). However, a short N−H···Br *inter*molecular hydrogen bond is present in the solid state, with an estimated length of 2.645(8) Å for H2···Br.

In the absence of strained cyclic rings, such as that observed in Re(CO)$_3$Cl(died) (died = *N*,*N'*-diisopropylethylenediimine), where the N−Re−N angle is as low as 72.72°[22], the *cis* octahedral angles about the rhenium atoms are fairly regular and range from 83.4(2) to 95.7(3)°. Analogously, the digonal geometry of the CO carbon atoms is also maintained [Re−C−O in the range 176.4(4)−179.0(5)°]. In all three compounds the Re−C distances are similar [1.881(6)−1.94(4) Å] and fall close to the mean value observed for the 28 ReC$_3$N$_2$X structures (X = F, Cl, Br) deposited in the CCDC file (1.907 Å). If a minor chemical effect is sought, one can envisage that the presence of a more basic[23] ligand (py) in **6** than in **4** (Hpz) slightly shortens the Re−C interactions [from 1.913 (**4**) to 1.888 Å (**6**), typical e.s.d.'s of 0.005 Å]; this effect, i.e. the presence of a stronger π back-donation in **6** than in **4**, can also be seen in the C−O values [1.152 (**4**) vs. 1.171 Å in **6**]. Re−N bond lengths lie in the range 2.183(4)−2.227(4) Å (CCDC avg. value, 2.208 Å).

### Crystal Structure of 3

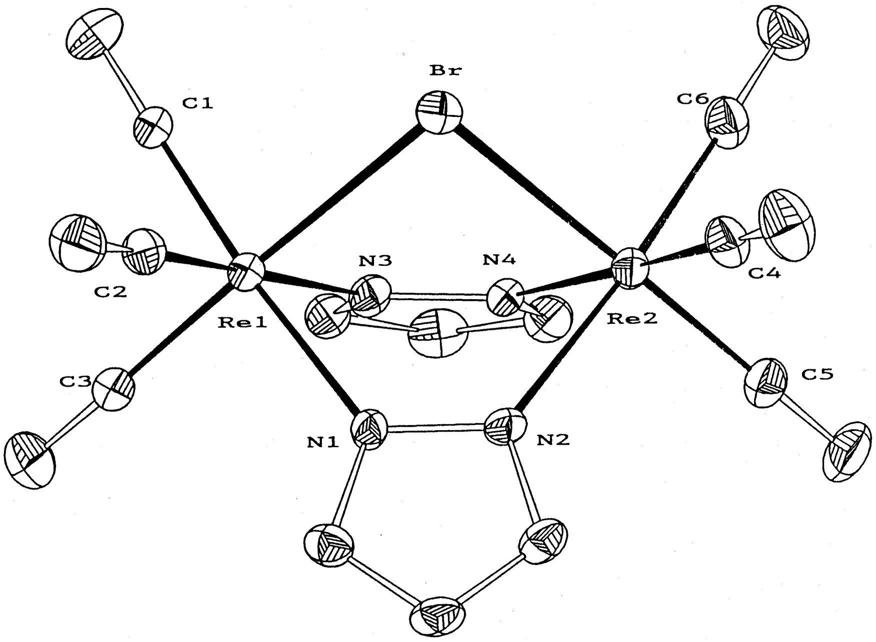
Crystals of **3** contain anionic, dinuclear [(CO)$_3$Re(μ-pz)$_2$(μ-Br)Re(CO)$_3$]$^-$ species and triethylammonium cations, packed in space by Coulombic forces and weak(er) van der Waals contacts. An ORTEP drawing of the anion is shown in Figure 4, together with a partial labelling scheme and a list of chemically relevant bond lengths and angles. The rhenium atoms in **3** exhibit an octahedral geometry, with *fac*-carbonyl ligands, and fulfil the 18-electron rule without the need for a

Table 2. Selected bond lengths [Å] and angles [°] for **1**, **4** and **6**; e.s.d.'s in parentheses

| | **1** | **4**[a] | **6** |
|---|---|---|---|
| Re−C avg. | 1.94 | 1.913 | 1.888 |
| Re−C1 | 1.94(4) | 1.924(5) | 1.882(6) |
| Re−C2 | 1.921(9) | 1.915(4) | 1.881(6) |
| Re−C3 | 1.913(5) | 1.902(6) | |
| Re2−C13 | | 1.902(5) | |
| Re2−C14 | | 1.913(5) | |
| Re2−C15 | | 1.910(5) | |
| C−O avg. | 1.13 | 1.152 | 1.171 |
| C1−O1 | 1.12(4) | 1.152(5) | 1.184(6) |
| C2−O2 | 1.132(10) | 1.156(5) | 1.171(6) |
| C3−O3 | 1.139(5) | 1.157(5) | |
| C13−O13 | | 1.161(5) | |
| C14−O14 | | 1.150(5) | |
| C15−O15 | | 1.152(5) | |
| Re−C1−O1 | 178(2) | 176.4(4) | 177.9(5) |
| Re−C2−O2 | 178.5(8) | 178.5(4) | 179.0(5) |
| Re−C3−O3 | 178.7(5) | 177.6(5) | |
| Re2−C13−O13 | | 176.2(4) | |
| Re2−C14−O14 | | 179.1(5) | |
| Re2−C15−O15 | | 178.4(4) | |
| Re−N1 | 2.187(6) | 2.187(3) | 2.183(4) |
| Re−N3 | 2.211(3) | 2.191(4) | |
| Re−N5 | 2.195(3) | 2.227(4) | |
| Re2−N7 | | 2.188(3) | |
| Re2−N9 | | 2.199(3) | |
| Re2−N11 | | 2.190(3) | |
| Re−Br | 2.641(5) | | |
| N···H···N | | 2.877(5) | 2.561(8) |
| | | 2.755(4) | |
| | | 2.883(6) | |
| | | 2.749(7) | |

[a] Two independent molecules in the asymmetric unit.

Figure 4. ORTEP drawing of the [Re$_2$(CO)$_6$(pz)$_2$(Br)]$^-$ anion with partial labelling scheme; thermal ellipsoids drawn at the 30% probability level[a]



[a] Selected bond lengths [Å] and angles [°]: Re···Re 3.825(1), Re(1)−Br 2.654(1), Re(2)−Br 2.641(1), Re−C avg. 1.895, C−O avg. 1.16; Re(1)−Br−Re(2) 92.51(4), Re−C−O 177(1)−180(1); hydrogen atoms are omitted for clarity.

direct metal−metal bond. The $[(CO)_3Re(\mu\text{-pz})_2(\mu\text{-Br})Re(CO)_3]^-$ anion represents the first structurally characterized species containing rhenium(I) atoms bridged by μ-pyrazolate ligands.

A similar rhenium(V) species $[ReO\{\eta^2\text{-B(pz)}_4\}(\mu\text{-pz})]_2(\mu\text{-O})$, has been recently reported[16], and showed a nonbonding Re···Re interaction of 3.425 Å. In addition, the synthesis and spectroscopic properties of an oxorhenium(VII) species, possibly a dimer containing two pz bridges, $[ReO_3(\mu\text{-pz})]_2$, have long been known[24], but, in the absence of single crystals of suitable quality, this species could not be characterized any further. Therefore, the observed nonbonding Re−Re separation, 3.825(1) Å, cannot usefully be compared to other cases. However, it appears, among pyrazolato-bridged complexes, to be rather long, even though rare examples with exceptionally distant metals (up to 4.56 Å) have been reported for polydentate complex pyrazolates[25]. In spite of the presence of a triple (pz, pz, Br) bridge which, avoiding overcrowding of ligands at the metal centres, should shorten the Re···Re distance, such a long Re···Re contact is certainly determined by the simultaneous presence of large metals (leading to Re−N distances of about 2.17 Å) and a rather bulky bridging anion, the bromide, with Re−Br interactions of about 2.65 Å. The above observations agree well with the coordination versatility of pz groups (which are known to form single- to quadruple-bridged[26] systems), capable of bridging metal atoms which are as close as 2.353 Å or even acting as *endo*bidentate $\eta^2$ ligands[9b][27]. Also in this case, *inter*molecular hydrogen bonds are found. Indeed, if the nitrogen-bonded proton is added to the triethylammonium cation in the ideal position, one can devise an N−H···Br contact with a Br···H distance of, say, 2.90 Å. During our studies of the crystal structure of **3**, a crystal which eventually was characterized as the product of bromine hydrolysis, containing hydroxo, rather than bromide, bridges[13] came fortuitously to our attention. In order to maintain the hydrogen-bond network, which properly stabilizes the crystal, an extra water molecule was found in its asymmetric unit, leading to a $\mu\text{-OH}\cdots(H_2O)\cdots H{-}N(Et)_3$ fragment replacing the $Br\cdots H{-}N(Et)_3$ contact of **3**. In **5**, as expected, replacement of Br by a smaller hydroxo group lowers the intermetallic distance to 3.659(1) Å.

## Conclusion

The synthesis and structural properties of a series of mononuclear and dinuclear pyrazolate complexes of rhenium(I) have been described. In particular, we foresee that the mononuclear derivatives $[Re(CO)_3(Hpz)_2(pz)]$ (**4**) and $[Re(CO)_3(Hdmpz)_2(dmpz)]$ (**6**) may act as useful synthetic precursors in building heteropolynuclear metal complexes.

In fact, **4** and **6** belong to a limited class of complexes that, from a coordination point of view, are comparable to the protonated tris(pyrazolyl)borate molecules[28]. The other members of this class, $[(\eta^5\text{-C}_5Me_5)Ir(Hpz)(pz)_2]$[17a], $[(\eta^6\text{-}p\text{-cymene})Ru(Hpz)(pz)_2]$[20] and $[(\eta^6\text{-mesitylene})Ru(Hpz)(pz)_2]$[29] when deprotonated to the anionic fragments $[(\eta^5\text{-C}_5Me_5)Ir(pz)_3]^-$, $[(\eta^6\text{-}p\text{-cymene})Ru(pz)_3]^-$ and $[(\eta^6\text{-mesitylene})Ru(pz)_3]^-$, have been shown to behave in some respect as the tris(pyrazolyl)borate anion, acting as organometallic ligands toward a variety of metal ions[29][30].

Accordingly, preliminary results[31] with group-7 and -11 metals show that, in the presence of appropriate deprotonating agents, complex **4** results in the dianionic species $[Re(CO)_3(pz)_3]^{2-}$, capable of coordination through the lone pairs of the three monodentate pyrazolate groups on a single or on two different metal centres, leading to bi- and trimetallic species. In this way, an analogy with the Kläui tripod-like metallorganic ligands such as $[(\eta^5\text{-C}_5H_5)M\{P(O)R_2\}_3]^-$ (M = Co, Rh) can be drawn[32]. Finally, the use of complexes **4** and **6** in the synthesis of bimetallic derivatives with potential catalytic applications is currently under investigation and will be the subject of a forthcoming paper.

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## Experimental Section

*General:* Solvents were dried and purified by standard methods. Pyrazole and 3,5-dimethylpyrazole (Aldrich Chemical Co.) were used as supplied. $[Re(CO)_5Br]$ was prepared according to literature procedures[33]. − Infrared spectra were taken with a BIO RAD FTIR 7 instrument. − $^1$H-NMR spectra were acquired with a Bruker AC-200 FT spectrometer operating at 200.13 MHz. − Elemental analyses (C, H, N) were performed at the Microanalytical Laboratory of this University. All reactions were carried out under dry nitrogen using standard Schlenk techniques.

*$[Re(CO)_3(Hpz)_2Br]$* (**1**): $[Re(CO)_5Br]$ (400 mg, 0.98 mmol) was dissolved in 10 ml of toluene and solid pyrazole (200 mg, 2.94 mmol) was added under stirring. The solution was kept at 80°C until no change in the IR spectrum was observed (about 4 h) and then concentrated to dryness. The white residue was treated with 3 ml of water, filtered off and dried under vacuum (414 mg, 87%). − $C_9H_8BrN_4O_3Re$ (486): calcd. C 22.23, H 1.66, N 11.53; found C 22.22, H 1.67, N 11.52. − Crystals suitable for X-ray structure analysis were obtained by slow diffusion of *n*-hexane into a dichloromethane solution of **1**.

*$[Re(CO)_3(Hdmpz)_2Br]$* (**2**): Prepared in a similar way, employing 3,5-dimethylpyrazole in place of pyrazole (yield 85% ). − $C_{13}H_{16}BrN_4O_3Re$ (542): calcd. C 28.78, H 2.98, N 10.33; found C 28.85, H 2.84, N 10.34.

*$(Et_3NH)[Re_2(CO)_6(pz)_2(Br)]$* (**3**): To a toluene solution of **1** (400 mg, 0.823 mmol) maintained at 50°C, triethylamine (0.5 ml) was added under stirring. In a few minutes a white precipitate formed. After 6 h, the solid was separated by filtration, washed with water (2 ml), and dried under vacuum (yield about 30%). − $C_{18}H_{22}BrN_5O_6Re_2$ (857): calcd. C 25.20, H 2.59, N 8.17; found C 25.28, H 2.65, N 8.21. − The mother liquors were concentrated to dryness and the residue treated with water. A mixture of variable amounts of **3** and **4** (on the basis of the IR spectrum) was always obtained (see text).

*$[Re(CO)_3(Hpz)_2(pz)]$* (**4**): $[Re(CO)_5Br]$ (1.03 g, 2.54 mmol) was added to a solution of pyrazole (0.920 g, 13.5 mmol) in toluene (20 ml) containing 0.5 ml of triethylamine. The solution was maintained

Table 3. Summary of X-ray single-crystal data and structure-refinement parameters

| Compound | **1** | **3** | **4** | **6** |
|---|---|---|---|---|
| Formula | $C_9H_8BrN_4O_3Re$ | $C_{18}H_{22}BrN_5O_6Re_2$ | $C_{12}H_{11}N_6O_3Re$ | $C_{14}H_{12}N_5O_3Re$ |
| Formula weight | 486.30 | 856.72 | 473.47 | 484.49 |
| Crystal system | Monoclinic | Monoclinic | Monoclinic | Monoclinic |
| Space group | $C2/c$ | $P2_1/n$ | $P2_1/n$ | $P2_1/n$ |
| $a$ [Å] | 7.247(3) | 8.189(2) | 15.699(3) | 9.049(4) |
| $b$ [Å] | 14.258(4) | 16.190(4) | 13.173(4) | 12.356(4) |
| $c$ [A] | 13.029(3) | 18.983(4) | 16.376(4) | 14.427(4) |
| β [°] | 91.31(4) | 99.53(2) | 115.13(2) | 93.17(2) |
| $V$ [$A^3$] | 1345.9(7) | 2482.1(10) | 3066.0(13) | 1610.6(10) |
| $Z$ | 4 | 4 | 8 | 4 |
| $F(000)$ | 896 | 1592 | 1792 | 920 |
| $D$(calcd.) [g $cm^{-3}$] | 2.400 | 2.293 | 2.051 | 1.998 |
| Temperature [K] | 293(2) | 293(2) | 293(2) | 293(2) |
| Diffractometer | CAD4 | SMART | SMART | SMART |
| Radiation [A] | 0.71069 | 0.71069 | 0.71069 | 0.71069 |
| Absorption coeff [$mm^{-1}$] | 12.002 | 11.396 | 7.948 | 7.566 |
| Crystal size [mm] | 400 × 80 × 50 | 200 × 100 × 100 | 200 × 80 × 20 | 40 × 40 × 40 |
| Scan method | ω | ω | ω | ω |
| Scan interval [°] | $1.0 + 0.35 \tan \theta$ | 0.30[a] | 0.30[a] | 0.30[a] |
| Max time per refl. [s] | 50 | 30[a] | 40[a] | 60[a] |
| θ range [°] | 3.13−24.97 | 1.66−26.90 | 1.51−26.84 | 2.17−26.97 |
| Index ranges | $-8 \le h \le 8, 0 \le k \le 16, 0 \le l \le 15$ | $-10 \le h \le 6, -16 \le k \le 19, -22 \le l \le 23$ | $-19 \le h \le 19, -16 \le k \le 12, -11 \le l \le 23$ | $-10 \le h \le 11, -15 \le k \le 12, -12 \le l \le 18$ |
| Reflections collected | 1185 | 12734 | 15039 | 8202 |
| Independent reflections | 1185 [$R$(int) = 0.0000] | 4786 [$R$(int) = 0.0324] | 5892 [$R$(int) = 0.0208] | 3093 [$R$(int) = 0.0391] |
| Crystal decay | none | none | none | none |
| Min. transmission factor | 0.294 | 0.637 | 0.621 | 0.804 |
| Refinement method | | *Full-matrix least-squares on $F_o^2$ | | |
| Obsd. reflection criterion | $> 2\sigma(I)$ | $> 2\sigma(I)$ | $> 2\sigma(I)$ | $> 2\sigma(I)$ |
| Data/restraints/parameters | 1185/0/96 | 4786/6/254 | 5892/0/397 | 3093/2/212 |
| Goodness-of-fit[b] on $F_o^2$ | 1.386 | 1.022 | 0.929 | 0.921 |
| $R$ indices[c] [$F_o > 4\sigma(F_o)$] $R1$, $wR2$ | 0.0230, 0.0924 | 0.0414, 0.0904 | 0.0199, 0.0434 | 0.0286, 0.0362 |
| $R$ indices (all data) $R1$, $wR2$ | 0.0252, 0.0939 | 0.0720, 0.1005 | 0.0291, 0.0444 | 0.0605, 0.0396 |
| Largest diff. peak and hole [e $A^{-3}$] | 1.017 and −1.036 | 1.220 and −1.249 | 0.327 and −1.272 | 0.495 and −0.513 |
| Weighting scheme[d] a | 0.0587 | 0.0494 | 0.0188 | 0.0085 |

[a] Frame width and exposure time per frame − [b] $GOF = [\Sigma w(F_o^2 - F_c^2)^2/(n - p)]^{1/2}$ (where $n$ is the number of reflections and $p$ is the number of refined parameters) − [c] $R1 = \Sigma \| F_o| - |F_c \| / \Sigma |F_o|$, $wR2 = [\Sigma w(F_o^2 - F_c^2)^2 / \Sigma w F_o^4]^{1/2}$. − [d] $w = 1/[\sigma(F_o^2) + (a\ P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$.

under stirring at 80°C for 6 h, the formation of $(Et_3NH)Br$, insoluble in the reaction medium, being observed. The solvent was then evaporated to dryness and the residue dissolved in the minimum amount of ethanol (2 ml). The addition of water caused the precipitation of **4** as a white product. The product was filtered, washed with water and dried under vacuum (yield 1.08 g, 90%). − $C_{12}H_{11}N_6O_3Re$ (474): calcd. C 30.38, H 2.34, N 17.72; found C 30.50, H 2.24, N 17.34.

*[Re(CO)$_3$(Hdmpz)$_2$(dmpz)]* (**7**): Obtained in a similar way employing Hdmpz (yield 90%). − $C_{18}H_{23}N_6O_3Re$ (558): calcd. C 38.70, H 4.15, N 15.05; found C 38.52, H 4.01, N 14.91. − Crystals suitable for X-ray structure analysis were obtained by slow concentration of toluene solutions of **4** or **7**.

*[Re(CO)$_3$(py)(Hpz)(pz)]* (**6**): Pyridine (1 ml) was added to a solution of **4** (300 mg, 0.634 mmol) in toluene. The clear solution was maintained under stirring at 50°C for 3 h. The solvent was then evaporated to dryness and the residue was dissolved in ethanol (1 ml). Addition of water caused the precipitation of **6** as a white product. The complex was filtered, washed with water and dried under vacuum (yield 240 mg, 78%). − $C_{14}H_{12}N_5O_3Re$ (485): calcd. C 34.64, H 2.49, N 14.43; found C 34.64, H 2.52, N 14.37. −Crystals suitable for X-ray structure analysis were obtained from an *n*-hexane solution of complex **6** kept at −25°C.

*[Re(CO)$_3$(Hdmpz)(dmpz)(py)]* (**8**): Obtained similarly starting from complex **7** (yield 80%). − $C_{18}H_{20}N_6O_3Re$ (555): calcd. C 38.91, H 3.63, N 15.14; found C 39.40, H 3.57, N 15.53.

*Crystallography*[34]: Crystals of **1**, **3**, **4** and **6** were studied by conventional single-crystal X-ray methods; an overview of the methodology used can be found in ref.[35]. A list of crystal data, refinement parameters and final agreement factors is reported in Table 3.

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