Preparation of rhenium hydride complexes with pyrazole and pyrazolato ligands

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Abstract

Hydride-pyrazolato ReH(Rpz)(HRpz)(NO)(PPh$_3$)$_2$ complexes (R = H (**1**), 5-Me (**2**)) were prepared by allowing the ReH$_2$(NO)(PPh$_3$)$_3$ derivative to react with pyrazole (HRpz) in refluxing toluene. The complexes were characterised spectroscopically (IR and NMR data) and by the X-ray crystal structure determination of the ReH(5-Mepz)(H-5-Mepz)(NO)(PPh$_3$)$_2$ derivative. An intramolecular hydrogen bond N–H···N between the pyrazolato and the pyrazole ligands was established both in the solid state and in solution. Protonation reaction with Brønsted acid of compound **1** was studied and led to the unstable bis(pyrazole) [ReH(Hpz)$_2$(NO)(PPh$_3$)$_2$]$^+$ cation. Acetylide-pyrazolato Re(C≡CAr)(Rpz)(HRpz)(NO)(PPh$_3$)$_2$ (**3**, **4**) complexes (Ar = Ph, *p*-tolyl; R = H, 5-Me) were also prepared by reacting hydride ReH(Rpz)(HRpz)(NO)(PPh$_3$)$_2$ species with terminal alkynes HC≡CAr in refluxing 1,2-dichloroethane.
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1. Introduction

Pyrazole (Hpz) and pyrazolato (pz) have been extensively used as ligands in transition metal chemistry and a number of complexes have been reported in the past 25 years [1–3]. These studies have been developed rapidly due to the potentialities of Hpz and pz as ligands. In fact, although being a poor base [4], pyrazole is a good σ-donor by acting as a monodentate ligand through its pyridinic nitrogen atom, or as either a monodentate or a bidentate bridging ligand in a pyrazolato anion [1–3]. Furthermore, the possibility of using substituents on the heterocyclic ring may modify the steric and electronic properties of the pyrazole ligand giving rise to versatile and varied chemistry.

The introduction of these ligands in the chemistry of transition metal hydrides [5], however, is somewhat restricted and in the case of rhenium, for example, only the hydride clusters [Re$_3$(μ-H)$_3$ (μ-η^2-pz)(CO)$_{10}$]$^-$ and [Re$_3$(μ-H)$_3$ (μ-η^2-pz)(CO)$_9$Hpz]$^-$ with pyrazole and pyrazolato have been recently described [3].

We are interested in the chemistry of classical and non-classical transition metal hydrides [6] and recently have devoted our studies to the synthesis and reactivity of hydride complexes of the iron triad containing N-donor ligands of the [MH(N–N)P$_3$]BPh$_4$, [MH(N–N)$_2$P]BPh$_4$ (M = Fe, Ru, Os; N–N = 2,2′-bipyridine, 1,10-phenanthroline) and RuH(Tp)P$_2$ [Tp = hydrido-tris(pyrazolyl)borate] (P = phosphite) types [7,8]. We have now extended these studies with the aim of

introducing pyrazole in the chemistry of hydride complexes and in this paper we report some results on rhenium as a central metal dealing with the synthesis and reactivity of the first mononuclear hydride complex containing pyrazole and pyrazolato as supporting ligands.

2. Results and discussion

Hydride $ReH_2(NO)(PPh_3)_3$ complex reacts with pyrazole (Hpz) in refluxing toluene to give the pyrazole-pyrazolato $ReH(pz)(Hpz)(NO)(PPh_3)_2$ (**1**) complex which was isolated in good yield and characterised (Scheme 1).

The reaction proceeds also with the substituted methylpyrazole H-3-Mepz to give the related ReH(5-Mepz)(H-5-Mepz)(NO)(PPh_3)_2 (**2**) complex, in which the nitrogen sites of the pyrazole ligand have been interchanged (see below) giving the final 5-methylpyrazole derivatives (Scheme 2).

Different rhenium hydrides of the $ReH_2(NO)$-$(PPh_2OEt)_3$ and $ReH_2(NO)L(PPh_3)_2$ [L = P(OEt)$_3$ and PPh(OEt)$_2$] types [9] were also treated with pyrazoles under different experimental conditions, but no reaction was observed and the starting hydride was almost quantitatively recovered. It seems, therefore, that only with the $ReH_2(NO)(PPh_3)_3$ precursor can the pyrazole-pyrazolato **1**, **2** derivatives be prepared.

The reaction of the triphenylphosphine Re-H$_2$(NO)(PPh$_3$)$_3$ complex with pyrazole giving **1**, **2** may be explained on the basis of the lability of the PPh$_3$ ligand, which can be substituted by pyrazole to give an [**A**] type intermediate (Scheme 3).
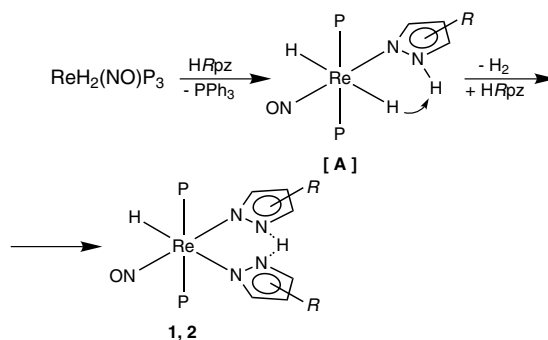
This intermediate [**A**] does give evolution of H$_2$, as determined by gas-chromatographic analysis, probably by interaction of the acidic N–H hydrogen of pyrazole with the Re–H hydride. The evolution of H$_2$ is followed by the coordination of another pyrazole molecule to the coordinatively unsaturated [ReH(pz)(NO)(PPh$_3$)$_2$] spe-
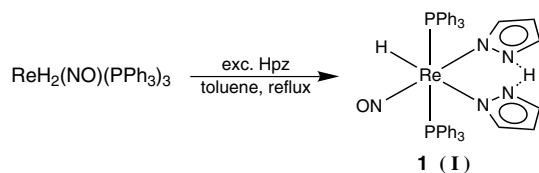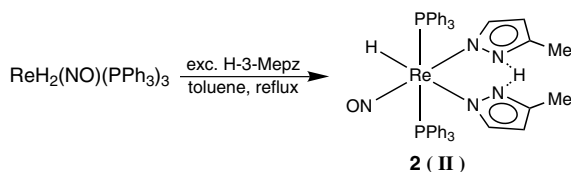
Scheme 3. P = PPh$_3$; R = H, 3-Me.

cies formed, giving the final complex **1** or **2**. Although the intermediate [**A**] was not spectroscopically detected in the reaction mixture, the evolution of H$_2$ along with the formation of free PPh$_3$ and the separation in good yield of **1** or **2**, support the reaction path proposed in Scheme 3. The formation of the ReH(5-Mepz)(H-5-Mepz)(NO)(PPh$_3$)$_2$ (**2**) compound also reflects the preference for the coordination of the less hindered nitrogen of the pyrazole ligand. It can also be noted that the pyrazole-pyrazolato complexes **1**, **2** are stable toward the further reaction with pyrazole and no tris(pyrazole) complex was detected. This is probably due to the formation of the hydrogen bond between the pyrazole and the pyrazolato groups which makes the pyrazole H-atom unreactive toward the hydride ligand.

Complexes **1**, **2** were isolated as yellow or orange solids stable in air and in solution of polar organic solvents, where they behave as non-electrolytes. The formulation of the compounds is supported by analytical and spectroscopic data (Tables 1 and 3) and by the single crystal X-ray structure determination of the methylpyrazole complex ReH(5-Mepz)(H-5-Mepz)(NO)(PPh$_3$)$_2$ (**2**) whose structure is shown along with the labelling scheme in Fig. 1. Table 2 reports the most relevant bond distances and angles regarding rhenium coordination. In ReH(5-Mepz)(H-5-Mepz)(NO)(PPh$_3$)$_2$ the metal coordination is octahedral, with the two phosphine ligands in apical positions, and the two heterocyclic ligands occupying the equatorial plane along with the NO and the hydride groups. The pyrazole and pyrazolato molecules are bonded to the rhenium atom in *cis* geometry, while a *trans* geometry is present for the hydride to the pyrazole and the NO ligand to the pyrazolato. In such systems it is difficult to define unambiguously the anionic or neutral nature of the 5-Mepz/H-5-Mepz moieties, since the proton can be easily exchanged between the two adjacent nitrogen sites [10]. Moreover, in the present case the experimental localisation of the –NH hydrogen atom was not straightforward, and in the end it has been introduced in a calculated position. The bond distances around the rings are affected by high standard deviations, so the real nature of the two ligands cannot be determined definitively. The present assignment is based

Scheme 1.

Scheme 2.

Table 1
Selected IR and NMR spectroscopic data for rhenium complexes

Compound	IR[a] (cm^{-1})	Assgnt.	^{1}H NMR[b,c] (ppm; J, Hz)	Assgnt.	^{31}P{^{1}H} NMR[c,d] (ppm; J, Hz)
ReH(pz)(Hpz)(NO)(PPh$_3$)$_2$ (**1**)	1948 m	ν_{ReH}	17.8 s, br	NH	23.7 s
	1663 s	ν_{NO}	7.05 d	H5	
			$J_{HH} = 1.55$		
			6.81 d	H3	
			$J_{HH} = 1.55$		
			5.45 t	H4	
			$J_{HH} = 1.86$		
			7.34 d	H5	
			$J_{HH} = 1.74$		
			7.20[e]	H3	
			6.08 t	H4	
			$J_{HH} = 2.13$		
			−1.35 t	ReH	
			$J_{PH} = 16$		
ReH(5-Mepz)(H-5-Mepz)(NO)(PPh$_3$)$_2$ (**2**)	1960 m	ν_{ReH}	17.7 s, br	NH	24.6 s
	1661 s	ν_{NO}	6.77 d	H3	
			$J_{HH} = 1.64$		
			5.21 d	H4	
			$J_{HH} = 1.64$		
			1.94 s	CH$_3$	
			7.23[e]	H3	
			5.81 d	H4	
			$J_{HH} = 1.01$		
			2.10 s	CH$_3$	
			−1.46 t	ReH	
			$J_{PH} = 16$		
Re(C≡CPh)(pz)(Hpz)(NO)(PPh$_3$)$_2$ (**3a**)	2071 m	$\nu_{C≡C}$	11.73 s, br	NH	18.2 s
	1653 s	ν_{NO}	7.31[e]	H5 Hpz	
			6.93 d	H3	
			$J_{HH} = 2.11$		
			5.20 t	H4	
			$J_{HH} = 2.25$		
			6.25 d	H5 pz	
			$J_{HH} = 2.51$		
			5.70 d	H3	
			$J_{HH} = 2.02$		
			4.96 t	H4	
			$J_{HH} = 2.38$		
Re(C≡Cp-tolyl)(pz)(Hpz)(NO)(PPh$_3$)$_2$ (**3b**)	2075 m	$\nu_{C≡C}$	11.58 s, br	NH	18.1 s
	1649 s	ν_{NO}	7.14[e]	H5 Hpz	
			5.88 d	H3	
			$J_{HH} = 2.11$		
			5.21 t	H4	
			$J_{HH} = 2.02$		
			6.25 d	H5 pz	
			$J_{HH} = 2.45$		
			5.66 d	H3	
			$J_{HH} = 1.82$		
			4.93 t	H4	
			$J_{HH} = 2.15$		
			2.28 s	CH$_3$	
Re(C≡CPh)(5-Mepz)(H-5-Mepz)(NO)(PPh$_3$)$_2$ (**4a**)	2066 m	$\nu_{C≡C}$	11.16 s, br	NH	16.2 s
	1653 s	ν_{NO}	7.63[e]	H3 HMepz	
			5.24 s, br	H4	
			1.63 s	CH$_3$	
			6.00 s, br	H3 Mepz	
			4.94 s, br	H4	
			2.22 s	CH$_3$	

Table 1 (continued)

Compound	IR[a] (cm^{-1})	Assgnt.	^{1}H NMR[b,c] (ppm; J, Hz)	Assgnt.	^{31}P{^{1}H} NMR[c,d] (ppm; J, Hz)
Re(C≡Cp-tolyl)(5-Mepz)(H-5-Mepz)-(NO)(PPh$_3$)$_2$ (4b)	2075 m	$\nu_{C≡C}$	11.02	NH	16.3 s
	1647 s	ν_{NO}	7.60[e]	H3 HMepz	
			5.97 d	H4	
			J_{HH} = 1.54		
			2.17 s	CH$_3$	
			5.95 d	H3 Mepz	
			J_{HH} = 1.93		
			4.89 d	H4	
			J_{HH} = 1.55		
			2.35 s	CH$_3$	
			2.28 s	CH$_3$ p-tolyl	

[a] In KBr pellets.
[b] Phenyl proton resonances omitted.
[c] In CD$_2$Cl$_2$ at 25 °C, unless otherwise noted.
[d] Positive shift downfield from 85% H$_3$PO$_4$.
[e] Partially overlapping the phenyl protons.

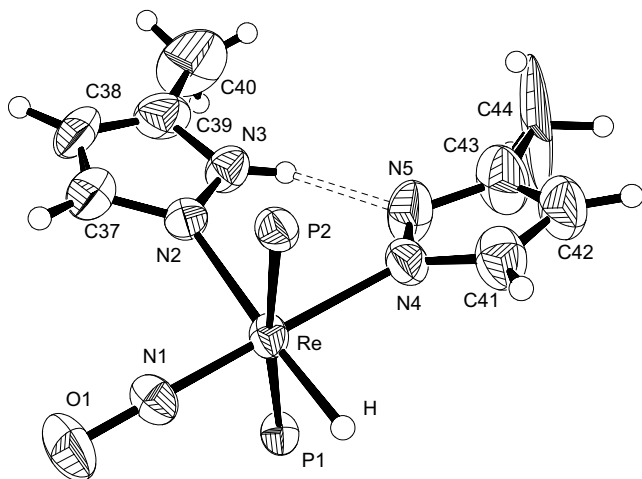Fig. 1. Perspective view of the molecular structure of 2. Phenyl groups omitted for clarity. Intramolecular hydrogen bond is dashed. Thermal ellipsoids at the 50% probability level.

on the analysis of the Re–N distances: the anionic pyrazolato 5-Mepz ligand is more strongly bonded to the metal (Re–N4 = 2.16(1) Å) than to the protonated pyrazole H-5-Mepz (Re–N2 = 2.24(1) Å). Although these values are also affected by the different *trans* influence of nitrosyl and hydride ligands, they are comparable to those observed in the similar tricarbonyl-bis-(3-phenylpyrazole-*N*)-(5-phenylpyrazolato-*N*)-rhenium(I) complex [11], where the ligand nature is unambiguous, and the Re–N distances are 2.14 and 2.16/2.23 Å, respectively, for the pyrazolato and the two pyrazole ligands. The most relevant structural feature of 2 regards the intramolecular hydrogen bond formed between the pyrazolic protonated NH group and the pyrazolato free nitrogen atom, N3–H···N5 (N···N = 2.67(2) Å, N–H···N = 140°). The two heterocyclic ligands form a

dihedral angle of 30°, which is the best balance between mutual steric hindrance and reciprocal attraction due to hydrogen bond stabilisation. However, this intramolecular hydrogen bond does not significantly affect the regularity of the coordination geometry, since the angle formed on the metal by the two cyclic ligands is close to 90°. A very similar situation is found in the above cited analogue pyrazole [10] and phenylpyrazole [11] complexes, where the reciprocal orientation of the heterocyclic rings is dictated by the presence of intramolecular N–H···N hydrogen bonds between them. Although a number of transition metal complexes with the H-3-Mepz ligand have been structurally described compound 2 seems to be the first one containing the deprotonated pyrazolato form 5-Mepz. The bond distances concerning the two heterocyclic ligands are reported in Table 2, however, due to the high standard deviations affecting the measured lengths, it is not possible to reliably discuss the structural effects of deprotonation on the system H-5-Mepz/5-Mepz.

The infrared spectra of the pyrazole-pyrazolato complexes 1, 2 show a band of medium intensity at 1960–1948 cm^{-1} attributed to ν(ReH) of the hydride ligand and one strong absorption at 1663–1661 due to ν(NO) of the nitrosyl ligand. The presence of the hydride ligand is confirmed by the ^{1}H NMR spectra which show a triplet at −1.35 (1) and at −1.46 (2) ppm due to the coupling with the phosphorus nuclei of the phosphine. In the high-frequency region of the spectra a slighter broad signal at 17.7–17.8 ppm, attributed to the NH proton of the pyrazole involved in a N–H···N hydrogen bond is also present. Inter- or intramolecular classical hydrogen bonds, in fact, can move the NH pyrazole signal at higher frequencies [3,10,12–14], as observed for free pyrazole involved in extensive intermolecular N–H···N interactions which thus confirms the existence, in solution, of

Table 2
Bond lengths (Å) and angles (°) for **2**, with s.u.'s in parentheses

Re–N1	1.74(1)
Re–N4	2.16(1)
Re–N2	2.24(1)
Re–P1	2.434(4)
Re–P2	2.446(4)
Re–H	1.7(2)
N1–O1	1.23(2)
N2–C37	1.34(2)
N2–N3	1.36(2)
N3–C39	1.37(2)
N4–C41	1.35(2)
N4–N5	1.36(2)
N5–C43	1.37(3)
C37–C38	1.33(2)
C38–C39	1.37(3)
C39–C40	1.51(3)
C41–C42	1.34(3)
C42–C43	1.38(3)
C43–C44	1.55(3)
N1–Re–N4	179.0(5)
N1–Re–N2	91.7(5)
N4–Re–N2	89.2(5)
N1–Re-P1	90.2(4)
N4–Re-P1	90.2(3)
N2–Re-P1	91.8(3)
N1–Re-P2	93.5(4)
N4–Re-P2	86.0(3)
N2–Re-P2	93.3(3)
P1–Re-P2	173.7(1)
H–Re-P1	88(6)
H–Re-P2	87(6)
H–Re-N1	92(6)
H–Re-N2	177(7)
H–Re-N4	87(6)
O1–N1–Re	174(1)
C37–N2–N3	104(1)
C37–N2–Re	132(1)
N3–N2–Re	123.4(9)
N2–N3–C39	110(1)
C41–N4–N5	108(1)
C41–N4–Re	130(1)
N5–N4–Re	122(1)
N4–N5–C43	106(1)
C38–C37–N2	112(2)
C37–C38–C39	107(2)
C38–C39–N3	106(1)
C38–C39–C40	135(2)
N3–C39–C40	120(2)
C42–C41–N4	111(2)
C41–C42–C43	105(2)
N5–C43–C42	110(2)
N5–C43–C44	125(2)
C42–C43–C44	125(2)

a geometry of type **I** or **II** (Schemes 1 and 2) as observed in the solid state (Fig. 1).

Support for a geometry with the hydride and the nitrosyl ligands in a mutually *cis* position and both *trans* to the pyrazole-pyrazolato groups came from the ^{1}H and ^{13}C NMR spectra of both pz and substituted-pz complexes **1**, **2**. The ^{1}H NMR spectra show, in fact,

two sets of signals for the H3, H4 and H5 protons of the two pyrazole rings in complex **1** whose assignment (Table 1) was confirmed by the multiplicity of the signals, COSY experiments, and literature comparations [3,10,12–14]. The magnetic non-equivalence of the methylpyrazole groups was also observed in the complex **2** whose ^{1}H spectra show two sets of signals either for the CH (H3, H4) or the CH_3 protons of the pyrazoles. At room temperature, however, no correlation was observed in the COSY experiment among the NH proton and the CH hydrogen atoms of the two pyrazole rings. Lowering the sample temperature does not change the profile of the spectra, but shows, in the COSY experiment of **2** at −40 °C, a correlation among the NH signal at 17.56 ppm and the two CH signals at 7.30 and at 5.81 ppm of one pyrazole group. No correlation was instead observed among the NH and the CH protons of the other pyrazole ring. These results may be explained on the basis of intramolecular H-exchange between the two pyrazole and pyrazolato ligands, which is fast at room temperature, but at −40 °C results to be in a low-exchange limit process. At this temperature, therefore, the pyrazole and the pyrazolato ligands are well distinguishable, as observed in the solid state and shown in Fig. 1. The ^{13}C NMR spectra confirmed these results and the HMQC and HMBC experiments allowed the easy assignment of all the carbon atoms of the N-donor ligands (Table 3). In the temperature range between +20 and −80 °C the ^{31}P{^{1}H} NMR spectra appear as a sharp singlet indicating the magnetic equivalence of the two phosphine ligands. We have also carried out NOESY experiments both at room temperature and at −40 °C, but unfortunately no correlation was observed between the proton signals of the pyrazole and pyrazolato ligands. However, the variable-temperature NMR data and the COSY experiments strongly suggest a geometry in solution of type **I** and **II**, like those observed in the solid state (Fig. 1). In this geometry a static conformation with the pyrazole H-hydrogen atom sharing the same uncoordinate pyrazolato N-atom has been proposed, although variable-temperature NMR spectra suggest an intramolecular exchange between the two pyrazole-pyrazolato ligands.

Metal complexes containing both pyrazole and pyrazolato ligands with intramolecular hydrogen bonds between them have already been reported for rhenium(I) and rhenium(V) [3,12b], osmium(II) [14g], iridium(III) [12a], palladium [13] and platinum [15] derivatives. The use of $ReH_2(NO)(PPh_3)_3$ as a precursor allows new types of complexes to be prepared containing the hydride as a supporting ligand.

2.1. Reactivity

Protonation of the $ReH(pz)(Hpz)(NO)(PPh_3)_2$ (**1**) complex with Brønsted acids was studied at variable

Table 3
^{13}C{^{1}H} NMR data for selected rhenium complexes

Compound	^{13}C{^{1}H} NMR[a,b] (ppm; J, Hz)	Assgnt.
ReH(pz)(Hpz)(NO)(PPh$_3$)$_2$ (**1**)	145.5 s	C3
	134.7 s	C5
	104.9 s	C4
	138.9 s	C5
	129.2 s	C3
	106.1 s	C4
ReH(5-Mepz)(H-5-Mepz)(NO)(PPh$_3$)$_2$ (**2**)	146.2 s	C3
	144.4 s	C5
	104.4 s	C4
	12.8 s	CH$_3$
	139.9 s	C5
	139.5 s	C3
	105.3 s	C4
	11.4 s	CH$_3$
Re(C≡CPh)(pz)(Hpz)(NO)(PPh$_3$)$_2$ (**3a**)	135.6 s	C3 pz
	128.6 s	C5
	105.6 s	C4
	140.8 s	C3 Hpz
	136.5 s	C5
	106.1 s	C4
	121.1 t $J_{31P13C} = 11.2$	Cα≡CPh
	106.9 s	C≡CβPh
Re(C≡CPh)(5-Mepz)(H-5-Mepz)(NO)(PPh$_3$)$_2$ (**4a**)	144.0 s	C3 Hpz
	140.3 s	C5
	106.4 s	C4
	10.97 s	CH$_3$
	135.7 s	C3 pz
	139.2 s	C5
	106.9 s	C4
	14.27 s	CH$_3$
	120.4 t $J_{31P13C} = 12.0$	Cα≡CPh
	108.0 s	C≡CβPh

[a] In CD$_2$Cl$_2$ at 25 °C.
[b] Phenyl carbon resonances omitted.

temperatures in a NMR tube and seems to proceed with the formation of the bis(pyrazole) [ReH(Hpz)$_2$-(NO)(PPh$_3$)$_2$]$^+$ cation, which is thermally unstable and cannot be isolated in the solid state (Scheme 4).

In the ^{1}H NMR spectra, the addition of an equimolar amount of HBF$_4$ · Et$_2$O to a CD$_2$Cl$_2$ solution of **1** at −80 °C causes the disappearance of the broad signal near 17 ppm of the N–H···N pyrazole proton atom and the appearance of two new slightly broad singlets at 10.1 and 9.6 ppm attributable to the NH protons of
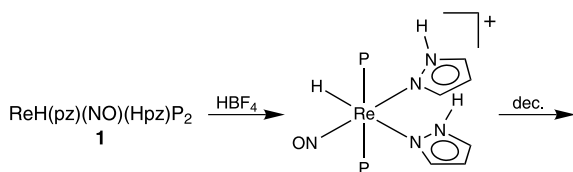
two Hpz ligands. The hydride signals do not change their multiplicity, but a change of the chemical shift of about 0.4 ppm, from −1.35 to −1.78 ppm, was observed. These data indicate that the protonation site in our pyrazole-pyrazolato complex **1** is not the hydride to give an η^2-H$_2$ complex [5e], but the pyrazolato ligand yielding a pyrazole Hpz molecule which remains bonded to the central metal in the resulting [ReH(Hpz)$_2$(NO)-(PPh$_3$)$_2$]$^+$ species. The pyrazolato group is the most basic among the ligands (H, NO, PPh$_3$, pz) in the starting ReH(pz)(Hpz)(NO)(PPh$_3$)$_2$ complex, and the reaction with HBF$_4$ · Et$_2$O yields a cationic bis(pyrazole) [Re-H(Hpz)$_2$(NO)(PPh$_3$)$_2$]$^+$ derivative. Unfortunately, this complex is thermally unstable and the NMR spectra of its solution show that some decomposition begins above −10 °C which prevents the separation of the complex.

The protonation study has also gone on after the formation of the [ReH(Hpz)$_2$(NO)(PPh$_3$)$_2$]$^+$ cation and

Scheme 4. P = PPh$_3$.

showed that this bis(pyrazole) complex is unstable in the presence of an excess of HBF$_4$ · Et$_2$O and gives decomposition products and formation of free pyrazole.

Reactivity studies of the new hydrides **1**, **2** were extended to the insertion reactions into the Re–H bond of several substrates such as aryldiazonium cations ArN$_2^+$, heteroallenes (CO$_2$, CS$_2$, ArNCS) and terminal alkynes (ArC≡CH). At room temperature, however, no reaction was observed and the starting hydrides **1**, **2** were recovered unchanged after several hours of reaction. This unreactivity, mainly towards aryldiazonium cations, is somewhat surprising because either the precursor ReH$_2$(NO)(PPh$_3$)$_3$ or other rhenium hydrides, such as ReH(CO)$_n$P$_{5-n}$ and ReH$_2$(NO)P$_3$ (P = phosphite), quickly react with ArN$_2^+$ to give the corresponding aryldiazene [Re]–NH=NAr derivatives [9,16]. The introduction of the N-donor pyrazole and pyrazolato ligands in rhenium hydride complexes changes the properties of the hydride group making, for example, the Re–H bond in complexes **1**, **2** unreactive toward the insertion of ArN$_2^+$ cations.

In refluxing 1,2-dichloroethane, instead, hydrides ReH(Rpz)(HRpz)(NO)(PPh$_3$)$_2$ (**1,2**) react with terminal alkynes to give the acetylide Re(C≡CAr)(Rpz)(HRpz)(NO)(PPh$_3$)$_2$ (**3**, **4**) complexes which were isolated and characterised (Scheme 5).

The formation of an acetylide from the reaction of a metal hydride with an excess of terminal alkyne may be explained through an initial step involving the insertion of the alkyne into the Re–H bond to give a vinyl intermediate [Re]–C(H)=C(H)Ar [**B**] complex (Scheme 6). Reaction of this vinyl complex with alkyne yields alkene ArCH=CH$_2$ and the final acetylide [17,18] [Re]–C≡CAr (**3,4**) derivative.

In order to support this reaction path, we monitored the progress of the reaction by ^{1}H NMR spectra, but did not observe any signals attributable to a vinyl intermediate [19]. However, the presence of styrene PhCH=CH$_2$ in the reaction with phenylacetylene was unambiguously detected in the reaction mixture, and
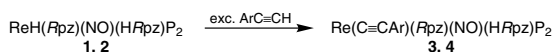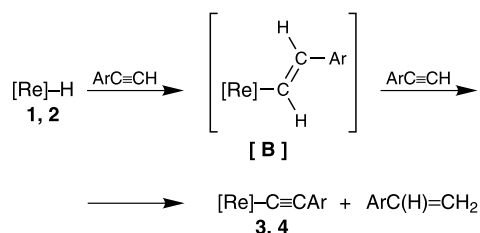
this result strongly supports the path proposed in Scheme 6 for the reaction.

Acetylide complexes **3**, **4** were isolated as orange solids stable in the air and in solution of common organic solvents where they behaved as non-electrolytes. Analytical and spectroscopic data (Table 1) support the proposed formulation. The IR spectra show a medium-intensity band at 2075–2066 cm^{-1} due to the v(C≡C) of the acetylide ligand [17,18]. In the spectra a strong absorption at 1653–1647 cm^{-1} attributed to v(NO) of the nitrosyl ligand is also present.

In the high-frequency region of the proton spectra of **3** a slightly broad signal appears at 11.73–11.58 ppm, which was attributed to the NH proton of the coordinate pyrazole ligand. In the spectra two sets of signals between 5 and 8 ppm are also present, one of which is correlated in the COSY experiment with the NH signal and was attributed to the CH protons of the coordinate Hpz ligand. The other set, instead, has been assigned to the CH protons of the pyrazolato (pz) ligand. In the spectra of the related methylpyrazole complexes **4**, two singlets for the 5-Me substituents are also present besides the NH resonances and the two sets of signals of the CH protons of the HRpz and Rpz ligands, respectively. The assignment of the pyrazole CH protons is supported by the multiplicity of the signals, the J_{HH} values, and COSY experiments and is reported in Table 1. A NOESY experiment on the methylpyrazole complexes **4** was also carried out and showed a strong correlation between the NH and the CH$_3$ of the methyl substituent of the pyrazole, in agreement with the presence of a H-5-Mepz ligand. Correlations between the CH$_3$ and the CH protons were also observed for both the pyrazole and the pyrazolato rings.

The ^{13}C spectra of **3** and **4** and the related HMQC and HMBC experiments confirm the presence of both the pyrazole and pyrazolato ligands, as well as of the acetylide group, and allow the assignment of all the carbon atoms of the N-donor and C≡CAr ligands to be achieved (Table 3).

The ^{1}H NMR spectra of **3** and **4** also highlight that, in contrast with the precursors **1**, **2**, a N–H···N hydrogen bond can be ruled out in these pyrazole-pyrazolato complexes owing to the low-frequency values of the signal of the NH hydrogen atom (11.73–11.02 ppm) which falls in the range generally observed for coordinate pyrazole (Hpz) [1–3]. The absence of a hydrogen bond can be explained on the basis of a mutually *trans* position of the pyrazolato and the pyrazole ligands. A vicinal (*cis*) position of the two ligands, in fact, should give rise to the N–H···N interaction, as observed in the related ReH(Rpz)(HRpz)(NO)P$_2$ (**1**, **2**) precursors. In the temperature range between +20 and −80 °C the ^{31}P{^{1}H} NMR spectra of **3** and **4** appear as a sharp singlet, in agreement with the presence of two magnetically equivalent phosphine ligands. On the basis of these data, a
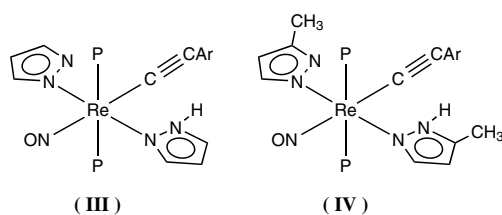
ReH(Rpz)(NO)(HRpz)P$_2$ $\xrightarrow{\text{exc. ArC≡CH}}$ Re(C≡CAr)(Rpz)(NO)(HRpz)P$_2$
1, 2 **3, 4**

Scheme 5. R = H **3**, 5-Me **4**; P = PPh$_3$; Ar = Ph **a**, p-tolyl **b**.

Scheme 6. [Re] = Re(Rpz)(NO)(HRpz)(PPh$_3$)$_2$.

Chart 1.

geometry of the type **III** and **IV** (Chart 1) can reasonably be proposed for our acetylide Re(C≡CAr)-(Rpz)(HRpz)(NO)(PPh₃)₂ (**3**, **4**) derivatives. Geometry **III** and **IV** also indicates that the reaction of hydrides **1**, **2** with terminal alkynes occurs with a change of the geometry of the complexes and loss of the hydrogen bond between Hpz and pz ligands.

3. Experimental

3.1. General comments

All synthetic work was carried out in an appropriate atmosphere (Ar, N₂) using standard Schlenk techniques or a vacuum atmosphere dry-box. Once isolated, the complexes were found to be relatively stable in air, but were stored in an inert atmosphere at −25 °C. All solvents were dried over appropriate drying agents, degassed on a vacuum line, and distilled into vacuum-tight storage flasks.

Pyrazole (Hpz), 3-methylpyrazole (H-3-Mepz) and other reagents were purchased from commercial sources (Aldrich, Fluka) in the highest available purity and used as received. Infrared spectra were recorded on a Nicolet Magna 750 FT-IR spectrophotometer. NMR spectra (^{1}H, ^{31}P, ^{13}C) were obtained on AC200 or AVANCE 300 Bruker spectrometers at temperatures between −90 and +30 °C, unless otherwise noted. ^{1}H and ^{13}C spectra are referred to internal tetramethylsilane; ^{31}P{^{1}H} chemical shifts are reported with respect to 85% H₃PO₄ with downfield shifts considered positive. The COSY, HMQC and HMBC NMR experiments were performed using their standard programs. The SwaN-MR software package [20] was used to treat NMR data. The conductivity of 10^{-3} mol dm^{-3} solutions of the complexes in CH₃NO₂ at 25 °C were measured with a Radiometer CDM 83.

3.2. Synthesis of complexes

The ReH₂(NO)(PPh₃)₃, ReH₂(NO)(PPh₂OEt)₃ and ReH₂(NO)L(PPh₃)₂ [L = P(OEt)₃, PPh(OEt)₂] hydrides were prepared following the methods previously reported [9,21].

3.2.1. ReH(pz)(Hpz)(NO)(PPh₃)₂ (1)

In a 50-mL three-necked round-bottomed flask were placed 603 mg (0.6 mmol) of ReH₂(NO)(PPh₃)₃, 204 mg (3 mmol) of pyrazole and 30 mL of toluene. The reaction mixture was refluxed for 1 h and then the solvent was removed under reduced pressure. The oil obtained was triturated with ethanol (8 mL) until an orange solid separated out, which was filtered and crystallised from CH₂Cl₂ and ethanol (350 mg, 66%). Found: C, 57.80; H, 4.31; N, 8.06%. C₄₂H₃₈N₅OP₂Re requires: C, 57.53; H, 4.37; N, 7.99.

3.2.2. ReH(5-Mepz)(H-5-Mepz)(NO)(PPh₃)₂ (2)

This complex was prepared exactly like the related pyrazole complex **1**, by using 3-methylpyrazole as a reagent (380 mg, 70%). Found: C, 58.35; H, 4.59; N, 7.64%. C₄₄H₄₂N₅OP₂Re requires: C, 58.40; H, 4.68; N, 7.74.

Suitable crystals for X-ray analysis were obtained by slow cooling from +20 to −18 °C of a saturated solution of the complex in 10 mL of ethanol and enough toluene to dissolve the solid.

3.2.3. Re(C≡CAr)(pz)(Hpz)(NO)(PPh₃)₂ (3) [Ar = Ph (a), p-tolyl (b)]

An excess of the appropriate alkyne ArC≡CH (1.7 mmol) was added to a solution of the ReH(pz)(Hpz)(NO)(PPh₃)₂ (**1**) hydride (300 mg, 0.34 mmol) in 1,2-dichloroethane (20 mL) and the resulting mixture was refluxed for 3 h and 30 min. The solvent was removed under reduced pressure to give an oil which was triturated with ethanol (5 mL). A brown solid slowly separated out from the resulting solution which was filtered and crystallised from CH₂Cl₂ and ethanol [250 mg, 75% (**3a**), 245 mg, 73% (**3b**)]. Found: C, 61.60; H, 4.38; N, 7.03%. C₅₀H₄₂N₅OP₂Re (**3a**) requires: C, 61.46; H, 4.33; N, 7.17. Found: C, 61.72; H, 4.34; N, 7.05%. C₅₁H₄₄N₅OP₂Re (**3b**) requires: C, 61.81; H, 4.47; N, 7.07.

3.2.4. Re(C≡CAr)(5-Mepz)(H-5-Mepz)(NO)(PPh₃)₂ (4) [Ar = Ph (a), p-tolyl (b)]

These complexes were prepared exactly like the related compounds **3** by reacting ReH(5-Mepz)(H-5-Mepz)(NO)(PPh₃)₂ (**2**) (300 mg, 0.33 mmol) with the appropriate alkyne (1.7 mmol) [275 mg, 80% (**4a**), 285 mg, 82% (**4b**)]. Found: C, 62.25; H, 4.73; N, 7.06%. C₅₂H₄₆N₅OP₂Re (**4a**) requires: C, 62.14; H, 4.61; N, 6.97. Found: C, 62.44; H, 4.65; N, 6.79%. C₅₃H₄₈N₅OP₂Re (**4b**) requires: C, 62.46; H, 4.75; N, 6.87.

3.2.5. Protonation reactions

The protonation of **1**, **2** hydrides was studied in a NMR tube by ^{1}H and ^{31}P spectra collected between +20 and −80 °C. A typical experiment involved the

addition of a CD_2Cl_2 solution (0.5 mL) of the appropriate ReH(Rpz)(HRpz)(NO)(PPh$_3$)$_2$ hydride ($R = H$, 5-Me) (30–40 mg, 0.03–0.04 mmol) in a screw-cap 5-mm NMR tube placed in a vacuum-atmosphere dry-box. The tube was sealed, cooled to −80 °C, and then one equivalent of HBF$_4$ · Et$_2$O was added by microsyringe. The tube was transferred into the instrument's probe pre-cooled to −80 °C and the spectra collected.

3.2.6. X-ray crystal structure determination of ReH(5-Mepz)(H-5-Mepz)(NO)(PPh$_3$)$_2$ (2)

A single crystal of **2** was mounted on a glass fiber and X-ray diffraction data were collected on a Bruker-Siemens SMART AXS 1000 equipped with CCD detector, using graphite-monochromated Mo Kα radiation ($\lambda = 0.71069$ Å). Data collection details are: crystal to detector distance = 5.0 cm, 2424 frames collected (complete sphere mode), time per frame = 40 s, oscillation $\Delta\Phi = 0.300°$. Crystal decay resulted negligible. Data reduction was performed up to $d = 0.90$ Å by the SAINT package [22] and data were corrected for absorption effects by the SADABS [23] procedure ($T_{max} = 1.000$, $T_{min} = 0.6275$). The phase problem was solved by direct methods [24] and refined by full-matrix least-squares on all F^2 [25], implemented in the WINGX package [26]. The triclinic centric unit cell contains also a toluene molecule disordered around the inversion centre, which was modelled with the aid of the 'squeeze' procedure implemented in the program Platon [27]. The toluene occupies a cavity of 300 Å^3, centered at (0.5, 0.5, 0.5), containing an electronic density summing up to 41 electrons; these values are consistent with the model considering one fully occupied, highly mobile molecule. Anisotropic displacement parameters were refined for all non hydrogen atoms, while hydrogen atoms were introduced in calculated positions, except for the hydride hydrogen, which was located from Fourier maps and refined isotropically. The final Fourier difference map contained a huge residual peak Q1 close to one aromatic carbon of one PPh$_3$ ligand (Q1···C33 = 2.00 Å), and other relevant peaks near other aromatic carbon atoms (distances ranging between 1.6 and 2.0 Å). No sensible interpretation was possible to assign these peaks to any chemical feature, and they were attributed to the poor data quality ($R_{int} = 0.109$) and to possible neglected absorption effects. Use of the Cambridge Crystallographic Database [28] facilities was made for structure discussion. Data collection and refinement results are summarised in Table 4.

4. Supplementary data

Crystallographic data in CIF format have been deposited with the Cambridge Crystallographic Data Centre, CCDC No. 266858.

Table 4
Crystal data and structure refinement for ReH(5-Mepz)(H-5-Mepz)-(NO)(PPh$_3$)$_2$ (**2**)

Empirical formula	$C_{44}H_{42}N_5OP_2Re \cdot 1/2C_7H_8$
Formula weight	951.03
Temperature (K)	293(2)
Wavelength (Å)	0.71073
Crystal system	triclinic
Space group	$P\bar{1}$
Unit cell dimensions	
a (Å)	9.813(3)
b (Å)	13.215(3)
c (Å)	18.472(5)
α (°)	79.420(4)
β (°)	83.852(4)
γ (°)	70.724(4)
Volume (Å^3)	2220(1)
Z	2
D_{calc} (Mg/m^3)	1.422
Absorption coefficient (mm^{-1})	2.849
$F(000)$	958
Theta range for data collection (°)	1.65–23.35
Reflections collected	17924
Independent reflections [R_{int}]	6374 [0.1091]
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	6374/34/449
Goodness-of-fit on F^2	1.052
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0975$, $wR_2 = 0.2489$
R indices (all data)	$R_1 = 0.1126$, $wR_2 = 0.2626$
Largest ΔF maximum/minimum (e Å^{-3})	10.634/−2.866

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