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Preparation and Reactivity of Hydridorhenium Complexes with Polypyridine and Phosphonite Ligands

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The hydrido complexes $[ReH(Cl)(N–N)P_3]BPh_4$ [P = $PPh(OEt)_2$; N–N = 2,2′-bipyridine (bpy), 5,5′-dimethylbipyridine (5,5′-Me_2bpy), 1,10-phenanthroline (phen)] have been prepared by allowing $ReCl_3P_3$ to react with the polypyridine in refluxing ethanol. The dihydrido $[ReH_2(bpy)P_3]BPh_4$ complex has also been prepared by treating $[ReHCl(bpy)P_3]^+$ cation with $NaBH_4$ in ethanol. Similarly, the hydrido tricarbonyl derivative $[ReH_2(bpy)(CO)_3]BPh_4$ has been synthesized by allowing $[ReH(bpy)(CO)_3]$ to react with $HBF_4·Et_2O$. All complexes have been characterized spectroscopically (IR and NMR spectroscopic data) and the $[ReHCl(bpy)\{PPh(OEt)_2\}_3]BPh_4$ derivative by X-ray crystallography. Protonation of both $[ReHCl(bpy)P_3]BPh_4$ and $[ReH_2(bpy)P_3]BPh_4$ with $HBF_4·Et_2O$ leads to the classical cations $[ReH_2Cl(bpy)P_3]^{2+}$ and $[ReH_3(bpy)P_3]^{2+}$, respectively. The vinyl complexes $[Re\{CH=C(H)R\}_2(bpy)P_3]BPh_4$ (R = Ph, *p*-tolyl, *tert*-butyl) have also been prepared by allowing the dihydrido derivative $[ReH_2(bpy)P_3]BPh_4$ to react with an excess of terminal alkyne in 1,2-dichloroethane.

Introduction

The chemistry of rhenium polyhydrido complexes has received considerable attention in recent years due to their various reactivity modes and unusual structural properties, including the presence of η^2-H_2 ligands.[1–4] The ancillary ligands used in this chemistry mainly involve π-acceptors such as carbonyls and mono- or polydentate tertiary phosphane groups.[1–4] In contrast, much less attention has been devoted to the use of nitrogen-donor ligands, and only one paper[5] has reported the use of polypyridines as supporting ligands[6,7] in rhenium polyhydrido complexes. This is somewhat surprising because rhenium complexes with polypyridine ligands are used in photo- and electrocatalytic reduction of CO_2.[6,7c,8] Changes in the nature of the ancillary ligands may also greatly change both the properties of complexes and the reactivity of the M–H bond, and recent results from our laboratory have confirmed the important influence of polypyridine ligands in the chemistry of classical and non-classical hydrido complexes of the iron triad.[9]

We have developed the chemistry of hydrido complexes of transition metals over several years using monodentate phosphites as supporting ligands.[9,10] Recently, in the case of rhenium, we reported the synthesis and reactivity of mono- and polyhydrido complexes of the type $[ReH(CO)_nP_{5-n}]$, $[Re(\eta^2\text{-}H_2)(CO)_nP_{5-n}]^+$, ReH_5P_3, ReH_3P_4, $Re_2H_8P_4$, and $[ReH_4(\eta^2\text{-}H_2)P_3]^+$ (P = phosphite; n = 1–4).[11] We have now extended these studies, with the aim of introducing nitrogen-donor ligands such as 2,2′-bipyridine and 1,10-phenanthroline into rhenium polyhydrido chemistry. Our results on the synthesis and reactivity of mixed-ligand cationic hydridorhenium complexes with phosphonite and polypyridine are reported here.

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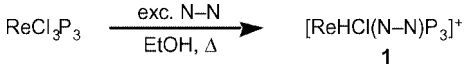
Results and Discussion

Synthesis of Hydrido Complexes

The trichlorido complex $[ReCl_3\{PPh(OEt)_2\}_3]$ was treated with an excess of polypyridine (N–N) in refluxing ethanol to give the cation $[ReHCl(N–N)\{PPh(OEt)_2\}_3]^+$, which was isolated as its BPh_4 salt and characterized (Scheme 1).



Scheme 1. P = $PPh(OEt)_2$; N–N = 2,2′-bipyridine (bpy) **a**, 5,5′-dimethyl-2,2′-bipyridine (5,5′-Me_2bpy) **b**, 1,10-phenanthroline (phen) **c**.

The reaction proceeds with substitution of the chlorido ligand by the polypyridine and formation of a heptacoordinate hydrido cation. The hydrido ligand presumably arises from abstraction of hydrogen from the ethanol solvent. Although this could not be proved conclusively, numerous precedents[1a] support this hypothesis.

The nature of the phosphane ligand is crucial for the synthesis of heptacoordinate hydrido complex **1**, which was obtained in pure form only with the phosphonite $PPh(OEt)_2$. The reaction of the related precursors $[ReCl_3(PPh_2OEt)_3]$ with polypyridines gave a mixture of products containing only small amounts of the $[ReHCl(N–N)(PPh_2OEt)_3]^+$ derivatives.

The hydrido complexes $[ReHCl(N–N)P_3]BPh_4$ (**1**) were treated with $NaBH_4$ in ethanol to give the dihydrido cations $[ReH_2(N–N)P_3]^+$ which, in the case of the bpy ligand, was isolated in good yield and characterized (Scheme 2). The reaction of **1** with $NaBH_4$ also proceeded with 5,5′-dimethylpyridine and 1,10-phenanthroline as a ligand but, in these cases, complexes **2** were rather unstable and decomposed during crystallization.

$$[ReHCl(N–N)P_3]^+ \xrightarrow[EtOH,\ \Delta]{NaBH_4} [ReH_2(N–N)P_3]^+$$
1 **2a**

Scheme 2. P = $PPh(OEt)_2$; N–N = 2,2′-bipyridine (bpy) **a**.

Hydridorhenium complexes containing polypyridine as a supporting ligand are rare[5,6] and the only known examples were obtained from polyhydrido $[ReH_7(PPh_3)_2]$ or $[ReCl(bpy)(CO)_3]$ precursors. The reaction of $[ReCl_3P_3]$ with polypyridine in ethanol is therefore a new method for preparing mixed-ligand hydridorhenium complexes.

Hydrido complexes **1** and **2a** are dark-green (**1**) or red-brown (**2a**) solids that are stable in air and in solution in polar organic solvents, where they behave as 1:1 electrolytes.[12] The analytical and spectroscopic (IR, NMR; Table 1) data confirm the proposed formulation for the complexes. Further support comes from the X-ray crystal structure of $[ReHCl(bpy)\{PPh(OEt)_2\}_3]BPh_4$ (**1a**), the cation of which is shown in Figure 1. The geometrical parameters of the anion were as expected and do not require further comment.

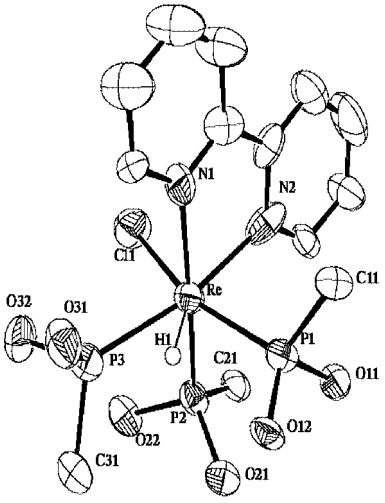


Figure 1. Perspective view of the crystal structure of the cation $[ReHCl(bpy)\{PPh(OEt)_2\}_3]^+$ **1a**, with thermal ellipsoids drawn at the 50% probability level. The ethyl and phenyl groups of the phosphites are omitted for clarity.

The rhenium atom in the cation is coordinated by three phosphorus atoms from three phosphonite ligands, two nitrogen atoms from the bipyridine ligand, and a chlorine atom. There is also significant residual electronic density close to the rhenium atom (at 1.23 Å; see Experimental Section), probably due to the presence of the hydrogen atom in this region, but unfortunately its position could not be refined due to the well-known inability of X-ray diffractometry to detect hydrido ligands coordinated to third-row transition metals. The presence of this ligand was also confirmed by the values of the angles around the metal, which are far from the theoretical values for an octahedron as a consequence of the heptacoordinate environment of the metal. Without knowing the position of the hydrido ligand it is difficult to propose a geometry around the metal. The N(1)–Re–P(2) axis [171.7(2)°], for example, could indicate a monocapped octahedron or a pentagonal bipyramid. The chelate angle N(1)–Re–N(2) has a value of only 75.7(4)° – virtually the same as that found in other 2,2′-bipyridine complexes of Re^{III}[13] – and is an important source of distortion since one of the nitrogen atoms is in the axis and the other in the equatorial plane. The angles in the plane for a pentagonal bipyramidal geometry should be close to 72°, although the different steric requirements of the hydrido and the rest of the ligands may enlarge these angles. The angles in the cation complex range from 79.2(2)° to 90.6(1)°. This, and the distortion of the axis, allows us to propose a monocapped octahedral geometry around the metal, with the hydrido ligand situated in the trigonal face occupied by the three phosphorus atoms.

The Re–N [2.172(10) and 2.180(9) Å] and Re–Cl [2.450(3) Å] bond lengths are slightly longer than those found for other octahedrally coordinated complexes,[13] as expected due to the increase in coordination number. The Re–P bond lengths range from 2.286(3) to 2.365(3) Å and are slightly shorter than those found in the cationic complex $[ReCl(PhN_2)\{PPh(OEt)_2\}_4]BPh_4$,[14] the only example of a complex containing both Re^{III} and a phosphonite $PPh(OEt)_2$ ligand found in the CCDC (version 5.27, update August 2006).[15] This shortening is due to the pseudo *trans* effect exerted by the nitrogen or chlorine atoms in the heptacoordinate complex when compared with the cited octahedral cation, which has the phosphonite ligands mutually *trans*.

The IR spectra of monohydrido complexes $[ReHCl(N–N)P_3]BPh_4$ (**1**) show the bands characteristic of polypyridine and phosphonite ligands (ν_{PO} = 1098–1020 cm^{-1}), but none attributable to the ν_{ReH} of the hydrido ligand. However, its presence was confirmed by the ^1H NMR spectra, which show signals for the $PPh(OEt)_2$ and polypyridine ligands and a multiplet between δ = –7.98 and –8.30 ppm that is characteristic of a hydrido ligand. As the $^{31}P\{^1H\}$ NMR spectrum is an A_2M multiplet for all complexes **1** in the temperature range between +20 and –80 °C, the hydrido pattern can be simulated by an A_2MX model (X = ^1H), with the parameters listed in Table 1. In addition, the values of the two $J_{P,H}$ coupling constants are similar, which suggests that the hydrido is in a mutually *cis* position with re-

Table 1. IR, ^1H and $^{31}P\{^1H\}$ NMR spectroscopic data for rhenium complexes.

Compound	^1H NMR[a] δ	Assignment	$^{31}P\{^1H\}$ NMR[a,b] Spin system	δ
$[ReHCl(bpy)\{PPh(OEt)_2\}_3]BPh_4$ (**1a**)	9.28–6.51 (m)	Ph + bpy	A_2M	δ_A = 126.8
	3.64 (m)	CH_2		δ_M = 119.9
	1.19 (t)	CH_3		$J_{A,M}$ = 37.7
	1.16 (t)			
	1.08 (t)			
	A_2MX	ReH		
	δ_X = –8.28			
	$J_{A,X}$ = 44			
	$J_{M,X}$ = 58			
$[ReHCl(5,5'\text{-}Me_2bpy)\{PPh(OEt)_2\}_3]BPh_4$ (**1b**)	9.57–6.15 (m)	Ph + bpy	A_2M	δ_A = 126.9
	3.68 (m)	CH_2		δ_M = 121.2
	2.34 (s)	CH_3 bpy		$J_{A,M}$ = 36.2
	2.22 (s)			
	1.21 (t)	CH_3 phos		
	1.19 (t)			
	1.08 (t)			
	A_2MX	ReH		
	δ_X = –8.30			
	J_{AX} = 44			
	J_{MX} = 58			
$[ReHCl(phen)\{PPh(OEt)_2\}_3]BPh_4$ (**1c**)	9.64–6.13 (m)	Ph + phen	A_2M	δ_A = 127.0
	3.70 (m)	CH_2		δ_M = 119.8
	1.28 (t)	CH_3		$J_{A,M}$ = 37.4
	1.03 (t)			
	A_2MX	ReH		
	δ_X = –7.98			
	$J_{A,X}$ = 42			
	$J_{M,X}$ = 58			
$[ReH_2(bpy)\{PPh(OEt)_2\}_3]BPh_4$ (**2a**)	9.27–6.86 (m)	Ph + bpy		141 m, b
	3.60 (m)	CH_2		
	3.31 (m)			
	0.96 (br. m)	CH_3		
	–5.20 (br. m)	ReH		
	9.20–6.80 (m)[c]	Ph + bpy	AM_2[c]	δ_A 145.7
	3.57 (m)	CH_2		δ_M 134.3
	3.23 (m)			$J_{A,M}$ = 27.0
	1.25 (t)	CH_3		
	0.98 (t)			
	AM_2X_2	ReH		
	δ_X –5.31			
	$J_{A,X}$ = 12			
	$J_{M,X}$ = 66			
$[ReH_2(bpy)(CO)_3]BPh_4$ (**3a**)[d]	9.03–7.68 (m)	Ph + bpy		
	–13.07 d	ReH_2		
	–17.47 d			
	$J_{H,H}$ = 3.4			
$[ReH_2Cl(bpy)\{PPh(OEt)_2\}_3]^{2+}$ (**4a**)	9.55–6.50 (m)[e]	Ph + bpy	AM_2[e]	δ_A = 163.4
	3.75 (m)	CH_2		δ_M = 124.1
	1.26 (m)	CH_3		$J_{A,M}$ = 52.3
	–5.50 (br. dt)	ReH_2	AM_2[e]	δ_A = 155.0
	–7.84 (br. m)			δ_M = 125.5
				$J_{A,M}$ = 49.4
$[ReH_3(bpy)\{PPh(OEt)_2\}_3]^{2+}$ (**5a**)	9.25–6.85 (m)[f]	Ph + bpy	A_2B[f]	δ_A = 127.8
	4.20–3.35 (m)	CH_2		δ_B = 126.5
	1.20 (m)	CH_3		$J_{A,B}$ = 31.0
	–2.2 (br. m)	ReH_3		
	–3.1 (br. m)			
$[Re\{CH{=}C(H)Ph\}_2(bpy)\{PPh(OEt)_2\}_3]BPh_4$ (**6a**)	7.30–6.82 (m)	Ph + bpy	AB_2	δ_A = 139.3
	7.08 (m)	$=CH_\alpha$		δ_B = 138.2
	6.47 (m)	$=CH_\beta$		$J_{A,B}$ = 32.6
	4.35–3.60 (m)	CH_2		
	1.52 (t)	CH_3		
	1.15 (t)			
	1.07 (t)			

Table 1. *(continued)*

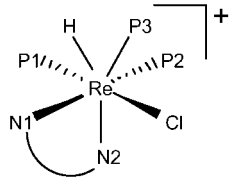
Compound	^{1}H NMR[a]		^{31}P{^{1}H} NMR[a,b]	
	δ	Assignment	Spin system	δ
[Re{CH=C(H)-*p*-tolyl}$_2$(bpy){PPh(OEt)$_2$}$_3$]BPh$_4$ (**7a**)	9.32–6.86 (m)	Ph + bpy	AB_2	δ_A = 136.4
	AB_2XY	=CH		δ_B = 135.2
	(X = H_α, Y = H_β)			$J_{A,B}$ = 31.8
	δ_X = 7.04			
	δ_Y = 6.45			
	$J_{A,X}$ = 4.0			
	$J_{A,Y}$ = 4.35			
	$J_{B,X}$ = 7.10			
	$J_{B,Y}$ = 5.20			
	$J_{X,Y}$ = 7.7			
	4.30–3.30 (m)	CH_2		
	2.44 (s)	CH_3 *p*-tolyl		
	1.51 (t)	CH_3 phos		
	1.15 (t)			
	0.99 (t)			
[Re{CH=C(H)-*tert*-butyl}$_2$(bpy){PPh(OEt)$_2$}$_3$]BPh$_4$ (**8a**)	9.28–6.87 (m)	Ph + bpy	AB_2	δ_A = 137.0
	AB_2XY	=CH		δ_B = 135.5
	(X = H_α, Y = H_β)			$J_{A,B}$ = 31.6
	δ_X = 7.09			
	δ_Y = 6.51			
	$J_{A,X}$ = 6.85			
	$J_{A,Y}$ = 3.60			
	$J_{B,X}$ = 8.10			
	$J_{B,Y}$ = 4.30			
	$J_{X,Y}$ = 8.40			
	4.32–3.32 (m)	CH_2		
	1.50 (t)	CH_3 phos		
	1.14 (t)			
	1.10 (t)			
	1.07 (s)	CH_3 *t*Bu		

[a] In CD_2Cl_2 at 25 °C, unless otherwise noted. Chemical shifts are given in ppm and coupling constants in Hz. [b] Positive shifts downfield from 85% H_3PO_4. [c] At –30 °C. [d] IR data for the complex in a KBr pellet: ν_{CO} = 2049 (s), 1989 (s), 1924 cm^{-1} (s). [e] At –50 °C. [f] At –70 °C.

spect to all the phosphonite ligands. Lastly, the two methyl substituents of the 5,5′-dimethyl-2,2′-bipyridine ligand are magnetically inequivalent in **1b** (two methyl singlets at δ = 2.34 and 2.22 ppm in the ^{1}H NMR spectrum of the complex).

The geometry of the heptacoordinate hydrido complexes **1** may be discussed in terms of three limiting structures, namely pentagonal bipyramidal, monocapped octahedral, or monocapped trigonal prismatic. The spectroscopic data do not allow us to distinguish between these possible structures, although it is plausible that the same geometry observed in the solid state for **1a** is also maintained in solution. A monocapped octahedral geometry of type **I**, which contains two magnetically equivalent phosphites that are different from the third and the hydrido ligand in a *cis* position with respect to each of the three phosphite groups, is in full accordance with the observed NMR spectroscopic data.

The ^{1}H and ^{31}P NMR spectra of the [ReH$_2$(bpy)P$_3$]$^+$ cation **2a** indicate that the complex is fluxional. The broad signals present at room temperature in the ^{31}P NMR spectrum resolve into an AM_2 multiplet at –30 °C, thereby suggesting the presence of two phosphonites that are magnetically equivalent and different from the third. At the same temperature, the ^{1}H NMR spectrum shows sharp signals



I

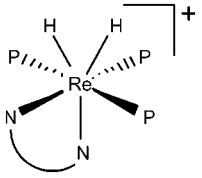
attributable to phosphonite and bpy ligands and a multiplet at δ = –5.31 ppm for the hydrido ligands. Variable-temperature T_1 measurements (200 MHz) on this signal gave a T_{1min} value of 104 ms (Table 2), in agreement[16] with the classical nature of the dihydrido derivative **2a**. The hydrido multiplet at δ = –5.31 ppm can also be simulated with an AM_2X_2 (X = ^{1}H) model, with the parameters listed in

Table 2. ^{1}H NMR spectroscopic data (200 MHz; δ values, ppm) in the hydrido region for some rhenium complexes.

Compound	T [K]	δ (M–H)	T_{1min} [ms]
[ReH$_2$(bpy){PPh(OEt)$_2$}$_3$]BPh$_4$ (**2a**)	205	–5.45	104
[ReH$_2$(bpy)(CO)$_3$]BPh$_4$ (**3a**)	198	–13.1	112
[ReH$_2$Cl(bpy){PPh(OEt)$_2$}$_3$]$^{2+}$ (**4a**)	200	–7.84	76
[ReH$_3$(bpy){PPh(OEt)$_2$}$_3$]$^{2+}$ (**5a**)	208	–2.15	65
	203	–3.10	83

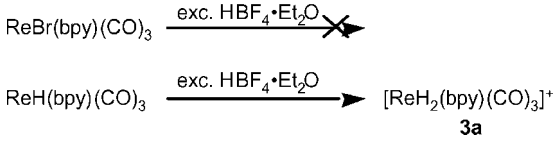
Table 1, and the good fit between experimental and calculated spectra indicates the magnetic equivalence of the two hydrido ligands.

The spectroscopic data strongly support the proposed formulation for complex **2a** but do not allow us to unambiguously assign its geometry in solution. However, by analogy with the related monohydrido **1**, a monocapped octahedral geometry of type **II** may also be proposed for dihydrido complex **2a**; this ligand arrangement fits the reported NMR spectroscopic data.



II

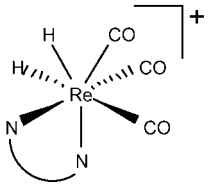
The easy synthesis of mono- and dihydridorhenium(III) complexes **1** and **2a** prompted us to extend our studies to related complexes containing carbonyl ligands. The method used was the protonation of Re^{I} compounds of the type $[ReH(bpy)(CO)_3]$[17] and $[ReBr(bpy)(CO)_3]$ (Scheme 3).



Scheme 3.

Although $[ReBr(bpy)(CO)_3]$ was found to be unreactive toward an excess of HBF_4, $[ReH(bpy)(CO)_3]$ reacts quickly with HBF_4 to give the dihydrido cation $[ReH_2(bpy)(CO)_3]^+$, which was isolated as its BPh_4 salt and characterized. Good analytical data were obtained for complex **3**, which is a yellow solid that is stable in air and in solution in polar organic solvents, where it behaves as a 1:1 electrolyte.[12] The IR spectrum of **3a** shows three strong absorptions in the ν_{CO} region attributable to three carbonyl ligands in a mutually *fac* position. Besides the signals of the bpy ligand and the BPh_4 anion, the ^1H NMR spectrum shows two doublets at δ = –13.07 and –17.47 ppm ($J_{H,H}$ = 3.4 Hz) for the two hydrido ligands, which means they are magnetically inequivalent. T_1 measurements on these hydrido signals were also performed and gave T_{1min} values near 112 ms, in good agreement[16] with the classical nature of these hydrido ligands. On this basis, we hypothesize that the reaction of $[ReH(bpy)(CO)_3]$ with HBF_4 does not proceed by protonation of the Re–H bond to give an η^2-H_2 ligand but involves the oxidative addition of H^+ to yield the formal cationic Re^{III} derivative $[ReH_2(bpy)(CO)_3]^+$. Oxidative addition of H^+ to a Re^{I} complex is rather rare[3e] as formation of the dihydrogen [Re]-η^2-H_2 complex is the more usual result of protonation.[3i,4a,11b] The presence of the bpy ligand probably strongly influences the course of the protonation reaction that leads to the Re^{III} species **3**.

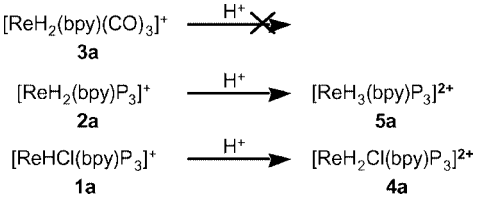
Although the IR and NMR spectroscopic data do not allow us to assign geometries to the complex, a monocapped octahedral geometry of type **III**, like those proposed for complexes **1** and **2a**, fits the spectroscopic data and may be tentatively proposed for the $[ReH_2(bpy)(CO)_3]^+$ derivative **3a**.



III

Reactivity

Protonation of the new hydrido complexes **1**, **2a**, and **3a** with a Brønsted acid was studied with the aim of testing whether η^2-H_2 complexes could be formed. The results show that, although $[ReH_2(bpy)(CO)_3]^+$ (**3a**) is unreactive towards an excess of HBF_4·Et_2O, phosphonite complexes **1a** and **2a** give the new Re^{V} hydrido complexes **4** and **5**, respectively, as shown in Scheme 4.



Scheme 4. P = $PPh(OEt)_2$.

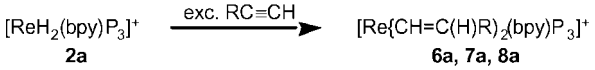
The protonation was carried out at variable temperature and was monitored by ^1H and ^{31}P NMR spectroscopy. The addition of HBF_4·Et_2O to a CD_2Cl_2 solution of the dihydrido cation $[ReH_2(bpy)P_3]^+$ (**2a**) at –80 °C caused the disappearance of the hydrido signal at δ = –5.4 ppm in the ^1H NMR spectrum and the appearance of two new multiplets with an intensity ratio of 2:1 at δ = –2.2 and at –3.1 ppm, respectively. Variable-temperature T_1 measurements (Table 2) on these signals gave T_{1min} values (200 MHz) of 65 and 83 ms, respectively, which suggests a classical structure for the protonated $[ReH_3(bpy)P_3]^+$ derivatives. Protonation of the dihydrido cation $[ReH_2(bpy)P_3]^+$ therefore proceeds by oxidative addition of H^+ to the metal center to give the octacoordinate Re^{V} trihydrido derivative **5a**. It should be noted that a twofold excess of HBF_4·Et_2O must be used to complete the formation of **5a**, the ^{31}P NMR spectrum of which shows an A_2B multiplet at –80 °C that can be simulated with the parameters listed in Table 1.

Addition of an excess of NEt_3 to a solution of **5a** regenerates the starting dihydrido complex $[ReH_2(bpy)P_3]^+$ and, although complex **5a** was not isolated, its spectroscopic data strongly support its formulation as the mixed-ligand rhenium(V) trihydrido complex $[ReH_3(bpy)P_3]^{2+}$, which contains three phosphonites and a bipyridine.

Protonation of cationic hydrido complexes has been reported previously[9,19] and often proceeds, in the presence of a large excess of Brønsted acid, to give η^2-H_2 derivatives. The relatively easy oxidative addition of H^+ to a cationic Re^{III} hydrido complex to yield a Re^V polyhydrido complex similar to **5a** may be due to the presence of the polypyridine ligand, which is able to stabilize classical dicationic hydrido complexes in a high oxidation state.

Reaction of the hydrido-chlorido $[ReH(Cl)(bpy)P_3]^+$ cation **1a** also proceeds with $HBF_4{\cdot}Et_2O$ at –80 °C to give the new hydrido cation $[ReH_2Cl(bpy)P_3]^{2+}$ (**4a**) (Scheme 4), although in this case a large excess of acid is required to complete the reaction. The ^1H and $^{31}P\{^1H\}$ NMR spectroscopic data also suggest the presence of two isomers for **4a**, which shows two multiplets at δ = –5.50 and –7.84 ppm in the ^1H NMR spectrum and two A_2M multiplets in the ^{31}P NMR spectrum. T_1 measurements on the hydrido proton multiplets (Table 2) confirmed the classical nature of the protonated complex, which suggests that oxidative addition of H^+ also takes place in the hydrido-chlorido complexes to yield the rhenium(V) polypyridine derivative **4a**. The two Re^{III} hydrido complexes **1a** and **2a**, which contain a polypyridine and phosphonites as supporting ligands, therefore show parallel behavior during the oxidative addition of H^+ and afford a dicationic octacoordinate polyhydrido Re^V complex.

Reactivity studies on hydrido cations **1** and **2a** were extended to substitution and insertion reactions, and the results revealed the relatively high stability of both complexes. Substitution reactions with carbonyl, phosphane, nitrile, or isocyanide ligands and insertion reactions with unsaturated molecules such as ArN_2^+, $RCH{=}CH_2$, CO_2, CS_2, etc. proved impossible for both complexes. However, one reaction was observed for **2a**, which reacts with terminal alkynes to give the bis(vinyl) derivatives $[Re\{CH{=}C(H)R\}_2(bpy)P_3]^+$ (**6a**, **7a**, and **8a**), as shown in Scheme 5.



Scheme 5. P = $PPh(OEt)_2$; R = Ph **6a**, *p*-tolyl **7a**, *tert*-butyl **8a**.

The reaction is quite slow at room temperature, and the synthesis of pure vinyl complexes **6a**–**8a** can be achieved only at reflux conditions. In every case, the reaction proceeds with the insertion of two alkynes into the Re–H bond to give only bis(vinyl) derivatives **6a**, **7a**, and **8a**. The absence of any mono-insertion product such as $[ReH\{CH{=}C(H)R\}_2(bpy)P_3]^+$ is probably due to a faster insertion rate of the second alkyne with respect to the first into the Re–H bond of **2a**. The need for reflux conditions to obtain the vinyl complexes may be explained by the fact that the mechanism proposed[20] for the insertion of an alkyne into an M–H bond usually requires a vacant site, and only at higher temperatures can the substitution of one ligand by an alkyne take place.

Vinyl complexes of rhenium are rare[21] and in some cases have been proposed only as intermediates.[22] Our reaction of dihydrido compound **2a** with a terminal alkyne provides new examples of this class of derivatives. Vinyl complexes **6a**–**8a** are green solids that are stable in air and in solution in polar organic solvents, where they behave as 1:1 electrolytes.[12] The analytical and spectroscopic data (Tables 1 and 3) support their proposed formulation. Thus, besides the signals of the polypyridine, phosphites, and the BPh_4 anion, the ^1H NMR spectrum shows a slightly broad multiplet at around δ = 6.45–6.51 ppm due to H_β of the vinyl ligand. This multiplet was correlated in a COSY experiment with a signal overlapping the phenyl resonances at δ = 7.04–7.09 ppm, which was attributed to the H_α proton of the vinyl ligand. As the ^{31}P NMR spectrum in the temperature range between +20 and –80 °C is an AB_2 multiplet, the H_α and H_β vinyl signals can be simulated with an AB_2XY (X = H_α, Y = H_β) model with the parameters listed in Table 1. The values of the proton-proton coupling constants $J_{X,Y}$ of 7.7 (**7a**) and 8.4 Hz (**8b**) also suggest a *cis* arrangement[23] of the two vinyl protons.

Table 3. $^{13}C\{^1H\}$ NMR spectroscopic data for vinyl complexes **7a** and **8a**.

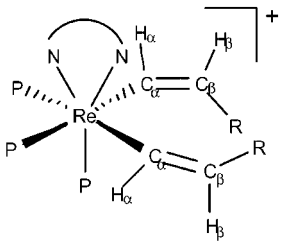
Compound	$^{13}C\{^1H\}$ NMR[a]	
	δ	Assignment
7a	165–122 (m)	Ph + bpy
	131.2 (s)	$=CH_\beta$
	128.6 (m)	$=CH_\alpha$
	67.4 (d)	CH_2
	66.4 (d)	
	16.6 (m)	CH_3 phos
	11.3 (s)	CH_3 *p*-tolyl
8a	163–122 (m)	Ph + bpy
	129.1 (m)	$=CH_\alpha$
	123.8 (s)	$=CH_\beta$
	67.4 (m)	CH_2
	65.4 (s)	$C(CH_3)_3$
	30.5 (s)	$C(CH_3)_3$
	16.9 (m)	CH_3 phos

[a] In CD_2Cl_2 at 25 °C. Chemical shifts are given in ppm and coupling constants in Hz.

The ^{13}C NMR spectra (Table 3) confirm the presence of the vinyl group in compounds **6**–**8** by the presence of a multiplet at δ = 128–129 ppm attributed to C_α and another at δ = 123–131 ppm attributed to C_β of the vinyl ligand. HMQC and HMBC experiments confirmed this assignment as the multiplets at δ = 123–131 ppm in the ^{13}C spectra are correlated to the proton signals near δ = 6.5 ppm due to the H_β vinyl resonance, whereas the ^{13}C signal at δ = 128–129 ppm is correlated with the signal at δ = 7.04–7.09 ppm due the H_α vinyl proton, in agreement with the proposed assignment of these signals.

These spectroscopic data strongly support the proposed formulation for the complexes but do not allow us to unambiguously assign geometries to the complexes. Assuming a monocapped octahedral geometry for these vinyl complexes as well, a structure of type **IV**, with two magnetically equiv-

alent vinyl groups and two magnetically equivalent phosphonites that are different from the third, fits the spectroscopic data. However, the absence of any X-ray crystal structure due to the poor quality of the obtained crystals means that geometry **IV** is only a tentative proposal.



IV

Conclusions

We have described the synthesis of the mixed-ligand hydridorhenium(III) complexes $[ReHCl(N–N)P_3]BPh_4$ (**1**) and $[ReH_2(N–N)P_3]BPh_4$ (**2a**), both of which contain phosphonite and polypyridine ligands. The hydrido carbonyl cations $[ReH_2(bpy)(CO)_3]^+$ have also been obtained by the oxidative addition of H^+ to Re^I derivatives. The structural parameters for the heptacoordinate $[ReHCl(bpy)P_3]^+$ cation have been obtained by X-ray crystallography. Among the properties shown by the new Re^{III} hydrido complexes we can highlight the easy protonation of cationic complexes **1** and **2a** to give classical Re^V hydrido derivatives, and the reaction of **2a** with terminal alkynes to afford new examples of vinyl complexes of rhenium.

Experimental Section

General: All synthetic work was carried out under an inert atmosphere (Ar, N_2) using standard Schlenk techniques or a dry box (Vacuum Atmospheres, Mecaplex, CH). All solvents were dried with appropriate drying agents, degassed on a vacuum line, and distilled into vacuum-tight storage flasks. $Re_2(CO)_{10}$ was a Pressure Chemical Co. (USA) product, while Re powder was purchased from Chempur (Germany); both were used as received. The phosphonite $PPh(OEt)_2$ and phosphinite PPh_2OEt were prepared according to Rabinowitz and Pellon.[24] Other reagents were purchased from commercial sources with the highest available purity and used as received. IR spectra were recorded with a Nicolet Magna 750 or Perkin–Elmer Spectrum One FT-IR spectrophotometer. NMR spectra (^1H, ^{31}P, ^{13}C) were obtained with an AC200 or Avance 300 Bruker spectrometer at temperatures between –80 and +30 °C, unless otherwise noted. ^1H and ^{13}C NMR spectra are referenced to internal tetramethylsilane; $^{31}P\{^1H\}$ chemical shifts are reported with respect to 85% H_3PO_4, with downfield shifts considered positive. The COSY, HMQC, and HMBC NMR experiments were performed using the standard programs. Values of T_{1min} (±10%) were determined by the inversion recovery method between –90 and +30 °C in CD_2Cl_2 with a standard 180°–τ–90° pulse sequence. The SwaN-MR software package[25] was used to treat NMR spectroscopic data. The conductivity of 10^{-3} M solutions of the complexes in CH_3NO_2 at 25 °C was measured with a Radiometer CDM 83. Elemental analyses were determined by the Microanalytical Laboratory of the Dipartimento di Scienze Farmaceutiche of the University of Padua, Italy.

Synthesis of Complexes: $[ReCl_3P_3]$, $[ReBr(CO)_5]$, and $[ReH(CO)_5]$ [P = $PPh(OEt)_2$, PPh_2OEt] were prepared following the previously reported methods.[11a,26]

$[ReHCl(N–N)\{PPh(OEt)_2\}_3]BPh_4$ (1) [N–N = 2,2′-bipyridine (bpy) (a), 5,5′-dimethylbipyridine (5,5′-Me_2bpy) (b), 1,10-phenanthroline (phen) (c)]: $[ReCl_3\{PPh(OEt)_2\}_3]$ (0.50 g, 0.56 mmol) and the appropriate polypyridine N–N (1.7 mmol) were placed in a 50-mL, three-necked, round-bottomed flask and dissolved in 30 mL of ethanol. The resulting mixture was refluxed for 5 h and then the solvent was removed under reduced pressure to give a brown solid from which the hydrido complex was extracted with five 10-mL portions of CH_2Cl_2. The combined extracts were evaporated to dryness to give an oil, which was treated with ethanol (5 mL) containing an excess of $NaBPh_4$ (1.7 mmol, 0.58 g). A dark-green solid separated out. This solid was filtered and crystallized from CH_2Cl_2 and ethanol. Yields: 0.45 g for **1a** (62%), 0.48 g for **1b** (65%), 0.33 g for **1c** (45%).

1a: $C_{64}H_{74}BClN_2O_6P_3Re$ (1292.7): calcd. C 59.47, H 5.77, Cl 2.74, N 2.17; found C 59.39, H 5.63, Cl 2.58, N 2.24. Λ_M = 54.9 $S\,cm^2\,mol^{-1}$.

1b: $C_{66}H_{78}BClN_2O_6P_3Re$ (1320.7): calcd. C 60.02, H 5.95, Cl 2.68, N 2.12; found C 59.87, H 6.02, Cl 2.80, N 2.21. Λ_M = 51.3 $S\,cm^2\,mol^{-1}$.

1c: $C_{66}H_{74}BClN_2O_6P_3Re$ (1316.7): calcd. C 65.38, H 5.66, Cl 2.69, N 2.13; found C 65.16, H 5.75, Cl 2.86, N 2.05. Λ_M = 52.8 $S\,cm^2\,mol^{-1}$.

$[ReH_2(bpy)\{PPh(OEt)_2\}_3]BPh_4$ (2a): $[ReCl_3\{PPh(OEt)_2\}_3]$ (0.50 g, 0.56 mmol) and 2,2′-bipyridine (0.266 g, 1.7 mmol) were placed in a 50-mL, three-necked, round-bottomed flask and 20 mL of ethanol was added. The mixture was stirred and refluxed for 5 h and then allowed to reach room temperature. An excess of $NaBH_4$ (0.211 g, 5.6 mmol) in ethanol (10 mL) was then added and the mixture refluxed for 1 h. The solvent was removed under reduced pressure to give an oil, from which the hydrido complex was extracted with five 10-mL portions of CH_2Cl_2. The extracts were evaporated to dryness to give an oil, which was triturated with ethanol (5 mL) containing an excess of $NaBPh_4$ (1.7 mmol, 0.58 g). A red-brown solid slowly separated out. This solid was filtered and crystallized from CH_2Cl_2 and ethanol. Yield: 0.40 g (57%). $C_{64}H_{75}BN_2O_6P_3Re$ (1258.2): calcd. C 61.09, H 6.01, N 2.23; found C 61.25, H 5.84, N 2.12. Λ_M = 54.7 $S\,cm^2\,mol^{-1}$.

$[ReH(bpy)(CO)_3]$: This compound was prepared by a new method rather than that reported in the literature.[6] Thus, $[ReH(CO)_5]$ (0.35 mL, 2.05 mmol) and one equivalent of 2,2′-bipyridine (0.32 g, 2.05 mmol) were placed in a 250-mL, three-necked, round-bottomed flask and 100 mL of toluene was added. The reaction mixture was refluxed for 4 h and then the solvent was removed under reduced pressure to give an oil, which was triturated with ethanol (5 mL). An orange solid slowly separated out from the resulting stirring solution. This solid was filtered and dried under vacuum. Yield: 0.307 g (35%). $C_{13}H_9N_2O_3Re$ (427.43): calcd. C 36.53, H 2.12, N 6.55; found C 36.71, H 2.05, N 6.42. IR (KBr): $\tilde{\nu}$ = 2032 (m), 1976 (s), 1912 cm^{-1} [s (ν_{CO})]. ^1H NMR (CD_2Cl_2, 25 °C): δ = 9.13–7.56 (m, bpy), –13.02 (s, ReH) ppm.

$[ReBr(bpy)(CO)_3]$: This compound was prepared by a slight modification of the reported method.[27] Thus, $[ReBr(CO)_5]$ (1 g,

2.46 mmol) and 2,2′-bipyridine (1.15 g, 7.38 mmol) were placed in a 100-mL, three-necked, round-bottomed flask and 30 mL of toluene was added. The mixture was stirred, refluxed for 5 h, and then allowed to reach room temperature. A yellow solid separated out which, after 1 h of stirring, was filtered and dried under vacuum. Yield: 1.01 g (81%). $C_{13}H_8BrN_2O_3Re$ (506.32): calcd. C 30.84, H 1.59, N 5.53; found C 30.66, H 1.68, N 5.40. IR (KBr): $\tilde{\nu}$ = 2012 (m), 1905 (s), 1882 cm^{-1} [s (ν_{CO})]. ^1H NMR (CD_2Cl_2, 25 °C): δ = 9.06–7.53 (m, bpy) ppm.

[ReH_2(bpy)$(CO)_3$]BPh_4 (3a): An excess of $HBF_4{\cdot}Et_2O$ (2.3 mmol, 0.33 mL of a 54% solution in diethyl ether) was added to a solution of [ReH(bpy)$(CO)_3$] (0.100 g, 0.23 mmol) in CH_2Cl_2 (7 mL) at –196 °C. The reaction mixture was then brought to room temperature and stirred for 2 h. The solvent was removed under reduced pressure to give an oil, which was triturated with ethanol (2 mL) containing an excess of $NaBPh_4$ (0.46 mmol, 0.157 g). A yellow solid slowly separated out from the resulting solution. This solid was filtered and crystallized from CH_2Cl_2 and ethanol; yield 0.134 g (78%). $C_{37}H_{30}BN_2O_3Re$ (747.67): calcd. C 59.44, H 4.04, N 3.75; found C 59.27, H 4.01, N 3.68. Λ_M = 53.5 $S cm^2 mol^{-1}$.

[ReH_2(Cl)(bpy){PPh$(OEt)_2$}$_3$]$^{2+}$ (4a) and [ReH_3(bpy){PPh$(OEt)_2$}$_3$]$^{2+}$ (5a): These cationic complexes were prepared in CD_2Cl_2 solution by protonation of the precursors [ReH(Cl)(bpy)P_3]BPh_4 (**1a**) and [ReH_2(bpy)P_3]BPh_4 (**2a**) with $HBF_4{\cdot}Et_2O$. In a typical experiment, a CD_2Cl_2 solution (0.5 mL) of **1a** or **2a** (30–40 mg, 0.02–0.03 mmol) was placed in a screw-cap 5-mm NMR tube placed in a dry box. The tube was sealed, cooled to –80 °C, and then increasing amounts (from one to four equivalents) of $HBF_4{\cdot}Et_2O$ were added with a microsyringe. The tube was then transferred into the instrument's probe, which had been pre-cooled to –80 °C, and the spectra collected.

[Re{CH=C(H)R}$_2$(bpy){PPh$(OEt)_2$}$_3$]BPh_4 (6–8) [R = Ph (6a), *p*-tolyl (7a), *tert*-butyl (8a)]: An excess of the appropriate alkyne RC≡CH (0.8 mmol) was added to a solution of [ReH_2(bpy){PPh$(OEt)_2$}$_3$]BPh_4 (0.100 g, 0.079 mmol) in 12 mL of 1,2-dichloroethane and the reaction mixture refluxed for 1 h. The solvent was removed under reduced pressure to give an oil, which was triturated with ethanol (2 mL) containing an excess of $NaBPh_4$ (0.2 mmol, 68 mg). A green solid slowly separated out from the resulting solution. This solid was filtered and crystallized from CH_2Cl_2 and ethanol. Yield 0.079 g for **6a** (68%), 0.081 g for **7a** (69%), 0.082 g for **8a** (73%).

6a: $C_{80}H_{87}BN_2O_6P_3Re$ (1462.5): calcd. C 65.70, H 6.00, N 1.92; found C 65.49, H 5.93, N 1.88. Λ_M = 53.1 $S cm^2 mol^{-1}$.

7a: $C_{82}H_{91}BN_2O_6P_3Re$ (1490.6): calcd. C 66.08, H 6.15, N 1.88; found C 65.91, H 6.24, N 1.80. Λ_M = 54.6 $S cm^2 mol^{-1}$.

8a: $C_{76}H_{95}BN_2O_6P_3Re$ (1422.5): calcd. C 64.17, H 6.73, N 1.97; found C 64.38, H 6.86, N 2.08. Λ_M = 52.8 $S cm^2 mol^{-1}$.

Crystallographic Analysis of [ReHCl(bpy){PPh$(OEt)_2$}$_3$]BPh_4 (1a): Data collection was performed on a SIEMENS Smart CCD area-detector diffractometer with graphite-monochromated Mo-K_α radiation. Absorption correction was carried out using SADABS.[28] The structure was solved and refined with the Oscail program[29] by Patterson methods and refined by a full-matrix least-squares procedure on F^2.[30] Non-hydrogen atoms were refined with anisotropic displacement parameters. Hydrogen atoms were included in idealized positions and refined with isotropic displacement parameters except that bonded to the rhenium atom, which was neither located nor included in the model. Atomic scattering factors and anomalous dispersion corrections for all atoms were taken from International Tables for X-ray Crystallography.[31] Details of crystal data and structural refinement are given in Table 4 and selected bond lengths and angles are listed in Table 5.

Table 4. Crystal data and structure refinement for [ReHCl(bpy){PPh$(OEt)_2$}$_3$]BPh_4 (**1a**).

Empirical formula	$C_{64}H_{74}BClN_2O_6P_3Re$
Formula weight	1292.68
Temperature	173(2) K
Wavelength	0.71073 Å
Crystal system	monoclinic
Space group	$P2_1/c$
Unit cell dimensions	a = 14.7335(18) Å b = 14.7029(19) Å c = 27.823(4) Å β = 90.929(4)°
Volume	6026.4(13) $Å^3$
Z	4
Density (calculated)	1.421 $Mg m^{-3}$
Absorption coefficient	2.192 mm^{-1}
F(000)	2636
Crystal size	0.25 × 0.16 × 0.10 mm^3
Theta range for data collection	1.38–28.02°
Index ranges	$-19 \le h \le 19$ $-13 \le k \le 19$ $-36 \le l \le 32$
Reflections collected	31483
Independent reflections	13368 [R(int) = 0.1562]
Reflections observed (>2σ)	3916
Data completeness	0.915
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	1.000 and 0.791
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	13368/0/709
Goodness-of-fit on F^2	0.692
Final R indices [$I > 2\sigma(I)$]	R_1 = 0.0659, wR_2 = 0.0835
R indices (all data)	R_1 = 0.2677, wR_2 = 0.1154
Largest diff. peak and hole	1.128 and –1.397 e $Å^{-3}$

Table 5. Selected bond lengths [Å] and angles [°] for [ReH(Cl)(bpy){PPh$(OEt)_2$}$_3$]BPh_4 (**1a**).

Re–N(2)	2.172(10)	Re–N(1)	2.180(9)
Re–P(1)	2.286(3)	Re–P(2)	2.316(3)
Re–P(3)	2.365(3)	Re–Cl(1)	2.450(3)
N(2)–Re–N(1)	75.7(4)	N(2)–Re–P(1)	80.2(2)
N(1)–Re–P(1)	99.9(2)	N(2)–Re–P(2)	101.3(3)
N(1)–Re–P(2)	171.7(2)	P(1)–Re–P(2)	87.06(10)
N(2)–Re–P(3)	168.7(3)	N(1)–Re–P(3)	98.7(3)
P(1)–Re–P(3)	110.68(11)	P(2)–Re–P(3)	82.84(10)
N(2)–Re–Cl(1)	79.2(2)	N(1)–Re–Cl(1)	84.7(2)
P(1)–Re–Cl(1)	157.02(10)	P(2)–Re–Cl(1)	87.09(10)
P(3)–Re–Cl(1)	90.58(10)		

CCDC-626730 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Center via www.ccdc.cam.ac.uk/data_request/cif.

Acknowledgments

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