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Water soluble phosphine rhenium complexes

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ABSTRACT

Reduction of $[NMe_4]_2[ReBr_5(NO)]$ (**1**) with zinc in acetonitrile leads to the known trisacetonitrile compound $[ReBr_2(CH_3CN)_3(NO)]$ (**2**). Attempts to turn **2** into a dihydrogen or a hydride complex applying direct reaction with H_2 or with H_2 and a base were unsuccessful. Complex **2** could be transformed into $[ReBr(BF_4)$*mer*-$(CH_3CN)_3(NO)]$ (**2a**) with $AgBF_4$ in acetonitrile and was used as a starting material in a ligand exchange reaction with the water soluble phosphine 1,3,5-triaza-7-phosphadamantane (PTA) to obtain the complex $[ReBr_2(NO)(PTA)_3]$ (**3**). When the reduction of **1** with zinc was carried out in the presence of PTA in acetonitrile, the disubstituted complex $[ReBr_2(CH_3CN)(NO)(PTA)_2]$ (**4**) was formed. The olefin-coordinated rhenium complexes $[ReBr_2(NO)(CH_2{=}CH_2)(PTA)_2]$ (**5a**) and $[ReBr_2(NO)(PhCH{=}CH_2)(PTA)_2]$ (**5b**) were obtained from the reaction of **4** with the corresponding olefins. Complex **4** reacts further with $NaHBEt_3$ in THF to give the dihydride $[ReH_2(THF)(NO)(PTA)_2]$ (**6**). In the presence of ethylene **6** is transformed into the ethyl hydride complex $[ReH(CH_2CH_3)(\eta^2\text{-}C_2H_4)(NO)(PTA)_2]$ (**7**). Complexes **6** showed catalytic activity in the hydrogenation of olefins.

1. Introduction

Catalysis in water possesses great ecological and economical advantages [1]. Recently developed water soluble hydrogenation catalysts are the $[RhCl(TPPMS)_3]$, where TPPMS is the water soluble triphenylphosphine monosulfonate and its PTA analogue $[RhCl(PTA)_3]$ [2–4]. PTA [5] is a neutral, strongly donating, small-cone-angle, polar, air and water stable phosphine ligand, first prepared in 1974 [6]. Rhenium based catalysts were recently shown to be active in hydrosilylations and in Ring Opening Metathesis Polymerization (ROMP) [7–10]. A phosphine nitrosyl rhenium chemistry is accomplished best starting from the paramagnetic salt $[NEt_4]_2[ReBr_5(NO)]$ reacting this in ligand exchange processes with different phosphines [8,11]. Related explorations on PTA substituted rhenium compounds were initiated to approach water soluble catalysis. In this paper we probed the $[NMe_4]_2[ReBr_5(NO)]$ salt and the dibromotris(acetonitrile)nitrosyl rhenium complex as a starting material.

2. Results and discussion

2.1. Bis- and tris-PTA nitrosyl rhenium complexes

Tetramethylammonium pentabromonitrosyl rhenate $[NMe_4]_2[ReBr_5(NO)]$ [9] (**1**) is indeed a versatile starting material to access rhenium nitrosyl compounds. Its facile preparation from rhenate (VII) salts and its high solubility in a variety of solvents, such as EtOH, MeOH, glyme, diglyme, CH_2Cl_2, acetone, CH_3CN (S = 47.5 g/L 25 °C) and THF (S = 267 g/L 25 °C), makes it an ideal reagent for this chemistry. It may be used in synthetic routes with primary introduction of the NO ligand, which seems to be in many respects superior over those routes applying nitrosylation at later stages of the synthetic pathway. Scheme 1 shows a variety of complexes with the water soluble 1,3,5-triaza-7-phosphadamantane ligand (PTA), which were prepared based on this material. Reduction of **1** with zinc in acetonitrile yielded the known dibromotris(acetonitrile)nitrosyl rhenium complex **2** [9]. One bromide of **2** could be exchanged with a BF_4^- ligand *via* the reaction with $AgBF_4$ in methylene chloride at room temperature, which resulted in the formation of the pseudo octahedral species $[ReBr(BF_4)$*mer*-$(CH_3CN)_3(NO)]$ (**2a**) possessing a coordinated BF_4^- ligand located *trans* to the nitrosyl ligand. The mixture was filtered and the solvent was removed. The resulting solid was washed several times with diethyl ether giving pure **2a**.

Subsequent treatment of **2** with three equivalents of PTA in refluxing dioxane gave entry to a water soluble chemistry producing the $[Re(PTA)_3Br_2(NO)]$ complex (**3**) in high yield. Complex **3** possesses a *mer* arrangement of the three phosphine groups. The ^1H NMR spectrum of **3** is consistent with the given structure. It exhibits a broad signal at 4.49 ppm for the 18 protons of the N–CH_2–N groups of all three PTA ligands. Two other broad signals at 4.34 and 4.14 ppm were assigned to the 12 protons of the P–CH_2–N groups of the two PTA in *trans* position and 6 protons of the P–CH_2–N group of the PTA in equatorial position. The

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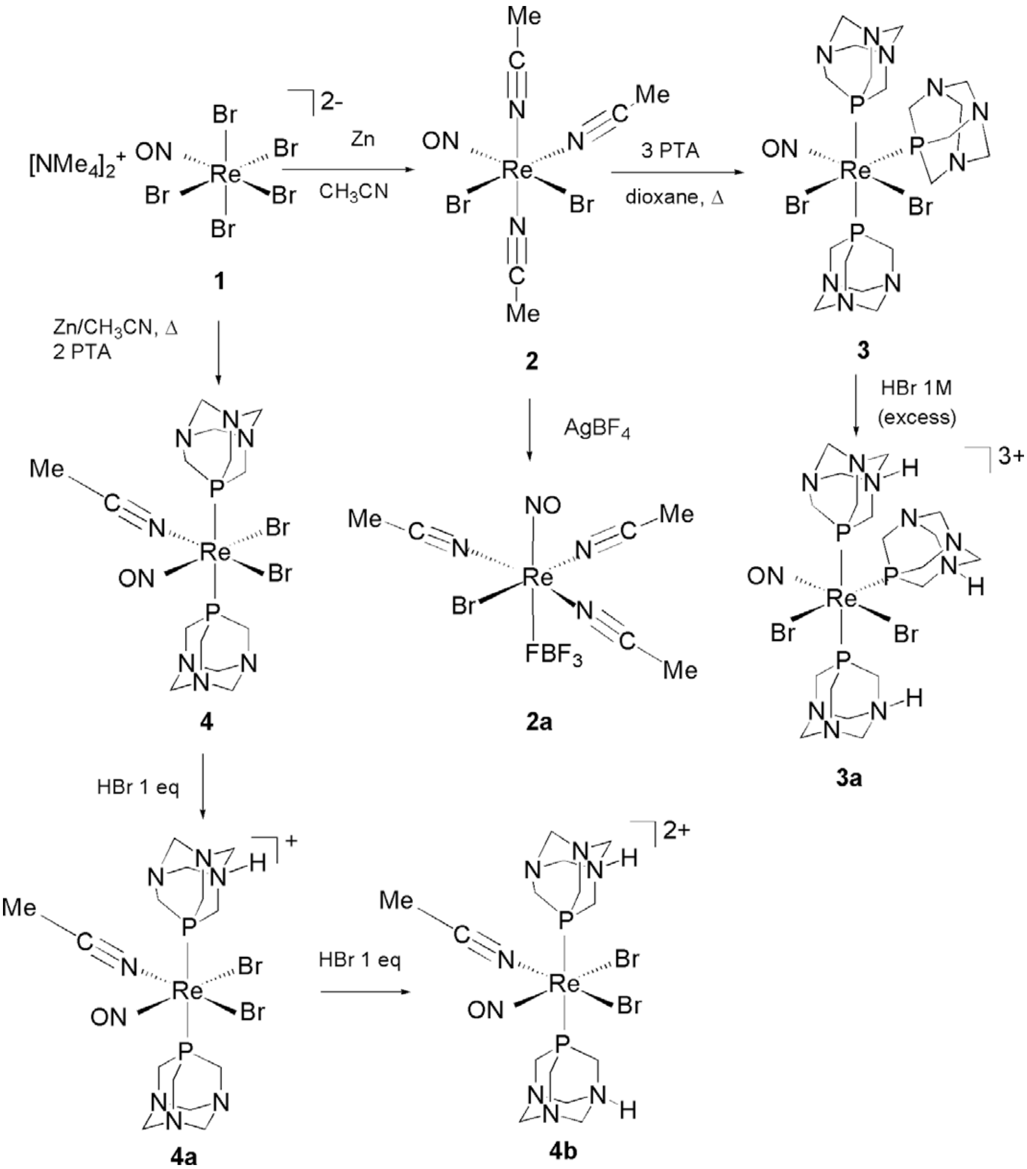


Scheme 1.

$^{31}P\{^1H\}$ NMR spectrum also confirmed the proposed structure exhibiting a characteristic doublet and triplet pattern in a 2:1 ratio at −70.4 and −88.0 ppm, respectively.

The $^{13}C\{^1H\}$ NMR spectrum of **3** exhibits the expected signals originating from the PTA ligand. Crystals of **3** suitable for a X-ray diffraction study could not be obtained, therefore we choose to crystallize its protonated derivative $[ReBr_2(NO)(PTAH)_3][Br]_3\cdot 4H_2O$ (**3a**) obtained from **3** *via* treatment with a 1 M HBr solution. The crystal structure of **3a** is shown in Fig. 1. Selected bond distances and angles are reported in Table 1. Complex **3a** exhibits a distorted octahedral geometry. The protonation of each PTA ligand occurs just at one nitrogen atom. Like at the free $PTAH^+$ cation further *N*-protonation of the $PTAH^+$ ligands does not occur [5]. As a consequence of the protonation, the C–N bond distances of the carbon atoms adjacent to the protonated nitrogen were elongated with mean values of 1.509(10) Å. The mean value of the C–N bond distances of the non-protonated nitrogen atoms is 1.451(15) Å. The same trends were observed in other related complexes with $PTAH^+$ ligands [11–16]. Protonation at the nitrogen atom of PTA can also be traced by NMR spectroscopy showing for the PTA ^1H and ^{31}P NMR signals shifts to lower fields, while the corresponding carbon resonances are found to be shifted downfield in the ^{13}C NMR spectra [16].

The pK_a value of the free $PTAH^+$ is reported to possess a value between 5.3 and 6.0 [17–19]. Coordinated $PTAH^+$ ligands are expected to be still more acidic [17,19,20]. To determine the pK_a values of **3**, NMR titration studies were sought *via* $^{31}P\{^1H\}$ NMR spectroscopic pursuit of the chemical shifts of the doublet and the triplet signal and plotting for both resonances δ versus pH (see Fig. 2 for the doublet). The results of the analysis for the two resonances were taken with confidence, since the $pK_a(1)$ and $pK_a(2)$ values found for the two types of PTA ligands were found to be quite close. The pK_a values of the doublet are: $pK_a(1) = 2.97 \pm 0.02$, $pK_a(2) = 4.04 \pm 0.02$, and those of the triplet: $pK_a(1) = 2.83 \pm 0.01$, $pK_a(2) = 4.02 \pm 0.05$. Their calculated weighted means are $pK_a(1) = 2.89 \pm 0.21$ and $pK_a(2) = 4.04 \pm 0.04$. Based on the $^{31}P\{^1H\}$ NMR chemical shifts, the $pK_a(2) = 4.04 \pm 0.04$ were assigned to the *trans* PTA ligands, which apparently are somewhat more basic. The $pK_a(1) = 2.89 \pm 0.21$ is assigned to the equatorial PTA ligand. Once **3a** was deprotonated by more than an aliquot of NaOH,

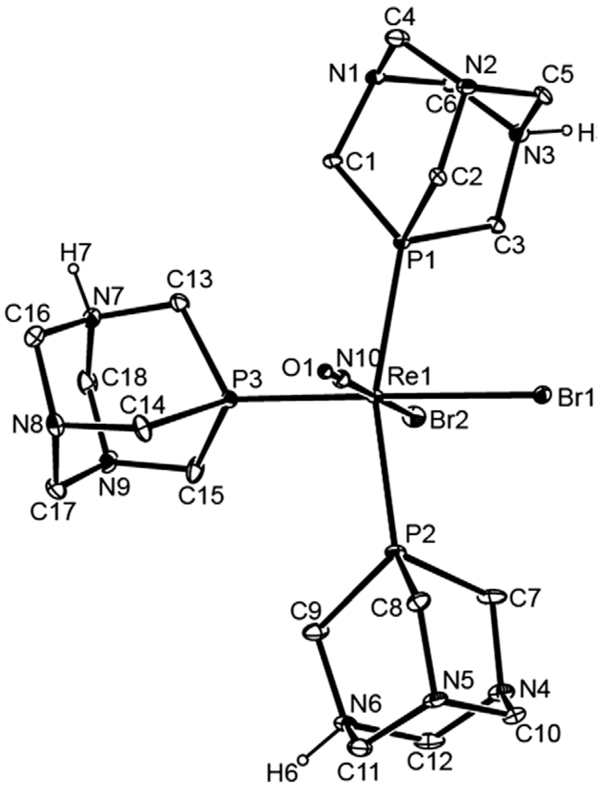


Fig. 1. Model of the X-ray structure of **3a**. ORTEP representation with selected atomic labels. Hydrogen atoms and disorder observed between some bromine ions and H_2O molecules are omitted for clarity except for the H_N atoms of the phosphine groups. The displacement ellipsoids are drawn with 10% probability.

Table 1
Selected bond distances (Å) and angles (°) for compound **3a**.

Selected bond distances (Å)			
Re(1)–N(10)	1.878(10)	N(6)–C(11)	1.52(2)
Re(1)–P(1)	2.441(3)	N(6)–C(12)	1.52(2)
Re(1)–P(2)	2.406(3)	N(5)–C(11)	1.418(19)
Re(1)–P(3)	2.361(3)	N(5)–C(10)	1.442(19)
Re(1)–Br(1)	2.6195(13)	N(5)–C(8)	1.461(17)
Re(1)–Br(2)	2.5422(16)	N(4)–C(7)	1.494(18)
N(10)–O(1)	0.796(9)	N(4)–C(10)	1.45(2)
N(6)–C(9)	1.488(18)	N(4)–C(12)	1.44(2)
Selected angles (°)			
N(10)–Re(1)–Br(2)	178.9(3)	P(2)–Re(1)–Br(2)	86.85(9)
P(2)–Re(1)–P(1)	162.47(12)	P(3)–Re(1)–P(2)	97.9(11)
P(3)–Re(1)–Br(1)	178.69(8)	P(2)–Re(1)–N(10)	93.7(3)
P(3)–Re(1)–P(1)	98.08(11)	O(1)–N(10)–Re(1)	179.2(11)

which means that one of the *trans* phosphines became partially deprotonated, a fast equilibration process of proton exchange was initiated between the two *trans* phosphines being fast on the NMR time scale at room temperature. The *trans* phosphines are not distinguished in their acid/base behaviour, therefore the determined $pK_a(2)$ value refers to a value for both *trans* PTA's.

Reduction of **1** with zinc in acetonitrile was carried out in the presence of two equivalents of PTA resulting in the formation of mainly **4**. Complex **4** was purified by low temperature chromatography (−14 °C) on a silica gel column. It is well soluble in CH_3CN, H_2O, MeOH and DMSO, whereas it decomposes in methylene chloride and THF [21,22]. Crystals of **4** were obtained from concentrated CH_3CN solutions. Its structure is shown in Fig. 3 and characteristic bond distances and angles are given in Table 2. The complex shows a pseudo-octahedral geometry with the PTA ligands arranged approximately *trans*. The P(1)–Re(1)–P(2) angle is found closed up to 168.52(7)°. The same structural feature was reported for related complexes [9,23,24]. Complex **4** can easily be protonated by dissolution in water and addition of one or two equivalent(s) of a strong acid, yielding the mono-protonated form **4a** or the di-protonated complex **4b**. As in the case of the **3**/**3a** pair, the protonation was pursued by NMR, but also by IR spectroscopy. The increasing positive charge on the complexes **4a** and **4b** was found to be mainly localized on the protonated ligands. The protonated ligands behave thus independent and have only little influence on other parts of the complexes. For this reason the expected blue shifts in the IR spectra

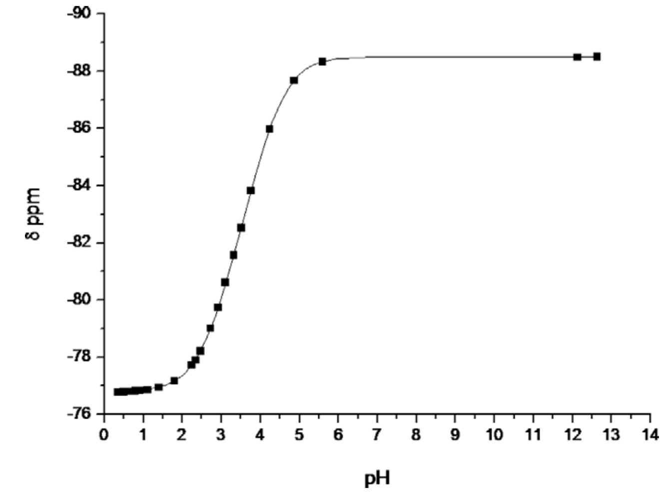


Fig. 2. Newton-Gauss non-linear least-squares fit of the titration curve of the **3/3a** acid/base pair. The solid line indicates the fitted titration curve, while the squares represent the experimental values. Pursuit of the intensity of the ^{31}P NMR doublet signals of the **3/3a** pair with changing pH: $pK_{a1} = 2.97 \pm 0.02$, $pK_{a2} = 4.04 \pm 0.02$.

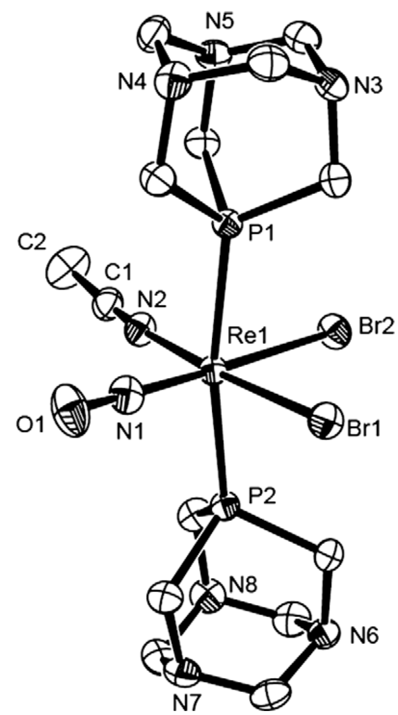


Fig. 3. X-ray structure of **4** (ORTEP representation with selected atomic labels. Hydrogen atoms are omitted for clarity). The displacement ellipsoids are drawn with 30% probability.

Table 2
Selected bond distances (Å) and angles (°) for compound **4**.

Selected bond distances (Å)	
Re(1)–N(2)	2.076(7)
Re(1)–N(1)	1.757(7)
Re(1)–P(1)	2.3988(19)
Re(1)–P(2)	2.4025(19)
Re(1)–Br(1)	2.5831(8)
Re(1)–Br(2)	2.6136(9)
N(1)–O(1)	1.175(9)
N(2)–C(1)	1.122(11)
Selected angles (°)	
P(1)–Re(1)–P(2)	168.52(7)
N(2)–Re(1)–Br(1)	173.7(2)
N(1)–Re(1)–Br(2)	178.2(2)
O(1)–N(1)–Re(1)	174.9(7)
N(2)–Re(1)–P(2)	91.05(19)
N(1)–Re(1)–Br(1)	89.7(2)
Br(1)–Re(1)–Br(2)	90.09(3)
C(1)–N(2)–Re(1)	174.5(7)

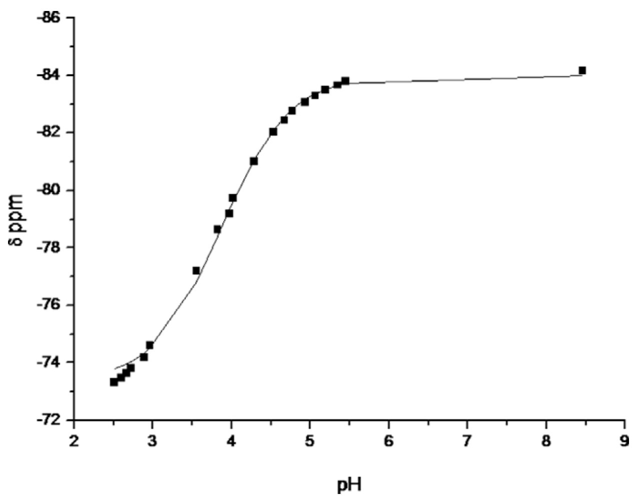


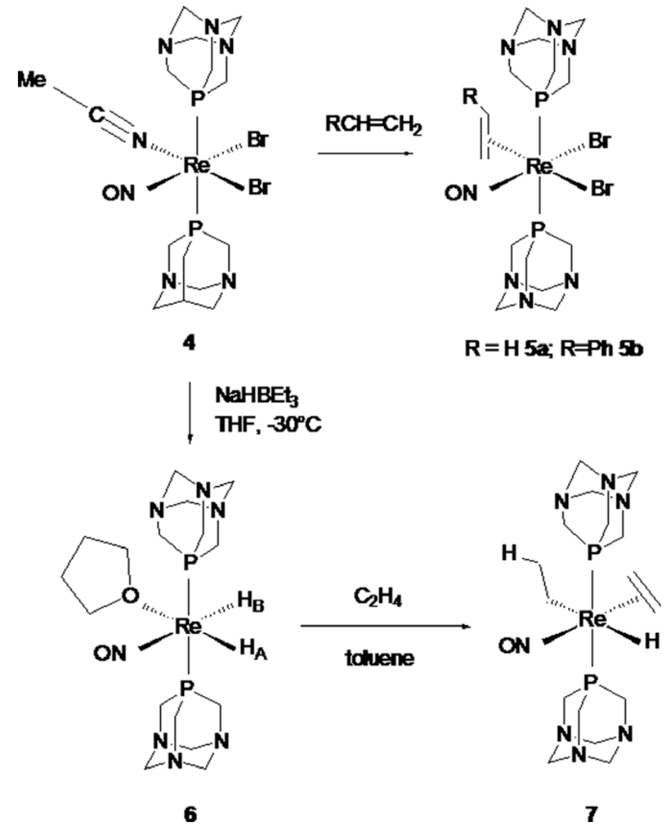
Fig. 4. Newton-Gauss non-linear least-squares fit of the titration curve of **4**. The solid line indicates the fitting curve, while the dashed line indicates the experimental values. pK_a = 3.86 ± 0.03.

of various stretching vibrations was found to be relatively small (ν(NO): 1675 cm^{-1}(**4**), 1681 cm^{-1} (**4a**) and 1682 cm^{-1} (**4b**)).

In the case of **4**, just one single pK_a value was found, presumably because the two phosphines are structurally related, but electronically quite independent from each other. The pK_a value obtained was 3.86 ± 0.03. The curve fitting of the NMR pH titration of **4** is presented in Fig. 4.

2.2. Olefin and hydride complexes with the trans-(PTA)$_2$(nitrosyl)rhenium fragment

Treatment of **4** with ethylene (1.2 bar) in THF for 1.5 h at 60 °C resulted in the formation of complex [$ReBr_2(NO)(CH_2CH_2)(PTA)_2$] (**5a**). The green powder **5a** was purified by washing the raw product several times with diethyl ether (Scheme 2). In the ^{1}H NMR spectrum the ethylene ligand was assigned to two triplets at 2.30 and 2.11 ppm, respectively. Reaction of **4** in THF with styrene for 8 h at 60 °C led to the formation of the [$ReBr_2(NO)(PhCHCH_2)(PTA)_2$] (**5b**). The light green powder **5b** was obtained in a similar way as described for **5a**. The formation of **5a** and **5b** indicates that the coordinated acetonitrile molecule is labile and that nitrosyl bisphosphine rhenium moieties have considerable affinity to olefins.



Scheme 2.

Various attempts failed to generate Re(I) dihydrogen and hydride complexes without the presence of PTA ligands applying the direct reaction with H_2 or with H_2 and a base were unsuccessful. However, the reaction of **4** with $NaHBEt_3$ in THF at −30 °C proceeded smoothly and was found to be completed after one hour. Formation of two species in an approximate 3:2 ratio was observed. One component was the dihydride [$ReH_2(THF)(NO)(PTA)_2$] (**6**) (40%) and the other species could not be identified yet. The isolated yield of **6** was 14%. The ^{1}H NMR spectrum of **6** exhibited two signals assigned to the hydride ligands with a dt pattern at −1.93 ppm (^2J(HH) = 8 Hz and ^2J(PH) = 32 Hz) and at −6.97 ppm (^2J(HH) = 8 Hz and ^2J(PH) = 36 Hz). The addition of water to **6** leads to the immediate evolution of H_2 proving a considerably hydridic character of the Re–H. The second unidentified product formed during the reaction to **6** does not correspond to a BEt_3 adduct with one of the PTA ligands, since the treatment of **4** with BEt_3·THF did not lead to noticeable conversion of **4**. As derived from the ^{31}P NMR spectrum the main product from this reaction with water has three *fac*-PTA ligands. The ^{31}P{1H} NMR spectrum gave rise to a doublet at −67.9 ppm and to a triplet at −72.9 ppm in a 2:1 ratio ($^2J_{PP}$ = 29 Hz).

Reaction of **6** with ethylene led to the formation of the complex [$ReH(CH_2CH_3)(\eta^2\text{-}C_2H_4)(NO)(PTA)_2$] (**7**) (Scheme 2). In the ^{1}H NMR spectrum the hydride ligand of **7** was assigned a triplet at −0.55 ppm with a coupling constant of ^2J(PH) = 37 Hz and for the coordinated ethylene molecule two sets of multiplets at 1.30 and 2.02 ppm were found indicating hindered rotation [9]. The ^{13}C{1H} NMR spectrum displayed only one signal for the ethylene carbon atoms at 28.0 ppm. Together with the ^{1}H NMR data a preferred orientation of the ethylene ligand along the P–Re–P axis was concluded. The same reaction can be also carried out with the mixture of **6** in the presence of ethylene. In this case the reaction product of the unknown component precipitates, while **7** stays in solution facilitating their separation. The spectroscopic yield of this reaction is 75% for **7**. The stability of **7** is anticipated to be primarily of kinetic nature. Only in *trans* position H and ethyl ligands can "survive" in one and the same coordination sphere, *cis* such ligands are expected to lead to spontaneous reductive elimination of ethane. *trans* to *cis* rearrangement of the H and ethyl ligands was attempted, but could not be induced by heating to 60 °C.

The catalytic activity of the two hydrides **6** and **7** were also tested for catalytic hydrogenation of olefins, ketones and imines. While **6** showed no activity, **7** revealed minor activity in the hydrogenation of olefins [25].

3. Conclusion

In summary, we have successfully developed a novel series of water soluble phosphine di- and trisubstituted rhenium complexes bearing PTA ligands. The disubstituted complex $[ReBr_2(CH_3CN)(NO)(PTA)_2]$ showed high affinity for olefins (C_2H_4 and $PhCHCH_2$) by replacement of the acetonitrile ligand. The dihydride complex $[ReH_2(THF)(NO)(PTA)_2]$ was obtained from $[ReBr_2(CH_3CN)(NO)(PTA)_2]$ *via* the reaction with $NaHBEt_3$. This complex also showed reactivity toward ethylene producing the monohydride $[ReH(Et)(C_2H_4)(NO)(PTA)_2]$. This dihydride complex displayed moderate catalytic activity in olefin hydrogenations under monophasic conditions in THF. Further investigation on the application of these water soluble complexes in organic transformations and catalysis are in progress.

4. Experimental

4.1. General comments

All manipulations were carried out under nitrogen in a dry box or using standard Schlenk techniques. All solvents (deuterated and non-deuterated) were deoxygenated and dried by standard methods [26]. H_2O, D_2O, HBr were deoxygenated by bubbling N_2 through the solutions. The chemical reagents were purchased from various commercial suppliers (Fluka, Aldrich, Merck, Erne-Chemie, Riedel-De Haën) and used as received. Preparation of PTA (1,3,5 triaza-7-phosphadamantane) was carried out as described in the literature [11,27].

4.2. Determination of acidity constants

Acidity constants of complexes **3** and **4** were determined in NMR titration experiments measuring the chemical shifts in $^{31}P\{^1H\}$ NMR experiments in H_2O in dependence of the pH (25 °C), which was changed by adding aliquots of NaOH 1 M or 10 M. The pH values were measured using a Metrohm 605 pH-meter equipped with a Hamilton Spintrode (pH 0–14, T = 0–80 °C) to detect the pH of the solutions directly in the NMR tubes, in air. Solutions were buffered with 50 μl of 2 M citric acid. A 48 mM solution of **3** was acidified with 2 equivalents of 0.1 M HBr to give the diprotonated compound **3b** and titrated back with 1 M or 10 M NaOH solutions in the pH range from about 3.0 to 9.0. About 31.4 mg of **4** were acidified with 0.7 ml of HBr 1 M to give the fully protonated complex **4a**, and titrated back with 1 M or 10 M NaOH solutions in the pH range from 0.35 to 12.89. The change in the chemical shift in the $^{31}P\{^1H\}$ NMR in dependence of the pH values was evaluated by a Newton-Gauss non-linear least-squares curve-fitting procedure. A better fit between experimental and theoretical data was obtained using Eqs. (1) and (2) [28,29], valid respectively for one or two deprotonation sites, and one or two pK_a values (pKA and pKAH) and adjusted to the present situation:

$$\delta_{obs} = \frac{\delta A + \delta AH * 10^{(pKA-x)}}{1 + 10^{(pKA-x)}} \quad (1)$$

$$\delta_{obs} = \frac{\delta A + \delta AH * 10^{(pKA-x)} + \delta AH_2 * 10^{(pKAH+pKA-2x)}}{1 + 10^{(pKA-x)} + 10^{(pKAH+pKA-2x)}} \quad (2)$$

where δ(A), δ(AH), $\delta(AH_2)$ are the chemical shifts of the neutral, mono- and diprotonated complexes.

4.3. Low temperature column chromatography

Low temperature column chromatography was carried out with silica gel (0.063–0.200 mm) as the stationary phase using a mixture of $MeOH/CH_2Cl_2$ (3:7) as eluent. The column was equipped with a cooling jacket, which was cooled to −14 °C. The separation was accomplished in air using non-degassed and non-dried solvents. The reaction mixture was dissolved in the eluent mixture and poured onto the cold column giving 3 different coloured zones. The first was orange, containing mainly compound **2**, the second was green-blue containing impurities and the third was yellow, containing compound **3**. Five litres of the eluent mixture were used to obtain almost 2 g of the pure product.

4.4. Preparations

4.4.1. Preparation of $[NMe_4]_2[ReBr_5(NO)]$ (1)

H_2O_2 (10 ml, 30%) was added dropwise to Re powder (3.03 g, 16.27 mmol) at 0 °C. $[NMe_4]Br$ (4.01 g, 26.03 mmol) was added to this solution without a further treatment. The solution was stirred for about 20 min to let the solution being homogeneous, then it was dried *in vacuo*. After drying the mixture, additional $[NMe_4]Br$ (4.06 g, 26.35 mmol) was added, and the solid dissolved in a 70:5 mL mixture of HBr (49%) and H_3PO_2 (50%). NO gas was bubbled through the solution at 110 °C, which turned dark green after 24 h. The reaction mixture was filtered and washed with MeOH (10 × 5 mL). The resulting apple green powder was dried under vacuum to yield 7.21 g (58%) of $[NMe_4]_2[ReBr_5(NO)]$. *Anal.* Calc. for $C_8H_{24}N_3OReBr_5$: C, 12.58; H, 3.17; N, 5.50. Found: C, 12.77; H, 3.22; N, 5.56%. IR (ATR): 1718 (ν_{NO}) cm^{-1}.

4.4.2. Preparation of $[ReBr_2(CH_3CN)_3(NO)]$ (2)

To a solution of $[NMe_4]_2[ReBr_5(NO)]$ (2.8 g, 3.9 mmol) in 50 mL of MeCN was added excess of Zn (2.56 g, 39 mmol) and the mixture was stirred at room temperature for 3 days. The orange solution was filtered and the solvent was evaporated under vacuum. The solid was washed with water and dried under vacuum. Yield of **2**: 1.38 g (70%). *Anal.* Calc. for $C_6H_9Br_2N_4ORe$: C, 14.44; H, 1.82; N, 11.22. Found: C, 14.60; H, 1.77; N, 11.14%. IR (ATR): 1691 (vs, ν_{NO}) cm^{-1}. ^1H NMR (300.1 MHz, CD_3CN): δ 2.96 (s, 6H), 2.94 (s, 3H) ppm. $^{13}C\{^1H\}$ NMR (125.8 MHz, CD_3CN): δ 134.3 (s, CN), 133.7 (s, 2CN), 4.23 (s, CH_3) ppm.

4.4.3. Preparation of $[ReBr(BF_4)mer-(CH_3CN)_3(NO)]$ (2a)

To a solution of $[Re(CH_3CN)_3Br_2(NO)]$ (52 mg, 0.10 mmol) in methylene chloride was added $AgBF_4$ (20.1 mg, 0.10 mmol). The mixture was stirred for 4 h at room temperature. The resulting solution was filtered and the solvent was removed *in vacuo* and the resulting solid was washed several times with diethyl ether to give rhenium complex **2a**. Yield: 43 mg (81%). A satisfactory elemental analysis could not be obtained. IR (CH_3CN): 2262 (ν_{CN}), 1724 (ν_{NO}) cm^{-1}. ^1H NMR (300 MHz, CD_3CN) δ 3.00 (s, 3H), 2.98 (s, 6H) ppm. $^{19}F\{^1H\}$ NMR (282.3 MHz, CD_3CN): δ 153.7, 151.8 ppm. $^{11}B\{^1H\}$ NMR (96.3 MHz, CD_3CN): δ 0.94 ppm. $^{13}C\{^1H\}$ NMR (500 MHz, CD_3CN): δ 135.9 (s, CN), 134.8 (s, 2CN), 4.57 (s, CH_3) ppm.

4.4.4. Preparation of [ReBr$_2$(NO)(PTA)$_3$] (**3**)

A stirred mixture of [ReBr$_2$(CH$_3$CN)$_3$(NO)] (212 mg, 0.43 mmol) and PTA (215 mg, 1.37 mmol) in 10 ml of dioxane was heated to 100 °C for 3 days. A yellow precipitate and a light yellow solution were formed. The mixture was cooled to room temperature. The solid produced was filtered, washed with MeOH (3 × 2 ml), washed with DMF (3 × 1 ml) and dried under vacuum. Yield: 288 mg (79%). *Anal.* Calc. for $C_{18}H_{36}Br_2N_{10}OP_3Re$: C, 26.00; H, 4.36; N, 16.84. Found: C, 26.14; H, 4.37; N, 16.66%. IR (ATR): 1691 (ν_{NO}), 2924 (ν_{asCH2}), 2870 (ν_{sCH2}) cm^{-1}. ^{1}H NMR (DMSO-d_6): δ 4.49 (broad, N–CH$_2$–N, 18H), 4.34 (broad, P–CH$_2$–N, 2 PTA-$_{trans}$12H), 4.14 (broad, P–CH$_2$–N, 1 PTA$_{eq}$ 6H) ppm. ^{31}P{1H} NMR (DMSO-d_6): δ −88.0 (d, ^2J = 10.7 Hz), −70.4 (t, ^2J = 11 Hz) ppm. ^{13}C{1H} NMR (DMSO-d_6): δ 51.3 (t, N–CH$_2$–P, 2 PTA$_{trans}$), 56.1 (d, N–CH$_2$–P, PTA$_{eq}$), 71.7 (d, N–CH$_2$–N, PTA$_{eq}$), 72.0 (s, N–CH$_2$–N, PTA$_{trans}$) ppm.

4.4.5. Preparation of [ReBr$_2$(NO)(PTAH)$_3$][Br]$_3$·4H$_2$O (**3a**)

A stirred solution of [ReBr$_2$(NO)(PTA)$_3$] (200 mg, 0.24 mmol) in 8 ml of HBr 1 M was stirred at room temperature for 20 min. The fine yellow precipitate formed in the round bottom flask was filtered off and the solution was concentrated *in vacuo* till 5 ml were left. The solution was left overnight at room temperature giving nice yellow crystals which were filtered off from the solution and dried *in vacuo*. Yield: 170 mg (65%). Presumably due to the water content a satisfactory elemental analysis could not be obtained. IR (ATR): 3363 (ν_{OH}), 1714 (ν_{NO}), 2330 (ν_{NH}), 2903 (ν_{sCH2}), 2962 (ν_{asCH2}) cm^{-1}. ^{1}H NMR (DMSO-d_6): δ 4.95 (broad, N–CH$_2$–N, PTA$_{eq}$ 6H), 4.91 (broad, N–CH$_2$–N, PTA$_{trans}$ 12H), 4.57 (broad, P–CH$_2$–N, PTA$_{trans}$ 12H), δ 4.43 (broad, P–CH$_2$–N, PTA$_{eq}$ 6H) ppm. ^{31}P{1H} NMR (DMSO-d_6): δ −76.94 (d, ^2J = 10.2 Hz), δ −63.3 (t, ^2J = 9.9 Hz, ^2J = 10.3 Hz) ppm. ^{13}C{1H} NMR (DMSO-d_6): δ 48.2 (broad, N–CH$_2$–P, 2 PTA$_{trans}$), 52.4 (d, N–CH$_2$–P, PTA$_{eq}$), 70.0 (b, N–CH$_2$–N, PTA$_{eq}$), 70.3 (s, N–CH$_2$–N, PTA$_{trans}$) ppm.

4.4.6. Preparation of [ReBr$_2$(CH$_3$CN)(NO)(PTA)$_2$] (**4**)

A stirred mixture of [NMe$_4$]$_2$[ReBr$_5$(NO)] (3.014 g, 3.94 mmol), PTA (1.24 g, 7.89 mmol) and a Zn excess (2.57 g, 3.94 × 10^{-2} mol) in 60 ml of CH$_3$CN was heated to 70 °C for 10 h. The reaction mixture was cooled to room temperature and filtered to remove the unreacted Zn and a yellow by-product; the filter was washed with CH$_3$CN (3 × 2 ml). The precipitate was removed and the filtered solution was dried under vacuum. The resulting solid was dissolved in a MeOH/CH$_2$Cl$_2$ solution (3:7) and poured onto a silica chromatographic column kept at −14 °C. The dark-yellow, orange fraction, that contained **3**, was collected. This solution was dried on a rotavapor leaving a yellow solid behind, which was washed with MeOH (3 × 5 ml) and dried *in vacuo*. Yield: 1.826 g (2.50 mmol) (63%). *Anal.* Calc. for $C_{14}H_{27}Br_2N_8OP_2Re$: C, 22.99; H, 3.72; N, 15.32. Found: C, 22.89; H, 3.81; N, 15.18%. IR (ATR): 1675 (ν_{NO}), 2942 (ν_{asCH2}), 2871 (ν_{sCH2}) cm^{-1}. ^{1}H NMR (CD$_2$Cl$_2$): δ 2.90 (s, 3H), 4.28 (N–CH$_2$–P, AB system, 12H, J = 15 Hz), 4.53 (N–CH$_2$–N, AB system, 12H, J = 12.9 Hz) ppm. ^{31}P{1H} NMR (CD$_2$Cl$_2$): δ −89.4 ppm. ^{13}C{1H} NMR (CD$_2$Cl$_2$): δ 4.7 (s, CH$_3$), 50.1 (virtual t, N–CH$_2$–P), 73.7 (broad, N–CH$_2$–N), 135.4 (s, CN) ppm.

4.4.7. Preparation of [ReBr$_2$(CH$_3$CN)(NO)(PTA)(PTAH)][Br] (**4a**)

A stirred mixture of [ReBr$_2$(CH$_3$CN)(NO)(PTA)$_2$] (200 mg, 0.274 mmol) was dissolved in water, the solution was stirred for 20 min at room temperature until complete dissolution. One equivalent of HBr 48% (15 μl) was added and the solution was stirred for 20 min at ambient temperature. The reaction mixture was dried *in vacuo* leaving a yellow solid. Yield: 169 mg (80%). *Anal.* Calc. for $C_{14}H_{28}Br_3N_8OP_2Re$: C, 20.70; H, 3.47; N, 13.79. Found: C, 20.78; H, 3.52; N, 13.74%. IR (ATR): 1681 (ν_{NO}) cm^{-1}. ^{1}H NMR (D$_2$O): δ 2.80 (s, 3H), 4.24 (N–CH$_2$–P, broad, 12H), 4.54 (N–CH$_2$–N, broad, 12H) ppm. ^{31}P{1H} NMR (D$_2$O): δ −80.1 ppm. ^{13}C{1H} NMR (D$_2$O): δ 3.2 (s, CH$_3$), 47.1 (virtual t, N–CH$_2$–P), 70.8 (broad s, N–CH$_2$–N), 129 (s, CN) ppm.

4.4.8. Preparation of [ReBr$_2$(CH$_3$CN)(NO)(PTAH)$_2$][Br]$_2$ (**4b**)

A stirred mixture of [ReBr$_2$(CH$_3$CN)(NO)(PTA)$_2$] (200 mg, 0.274 mmol) was dissolved in water, the solution was stirred for 20 min at room temperature until complete dissolution. Two equivalent of HBr 48% (29.3 μl) were added and the solution was stirred further for 20 min at ambient temperature. It was dried *in vacuo* leaving a yellow solid. Yield: 169 mg (80%). *Anal.* Calc. for $C_{14}H_{29}Br_4N_8OP_2Re$: C, 18.83; H, 3.27; N, 12.54. Found: C, 19.01; H, 3.24; N, 12.72%. IR (ATR): 1682 (ν_{NO}) cm^{-1}. ^{1}H NMR (D$_2$O): δ 2.80 (s, 3H), 4.30 (N–CH$_2$–P, broad, 12H), 4.64 (N–CH$_2$–N, broad, 12H) ppm. ^{31}P{1H} NMR (D$_2$O): δ −76.7 ppm. ^{13}C{1H} NMR (D$_2$O): δ 3.3 (s, CH$_3$), 46.8 (virtual t, N–CH$_2$–P), 70.9 (broad s, N–CH$_2$–N), 136.8 (s, CN) ppm.

4.4.9. Preparation of [ReBr$_2$(NO)(CH$_2$CH$_2$)(PTA)$_2$] (**5a**)

To a solution of [ReBr$_2$(NO)(CH$_3$CN)(PTA)$_2$] (200 mg, 0.274 mmol) in THF was pressurized with ethylene. The mixture was stirred for 1.5 h at 60 °C. The resulting solution was filtered and the solvent was removed *in vacuo* and the resulting solid was washed several times with diethyl ether to give green powder. Yield: 171 mg (87%). *Anal.* Calc. for $C_{14}H_{28}Br_2N_7OP_2Re$: C, 23.41; H, 3.93; N, 13.65. Found: C, 23.61; H, 3.73; N, 13.35%. IR (CD$_2$Cl$_2$): 1712 (ν_{NO}) cm^{-1}. ^{1}H NMR (CD$_2$Cl$_2$): δ 4.50 (N–CH$_2$–P, AB system, 12H, J = 15.9 Hz), 4.22 (N–CH$_2$–N, AB system, 12H, J = 13.2 Hz), 2.30 (t, J = 2.4 Hz, 2H), 2.11 (t, J = 3.3 Hz, 2H) ppm. ^{31}P{1H} NMR (CD$_2$Cl$_2$): δ −94.8 ppm. ^{13}C NMR (CD$_2$Cl$_2$): δ 128.7, 127.9, 73.9(d), 50.8(t) ppm.

4.4.10. Preparation of [ReBr$_2$(NO)(PhCHCH$_2$)(PTA)$_2$] (**5b**)

To a solution of [ReBr$_2$(NO)(CH$_3$CN)(PTA)$_2$] (200 mg, 0.274 mmol) in THF was added styrene (0.30 mmol). The mixture was stirred for 8 h at 60 °C. The resulting solution was filtered and the solvent was removed *in vacuo* and the resulting solid was washed several times with diethyl ether to give light green powder. Yield: 176 mg (81%). *Anal.* Calc. for $C_{20}H_{32}Br_2N_7OP_2Re$: C, 30.24; H, 4.06; N, 12.34. Found: C, 30.32; H, 4.10; N, 12.37%. IR (benzene-d_6): 1685 (ν_{NO}) cm^{-1}. ^{1}H NMR (benzene-d_6): δ 7.09–7.02 (m, 5H), 4.75 (N–CH$_2$–P, AB system, 12H, J = 15.9 Hz), 3.96 (N–CH$_2$–N, AB system, 12H, J = 13.2 Hz), 2.82 (t, J = 2.4 Hz, 1H), 2.57 (dd, J = 5.4 Hz, 2H) ppm. ^{31}P{1H} NMR (benzene-d_6) δ: −96.9 ppm. ^{13}C NMR (benzene-d_6): δ 178.8, 144.1, 128.7, 128.3, 127.7, 73.0(d), 50.0(t), 49.3(t) ppm.

4.4.11. Preparation of [ReH$_2$(THF)(NO)(PTA)$_2$] (**6**)

To 6 ml of a stirred THF solution of [ReBr$_2$(CH$_3$CN)(NO)(PTA)$_2$] (201 mg, 0.27 mmol), a solution of NaHBEt$_3$ 1 M in THF (0.36 ml, 0.36 mmol) at −30 °C was added. The orange solution was left at −30 °C for 1 h. The solution was dried *in vacuo* leaving an orange precipitate, which was extracted using toluene (5 × 2 ml). The filtrate was dried *in vacuo* and dissolved in a minimum amount of THF and then layered with 3 ml of pentane to induce the precipitation of the dihydride and to purify it from a small excess amount of NaHBEt$_3$. The layered solution was left in the freezer at −30 °C overnight. This procedure was repeated three times. An orange precipitate was collected that was dried *in vacuo* yielding 23.5 mg (14%) of pure **6**. *Anal.* Calc. for $C_{16}H_{34}N_7O_2P_2Re$: C, 31.78; H, 5.67; N, 16.22. Found: C, 31.45; H, 5.31; N, 15.91%. IR (ATR): 2926 (ν_{asCH2}), 2860 (ν_{sCH2}), 1836 (ν_{ReH}), 1615 (ν_{NO}) cm^{-1}. ^{1}H NMR (THF-d_8): δ −1.93 (dt, H$_B$, 1H), −6.97 (dt, H$_A$, 1H), 1.63 (m, THF, 4H), 3.61 (m, THF, 4H), 4.13 (s, PCH$_2$N, 12H); 4.55 (AB system, NCH$_2$N, 12H) ppm. ^{31}P{1H} NMR (THF-d_8): δ −68.5 ppm. ^{13}C{1H} NMR (THF-d_8): δ 58.1 (t, PCH$_2$N), 73.7 (t, NCH$_2$N) ppm.

*4.4.12. Preparation of [ReH(^{2}-C_2H_4)(Et)(NO)($PTA)_2$] (**7**)*

An impure mixture (3:2) of complex **5** with an unknown complex (84.4 mg, ≅0.05 mmol of **5** was dissolved in 4 ml of toluene in a young tap Schlenk tube and sealed under 1 bar of C_2H_4. The solution was stirred at room temperature for 3 h. The gas was removed under reduced pressure. The solution was filtered off from the precipitate and the precipitate was washed with toluene (5 × 2 ml), the solution was dried *in vacuo*. Yield: (27.6 mg 75%). *Anal.* Calc. for $C_{16}H_{34}N_7OP_2Re$: C, 32.65; H, 5.82; N, 16.66. Found: C, 33.05; H, 5.98; N, 14.39%. IR (ATR): 2924 (ν_{asCH2}), 2850 (ν_{sCH2}), 1852 (ν_{ReH}), 1626 (ν_{NO}) cm^{-1}. ^{1}H NMR (toluene-d_8): δ 4.15 (AB system, NCH_2N, 12H), 4.05 (AB system, PCH_2N, 12H), 1.36 (m, CH_2CH_3, 2H); 1.22 (t, CH_2CH_3, 3H), 0.55 (t, H, ^2J(PH) = 37 Hz, 1H); 1.30 (m, $H_2C{=}CH_2$, 2H), 2.02 (m, $H_2C{=}CH_2$, 2H) ppm. ^{31}P{1H} NMR (toluene-d_8): δ −75.0 ppm. ^{13}C{1H} NMR (toluene-d_8): δ 2.5 (CH_2CH_3, t), 23.0 (CH_2CH_3, s), 28.0 ($H_2C{=}$, s), 55.0 (PCH_2N, s), 72.8 (NCH_2N, s) ppm.

4.5. Catalytic hydrogenations in THF

The reactions were carried out in a steel autoclave. About 0.01 mmol of the catalysts were dissolved in THF-d_8 and 1 mmol of 1-hexene, cyclohexene, acetophenone or *N*-benzylidenemethylamine were added by a micro syringe. The autoclave was pressurized with different H_2 pressures (15–40 bar) and the reaction mixture was stirred and heated at 70 °C for 6–20 h. The reaction mixture was analysed by NMR spectroscopy at given reaction times.

4.6. Catalytic hydrogenations in water/benzene

The reactions were carried out in a steel autoclave in a biphasic mixture to allow the catalyst to stay in the water phase and the unsaturated substrate in the organic phase. A mixture D_2O:benzene-d_6 (1:1) and 1 mmol of 1-hexene, acetophenone or *N*-benzylidenemethylamine were added to an autoclave vessel which was frozen at −30 °C. A 0.01 mmol of catalysts were added to the previous mixture and the autoclave was again frozen in liquid nitrogen before being pressurized. The autoclave was pressurized with different H_2 pressures (20–45 bar) and the catalytic reactions were carried out for 8–16 h stirring and heating at 70 °C. The reaction mixture was analysed by NMR spectroscopy at given reaction times.

4.7. X-ray diffraction analyses

The selected single crystals were mounted using polybutene oil on the top of a glass fiber fixed on a goniometer head and transferred to a Stoe IPDS diffractometer (Imaging Plate Detector System with graphite-monochromated Mo Kα radiation, λ = 0.71073 Å) [30] and cooled to 183(2) K using a cold N_2-gas stream from an Oxford Cryogenic System. Data collections were performed with the program EXPOSE and the crystal systems and unit cell parameters were determined with the programs DISPLAY, INDEX and CELL [30]. Lorentz, polarization and numerical absorption [31] corrections (based on measured and indexed crystal faces) were applied with the programs FACEITVIDEO and XRED [29]. The Patterson method was used to solve the crystal structures by applying the software options of the program SHELXS-97 [32]. The structure refinement was performed with the program SHELXL-97 [32]. The program PLATON [33,34] was used to check the result of the X-ray analyses and the program ORTEP [35] used to give a representation of the structures. Table 3 summarizes crystal data and structure determination results.

Table 3
Crystallographic data for **3a** and **4**.

	3a	**4**
Empirical formula	$C_{18}H_{39}Br_2N_{10}OP_3Re$, 3(Br), 4($H_2O$)	$C_{14}H_{27}Br_2N_8OP_2Re$, C_2H_3N
Formula weight (g mol^{-1})	1162.28	772.44
Temperature (K)	183(2)	183(2)
Wavelength (Å)	0.71073	0.71073
Crystal system, space group	Monoclinic, $P2_1/c$	Monoclinic, $P2_1/c$
a (Å)	20.3510(11)	9.7242(7)
b (Å)	12.6178(7)	21.7605(12)
c (Å)	14.9204(8)	13.6191(10)
α (°)	90	90
β (°)	111.069(6)	119.143(7)
γ (°)	90	90
Volume (Å^3)	3575.2(4)	2517.0(3)
Z, D_{calc} (mg m^{-3})	4, 2.159	4, 2.038
Absorbed coefficient (mm^{-1})	9.166	8.158
F(0 0 0)	2240	1488
Crystal size (mm^3)	0.43 × 0.35 × 0.24	0.20 × 0.15 × 0.12
θ Range (°)	2.7–30.3	2.4–25.9
Reflections collected	41387	27834
Reflections unique	10601 [R_{int} = 0.0932]	4857 [R_{int} = 0.1042]
Completeness to θ (%)	98.9	99.3
Absorption correction	Numerical	Numerical
Maximum and minimum transmission	0.206 and 0.093	0.429 and 0.271
Data/restraints/parameters	10601/2/356	4857/0/282
Goodness-of-fit on F^2	1.045	1.019
Final R_1 and wR_2 indices [$I > 2\sigma(I)$]	0.0826, 0.2000	0.0407, 0.1173
R_1 and wR_2 indices (all data)	0.1503, 0.2179	0.0485, 0.1195

The unweighted *R*-factor is $R_1 = \Sigma(F_o - F_c)/\Sigma F_o$; $I > 2\sigma(I)$ and the weighted *R*-factor is $wR_2 = \{\Sigma w(F_o^2 - F_c^2)^2/\Sigma w(F_o^2)^2\}^{1/2}$.

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Appendix A. Supplementary material

CCDC 745331 and 745332 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jorganchem.2009.11.031.

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[25] The dihydride 6 was applied in catalytic reactions in the mixture (3:2) with the unknown complex. It was assured that the second component was unreactive toward H_2. The aqueous biphasic catalytic hydrogenations (water/benzene) of 1-hexene and a cetophenone were conducted in a steel autoclave under 20 bar H_2 pressure. However, in both cases no reactions were observed. When the hydrogenation of olefins, ketones and imines were tested for catalytic hydrogenations in THF under H_2 pressure (15–40 bar), only olefins showed moderate activity. For example 1-hexene showed a 85% conversion to hexane in 16 h at 70 °C with a H_2 pressure of 15 bar. In contrast to this catalytic hydrogenation reactions of alkenes or imines in THF or in the biphasic water/benzene system using 1% of 7 as a catalyst and H_2 pressure were not successful, presumably, because 7 possesses a too stable 18 e^- coordination sphere and facile rearrangement seems not possible.
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