Iminophosphorane based [P_2N_2] rhodium complexes: synthesis, reactivity, and application in catalysed transfer hydrogenation of polar bonds.†

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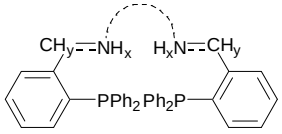
[Rh(P_2N_2)X] complexes (**2-X,** X = Cl, BF_4) featuring tetradentate iminophosphorane phosphine ligand were synthesised and characterised. The X-Ray analysis evidences a square planar geometry without coordination of the chloride anion. These complexes proved to be air-sensitive, and their oxidation to Rh(III) complexes **3-X** was observed in air. The controlled reaction of **2-BF_4** with one equivalent hexachloroethane also yielded [Rh(P_2N_2)Cl_2(BF_4)] (**3-BF_4**). The direct synthesis of **3-Cl** can be realised by coordination of the [P_2N_2] ligand to [RhCl(THT)$_3$] (THT= tetrahydrothiophene) as well. The reactivity of Rh(I) complexes **2** was further investigated, and no reaction was observed with silanes, arylhalides, or pinacolborane while the decomposition of the complex was observed under 1 atm of H_2 upon prolonged heating. Interestingly, the reduction of complex **3-Cl** was observed in NMR when reacting with silanes or sodium isoproxide. Therefore, complex **3-Cl** was used for catalytic transfer hydrogenation of polar bonds. The reduction of aromatic and aliphatic ketones can be carried out using 1% catalyst and 10% sodium isopropoxide. In these conditions an imine can be partially reduced.

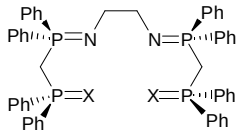
INTRODUCTION

Tetradentate ligand systems featuring two phosphines and two nitrogen donors either amine or amide functions have been widely studied for almost 30 years (Chart 1).[1] Furthermore, efficient enantioselective catalysts have been developed *via* the introduction of chirality within their carbon backbone; main successes being obtained with iridium,[2] palladium,[3] or ruthenium[4] complexes. More recently, Morris and coworkers have developed iron based systems able to achieve the efficient asymmetric transfer hydrogenation of polar bonds.[5] Motivated by these results, we have recently started to investigate their phosphorus analogues, namely [P_2N_2] ligands exhibiting iminophosphorane group instead of amine or imine functionalities (Chart 1). We anticipated that the electronic and steric properties of these new ligands will markedly differ from those of classical imine derivatives. Indeed, iminophosphoranes behave as strong σ and π donors because of the presence of two lone pairs at the nitrogen atom. Moreover, they do not present any π acceptor character because of the absence of a real π system. Clearly, iminophosphorane based ligands are much less exploited in catalysis than their carbon analogues, nevertheless their potential in coordination chemistry is now well established,[6] and they were successfully employed in a number of different catalytic processes.[7] Noteworthy, most iminophosphorane based ligand preparations rely on the Staudinger reaction involving the addition of an azide to a phosphine.[8] This methodology, though very clean, induces severe limitations concerning the substitution pattern at the nitrogen atom, because of the limited availability of azides. We have favoured synthetic strategies involving the Kirsanov reaction which allows the use of amines as the nitrogen source.[9] This has allowed a high-yielding two steps synthesis of tetradendate mixed phosphine-iminophosphorane [P_2N_2] ligands, which was first coordinated to group 10 metal centers (Pd, Ni). The obtained complexes were shown to be extremely stable and were able to catalyze Suzuki couplings in aqueous biphasic medium.[7m] Then, a series of iron(II) complexes was synthesised from tetradentate ligands combining iminophosphorane with phosphine, thiophosphine, or phosphine oxide groups, and was used for the catalytic transfer hydrogenation of acetophenone.[7p] Pursuing our investigations concerning this tetradentate mixed phosphine-iminophosphorane ligand, we report here its coordination to Rh(I) and Rh(III) centers. The reactivity of these complexes was investigated and their catalytic performances in the catalysed transfer hydrogenation of polar bonds are presented.



x = 0, y = 1
x = 1, y = 2

Carbon-based tetradentate [P_2N_2] ligands



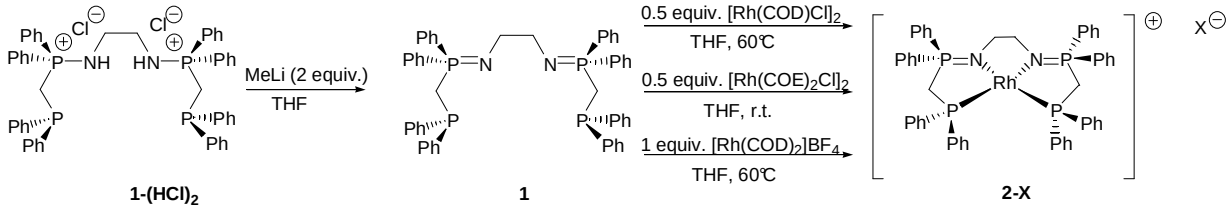
X = lone pair, S, O

Phosphorus based tetradentate ligands

Chart 1: Tetradentate [P_2N_2] ligands

RESULTS AND DISCUSSION

A Coordination and reactivity studies



Scheme 1 Synthesis of complex **2-X**

All coordination experiments were realised by addition of a rhodium precursor to a THF solution of ligand **1**, which was obtained by *in situ* deprotonation of bis(aminophosphonium) adduct **1-(HCl)$_2$** using 2 equivalents of MeLi (Scheme 1). To synthesise the Rh(I) complexes, different metal precursors were employed. [(P_2N_2)RhCl] complex **2-Cl** was synthesised by addition of half an equivalent of the [Rh(COD)Cl]$_2$ or the [Rh(COE)$_2$Cl]$_2$) precursors**.** After elimination of the lithium salts, and washing with diethyl ether, complex **2-Cl** was isolated in 84% yield. However, the reaction conditions were found to be highly dependent on the nature of the precursor. Thus, with the cyclooctadiene dimer 6h of heating at 60°C was required whereas with cyclooctene complex the reaction occured smoothly and was achieved within 6h at room temperature or 2h heating (60°C). The coordination of the phosphine and iminophosphorane arms could be inferred from the AA'BB' signal pattern observed in the ^{31}P{H} NMR spectrum. This complex **2-Cl** indeed logically appears as a doublet ($^2J_{PRh}$= 18.5 Hz) of virtual triplets ($^2J_{PP}$= $^3J_{PP}$ = 13.0 Hz) centred at δ_p(THF)= 38.2 ppm corresponding to the P=N groups and a doublet of doublet of doublet centred at δ_p(THF)= 41.5 ppm ($^2J_{PP}$= 19.5 Hz, $^2J_{PP}$= 13.0 Hz, $^1J_{PRh}$= 171.0 Hz) for the phosphines. This new complex was further characterised by multinuclear NMR spectroscopy (^{31}P, ^{1}H, ^{13}C) and elemental analyses. Moreover, monocrystals suitable for X-Ray analysis were obtained by slow diffusion of hexanes solution into concentrated dichloromethane solution of **2-Cl**. An Ortep view of one molecule is presented in figure 1.

As can be seen, complex **2-Cl** is a cationic species which adopts a square planar geometry, as expected for a d^8 complex, with the chloride anion being being more than 4 Å away from the metal centre. The deviation from planarity is very small 0.98(11)° for the P2-N1-N2-P4 dihedral angle. The two five-membered Rh-N-P-C-P metallacycles present similar bond lengths and angles. Moreover, the observed structural parameters are in the range of those measured by Cavell and coworkers for Rh(I) complexes bearing bidentate phosphine-iminophosphorane ($PPh_2CH_2PPh_2$=NR) ligand.[10] In particular, the N-Rh and P-Rh bond distances in **2-Cl** were measured respectively at 2.079 and 2.1915 Å on average, which are only slightly shorter than those observed by Cavell.

The tetrafluoroborate derivative of complex **2** was also synthesised by reacting ligand **1** (free of LiCl salt or prepared from **1-(HBF$_4$)$_2$**, with one equivalent of [Rh(COD)$_2$](BF$_4$) (Scheme 1). This way, complex **2-BF$_4$** was isolated as a yellow powder in 75% yield after classical work-up. Its NMR data are similar to those of **2-Cl**, and its X-Ray structure (see supporting information) is almost identical to that of **2-Cl**, aside from the tetrafluoroborate anion replacing the chloride one.

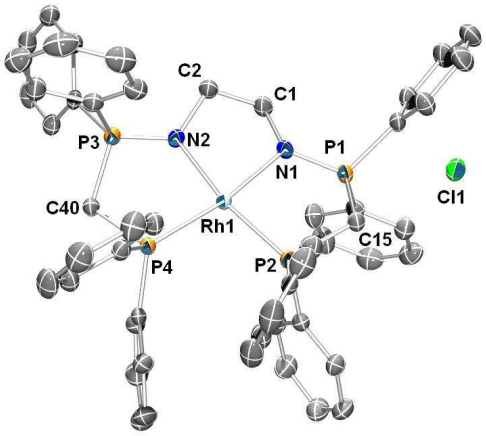


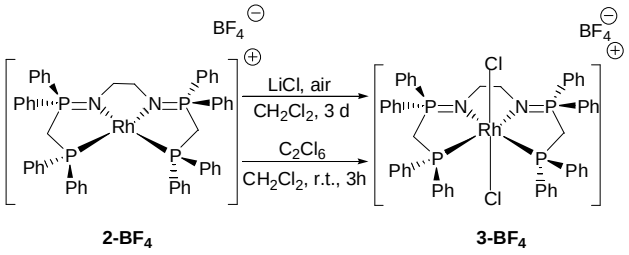
Figure 1: Molecular structure of complex **2-Cl**. Thermal ellipsoids drawn at the 50% probability level. Hydrogen atoms have been omitted for clarity. Selected distances (Å) and angles (◦): P2-Rh1 2.1935(6), N1-Rh1 2.075(2), N2-Rh1 2.082(2), P4-Rh1 2.1896(6), Rh1-Cl1 6.434, P1-N1 1.604(2), P3-N2 1.603(2), P1-C15 1.805(3), P2-C15 1.873(2), P3-C40 1.805(3), P4-C40 1.879(2); P4-Rh1-P2 100.40(2), N1-Rh1-N2 80.39(8), P4-Rh1-N2 89.66(6), P2-Rh1-N1 89.55(6), P1-N1-Rh1118.2(1), N1-P1-C15 105.1(1), P1-C15-P2 107.4(1), C15-P2-Rh1 105.57(8), C40-P4-Rh1 105.21(8), P4–C40–P3 106.4(1), C40-P3-N2 105.1(1), P3-N2-Rh1 117.4(1), N1-P2-P4-N2 -0.78(9), P1-P2-P4-P3 -17.72(4), P2-N1-N2-P4 -0.98(11), P2-P1-P3-P4 -10.36(4).

Finally, we found that syntheses of both complexes could be conveniently carried out in dichloromethane using **1** and the required rhodium precursor, a procedure which avoids solvent exchange to remove the lithium salts. In this case, one night stirring at room temperature was necessary to drive the reaction to completion. Note that usually iminophosphorane derivatives decompose when standing in dichloromethane, which stresses out the particular stability of the [P_2N_2] ligand.

Complexes **2-Cl** and **2-BF$_4$** were found to be oxygen sensitive. When exposed to air, CH_2Cl_2 solutions of complex **2-Cl** and **2-BF$_4$** with traces of chloride salts evolved towards the formation of a new complex **3**. In ^{31}P{H} NMR, this new species also exhibits a AA'BB' spin system pattern in which the chemical shifts of the coordinated phosphine ligand P(III) and the iminophosphorane P(V) are inversed. Thus in **3**, the signal corresponding to the coordinated phosphine group is centred at δ_p(THF)= 19.4 ppm and appears as a doublet ($^1J_{PRh}$ = 104.0 Hz) of virtual triplet ($^2J_{PP}$ = $^3J_{PP}$ = 15.0 Hz). The P(V) atoms resonate at δ_p(THF)= 41.2 ppm and logically the signal appears as a virtual triplet (J_{PP} = 15.5 Hz) of doublets ($^2J_{PRh}$ =

6.5 Hz). Noteworthy, the coupling constant between the phosphine ligand and the rhodium ($^1J_{PRh}$) is lower in **3** ($^1J_{PRh}$= 104 Hz) than in **2** ($^1J_{PRh}$= 171 Hz), this may be attributed to the oxidation of the rhodium centre according to the literature.[11]

This hypothesis was confirmed by parallel experiments aiming at the synthesis of complexes **3** through a controlled oxidation process (Scheme 2). Reactions of **2-BF$_4$** with one equivalent of hexachloroethane in dichloromethane cleanly yielded the expected complex **3-BF$_4$** in good yield (96%). Definitive evidence concerning the structure of **3-BF$_4$** was obtained by X-Ray analysis. An Ortep view of the molecular structure is presented in figure 2 together with the most relevant structural parameters.



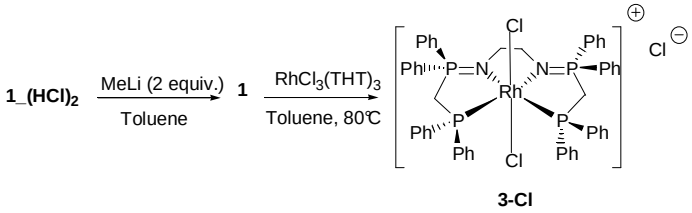
2-BF$_4$ **3-BF$_4$**

Scheme 2 Oxidation of complex **2-BF$_4$**

Figure 2 : Molecular structure of complex **3-BF$_4$**. Thermal ellipsoids drawn at the 50% probability level. Hydrogen atoms have been omitted for clarity. Selected distances (Å) and angles (°):P2–Rh1 2.2974(7), N1–Rh1 2.077(2), N2–Rh1 2.080(2), P4–Rh1 2.3097(7), Rh1–Cl1 2.3653(7), Rh1–Cl2 2.3616(7), Rh1–B1 7.040, P1–N1 1.591(2), P3–N2 1.585(2), P1–C15 1.803(3), P2–C15 1.848(3), P3-C40 1.806(3), P4–C40 1.851(3); P4–Rh1–P2 106.56(3), N1–Rh1–N2 80.5(1), P4–Rh1–N2 86.67(7), P2–Rh1–N1 86.85(7), Cl1–Rh1–Cl2 173.23(3), Cl1–Rh1–P2 98.02(2), Cl1–Rh1–P4 85.73(3), P(3)-N(2)-Rh(1) 123.3(1); N(2)-P(3)-C(40) 103.4(1); C(40)-P(4)-Rh(1) 100.3(1); C(15)-P(2)-Rh(1) 101.3(1); N(1)-P(1)-C(15) 104.3(1); P(1)-N(1)-Rh(1) 122.9(1);P1–C15–P2 109.2(1), P4–C40–P3 109.3(1), N1–P2–P4–N2 7.31(5), P1–P2–P4–P3 7.77(3); P2-N1-N2-P4 10.03(14), P2-P1-P3-P4 4.93(3).

The resulting complex is cationic and features an octahedral geometry around the metal center, with coordination of the [P_2N_2] in the median plane and two chlorine atoms in the apical positions. The deviation from planarity is slightly more pronounced than in **2** (N1-P2-P4-N2 7.31(5)). The oxidation is accompanied by a decrease of most the inner angles in the five membered metallacycle in particular the C-P-Rh and N-Rh-P angles go from respectively 105.39° and 89.61° on average in **2-Cl** to 100.8° and 86.77° on average in **3-BF$_4$**. Only the P-C-P angle widens after oxidation (from 107.4(1)° in **2-Cl** to 109.2(1) in **3-BF$_4$**). This accompanies an elongation of the P-Rh bond lengths (from 2.19 Å on average in **2** versus 2.30 Å on average in **3**), and a shortening of the P_{III}-C bonds (from 1.876 Å in the Rh(I) complex to 1.850 Å on average in the Rh(III) derivative). No substantial evolution is observed for the N-Rh and P-N bond lengths.

Interestingly complex **3-Cl** was directly obtained by reacting ligand **1** with one equivalent of [$RhCl_3(THT)_3$] (THT: tetrahydrothiophene) complex (Scheme 3). In this case heating overnight at 80°C was required to complete the reaction. Complex **3-Cl** precipitated from the reaction mixture and was isolated in 90% yield after washing with diethyl ether. This complex proved to be poorly soluble in most organic solvents (toluene, THF, CH_2Cl_2, or $CDCl_3$), nevertheless complete NMR characterisation was achieved using saturated solution of the compound in CD_2Cl_2. These NMR data are identical to those of **3-BF$_4$**. X-Ray diffraction analysis revealed that the molecular structure of **3-Cl** is also very similar to that of **3-BF$_4$** (see Supporting Information). Contrary to complexes **2** which are rather sensitive to air and moisture, complexes **3** can be handled and stored without particular precaution on the bench.



3-Cl

Scheme 3 Synthesis of complex **3-Cl**

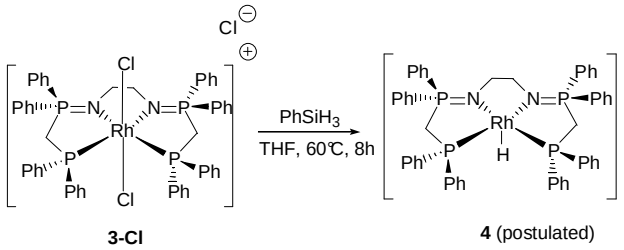
The reactivity of Rh(I) complexes **2** towards arylhalides, pinacolborane, and silane (Et_3SiH, Ph_2SiH_2) was investigated but no reaction was observed even at high temperature. Under H_2 atmospher (1atm), decomposition was observed upon prolonged heating (50° C). In the end, as mentioned above, only the oxidation to the Rh(III) species could be cleanly performed.

More significant results were obtained by reacting a suspension of **3-Cl** in THF with one equivalent of silane ($PhSiH_2$ or $EtSiH_3$). After 8h heating at reflux a colour change of the reaction mixture from yellow to brown-green was observed. The $^{31}P\{H\}$ NMR spectrum of the crude mixture evidenced a signal pattern similar to that observed for **2-Cl** and **2-BF$_4$** suggesting that a reduction to Rh(I) occurred. Importantly, the ^1H NMR spectrum of the reaction mixture (in d_3-acetonitrile) revealed the presence of a hydride which

Table 1. Crystal data and structural refinement details for complexes **2-Cl** and **3-BF$_4$**

Compound	**2-Cl**	**3-BF$_4$**
Molecular formula	$C_{52}H_{48}N_2P_4Rh$, 4(CH_2Cl_2), Cl	$C_{52}H_{48}Cl_2N_2P_4Rh$, 3($CHCl_3$), BF_4
Molecular weight	1302.87	1443.53
Crystal system	monoclinic	monoclinic
Space group	$P2_1/c$	$P\ 2_1/c$
a(Å)	11.715(1)	10.806(1)
b(Å)	21.218(1)	35.589(1)
c(Å)	23.598(1)	16.434(1)
α(°)	90.00	90.00
β(°)	91.563(1)	100.108(1)
γ(°)	90.00	90.00
V(Å^3)	5863.5(6)	6222.0(7)
Z	4	4
Reflections measured	13346	40501
Unique data	13346	17688
Rint	0.0329	0.0373
R1	0.0376	0.0476
CCDC number	772851	772853

appears as a complicated multiplet centred at $\delta_p(CD_3CN)$= -16.18 ppm). In the $^1H\{^{31}P\}$ spectrum, this hydride appears as a (broad doublet $J_{H,Rh}$ = 19.0 Hz) thus confirming the presence of a Rh-H bond. Unfortunately the poor solubility of this complex in acetonitrile or THF combined with its instability precluded the recording of its ^{13}C NMR spectrum and a full characterisation. Several crystallization attempts were also made but suitable crystals for an X-ray structural analysis could not be obtained. Based on these NMR indications, we nevertheless propose that this complex is the hydride derivative **4** (Scheme 4).



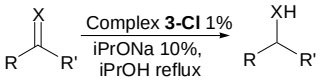
Scheme 4 Reduction of **3-Cl**

Importantly when reacting the Rh(III) complex **3** with two equivalents of sodium isopropoxide in a mixture of isopropanol/THF (1:1) (for solubility purpose) at 60°C for some hours, the ^{31}P NMR of the crude mixture evidenced the formation of a Rh(I) complex, since signals similar to those of **2** were observed (38.4 (vtd, J_{RhP}= 18.5.0 Hz, J_{PP} = J_{PP} = 12.5 Hz); 41.5 (ddd, J_{RhP}= 170.0 Hz, J_{PP} = 14.0 Hz, J_{PP} =19.5 Hz)). Unfortunately this Rh(I) complex could not be isolated. This last observation prompted us to investigate the reactivity of these rhodium complexes in the catalysed transfer hydrogenation of polar bonds.

B Catalytic Transfer hydrogenation experiments

Reactions were conducted using 1% of complex **3-Cl** as the catalyst, 10% isopropoxide as the base in refluxed isopropanol (reaction were very sluggish at room temperature or even 50°C). The progress of the reaction was monitored by ^1H NMR and these data are gathered in table 2. For example acetophenone is reduced in 90% after 4h (entry 1) using complex **3-Cl** as the catalyst and full conversion is achieved in 18h. As expected, the same reaction carried out with Rh(I) complex **2-Cl** was more rapid leading to total conversion after 4h (entry 2). Note that in the employed conditions ([iPrONa]~0.03 mol L^{-1}), only half-conversion can be achieved after 18h in the absence of any catalyst.[12] Because Rh(III) complex **3-Cl** gave satisfactory results and was by far easier to handle than complex **2-Cl**, it was used for the rest of the study. With 1% of **3-Cl** catalyst loading, the hydrogenation of *para*-substituted acetophenone was also efficiently achieved (entries 3-5), the reaction being more rapid for 4-methylacetophenone (99 % conversion after 8h).

Table 2 Catalytic transfer hydrogenation[a]



Entry	X	R	R'	Conversion after 4h, 8h, 18h (%)[b]
1	O	Ph	CH_3	90, 97, 99
2	O[c]	Ph	CH_3	100 (4h)
3	O	*p*-Cl-Ph	CH_3	44,51, 99
4	O	*p*-Me-Ph	CH_3	98, 99 (8h)
5	O	*p*-OMe-Ph	CH_3	74, 86, 96
6	O	Ph	*i*Pr	51, 55, 71
7	O	CH_3	*i*Pr	47, 65, 85 (94% after 24h)
8	NPh	Ph	H	22,32, 58 (67% after 24h)

[a] typical catalyst runs were performed with 1.4 mmmol of substrate, 1% of **3-Cl** as catalyst, 10% iPrONa (0.03 mol L^{-1}), $_i$PrOH (5mL) at reflux (82 °C),[b] Conversion into reduction product determined by ^1H NMR, average of two runs, [c] Same conditions except complex **2-Cl** was used as catalyst in place of **3-Cl**

Isobutyrophenone was also hydrogenated but only 71% conversion was observed after 18h (entry 6). These performances compare favorably with the ones reported by Gao for Rh(I) complexes bearing tetradentate aminophosphine ligands. Indeed, with these carbon based ligand 86 %, 49%, and 38% conversions were observed for acetophenone, 4-methoxylacetophenone and isobutyrophenone respectively (conditions: 22h in isopropanol at reflux with 1% catalyst and 1% potassium isopropanolate).[13] Nevertheless, other rhodium based catalytic systems have been shown to efficiently

catalysed the reduction of aromatic ketones under milder conditions.[14]

Interestingly complex **3-Cl** is also able to catalyse the transfer hydrogenation of 3-methyl-but-2-one, allowing 94 % conversion after 1 day reaction (entry 7). Moreover the reduction of *N*-benzylideneaniline can be also performed yielding 67% of amine after 24h.

Regarding the mechanism of the catalytic reaction, the reduction of **3-Cl** by isopropoxide was established independently by NMR experiments. In addition the monitoring of a catalytic test by $^{31}P\{H\}$ NMR spectroscopy confirmed the presence of a $[P_2N_2]$ rhodium (I) complex. Despite those evidences, the formation of a hypothetical hydride active species remains difficult to explain, since no vacant site is indeed available to allow the transfer of a hydride on the rhodium. An active role of the ligand can not be ruled out, the iminophosphorane function being able to act as a masked amide by the nitrogen atom or as an electrophilic site by the phosphorus one. Another possibility would be the liberation of one coordination site by a transitory phosphine decoordination. A stoechimetric reaction between complex **2-Cl** and one equivalent of isopropoxide was carried out in THF-d_8 at room temperature and then at 60°C to shed light on this question. Unfortunatly, the analysis of the crude mixture by $^{31}P\{H\}$ and ^{1}H NMR spectroscopy was rather difficult. However, no free phosphine nor hydride was seen. Several signals with complicated coupling patterns were observed which may indicate a desymmetrization of the complex. The elucidation of this mechanism may require a complete theoretical study.

CONCLUSION

In conclusion we have synthesised rhodium(I) and (III) complexes **2** and **3** respectively featuring tetradentate iminophosphorane based ligands. The reactivity of these complexes was investigated. **2** did not react with arylhalides, silanes, nor pinacolborane. Under 1 atm of H_2 and high temperature, decomposition of the complex was observed. Only the oxidation of Rh(I) derivatives into the corresponding Rh(III) complex was neatly carried out. Moreover, the reduction of complex **3** **u**sing silanes or isopropoxide was inferred from *in situ* NMR spectroscopy analysis. This prompted us to investigate the transfer hydrogenation of polar bonds using the stable Rh(III) complex **3**. Transfer hydrogenations of substituted aromatic ketones and an alkyl substituted ketone were achieved. Partial hydrogenation of *N*-benzylideneaniline was also realised. Additional experiments could not fully rationalize the observed hydride formation and the hydrogene transfer but a complete theoretical study may cast some light on those aspects.

EXPERIMENTAL

Synthesis

All experiments were performed under an atmosphere of dry nitrogen or argon using standard schlenk and glove box techniques. Solvents were freshly distilled under dry nitrogen from Na/benzophenone (THF, diethylether, petroleum ether), from P_2O_5 (dichloromethane). Aminophosphonium salt **1-(HCl)$_2$**,[9] $[Rh(COD)Cl]_2$ (COD= cyclooctadiene),[15] $[Rh(COE)_2Cl]_2$ (COE= cyclooctene),[16] $[Rh(COD)_2BF_4]$,[17] and $RhCl_3(THT)_3$] (THT = tetrahydrothiophene),[18] were prepared according to literature procedure. All other reagents and chemicals were obtained commercially and used without further purification, except for isopropanol which was distilled under dry nitrogen from calcium hydride. Nuclear magnetic resonance spectra were recorded on Bruker Avance 300 spectrometre operating at 300 MHz for ^{1}H, 75.5 MHz for ^{13}C and 121.5 MHz for ^{31}P. Solvent peaks were used as internal references for ^{1}H and ^{13}C chemical shifts (ppm). ^{31}P are relative to a 85% H_3PO_4 external reference. Coupling constant are expressed in hertz. The following abbreviations are used: b, broad; s, singlet; d, doublet; dd, doublet of doublets; t, triplet; m, multiplet; v, virtual. Elemental analyses were performed by the "Service d'analyse du CNRS", at Gif sur Yvette, France.

Synthesis of complex 2

2-Cl: MeLi (140 µl, 0.223 mmol) was added to a suspension of **1-(HCl)$_2$** (100 mg, 0.111 mmol) in THF (5 mL) cooled at -78°C, and the suspension was stirred at room temperature for 15 minutes. $[Rh(COE)Cl]_2$ (40 mg, 0.056 mmol) was added, and the solution turned yellow. After heating for 2h at 60°C, all volatiles were removed in vacuo and dichloromethane was added to filtrate off precipitated LiCl salts. After evaporation of CH_2Cl_2, the obtained solid was washed with petroleum ether (3x10 mL) to deliver **2-Cl** as a yellow solid (90 mg, 84%).^{31}P $\{^{1}H\}$ NMR (CD_2Cl_2) δ 37.8 (dvt, $^{2}J_{RhP}$ = 31.5 Hz, $^{2}J_{PP} = {}^{3}J_{PP}$ = 13.0 Hz, $P^{(V)}$), 41.5 (ddd, $^{1}J_{RhP}$ = 170.0 Hz, $^{2}J_{PP}$ = 13.0 Hz, $^{2}J_{PP}$ = 19.0 Hz, $P^{(III)}$) ppm. ^{1}H NMR (CD_2Cl_2) δ 3.20 (4H, t, $^{3}J_{PH}$= 4.5 Hz, N-C*H*$_2$), 3.53 (4H, dd, $^{2}J_{PH}$= 3.5 Hz, $^{2}J_{PH}$= 8.5 Hz, PC*H*$_2$P), 6.94 (4H, t, $^{3}J_{HH}$= 7.5 Hz, *p-H* ($Ph_2P^{(III)}$)) 7.07 (8H, dd, $^{3}J_{HH}$= 7.5 Hz, $^{4}J_{PH}$= 8.5 Hz, *m-H* ($Ph_2P^{(III)}$)), 7.14 (8H, dd, $^{3}J_{HH}$= 7.5 Hz, $^{3}J_{PH}$= 11.0 Hz, *o-H* ($Ph_2P^{(III)}$)), 7.34 (12H, vtd, $^{3}J_{HH}$= 7.5 Hz, $^{4}J_{PH}$= 2.0 Hz, *p*-H, *m-H* ($Ph_2P^{(V)}$)), 7.50 (8H, dd, J_{PH}= 11.5 Hz, $^{3}J_{HH}$= 7.5 Hz, *o-H* ($Ph_2P^{(V)}$)) ppm. ^{13}C $\{^{1}H\}$ NMR (CD_2Cl_2) δ = 39.8 (dd, $^{1}J_{PC}$= 4.5 Hz, $^{2}J_{PC}$= 87.0 Hz, P*C*H$_2$P), 53.5 (d, $^{2}J_{PC}$= 14.0 Hz, N*C*H$_2$), 126.0 (d, J_{PC}= 83.5 Hz, C^{IV} $Ph_2P^{(III)}$), 127.1 (vt, $^{4}J_{PC}$= 5 Hz, *p-C*H-($Ph_2P^{(III)}$)), 128.3 (d, $^{2}J_{PC}$ = 12.0 Hz, *o-C*H-($Ph_2P^{(III)}$)), 129.0 (s, p-*C*H-($Ph_2P^{(V)}$)), 131.5 (d, $^{3}J_{PC}$= 9.5 Hz, *m-C*H-($Ph_2P^{(III)}$)), 132.0 (d, $^{3}J_{PC}$= 6.5 Hz, *m-C*H-($Ph_2P^{(V)}$)), 132.1 (d, $^{2}J_{PC}$= 13.0 Hz, *o-C*H-($Ph_2P^{(V)}$)), 134.6 (C^{IV}($Ph_2P^{(V)}$) J not measurable). $C_{52}H_{48}ClN_2P_4Rh$, calcd : C 64.84, H 5.02, N 2.91 ; found : C 65.08, H 4.86, N 2.64.

2-BF$_4$: This complex was obtained with a similar procedure using $[Rh(COD)_2BF_4]$ (45 mg, 0.111 mmol) as the rhodium(I) precursor and either **1-(HBF$_4$)$_2$** or **1-(HCl)$_2$** as the reagent. When using **1-(HCl)$_2$**, the lithium salts have to be removed before the addition of the metal precursor. **2-BF$_4$** was obtained as a yellow solid (89 mg, 75 %) and present NMR data similar to those of **2-Cl**. $C_{52}H_{48}BF_4RhN_2P_4$, calcd : C 61.56, H 4.77, N 2.76 ; found : C 61.71, H 4.63, N 2.54.

For both compounds crystals suitable for X-ray diffraction

analysis were grown by diffusion of hexanes solution in concentrated dichloromethane of the complex (see ESI).

Synthesis of complex 3

3-BF$_4$: C_2Cl_6 (23 mg, 0.099 mmol) was added to a solution of **2-BF$_4$** (100 mg, 0.099 mmol) in dichloromethane (5 mL). After 3h stirring at room temperature, solvents were removed in vacuo and the obtained solid was washed with hexanes (3x5 mL) to give **3-BF$_4$** as a yellow solid (103 mg, 96%). ^{31}P {^{1}H} NMR (CD_2Cl_2) δ 19.4 (dvt, $^1J_{RhP}$= 104.0 Hz, $^2J_{PP}$ = $^2J_{PP}$ = 15.5 Hz, P$^{(III)}$), 41.2 (vtd, $^2J_{PP}$ = $^3J_{PP}$ = 15.5 Hz, $^2J_{RhP}$ = 6.5 Hz, P$^{(V)}$) ppm. ^{1}H NMR (CD_2Cl_2) δ 3.15 (4H, vt, $^3J_{PH}$= 5.5 Hz, N-C*H*$_2$), 4.23 (4H, td, $^2J_{PH}$= 11.5 Hz, $^4J_{PH}$= 1.0 Hz, PC*H*$_2$P), 7.10 (4H, t, $^3J_{HH}$= 7.5 Hz, *p-H* Ph$_2$P$^{(V)}$) 7.19 (8H, vt, $^3J_{HH}$= 7.5 Hz, $^4J_{PH}$= 7.5 Hz, *o-H* (Ph$_2$ P$^{(III)}$)), 7.36 (4H, t, $^3J_{HH}$= 7.5 Hz, *p-H* (Ph$_2$ P$^{(III)}$)), 7.56 (8H, td, $^3J_{HH}$= 7.5 Hz, $^3J_{PH}$= 2.5 Hz, *m-H* Ph$_2$P$^{(V)}$), 7.67 (8H, td, $^3J_{HH}$= 7.5 Hz, $^4J_{PH}$= 1.5 Hz, *m-H* (Ph$_2$ P$^{(III)}$)), 7.96 (8H, dd, $^3J_{HH}$= 7.5 Hz, $^3J_{PH}$= 12.5 Hz, *o-H* (Ph$_2$P$^{(V)}$)). ^{13}C {^{1}H} NMR (CD_2Cl_2) δ 52.0 (s, N*C*H$_2$), 105.2 (t, $^1J_{PC}$= 38.0 Hz, P*C*H$_2$P), 128.1 (vt, $^4J_{PC}$= 5.0 Hz, *p-C*H (Ph$_2$ P$^{(V)}$)), 128.8 (*C*^{IV}(Ph$_2$P$^{(III)}$ J not measurable), 129.4 (d, $^3J_{PC}$= 12.0 Hz, *m-C*H (Ph$_2$P$^{(V)}$)), 131.2 (*C*^{IV}(Ph$_2$P$^{(V)}$) J not measurable), 131.4 (s, *p-C*H-(Ph$_2$P$^{(III)}$)), 133.4 (d, $^2J_{PC}$= 11.5 Hz, *o-C*H-(Ph$_2$P$^{(V)}$)), 133.7 (d, $^2J_{PC}$= 10.0 Hz, *o-C*H-(Ph$_2$P$^{(III)}$)), 133.9 (bs, *m -C*H-(Ph$_2$P$^{(III)}$)). $C_{52}H_{48}Cl_2BF_4RhN_2P_4$, calcd : C 57.54, H 4.46, N 2.58 ; found : C 57.37, H 4.68, N 2.73.

3-Cl: MeLi (140 µl, 0.223 mmol) was added to a suspension of **1-(HCl)$_2$** (100 mg, 0.111 mmol) in toluene (5 mL) cooled at -78°C, After warming to room tempereature stirring was pursued 15 minutes, then the lithium salts were filtrated off. [$RhCl_3(THT)_3$] (52 mg, 0.110 mmol) was subsequently added to the ligand solution inducing a red coloration. After heating 12h at 80°C, the complex which precipitated from the reaction mixture was filtered and washed with hexanes (3x5 mL). **3-Cl** is obtained as an orange solid after drying in vacuo (100 mg, 90 %). Monocrystals were grown by diffusion of diethyl ether in acetonitrile solution of the complex. NMR data are similar to those of **3-BF$_4$**. $C_{52}H_{48}Cl_3N_2P_4Rh$, calcd : C 60.40, H 4.68, N 2.71 ; found : C 60.27, H 4.92, N 2.51.

General procedure for the transfer hydrogenation of polar bonds

A schlenk was charged under nitrogen atmosphere with **3-Cl** (8.0 mg, 0.07 mmol) and sodium isopropoxide (6.3 mg, 0.07 mmol). Isopropanol (2.5 mL) and ketone or imine (0.7 mmol) were then added and the reaction mixture was vigorously stirred under isopropanol reflux (82 °C). The progress of the reaction was monitored by ^{1}H NMR. At the appropriate time, an aliquot was taken from the reaction mixture, dried up under vacuum, flushed on a short silica column with $CDCl_3$ to remove the rhodium complexes, and then analysed by ^{1}H NMR. For the transfer hydrogenation of 3-methyl-but-2-one, the progress the reaction was monitored on crude mixture without any evaporation due to the low boiling point of the substrate.

Table 3: ^{1}H NMR chemical shifts considered to monitor the on-going conversion of catalytic reactions[a]

Subtrate	δ	Product	NMR signal
Acetophenone	2.58 (s,3H)	1-phenylethanol	1.47 (d, 3H)
p-Cl-acetophenone	2.58 (s,3H)	1-(p-chlorophenyl)ethanol	1.47 (d, 3H)
p-Me-acetophenone	2.54 (s,3H)	1-(p-methylphenyl)ethanol	1.46 (d, 3H)
p-OMe-acetophenone	2.55 (s,3H)	1-(p-methoxyphenyl)ethanol	1.47 (d, 3H)
3-methyl-butan-2-one	2.45 (sept,1H)	3-methyl-butan-2-ol	1.46 (oct.[b], 1H)
N-benzylideneaniline	8.47 (s, 1H)	*N*-benzylbenzenamine	4.35 (s, 2H)

[a] chemical shift in $CDCl_3$ (ppm); [b] oct: octuplet

X-ray Crystallography

General consideration: Data were collected on a Nonius Kappa CCD diffractometer using a Mo Kα (λ = 0.71073 Å) X-ray source and a graphite monochromator. Crystal data and structural refinement details are gathered in table 1 or in table S1. CCDC 772851 to 772854 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html [or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; fax: +44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk].The crystal structure was solved using SIR 97[19]and Shelxl-97.[20]ORTEP drawings were made using ORTEP III for Windows.[21]

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Notes and references

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† Electronic Supplementary Information (ESI) available: [CIF files, ORTEP plot and tables giving crystallographic data for **2-BF$_4$** and **3-Cl**, including atomic coordinates, bond lengths, angles, and anisotropic displacement parameters.]. See DOI: 10.1039/b000000x/

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