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 a tetradentate iminophosphorane phosphine ligand were synthesised and characterised. X-Ray analysis provides evidence for 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 of hexachloroethane yielded [Rh(P_2N_2)Cl_2(BF_4)] (**3-BF_4**). Direct synthesis of **3-Cl** can also be achieved by coordination of the [P_2N_2] ligand to [RhCl(THT)$_3$] (THT = tetrahydrothiophene). The reactivity of Rh(I) complexes **2** was further investigated, and no reaction was observed with silanes, aryl halides, or pinacolborane, although decomposition was observed under 1 atm of H_2 upon prolonged heating. Interestingly, reduction of complex **3-Cl** was observed by NMR upon treatment with silanes or sodium isopropoxide. 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, while imines are partially reduced under these conditions.

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 by the introduction of chirality to their carbon backbone, the main successes having been obtained with iridium,[2] palladium,[3] and 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 an iminophosphorane group instead of amine or imine functionalities (Chart 1). We anticipated that the electronic and steric properties of these new ligands would 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 true π system. Although iminophosphorane-based ligands are much less exploited in catalysis than their carbon analogues, their potential in coordination chemistry is now well established,[6] and they have been successfully employed in a number of different catalytic processes.[7]

It is noteworthy that 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-step synthesis of tetradentate mixed phosphine-iminophosphorane [P_2N_2] ligands, which were first coordinated to group 10 metal centers (Pd, Ni). The complexes obtained were shown to be extremely stable and were able to catalyze Suzuki couplings in aqueous biphasic media.[7m] Then, a series of iron(II) complexes was synthesised from tetradentate ligands combining iminophosphorane with phosphine, thiophosphine, or phosphine oxide groups, and these were 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 is investigated and their catalytic performance in the catalysed transfer hydrogenation of polar bonds is presented.

Results and discussion

Coordination and reactivity studies

All coordination experiments were carried out 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).

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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. CCDC reference numbers 772851–772854. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c0nj00299b

‡ Deceased.

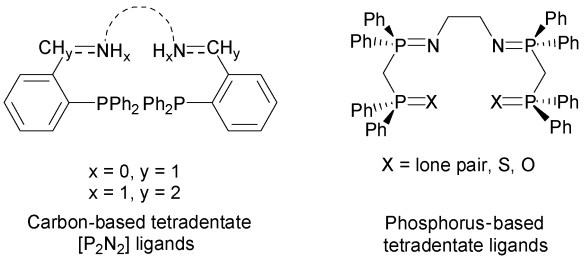


Chart 1 Tetradentate $[P_2N_2]$ ligands.

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 $[Rh(COE)_2Cl]_2$) 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 6 h of heating at 60 °C was required, whereas with cyclooctene complex the reaction occurred smoothly and was achieved within 6 h at room temperature, or 2 h at 60 °C. The coordination of the phosphine and iminophosphorane arms could be inferred from the AA′BB′ signal pattern observed in the $^{31}P\{^1H\}$ NMR spectrum. This complex **2-Cl** indeed logically appears as a doublet ($^2J_{RhP}$ = 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 doublets centred at δ_p(THF) = 41.5 ppm ($^2J_{PP}$ = 19.5 Hz, $^2J_{PP}$ = 13.0 Hz, $^1J_{RhP}$ = 171.0 Hz) for the phosphines. This new complex was further characterised by multinuclear NMR spectroscopy (^{31}P, ^1H, ^{13}C) and elemental analyses. Moreover, single crystals suitable for X-ray analysis were obtained by slow diffusion of hexanes into a concentrated dichloromethane solution of **2-Cl**. An ORTEP view of one molecule is presented in Fig. 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 more than 4 Å away from the metal centre. The deviation from planarity is very small – only 0.98(11)° for the P2–N1–N2–P4 dihedral angle. The two five-membered Rh–N–P–C–P metallacycles have 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 on average 2.079 and 2.1915 Å, respectively – 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

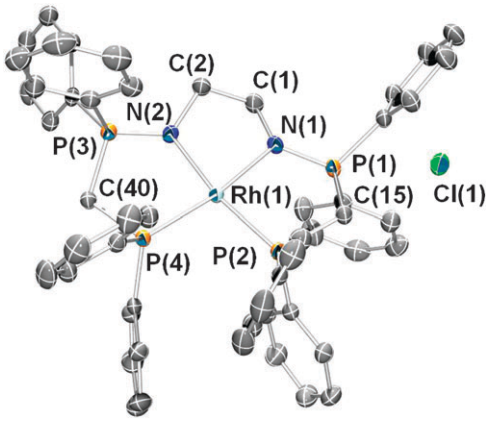
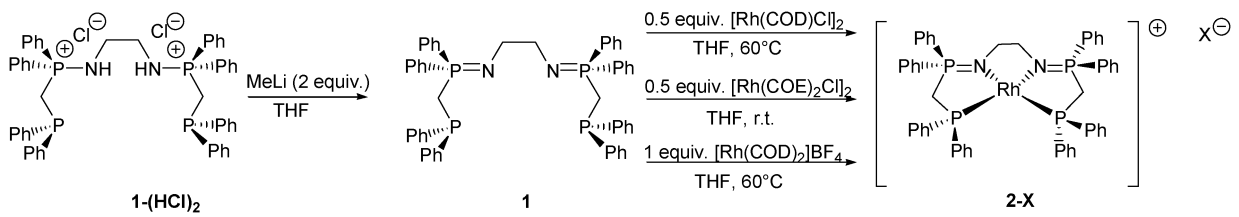


Fig. 1 Molecular structure of complex **2-Cl**. Thermal ellipsoids drawn at the 50% probability level. Hydrogen atoms have been omitted for clarity. Selected distances (Å) and angles (°): P2–Rh1 2.1935(6), N1–Rh1 2.075(2), N2–Rh1 2.082(2), P4–Rh1 2.1896(6), Rh1–Cl1 6.434, P1–N1 1.604(2), P3–N2 1.603(2), 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).

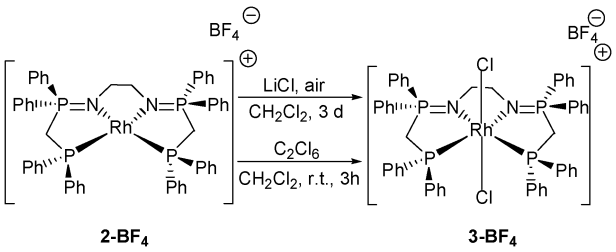
from **1-(HBF$_4$)$_2$**, with one equivalent of $[Rh(COD)_2](BF_4)$ (Scheme 1). This way, complex **2-BF$_4$** was isolated as a yellow powder in 75% yield after standard work-up. Its NMR data are similar to those of **2-Cl**, and its X-ray structure (see ESI†) is almost identical to that of **2-Cl**, apart from that tetrafluoroborate replaces chloride.

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, overnight stirring at room temperature was necessary to drive the reaction to completion. Note that iminophosphorane derivatives usually decompose when standing in dichloromethane, which emphasises 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 **2-Cl** and **2-BF$_4$** with traces of chloride salts underwent transformation to a new complex, **3**. In the $^{31}P\{H\}$ NMR, this new species also exhibits a AA′BB′ spin system, in which the chemical shifts of the coordinated phosphine ligand P(III) and the iminophosphorane P(V) are inverted. 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 ($^1J_{RhP}$ = 104.0 Hz) of virtual triplets



Scheme 1 Synthesis of complexes **2-X**.



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

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

This hypothesis was confirmed by parallel experiments aimed 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 Fig. 2 together with the most relevant structural parameters.

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

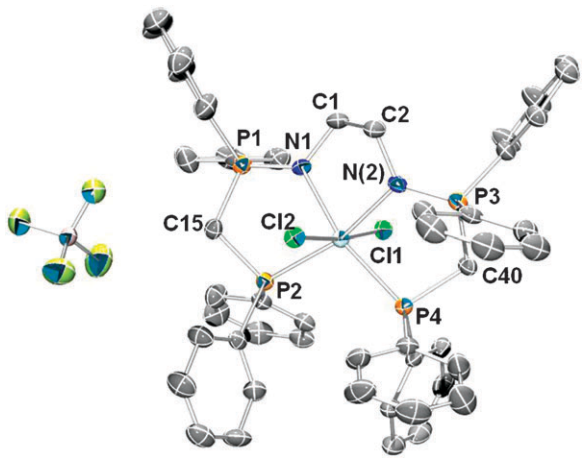
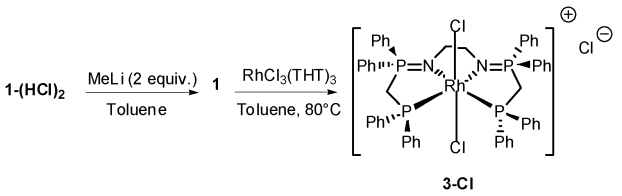


Fig. 2 Molecular structure of complex **3-BF$_4$**. Thermal ellipsoids drawn at the 50% probability level. Hydrogen atoms have been omitted for clarity. Selected distances (Å) and angles (°): P2–Rh1 2.2974(7), N1–Rh1 2.077(2), N2–Rh1 2.080(2), P4–Rh1 2.3097(7), Rh1–Cl1 2.3653(7), Rh1–Cl2 2.3616(7), Rh1–B1 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).



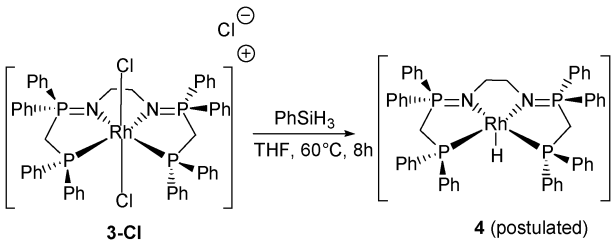
Scheme 3 Synthesis of complex **3-Cl**.

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 of the inner angles in the five-membered metallacycle; in particular, the average C–P–Rh and N–Rh–P angles change from 105.39° and 89.61° (respectively) in **2-Cl** to 100.8° and 86.77° 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 change 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 $CDCl_3$), but complete NMR characterisation was achieved using a 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 ESI†). In contrast to complexes **2**, which are rather sensitive to air and moisture, complexes **3** can be handled and stored without particular precautions.

The reactivity of Rh(I) complexes **2** towards aryl halides, pinacolborane, and silanes (Et_3SiH, Ph_2SiH_2) was investigated, but no reaction was observed even at high temperature. Under H_2 atmospher (1 atm), decomposition was observed upon prolonged heating (50° C). Ultimately, 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 ($PhSiH_3$ or $EtSiH_3$). After 8 h heating at reflux, a colour change of the reaction mixture from yellow to brown-green was observed. The $^{31}P\{^1H\}$ NMR spectrum of the crude mixture showed a signal pattern similar to that observed for **2-Cl** and **2-BF$_4$**, suggesting that a reduction to Rh(I) had occurred. Importantly, the ^1H NMR spectrum of the reaction mixture (in d_3-acetonitrile) revealed the presence of a hydride which 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_{RhH} = 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



Scheme 4 Reduction of **3-Cl**.

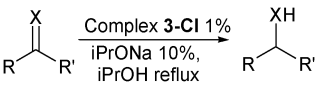
and a full characterisation. Several crystallization attempts were also made, but suitable crystals for an X-ray structural analysis could not be obtained. Based on these NMR indications, we nevertheless propose that this complex is the hydride derivative **4** (Scheme 4).

Importantly, when reacting the Rh(III) complex **3** with two equivalents of sodium isopropoxide in a mixture of isopropanol–THF (1 : 1) (for solubility purposes) at 60 °C for some hours, the ^{31}P NMR of the crude mixture indicated the formation of a Rh(I) complex, since signals similar to those of **2** were observed (δ 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) ppm). 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.

Catalytic transfer hydrogenation experiments

Reactions were conducted using 1% of complex **3-Cl** as the catalyst, and 10% isopropoxide as the base, in refluxing isopropanol (reactions were very sluggish at room temperature or even at 50 °C). The progress of the reaction was monitored by ^{1}H NMR, and these data are gathered in Table 1. For example, acetophenone was reduced in 90% yield after 4 h (entry 1) using complex **3-Cl** as the catalyst, with full conversion being achieved after 18 h. As expected, the same reaction carried out with Rh(I) complex **2-Cl** was more rapid, leading to total conversion after 4 h (entry 2). Note that under the employed conditions ([*i*PrONa] ~0.03 mol L^{-1}), only half-conversion was achieved after 18 h 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, hydrogenation of *para*-substituted acetophenone was also achieved efficiently (entries 3–5), the reaction being most rapid for 4-methylacetophenone (99% conversion after 8 h).

Table 1 Catalytic transfer hydrogenation[a]



				Conversion (%)[b]			
Entry	X	R	R′	4 h	8 h	18 h	24 h
1	O	Ph	Me	90	97	99	—
2	O[c]	Ph	Me	100	—	—	—
3	O	*p*-Cl–C_6H_4	Me	44	51	99	—
4	O	*p*-Me–C_6H_4	Me	98	99	—	—
5	O	*p*-MeO–C_6H_4	Me	74	86	96	—
6	O	Ph	*i*Pr	51	55	71	—
7	O	Me	*i*Pr	47	65	85	94
8	NPh	Ph	H	22	32	58	67

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

Isobutyrophenone was also hydrogenated, but only 71% conversion was observed after 18 h (entry 6). These performances compare favorably with those reported by Gao for Rh(I) complexes bearing tetradentate aminophosphine ligands. Indeed, with these carbon-based ligands 86%, 49%, and 38% conversions were observed for acetophenone, 4-methoxylacetophenone and isobutyrophenone respectively (conditions: 22 h in isopropanol at reflux with 1% catalyst and 1% potassium isopropoxide).[13] Nevertheless, other rhodium-based catalytic systems have been shown to efficiently catalyse the reduction of aromatic ketones under milder conditions.[14]

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

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{^{1}H} NMR spectroscopy confirmed the presence of a [P_2N_2] rhodium(I) complex. Despite this evidence, the formation of a hypothetical hydride active species remains difficult to explain, since no vacant site is available to allow the transfer of a hydride on the rhodium. An active role of the ligand can not be ruled out, as the iminophosphorane function could act as a masked amide through the nitrogen or as an electrophilic site through the phosphorus. Another possibility would be the liberation of one coordination site by a transitory phosphine decoordination. A stoichiometric reaction between complex **2-Cl** and one equivalent of isopropoxide was carried out in d_8-THF at room temperature and then at 60 °C to shed light on this question. Unfortunately, the analysis of the crude mixture by ^{31}P{^{1}H} and ^{1}H NMR spectroscopy was rather difficult, but no free phosphine or 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 therefore benefit from a complete theoretical study.

Conclusion

In conclusion, we have synthesised rhodium(I) and rhodium (III) complexes **2** and **3** respectively, featuring tetradentate iminophosphorane-based ligands. The reactivity of these complexes was investigated. Complex **2** did not react with aryl halides, silanes, or 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) complexes proceeded smoothly. The reduction of complex **3** using silanes or isopropoxide was inferred from *in situ* NMR spectroscopy analysis, which 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 achieved. Additional experiments could not fully explain the observed hydride formation and the hydrogen transfer, but a complete theoretical study may cast some light on these 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, diethyl ether, 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 procedures. 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 spectrometer 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 constants 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 to −78 °C, and the suspension was stirred at room temperature for 15 min. $[Rh(COE)Cl]_2$ (40 mg, 0.056 mmol) was added, and the solution turned yellow. After heating for 2 h at 60 °C, all volatiles were removed *in vacuo* and dichloromethane was added to filter off precipitated LiCl salts. After evaporation of CH_2Cl_2, the obtained solid was washed with petroleum ether (3 × 10 mL) to deliver **2-Cl** as a yellow solid (90 mg, 84%). ^{31}P {^{1}H} NMR (CD_2Cl_2) δ 37.8 (dvt, $^2J_{RhP}$ = 31.5 Hz, $^2J_{PP}$ = $^3J_{PP}$ = 13.0 Hz, $P^{(V)}$), 41.5 (ddd, $^1J_{RhP}$ = 170.0 Hz, $^2J_{PP}$ = 13.0 Hz, $^2J_{PP}$ = 19.0 Hz, $P^{(III)}$) ppm. ^{1}H NMR (CD_2Cl_2) δ 3.20 (4H, t, $^3J_{PH}$ = 4.5 Hz, N-CH_2), 3.53 (4H, dd, $^2J_{PH}$ = 3.5 Hz, $^2J_{PH}$ = 8.5 Hz, PCH_2P), 6.94 (4H, t, $^3J_{HH}$ = 7.5 Hz, *p-H* ($Ph_2P^{(III)}$)) 7.07 (8H, dd, $^3J_{HH}$ = 7.5 Hz, $^4J_{PH}$ = 8.5 Hz, *m-H* ($Ph_2P^{(III)}$)), 7.14 (8H, dd, $^3J_{HH}$ = 7.5 Hz, $^3J_{PH}$ = 11.0 Hz, *o-H* ($Ph_2P^{(III)}$)), 7.34 (12H, vtd, $^3J_{HH}$ = 7.5 Hz, $^4J_{PH}$ = 2.0 Hz, *p*-H, *m-H* ($Ph_2P^{(V)}$)), 7.50 (8H, dd, J_{PH} = 11.5 Hz, $^3J_{HH}$ = 7.5 Hz, *o-H* ($Ph_2P^{(V)}$)) ppm. ^{13}C {^{1}H} NMR (CD_2Cl_2) δ = 39.8 (dd, $^1J_{PC}$ = 4.5 Hz, $^2J_{PC}$ = 87.0 Hz, PCH_2P), 53.5 (d, $^2J_{PC}$ = 14.0 Hz, NCH_2), 126.0 (d, J_{PC} = 83.5 Hz, C^{IV} $Ph_2P^{(III)}$), 127.1 (vt, $^4J_{PC}$ = 5 Hz, *p*-CH–($Ph_2P^{(III)}$)), 128.3 (d, $^2J_{PC}$ = 12.0 Hz, *o*-CH–($Ph_2P^{(III)}$)), 129.0 (s, *p*-CH–($Ph_2P^{(V)}$)), 131.5 (d, $^3J_{PC}$ = 9.5 Hz, *m*-CH–($Ph_2P^{(III)}$)), 132.0 (d, $^3J_{PC}$ = 6.5 Hz, *m*-CH–($Ph_2P^{(V)}$)), 132.1 (d, $^2J_{PC}$ = 13.0 Hz, *o*-CH–($Ph_2P^{(V)}$)), 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 by 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 had 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 into a 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 3 h stirring at room temperature, solvents were removed *in vacuo* and the obtained solid was washed with hexanes (3 × 5 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–CH_2), 4.23 (4H, td, $^2J_{PH}$ = 11.5 Hz, $^4J_{PH}$ = 1.0 Hz, PCH_2P), 7.10 (4H, t, $^3J_{HH}$ = 7.5 Hz, *p-H* $Ph_2P^{(V)}$) 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* $Ph_2P^{(V)}$), 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* ($Ph_2P^{(V)}$)). ^{13}C {^{1}H} NMR (CD_2Cl_2) δ 52.0 (s, NCH_2), 105.2 (t, $^1J_{PC}$ = 38.0 Hz, PCH_2P), 128.1 (vt, $^4J_{PC}$ = 5.0 Hz, *p-C*H (Ph_2 $P^{(V)}$)), 128.8 (C^{IV}($Ph_2P^{(III)}$, *J* not measurable), 129.4 (d, $^3J_{PC}$ = 12.0 Hz, *m-C*H ($Ph_2P^{(V)}$)), 131.2 (C^{IV}($Ph_2P^{(V)}$), *J* not measurable), 131.4 (s, *p-C*H-($Ph_2P^{(III)}$)), 133.4 (d, $^2J_{PC}$ = 11.5 Hz, *o-C*H–($Ph_2P^{(V)}$)), 133.7 (d, $^2J_{PC}$ = 10.0 Hz, *o-C*H–($Ph_2P^{(III)}$)), 133.9 (bs, *m-C*H–($Ph_2P^{(III)}$)). $C_{52}H_{48}Cl_2BF_4RhN_2P_4$, 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 to −78 °C. After warming to room temperature, stirring was continued for 15 min, and then the lithium salts were filtered off. $[RhCl_3(THT)_3]$ (52 mg, 0.110 mmol) was subsequently added to the ligand solution, inducing a red coloration. After heating 12 h at 80 °C, the complex which precipitated from the reaction mixture was filtered and washed with hexanes (3 × 5 mL). **3-Cl** was obtained as an orange solid after drying *in vacuo* (100 mg, 90%). Single crystals were grown by diffusion of diethyl ether into an 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 flask was charged under nitrogen atmosphere with **3-Cl** (8.0 mg, 0.007 mmol) and sodium isopropoxide

Table 2 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	$P2_1/c$	$P2_1/c$
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
R_{int}	0.0329	0.0373
$R1$	0.0376	0.0476
CCDC number	772851	772853

(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 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 under vacuum, flushed through 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-methylbut-2-one, the progress of the reaction was monitored on the crude mixture without any evaporation due to the low boiling point of the substrate.

X-Ray crystallography

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 2 and in Table S1†. CCDC 772851–772854 contain the supplementary crystallographic data for this paper†. The crystal structure was solved using SIR 97[19] and Shelxl-97.[20] ORTEP drawings were created using ORTEP III for Windows.[21]

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