'A rendezvous with an old flame': revisiting olefin hydrogenation with new rhodium and iridium catalysts

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Most of this work was carried out under the direction of John A. Osborn before he passed away on 23 April 2000. His co-workers dedicate this paper to the memory of John, a long-term teacher, mentor and friend.

Abstract – A novel tridentate hemilabile ligand **2** containing phosphine, imine and pyridyl donor groups has been prepared in analogy with the synthesis of the known related ligand **1**. The reaction of **1** or **2** with $[Rh(COE)_2Cl]_2$ resulted in the formation of the neutral complexes $[Rh(L)Cl]$. By a method using $[M(diene)Cl]_2$ as starting material, cationic complexes of the type $[M(diene)(L)]X$ were also obtained (M = Rh, diene = NBD, L = **1**, **2**; M = Ir, diene = COD, L = **1**; X = BF_4, OTf). A comparative study of the catalytic activity of the new complexes towards the hydrogenation of various olefins has been reported. In particular, the catalysts of the type $[Rh(L)Cl]$ are remarkably active when prepared in situ, especially for the reduction of hindered olefins. ***To cite this article: J.-P. Masson et al., C. R. Chimie 5 (2002) 303–308*** © 2002 Académie des sciences / Éditions scientifiques et médicales Elsevier SAS

rhodium / iridium / hemilabile tridentate ligand / catalytic hydrogenation / olefins

Résumé – Un nouveau ligand tridentate hémilabile **2** portant les fonctions phosphine, imine et pyridyl comme groupements donneurs a été synthétisé selon une procédure comparable à celle décrite pour un ligand similaire **1**. La réaction de **1** ou **2** en présence de $[Rh(COE)_2Cl]_2$ conduit à la formation de complexes neutres $[Rh(L)Cl]$. Par une méthode impliquant $[M(diene)Cl]_2$ comme précurseur, les complexes cationiques de type $[M(diene)(L)]X$ ont également été synthétisés (M = Rh, diene = NBD, L = **1**, **2**; M = Ir, diene = COD, L = **1**; X = BF_4, OTf). Une étude comparative de l'activité catalytique des nouveaux complexes en hydrogénation de différentes oléfines a été menée. Les catalyseurs de type $[Rh(L)Cl]$, préparés in situ, sont remarquablement actifs, et plus particulièrement pour la réduction d'oléfines encombrées. ***Pour citer cet article : J.-P. Masson et al., C. R. Chimie 5 (2002) 303–308*** © 2002 Académie des sciences / Éditions scientifiques et médicales Elsevier SAS

rhodium / iridium / ligand tridentate hémilabile / hydrogénation catalytique / oléfines

1. Introduction

In recent years, much attention has been paid to the search of new chelated ligands containing mixed functionalities as a potential tool to achieve more efficient and selective catalytic reactions. In particular, the use of the so-called hemilabile ligands [1] represents a step forward in catalysis as they may induce a higher reactivity of their transition metal complexes and allow the stabilisation of reactive transition metal centres. Due to the intrinsic nature of such ligands, the labile group can be displaced easily and reversibly
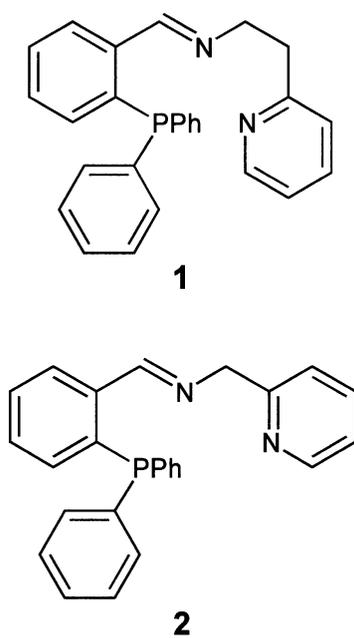

Fig. 1. Representation of ligands **1** and **2**.

from the metal centre, thereby allowing a catalytic reaction to occur. Such a potential has been widely used for bidentate ligands [2] but much less for tridentate ones [3, 4]. However, Mathieu and al. reported on the use of ruthenium complexes bearing a tridentate P–N–O ligand in the catalytic transfer hydrogenation of ketones [5]. More recently, the groups of Vrieze and van Leeuwen have described interesting reactivity properties for palladium complexes of a new hemilabile P–N–N ligand containing phosphine, imine and pyridyl donor groups [6, 7]. These findings prompted us to synthesise a novel closely related ligand **2** and to investigate the coordination properties of **1** and **2** shown in Fig. 1, in the presence of rhodium (I) and iridium (I), as a first step towards a more detailed study of their catalytic properties.

Herein, we describe preliminarily the synthetic routes to achieve this goal and report on the catalytic activity of the new complexes towards the hydrogenation of linear olefins, cyclic olefins and sterically demanding olefins.

2. Experimental

2.1. General considerations

All syntheses were performed under a pure dinitrogen or argon atmosphere using Schlenk techniques on an inert gas/vacuum manifold or in a dry box equipped with a dry-train HE-493 inert gas purifier. Solvents were dried by standard methods and distilled

under nitrogen. $AgBF_4$ and $AgSO_3CF_3$ were purchased from Strem and used as received. $[Rh(COE)_2Cl]_2$ [8], $[Rh(NBD)Cl]_2$ [9], and $[Ir(COD)Cl]_2$ [10] were prepared according to published methods. NMR spectra were recorded at ambient probe temperature on a Bruker AC-300 spectrometer operating at 300 MHz for ^1H, 75 MHz for ^{13}C and 121.5 MHz for $^{31}P\{^1H\}$. Chemical shifts are reported in parts per million versus $SiMe_4$ for ^1H and ^{13}C calibrated against the residue solvent resonance as an internal reference. ^{31}P NMR spectra were referenced to 85% aqueous H_3PO_4.

The analyses of the catalytic reactions were carried out using a Hewlett Packard 5890 Series II Gas Chromatograph equipped with a flame ionisation detector (FID) and a methyl silicone gum column of length 10 m, diameter 0.53 mm and 2.65 μm film thickness.

2.2. General procedure for the hydrogenation studies

A typical experiment was set up using a stainless steel autoclave containing 21 μmol of catalyst in 15 ml of distilled and degassed solvent, and the substrate in excess (500 equiv). The apparatus was degassed and refilled three times with H_2 and pressurized adequately. The autoclave that was equipped with a pressure gauge and an internal thermocouple was maintained in an oil bath at a given temperature. The hydrogenation reactions were followed by ^1H NMR and GC analyses on samples that were taken out regularly. Except for the *trans*-stilbene, which, as a solid, was used without purification, traces of peroxides were removed from all the liquid olefins by passing through an alumina column. A trap-to-trap distillation followed by the classical freeze-pump-thaw technique for removal of oxygen allowed storage of the substrates under inert atmosphere.
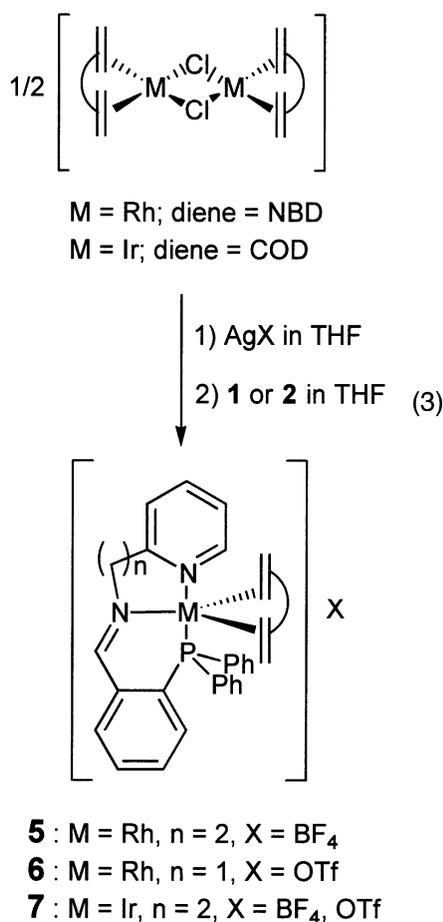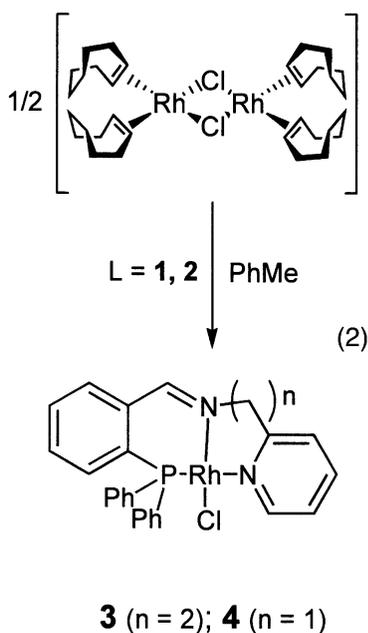
In the catalytic runs, the catalysts were isolated prior to use as described above or generated in situ. In the latter case, a catalytically active solution was prepared as follows: after dissolution of 1 equiv of $[Rh(COE)_2Cl]_2$ in the appropriate solvent, a solution of 2 equiv of the ligand **1** or **2** was added dropwise under nitrogen and allowed to react for 15 min, before addition of the substrate, and eventually the co-catalyst.

3. Results and discussion

In analogy with the synthesis by Vrieze et al. [6, 7], the new ligand **2** was obtained according to equation (1), by condensation reaction of 2-(diphenylphosphino)benzaldehyde and 2-(2-aminomethyl) pyridine in good yield (79%).
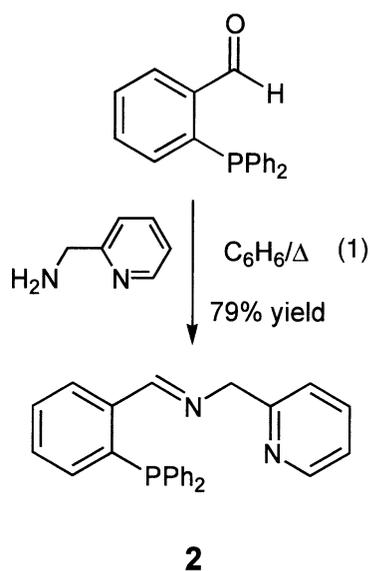
The complexation studies of **1** and **2** in the presence of rhodium and iridium have been carried out in a straightforward manner as shown in equations (2) and (3). Treatment of the rhodium precursor [Rh(COE)$_2$Cl]$_2$ with **1** and **2** in toluene yields the neutral complexes **3** and **4**, respectively. The cationic rhodium and iridium complexes **5**–**7** were prepared by halide abstraction with AgCF$_3$SO$_3$ or AgBF$_4$, followed by displacement of the diene ligand by **1** or **2**.

M = Rh; diene = NBD
M = Ir; diene = COD

1) AgX in THF

2) **1** or **2** in THF   (3)

5 : M = Rh, n = 2, X = BF$_4$
6 : M = Rh, n = 1, X = OTf
7 : M = Ir, n = 2, X = BF$_4$, OTf

Ligand **2** and complexes **3**–**7** were characterised by multinuclear NMR, IR, FAB–MS and elemental analysis. All the data are fully consistent with the structural formula and will be reported and discussed in detail elsewhere. Furthermore, X-ray crystallographic analysis of **5** and **7** confirms the tridentate coordination of ligand **1** and indicates a bipyramidal geometry around rhodium or iridium.

In order to investigate the reactivity of the new complexes, we firstly explored the behaviour of [Rh(**1**)Cl] in the presence of H$_2$. Interestingly, exposing a degassed C$_6$H$_6$ solution of **3** to H$_2$ (10 bar), with stirring for 2 h, resulted in the formation of [Rh(**1**)H$_2$Cl], as shown in equation (4).

C$_6$H$_6$/Δ   (1)

79% yield

2

L = **1**, **2** | PhMe

(2)

3 (n = 2); **4** (n = 1)

H$_2$
C$_6$H$_6$

(4)

3

3'
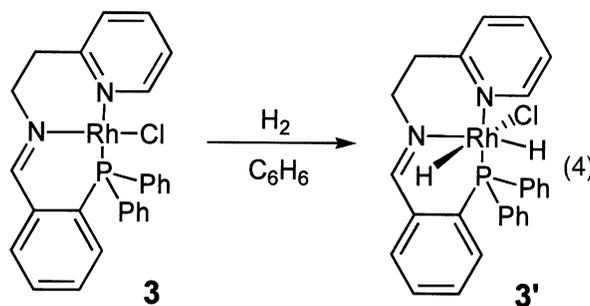
The new species is characterised in C_6D_6 by its $^{31}P\{^1H\}$ NMR spectrum, which displays a doublet at 39.02 ppm ($^1J_{Rh-P} = 136.6$ Hz) and by its ^1H NMR pattern, which appears as two sets of resonances: a doublet of doublet at –17.35 ppm ($^1J_{Rh-H} = 17.1$ Hz, $^2J_{P-H} = 9.4$ Hz) and a multiplet at –15.60 ppm. The above data are consistent with two hydride ligands in a cis position.
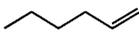
These results prompted us to test the catalytic activities of the new complexes. Preliminary experiments with all the iridium compounds have indicated a low activity towards the hydrogenation of imines and olefins. Our efforts have then been concentrated in the study of the rhodium complexes as potential hydrogenation catalysts towards various olefins including an easily reduced linear olefin (1-hexene), cyclic olefins (cyclohexene, cyclopentene or cyclooctene), and sterically demanding olefins (1-methyl-cyclohexene, α-methylstyrene or *trans*-stilbene). The data relative to the catalytic properties of the neutral complexes [Rh(**1**)Cl] **3** and [Rh(**2**)Cl] **4** are listed in Tables 1 and 2, and those concerning the anionic compound [Rh(NBD)(**1**)](BF$_4$) **5** in Table 3.

The catalytic reactions were carried out in an autoclave, usually under mild temperature and pressure conditions, using the catalyst (21 μmol), either previously isolated or prepared in situ, and combined with the substrate (500 equiv) in various solvents, although methanol was proven to be the best choice in many cases. The evolution of all reactions was monitored by ^1H NMR and GC analyses on samples withdrawn regularly from the autoclave. Details are included in the experimental section.
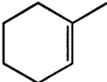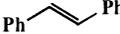
On the basis of a comparative analysis concerning the behaviour of the various catalysts reported herein, it is clear that the cationic complex **5** is less active than the neutral ones **3** and **4**, although conversion rates close to 100% have been observed in all cases. Moreover, in order to achieve the completion of the catalytic reaction, the reaction times appeared to be relatively long, especially with simple olefins such as 1-hexene. We thus have focused our attention towards the more promising catalysts **3** and **4**, which were found to be very efficient catalytic systems for the hydrogenation of a wide variety of olefins. The linear and cyclic olefins undergo rapid reduction under mild conditions, with conversion rates of nearly 100%, as depicted in Table 1. Notably, in the case of 1-hexene, the classical isomerisation side-reaction leading *cis* and *trans*-2-hexene is disfavoured, which explains the unusual high yields in production of hexane up to almost 100%. The results obtained with the sterically demanding olefins, which are known to be difficult to reduce, are also remarkable in terms of total conversion. However, the *trans*-stilbene requires higher pressures and longer reactions times, although the initial

Table 1. Hydrogenation[a] of 1-hexene and cyclic olefins in the presence of **3** and **4**.

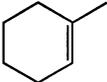| Entry	Substrate	Catalyst[I/II]	P_{H2} (atm)	Time (h)	Conversion (%)	$t_{1/2}$ (h)[c]	iTOF (h^{-1})[d]
1		**3**[I]	5[e]	70	99	14.5	50
2		**3**[I, b]	5	15	99	3	180
3		**3**[II]	2	11	99	4	190
4		**3**[II, b]	2	7	100	4	290
5		**3**[II]	5	5	99	0.75	360
6		**3**[II, b]	5	3	100	0.35	870
7		**4**[I]	2	1	99	0.35	620
8		**4**[II]	2	1.75	99.5	0.3	740
9		[Rh(PPh$_3$)$_3$Cl][f]	2	1.7	99	—	600
10		**3**[I]	5	70	94	18	10
11		**3**[II]	5	6	100	2.2	770
12		**3**[II]	2	8	100	5	200
13		**3**[II, b]	2	8	100	3.5	30
14		**4**[II]	2	4.5	100	1	410
15		**4**[II]	5	2	100	0.8	690
16		[Rh(PPh$_3$)$_3$Cl][f]	1.5	1.9	96	–	840
18		**3**[II]	2	1.25	100	0.5	710
19		**4**[II]	2	1.25	100	0.35	860
20		**3**[II]	2	4.25	100	2.2	310
21		**4**[II]	2	5.25	100	2.4	250

I: Isolated catalyst; **II**: in situ catalyst. [a] Standard conditions: 21 μmol of catalyst in 15 ml of methanol; ratio substrate/catalyst = 500; $T = 30$ °C (unless stated otherwise). [b] 5 equiv NEt$_3$ per Rh. [c] Time for 50% conversion. [d] iTOF = initial Turnover Frequency, the value of which was determined at $t = 0.25$. [e] $T = 20$ °C. [f] Conditions: 25.6 μmol of catalyst in MeOH; S/Cata = 500 [11–12].

Table 2. Hydrogenation[a] of sterically demanding olefins in the presence of **3** and **4**.

Entry	Substrate	Catalyst[I/II]	P_{H2} (atm)	Time (h)	Conversion (%)	$t_{1/2}$ (h) [c]	iTOF (h^{-1}) [d]
1		**3**[I]	10	72	14	–	10
2		**3**[II]	10	23	100	2.5	90
3		**3**[II, b]	10	32	99	3	160
4		**4**[I]	10	48	98	18	100
5		**4**[II]	10	25	100	3.6	120
6		**4**[II]	5	24	100	3	90
7		[Rh(PPh$_3$)$_3$Cl][f]	0.8	150	100	–	12
8		**3**[II]	2	47	100	24.5	50
9		**3**[II]	5	27	100	12.5	60
10	Ph	**3**[II, b]	5	24	100	12	5
11	Ph—Ph	**3**[II, e]	70	36	90	0.75	300
12		**3**[II, b, e]	70	38	93	0.4	840

I: Isolated catalyst; **II**: in situ catalyst. [a] Standard conditions as in Table 2. [b] 5 equiv NEt$_3$ per Rh. [c] Time for 50% conversion. [d] iTOF = initial Turnover Frequency, the value of which was determined at $t = 0.25$. [e] MeOH/C$_6$H$_6$ in 4:1 ratio. [f] Conditions: 500 µmol of catalyst in MeOH/C$_6$H$_6$; S/Cata = 1000, $T = 25°C$ [11–12].

Table 3. Hydrogenation[a] of selected olefins in presence of **5**.

Entry	Substrate	Solvent	P_{H2} (atm)	Time (h)	Conversion (%)	$t_{1/2}$ (h)	iTOF (h^{-1})
1		CH$_2$Cl$_2$	5	25	99.5	8	<5
2		MeOH	5	30	99	14	45
3		CH$_2$Cl$_2$	5	108	99	34	60
4		CH$_2$Cl$_2$	10	17	100	8.5	60
5		CH$_2$Cl$_2$	10	137	99	60	5

[a] Standard conditions as in Table 1.

rate remains generally high. In this case, the reaction slows down drastically after 75% conversion.

Several points of interest concerning the activities of **3** and **4** need to be pointed out.

1. The influence of the addition of triethylamine (5 equiv) as a cocatalyst can be summarised as follows. In the hydrogenation reaction of 1-hexene, it results in slightly increased initial and overall rates (entries 1–2, 3–4, 5–6 in Table 1). However, with cyclohexene as substrate, a negative effect is mainly detected on the initial rate (entries 12–13 in Table 1). In the case of 1-methylcyclohexene (entries 2–3 in Table 2), the conversion rate decreases, whereas with α-methylstyrene, the catalyst is slower (entries 9–10 in Table 2). The overall negative effect of a base added as cocatalyst is likely to indicate that during the catalytic cycle, no deprotonation reaction is involved.

2. In all cases, better activities and higher rates are obtained when the catalyst is generated in situ, instead of the preliminarily isolated catalyst. This difference is probably related to its sensitivity towards oxygen

and/or to some instability of the complexes in solution as noticed in the course of their NMR characterisation.

3. Finally, the [Rh(**2**)Cl] catalyst was found to be significantly more efficient than the related [Rh(**1**)Cl] catalyst. Such a marked improvement in activity may be the result of the size of the chelate around the metal. As opposed to a 6-membered ring around the rhodium in **3**, the constrained 5-membered ring encountered in **4** may allow a better accessibility to the substrate on the opposite side of the rhodium, yielding a better activity as observed.

Overall, complexes **3** and **4** are very active catalysts in hydrogenation reactions. In particular, the activity of **4** towards 1-hexene is comparable with that of the well-known Wilkinson's catalyst [11, 12]. However, if one refers to Crabtree's iridium catalyst [13, 14], our system appears less competitive. In presence of cyclohexene, the same trend is observed, although, based on a higher conversion rate, our catalyst represents an improvement on the results obtained with [Rh(PPh$_3$)$_3$Cl]. It is also noteworthy that the reactivity

of our catalysts depends upon the size of the cycle of the olefin in the order cyclopentene > cyclohexene > cyclooctene. Furthermore, [Rh(**2**)Cl] is by far a better catalyst than [Rh(PPh₃)₃Cl] towards the hydrogenation of α-methylcyclohexene, but not as good as Crabtree's catalyst, in spite of the conversion rate of 100% observed in our systems and of their robustness. Finally, **3** also exhibits a good catalytic activity towards α-methylstyrene and *trans*-stilbene, for which to our knowledge rare data have been reported in the literature until recently [15].

Although the detailed mechanism of hydrogenation of olefins in these catalytic systems is not fully understood, we propose the catalytic cycle presented in Fig. 2. The first step would involve oxidative addition of H₂ on the active species **3** or **4**, resulting in the formation of a dihydride compound (**I**). Convincing evidence for the existence of such a species was obtained by studying the reaction of **3** with H₂ which also gives rise to a complex containing two *cis*-hydride ligands on the basis of the ¹H and ³¹P{¹H} NMR analyses. Olefin coordination will then be facilitated by the hemilabile character of the ligand, as represented in (**II**). The formation of an alkyl derivative (**III**) via olefin insertion into one of the Rh–H bond follows. Finally, the active species is regenerated via reductive elimination of the alkane.

In conclusion, the new neutral rhodium complexes [Rh(L)Cl] are remarkably active for the hydrogenation of olefins. Higher activities are generally observed for [Rh(**2**)Cl] compared to [Rh(**1**)Cl], especially if the catalyst is prepared in situ. In the presence of 1-hexene, our catalyst performance competes well with that of the worldwide known Wilkinson's catalyst
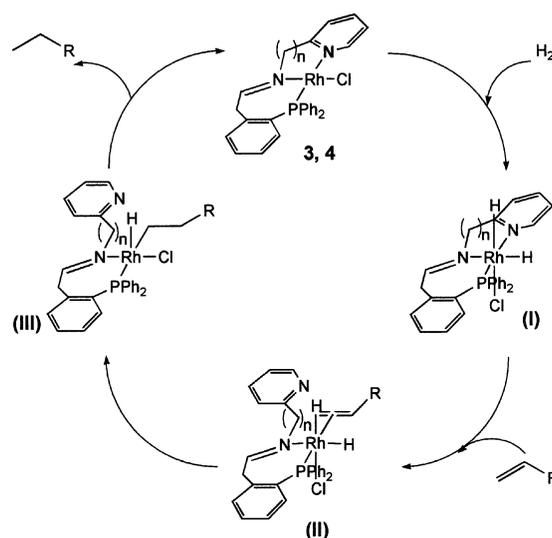

Fig. 2. Proposed mechanism for the hydrogenation of olefins in presence of **3** and **4**.

[11]. When cyclic olefins are involved, reducing the size of the cycle leads to a higher activity, and also the conversion rates of 100% represent a real improvement with respect to [Rh(PPh₃)₃Cl]. Finally, based on the overall rate and the conditions used for the reduction of hindered olefins, our systems may also be considered as better catalysts than [Rh(PPh₃)₃Cl].

This small contribution was meant to illustrate that, more than 30 years after the discovery of Wilkinson's catalyst, John Osborn's passion for organometallic chemistry has never been altered and his scientific roots have always been firmly anchored.

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