Cationic rhodium(I) complexes containing 4,4′-disubstituted 2,2′-bipyridines: A systematic variation on electron density over the metal centre

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Abstract

A series of $[Rh(COD)(X_2\text{-bipy})]BF_4$ complexes (COD = 1,5-cyclooctadiene; X_2-bipy = 4,4′-disubstituted 2,2′-bipyridines; X = OCH_3, CH_3, H, Cl or NO_2) has been prepared from $[Rh(COD)Cl]_2$. The complexes for X = OCH_3, Cl and NO_2 have not been described previously in the literature. All complexes have been characterised by elemental analysis, IR, ^{1}H NMR and UV–Vis spectrometry. This series of complexes presents a wide variation on electron density over the metal centre with virtually no variation on its steric environment which discloses interesting possibilities for catalytic and electro-catalytic studies. A preliminary evaluation of these complexes on the hydroformylation of camphene and β-pinene showed that under the rather drastic conditions employed the complexes acted as a precursor for $[Rh(CO)_3H]$, which accounts for most of the catalytic activity.
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Keywords: Cationic rhodium(I) complexes; Substituted bipyridine; Hydroformylation; Rhodium catalysts

1. Introduction

Cationic rhodium(I) complexes have long been acknowledged as catalysts precursors for many reactions such as hydrogenation [1] or transfer hydrogenation [2] of double-bonds, water gas shift reaction [3], amination [4], hydroamination [5], hydroformylation [6–8], among others. Although phosphorus ligands are more widely used for these reactions, in many instances nitrogen-donors such as 2,2′-bipyridines have been successfully employed [9–20].
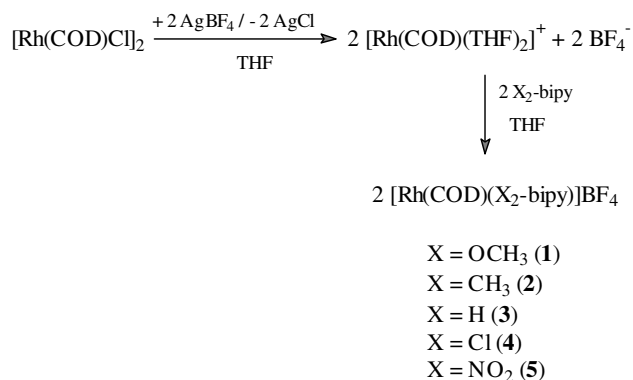
We have been studying the diastereoselective hydroformylation of monoterpenes as a way of better understanding the diastereoselectivity control in hydroformylation employing rhodium complexes [21] or platinum/tin systems [22,23] as catalysts. In a previous work [21] we described

the rhodium-catalysed hydroformylation of β-pinene and camphene in the presence of various phosphines and phosphites ancillaries. It has been demonstrated that the diastereoisomeric excess for the *cis* aldehyde is directly related to the electron-donating ability of the ancillary measured as described by Tolman [24]. Nevertheless, no clear correlation was found for its steric parameter (cone angle). In order to investigate whether or not this influence is purely electronic we decided to synthesise rhodium(I) complexes containing various 2,2′-bipyridines disubstituted in the 4,4′ positions by the methoxy, methyl, chloro, or nitro groups. In this series there is a considerable variation on the electron-donating ability of the ligands with virtually no variation on their steric parameters.

In this work, we describe the synthesis and the spectroscopic characterisation of rhodium complexes of the type $[Rh(COD)(X_2\text{-bipy})]BF_4$ (COD = 1,5-cyclooctadiene; X_2-bipy = 2,2′ bipirydine or 2,2′ bipirydine 4,4′-disubstituted by Cl, OCH_3, NO_2, CH_3), as well as their use as a catalyst for the hydroformylation camphene and β-pinene.

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$$[Rh(COD)Cl]_2 \xrightarrow[\text{THF}]{+\,2\,AgBF_4\,/\,-\,2\,AgCl} 2\,[Rh(COD)(THF)_2]^+ + 2\,BF_4^-$$

$$\downarrow \begin{array}{c} 2\,X_2\text{-bipy} \\ \text{THF} \end{array}$$

$$2\,[Rh(COD)(X_2\text{-bipy})]BF_4$$

X = OCH₃ (**1**)
X = CH₃ (**2**)
X = H (**3**)
X = Cl (**4**)
X = NO₂ (**5**)

Scheme 1.

2. Results and discussion

2.1. Synthesis of the complexes

For the synthesis of the complexes a straightforward route was employed. Firstly, [Rh(COD)Cl]₂ was reacted with silver tetrafluoroborate in tetrahydrofuran which acts as a labile stabilising ligand. The addition of a stoichiometric amount of the substituted bipyridines to the rhodium solution after silver chloride removal resulted in the immediate formation of desired compounds in high yield. (Scheme 1).

The stripping of the solvent and washing with fresh portions of THF resulted in sufficiently pure compounds, which was confirmed by the narrow melting point and elemental analysis. It is interesting to observe that only for 2,2′-bipyridine as ligand the solid showed by ¹H NMR a molecule of THF as a crystallization solvent, which was easily removed by recrystallization in methanol. The complexes present low solubility in toluene, chloroform, and tetrahydrofuran, moderate solubility in dichloromethane and are soluble in methanol and ethanol.

2.2. Infrared spectroscopy

The IR spectra of the complexes in the range of 5000–400 cm⁻¹ are similar to those of the free ligands (Table 1). The most significant shifts are related to the absorptions assigned to the aromatic ring stretching of the bipiridinic

Table 1
Selected bands, cm⁻¹, and assignments for the infrared spectra for the free ligands and their complexes

Free ligand		Complex[a]					Assignments[d]
X₂-bipy[b]	COD[c]	1	2	3	4	5	
3100–3080w		3100vw	3090w	3090vw	3090vw	3100w	v CH$_{ar}$
	3000–2850s	2920vs, 2850vs	2920vs, 2850vs	2920vs, 2850vs	2920vs, 2850vs	2920vs, 2850vs	CH$_{al}$
1530vs						1540	v_{asy}NO₂
1520vs		1470s	1460s	1470s	1470s	1470s	v ring$_{ar}$
	1430s	1380m	1380s	1390m	1380s	1370s	v C=C$_{al}$
1340vs						1350s	v_{sy} NO₂
1230s		1250m					v_{asy} COC
1080m					1080s		v CCl
1050vs		1050s					v_{sy} COC

[a] From Nujol mulls.
[b] From KBr pellets.
[c] From the literature.
[d] From the literature [25], v, axial stretching vibration; sy, symmetry vib.; asy, anti-symmetry vib.; ar, aromatic; al, aliphatic.

Table 2
Proton chemical shifts[a] for the free ligands (L)[b] and their complexes [Rh(COD)(X₂-bipy)]BF₄(C)[c]

Complex	X	H$_{3,3'}$		H$_{5,5'}$		H$_{6,6'}$		Substituent 4,4′		H$_a$		H$_b$	
		L	C	L	C	L	C	L	C	L	C	L	C : H$_{b'}$/H$_{b''}$
1	CH₃O	7.98d (0.00)[d]	7.98d	6.84dd (0.34)	7.18dd	8.46d (−0.68)	7.78dd	3.94s (0.14)	4.08s	5.54m (−1.02)	4.52m	2.34m	2.57m/2.17m J = 0.40
2	CH₃	8.23d (0.08)	8.31d	7.11dd (0.39)	7.50dd	8.52d (−0.71)	7.81d	2.41s (0.16)	2.57s	5.54m (−0.93)	4.61m	2.34m	2.60m/2.19m J = 0.41
3	H	8.40d (0.05)	8.45d	7.30dt (0.39)	7.69dt	8.69d (−0.69)	8.00d	7.81dt (0.43)	8.24dt	5.54m (−0.86)	4.68m	2.34m	2.62m/2.24m J = 0.38
4	Cl	8.47d (0.19)	8.66d	7.37dd (0.41)	7.78dd	8.60d (−0.66)	7.94dd			5.54m (−0.88)	4.66m	2.34m	2.69m/2.21m J = 0.48
5	NO₂	9.21d (0.17)	9.38d	8.12dd (0.33)	8.45dd	9.03d (−0.66)	8.37dd			5.54m (−0.86)	4.68m	2.34m	2.62m/2.29m J = 0.33

[a] In ppm downfield from TMS.
[b] In chloroform-d.
[c] In methanol-d_4.
[d] Values in parentheses are coordination induced shifts (c.i.s.).

ligands (from 1520 to 1470–1460 cm^{-1}) and the double bond stretching of the 1,5-COD (from 1430 to 1390–1370 cm^{-1}).

2.3. Nuclear magnetic resonance

The ^{1}H NMR spectra of the complexes exhibit resonances due to X$_2$-bipy and COD hydrogen. The comparison of these data with uncoordinated ligands (Table 2) showed induced shifts due to coordination to metal (c.i.s. $= \delta_{\text{coordinated ligand}} - \delta_{\text{free ligand}}$) [26]. In **X$_2$-bipy** ligands, the c.i.s. were positive in H$_{3,3'}$ and H$_{5,5'}$ (downfield). This indicates a diminution of electron density in the ring due to the donation to the metal. On the other hand, H$_{6,6'}$ undergo a upfield shift after coordination probably due to the anisotropic effect of the metal atom in the neighbourhood. A shielding effect is also observed for the H$_a$ signal for the co-ordinated COD: the more electron-donating the X-substituents, the higher the shielding. H$_b$ appears as a single multiplet for the free ligand which is split in two for the co-ordinated ligand as the hydrogen atoms are no longer equivalent. The vicinal J-couplings are in the range of 0.33–0.41 ppm. These results are in accordance with the previously reported for analogous complexes [11]. These data confirm that after addition of **X$_2$-bipy** ligands in complex preparation, COD keeps the η^4-bonding to rhodium, like its precursor, in which the hydrogens bound to the secondary carbons are sterically distinct (H$_{b'}$ and H$_{b''}$), as showed in Fig. 1. The H$_{b''}$ is under the shielding effect of the double bound and has the lower δ values.

2.4. UV–Vis spectroscopy

A clear evidence for the changes in the electronic levels on the metal as X varies is the remarkable change in colour
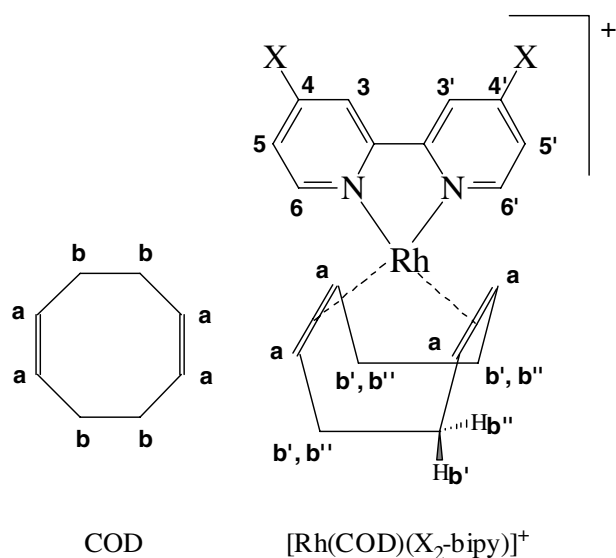

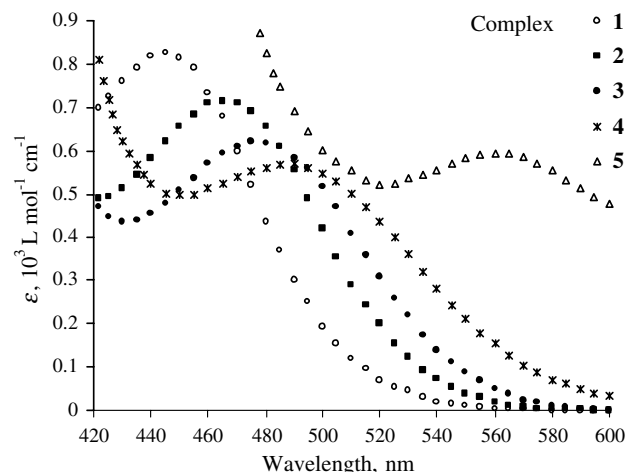Fig. 2. Visible absorption spectra of **1**–**5** (ε multiplied by 1.15 for **5**).

along the ligand series. It is noteworthy the difference in colours among the complexes depending on the X-substituent: X = OCH$_3$, yellow; CH$_3$, orange; H, red; Cl, purple; NO$_2$, dark green. The absorption maxima ($\lambda_{\max}$) are observed in the range 444–562 nm (Fig. 2) and were assigned to rhodium d–d transitions. The $\varepsilon_{\max}$ (ca. 10^2 L mol^{-1} cm^{-1}) is high, considering that this transition is spin-forbidden for d^8 configuration of Rh(I), but there is a relaxation of the selection rule due to the spin–orbit coupling usually observed in heavy d-metals complexes [27]. There is a general tendency to increase $\lambda_{\max}$ with the increase of the electron-withdrawing ability of the substituent. In attempting to quantify this effect, we choose the Hammett parameter (σ_p) which is a measure of the electron-withdrawing capacity of a substituent in an aromatic ring. Groups with a better electron-withdrawing ability than hydrogen will have positive values for σ_p, and negative values correspond to groups with a better electron-donating ability than hydrogen [28].

Indeed, there is a fairly good linear correlation between σ_p and the $\lambda_{\max}$ of the complexes in visible spectra (Table 3 and Fig. 3). This can be interpreted as the increase of the splitting between d$_{xy}$ and d$_{x^2-y^2}$ orbitals of the metal with the increase in electron density of the ligand. Fig. 4 shows the correlation between $\lambda_{\max}$ and the pK_a for each **X$_2$-bipy**. There is a general tendency to reduce $\lambda_{\max}$ with the increase in pK_a of the ligand. There is a good linear correlation between these parameters for X = CH$_3$O, CH$_3$, or H. This

COD   [Rh(COD)(X$_2$-bipy)]$^+$

Fig. 1. Numbering for ^{1}H NMR assignments.

Table 3
Hammett parameters, σ_p, for X in X$_2$-bipy and absorption maxima, $\lambda_{\max}$, of the complexes

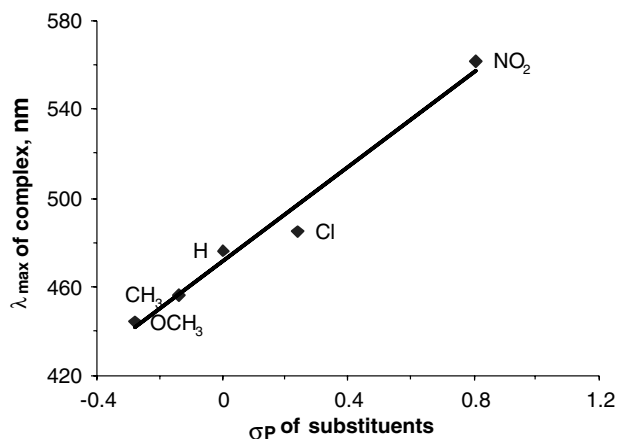| Complex	X	σ_p	$\lambda_{\max}$ (nm)
1	OCH$_3$	−0.28	444
2	CH$_3$	−0.14	456
3	H	0	476
4	Cl	0.24	485
5	NO$_2$	0.81	562

Fig. 3. Correlation between Hammett parameters (σ_p) for X in X_2-bipy and absorption maxima (λ_{max}) of the complexes.
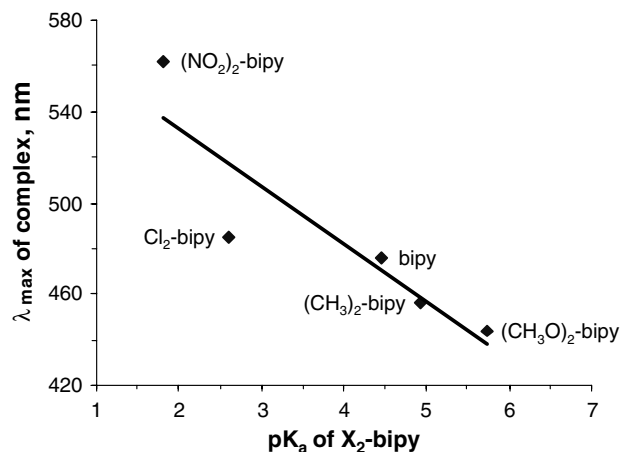

Fig. 4. Correlation between pK_a of X_2-bipy and absorption maxima (λ_{max}) of the complexes.

Table 4
Hydroformylation of β-pinene (6) catalyzed by [Rh(COD)(X_2-bipy)]BF$_4$[a]

Complex	X	Conversion (%)	Product distribution (%)			
			7	8	9	Others
1	–OCH$_3$	99	43	6	45	6
2	–CH$_3$	99	42	5	46	7
3	–H	99	46	5	39	10
4	–Cl	99	46	5	39	10
5	–NO$_2$	99	39	5	50	6

[a] β-Pinene = 10 mmol; catalyst = 1.00×10^{-2} mmol; dichloromethane = 20.0 mL; 80 °C; 80 atm (CO:H$_2$ = 1:1); 24 h.
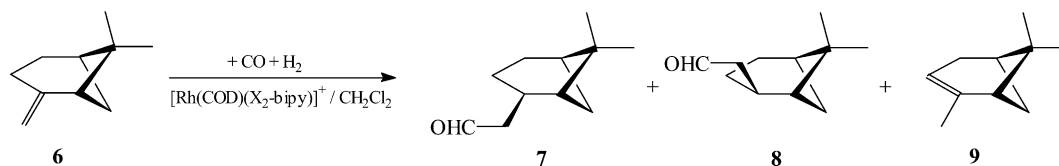
suggests that the separation in the energy level for this transition is predominantly determined by the σ bonding Rh-(X_2-bipy) which would be similar to an H$^+$-X_2-bipy bonding. Nevertheless, for X = Cl or NO$_2$, which are electron-withdrawing groups, the metal-to-ligand backbonding may play an important role, and this similarity is no longer valid.

2.5. Hydroformylation of β-pinene and camphene catalysed by the rhodium complexes 1–5

In a previous work we demonstrated that β-pinene and camphene can be hydroformylated employing the complex [(μ-acetato)(1,5-cyclooctadien)rhodium(I)] as a catalyst precursor with or without phosphor(III) ancillaries [21]. The results for the hydroformylation of β-pinene (6) employing the complexes 1–5 as catalyst precursors at 80 °C and 80 atm of CO/H$_2$ (1:1) are shown in Table 4

and Scheme 2. The aldehydes 7 and 8 were formed, accompanied by about 50% of the double-bond isomerization product, α-pinene (9). Although the conversion was complete after 1 h of reaction for all the complexes, the reaction was kept for additional 23 h to check for α-pinene hydroformylation. Indeed, along this reaction time α-pinene is slowly converted to the corresponding aldehydes accounted as "others" in Table 4. It is surprising that the selectivity of this reaction shows little dependence on the ligand, as we have demonstrated that employing the system [[(μ-acetato)(1,5-cyclooctadien)rhodium(I)]/PR$_3$ the selectivity depends strongly on the donation ability of PR$_3$: the more donating the ancillary, the greater the chemoselectivity for hydroformylation and the diastereoselectivity for 8 are. These complexes have a very similar behaviour to the unpromoted system where the complex [(μ-acetato)(1,5-cyclooctadien)rhodium(I)] readily generate [Rh(CO)$_3$H] under hydroformylation conditions [21].

In order to study the hydroformylation separately from double bond isomerization, camphene (10) was chosen for the kinetic studies because its double bond is similar to the β-pinene one but isomerization is not possible due to the lack of a neighbour secondary carbon to it. Its hydroformylation products are two diasteromeric aldehydes 11 and 12 (Scheme 3). In Table 5, it can be noticed that the complexes containing bipyridines with electron-withdrawing substituents (NO$_2$, Cl) led to a faster conversion of the substrate, having, therefore, a higher turnover frequency (TF = mol of substrate converted per mol of catalyst per hour). On the other hand, for the substituents containing electron-donating groups (CH$_3$O, CH$_3$), the
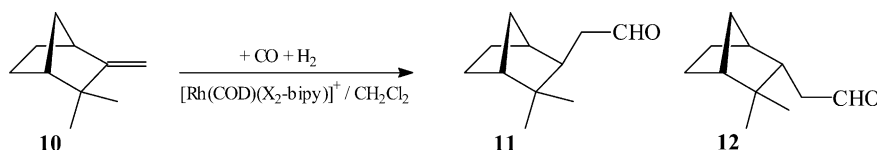

Scheme 2.

$$\text{10} \xrightarrow[\text{[Rh(COD)(X}_2\text{-bipy)]}^+ \text{/ CH}_2\text{Cl}_2]{+ \text{CO} + \text{H}_2} \text{11} \quad \text{12}$$

Scheme 3.

Table 5
Hydroformylation of camphene (**10**) catalyzed by [Rh(COD)(X$_2$-bipy)]BF$_4$[a]

Complex	X	Conversion (%)	TF (h^{-1})[b]	Product distribution (%)	
				11	12
1	–OCH$_3$	55	530	52	48
2	–CH$_3$	57	570	53	47
3	–H	74	740	52	48
4	–Cl	74	740	52	48
5	–NO$_2$	74	740	52	48

[a] Camphene = 10 mmol; catalyst = 1.00×10^{-2} mmol; dichloromethane = 20.0 mL; 80 °C; 80 atm (CO:H$_2$ = 1:1); 1 h.
[b] Turnover frequency: mol of substrate converted per mol of catalyst precursor per hour.

conversion of the substrate is slower and the turnover rate is lower.

These results suggest that the bipyridine complexes are acting as a precursor for [Rh(CO)$_3$H], which carries the fastest catalytic cycle and even at low concentration can account for the observed product distribution. In other words, the complexes containing bipyridines, have low activity compared to [Rh(CO)$_3$H]. Differences in turnover rates observed for camphene hydroformylation may be related to the ability of the complex to deliver the true catalyst: the stronger the X$_2$-bipy-Rh bound, the slower the formation of [Rh(CO)$_3$H] is, and, as a consequence, the turnover frequency will be lower.

3. Conclusion

Three new rhodium complexes with 4,4′-disubstituted 2,2′-bipyridines have been synthesised and characterised. A remarkable influence of the substituents on the electron density over the metal centre can be inferred from IV, ^{1}H NMR, and UV–Vis spectrometry. A preliminary evaluation on the catalytic behaviour of this series of complexes on camphene hydroformylation showed that the catalytic activity decreases with the increase of the Rh-bipy bond strength. The selectivity on β-pinene hydroformylation indicates that most of the catalytic activity is carried out by [Rh(CO)$_3$H] which is formed in situ from the bipy complexes under the rather harsh reaction conditions employed. Nevertheless, this series of complexes is promising for basic catalytic and electrocatalytic studies as there is a great variation on electron density in the metal centre with virtually no variation in its steric environment. Further studies are in progress in our laboratory.

4. Experimental

4.1. General procedures

All chemicals were purchased from Aldrich and used as received, unless otherwise indicated. Bis[(1,5-cyclooctadiene)(μ-chloride)rhodium(I)], [Rh(COD)Cl]$_2$ [29], 4,4′-dichloro-2,2′-bipyridine [30] 4,4′-dimethoxy-2,2′-bipyridine, and 4,4′-dinitro-2,2′-bipyridine [31–33] were prepared by published procedures. For convenience, a general sketch for bipyridines synthesis is depicted in Scheme 4. Tetrahydrofuran and toluene were purified under reflux with sodium wire/benzophenone for 6 h and then distilled under nitrogen. Dichloromethane was distilled under N$_2$ atmosphere over phosphorous pentoxide. The syntheses of the complexes were carried out under nitrogen atmosphere employing standard Schlenk techniques.

NMR spectra were obtained using a Brucker DRX 200 MHz spectrometer in CDCl$_3$ (bipyridines) or methanol-d_4 (Rh-complexes). IR spectra were obtained in a Mattson FTIR 3000-Galaxy Series spectrometer in KBr disks (bipyridines) or in a Nujol mull (Rh-complexes). UV–Vis spectra were taken in a Hewlett-Packard 8453 spectrometer (methanol solution 1.00 mmol L^{-1} in quartz cell of 1 cm). Elemental analysis was performed in a Carlo Erba Instrumentos EA 1110 CHNS-O. Gas chromatography (GC) was performed in a Shimadzu 17B instrument fitted with a Carbowax 20 M capillary column and a flame ionization detector. Mass spectra were obtained on a Hewlett-Packard MSD 5890/Series II instrument operating at 70 eV.

4.2. Synthesis of rhodium complexes

A solution of silver tetrafluoroborate (0.2745 g, 1.410 mmol) in 10 mL of THF was added dropwise with a syringe to a Schlenk flask containing a solution of [Rh(COD)Cl]$_2$ (0.3475 g, 0.7050 mmol) in 20 mL of THF. A white solid immediately precipitated and the mixture was magnetically stirred for 20 min to complete the precipitation of AgCl. After decanting, the yellow supernatant was filtered off to another Schlenk flask, and the solid was washed twice with 2 mL of THF in order to transfer quantitatively the soluble rhodium complex. A THF solution of bipyridinic ligand (1.410 mmol) was added dropwise with a syringe to the yellow solution. An immediate change in colour occurred and the solution was stirred for 30 min at room temperature. The solvent was carefully evaporated under vacuum at room temperature to yield the
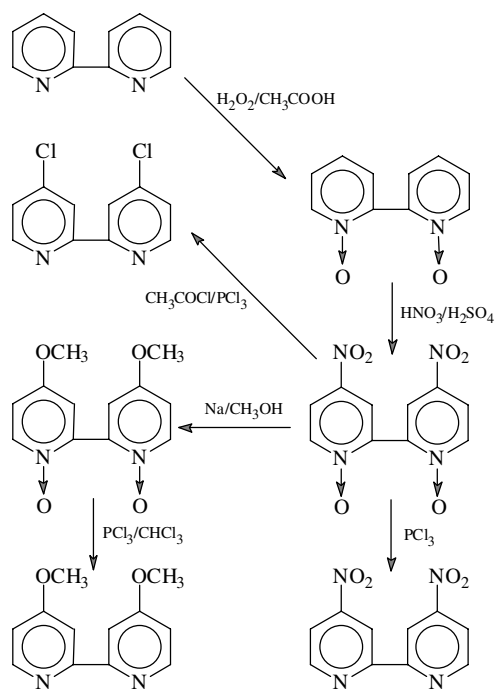
Scheme 4.

respective bipyridine complex which was washed twice with 2 mL of THF and dried overnight under vacuum.

4.2.1. [Rh(COD)(4,4'-dimethoxy-2,2'-bipyridine)]BF$_4$ (**1**)
Bright yellow crystals (0.6643 g, 92% yield) m.p. 263–264 °C. Elemental analysis: Calc. for BC$_{20}$F$_4$H$_{24}$N$_2$O$_2$Rh (512.12 g/mol): C, 46.2; H, 4.8; N, 5.1. Found: C, 46.7; H, 4.7; N, 5.4%.

4.3. [Rh(COD)(4,4'-dimethyl-2,2'-bipyridine)]BF$_4$ (**2**)

Bright orange crystals (0.6296 g, 93% yield) m.p. 269–270 °C. Elemental analysis: Calc. for BC$_{20}$F$_4$H$_{24}$N$_2$Rh (480.12): C, 49.8; H, 5.0; N, 5.8. Found: C, 49.2; H, 5.1; N, 5.2%.

4.4. [Rh(COD)(2,2'-bipyridine)]BF$_4$ (**3**)

Reddish orange solid (0.6018 g, 94% yield), dec. ∼300 °C Recrystallized from methanol. Red crystals were obtained, m.p. 286–288 °C (dec). Elemental analysis: Calc. for BC$_{18}$F$_4$H$_{20}$N$_2$Rh (454.08): C, 47.6; H, 4.4; N, 6.2. Found: C, 45.9; H, 4.4; N, 5.8%.

4.4.1. [Rh(COD)(4,4'-dichloro-2,2'-bipyridine)]BF$_4$ (**4**)
Purple crystals (0.6636 g, 90% yield), m.p. 253–254 °C. Elemental analysis: Calc. for BC$_{18}$Cl$_2$H$_{18}$F$_4$N$_2$Rh (522.97): C, 41.3; H, 3.4; N, 5.4. Found: C, 40.4; H, 3.6; N, 5.3%.

4.4.2. [Rh(COD)(4,4'-dinitro-2,2'-bipyridine)]BF$_4$ (**5**)
Dark green crystals (0.6904 g, 90% yield), dec. ∼300 °C. Elemental analysis: Calc. for BC$_{18}$F$_4$H$_{18}$N$_4$O$_4$Rh (544.08): C, 39.7; H, 3.3; N, 10.3. Found: C, 39.5; H, 3.3; N, 9.9%.

4.5. Catalytic runs

In a typical run [Rh(COD)(X$_2$-bipy)]BF$_4$ (1.0 × 10^{-2} mmol), β-pinene (10.0 mmol), dichoromethane (20.0 ml) were added in a Schlenk tube under nitrogen and stirred for 10 min at room temperature. The mixture was transferred into a stainless steel magnetic stirred reactor under nitrogen. The reactor was pressurized to 8.0 MPa total pressure (CO/H$_2$ = 1/1), placed in an oil bath at 80 °C and the mixture was magnetically stirred for 24 h. Reactions were followed by sampling the liquid phases under pressure. After carrying out the reaction and cooling the reactor to room temperature, the excess CO and H$_2$ was slowly vented. The solution was analyzed by GC and GC/MS and the products' identity was confirmed by comparison with authentic samples obtained as described previously [21].

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