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# Rigid, non-porous and tunable hybrid *p*-aminobenzoate/TiO<sub>2</sub> materials: Toward a fine structural determination of the immobilized $RhCl(Ph_3)_3$ complex

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## Introduction

Ample consideration has been made for developing the immobilization of catalysts on various supports to combine the advantages of both homogeneous and heterogeneous catalysis [1]. While metal complexes can be grafted directly on the carrier and result in true "Surface OrganoMetallic Complexes", some will require an anchor often provided by a derivatized support for both the tethering and tailoring of the metal center and provide "Supported Homogeneous Complexes" [2]. These so-called "post-functionalized" hybrid supports are generally prepared by reacting the surface hydroxyl groups of an inorganic oxide with an organic spacer (frequently an organosilane) presenting a coordinating function such as phosphanes, thiols or amines [3]. The latter proved to generate stability and catalytic activity of late transition metals. For this purpose, diverse sophisticated aminated materials were reported, e.g. polyamidoamine (PAMAM) dendrimers supported on silica [4]. However, such systems generally suffer from non-

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## ABSTRACT

By exchange of ligands, Wilkinson complex RhCl(PPh<sub>3</sub>)<sub>3</sub> are immobilized on *p*-aminobenzoate/TiO<sub>2</sub> with different organic loading (6, 11 and 16%). This new hybrid material exhibit a linear correlation between the ligand content of the starting TiO<sub>2</sub> and the rhodium loading, showing the accessibility of all surfaces amines fonctions on the non-porous parent materials. <sup>1</sup>H, <sup>13</sup>C, and <sup>1</sup>D, <sup>2</sup>D INAQUEDATE refocused and *J*-resolved <sup>31</sup>P solid-state NMR confirm the well-defined structure  $[(\equiv TiO)_2(n^2-O_2C-C_6H_4-NH_2)RhCl-cis-(PPh_3)_2]$ . New immobilized catalysts show interesting activity in cyclohexene hydroformylation.

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homogeneously (inaccessible) distributed functions which do not warranty a homogeneous grafting of any metal, the flexibility of the alkyl linkers, and also the presence of unreacted siloxanes moieties [5], limiting the complete structural determination of the metal center. Therefore, the development of well-defined aminated supports is a necessary requirement for a full investigation of the final material for "catalysis by design" to achieve structure/activity relationship and go beyond the "making sure that the immobilization worked" suggested by Blümel et al. [6].

Among the conventional processes for the development of hybrid support, Sol–gel chemistry could be an alternative strategy [7]. Through the hydrolysis of organically modified titanium isopropoxide, Rahal et al. published a one pot synthesis at low temperature of a series of non-porous *p*-aminobenzoate/TiO<sub>2</sub> hybrid materials, denoted [( $\equiv$ TiO)<sub>2</sub>( $\eta^2$ -O<sub>2</sub>C–C<sub>6</sub>H<sub>4</sub>–NH<sub>2</sub>)], presenting rigid aromatic tethers and controlled amine content [8]. Here we report the use of these tunable hybrid aminated supports as a mean to overcome all the above mentioned disadvantages of classical complexes heterogenization. The choice of the Wilkinson complex RhCl(PPh<sub>3</sub>)<sub>3</sub> has just been the result of a simple proof of concept. The morphology of these materials and the fine chemical design of the supported organometallic moiety have been characterized by BET, TEM, XRD, TGA, mass balance analysis, IR, solid state NMR (<sup>1</sup>H MAS, <sup>13</sup>C CP/MAS and <sup>31</sup>P MAS, CP/MAS, 2D refocused INADEQUATE







and J-resolved). The accessibility and the loading effect of the amine functions on the nature and the surface coverage of the tethered complex were also studied as well as their catalytic performance in cyclohexene hydroformylation.

# **Results and discussion**

The *p*-aminobenzoate/TiO<sub>2</sub> with an organic loading of 6, 11 and 16% (**I**, **II** and **III**), were synthetized as reported previously (Scheme S1 in Supporting information) [8a]. The corresponding (**I-III**)-**Rh** complexes were obtained by refluxing a toluene solution of the Wilkinson complex RhCl(PPh<sub>3</sub>)<sub>3</sub> with **I–III** (see Experimental section, Fig. S2). The N<sub>2</sub> adsorption desorption isotherms of (**I–III**)-**Rh** complexes correspond to a mesoporous structure, similar to that of the starting materials (**I–III**) (see Fig. S3) [8a]. **I-Rh** gives a type-IV isotherm with capillary hysteresis loops of type-H2. **II-Rh** and **III-Rh** present the same type-IV isotherm and hysteresis loops of type-H4. Upon increasing the organic loading, the hysteresis which is assumed to be an intrinsic property of the pores, varies from type-H2 to type-H4. This can be explained by the disorder occurring in the pore network due to the increase of their aggregation state [9].

After reaction with the Wilkinson complex, the BET surface area and the total pore volume decrease dramatically respectively from 220, 58 and 16 m<sup>2</sup> g<sup>-1</sup> to 153 m<sup>2</sup> g<sup>-1</sup> (0.22 cm<sup>3</sup> g<sup>-1</sup>), 58 m<sup>2</sup> g<sup>-1</sup> (0.09 cm<sup>3</sup> g<sup>-1</sup>) and 16 m<sup>2</sup> g<sup>-1</sup> (0.05 cm<sup>3</sup> g<sup>-1</sup>) for (**I–III**)-**Rh**, respectively (Table 1). This phenomenon is likely related to the fact that the numerous phenyl groups coming from the Wilkinson complex reinforce inter-granular interactions and aggregation.

Transmission electron microscopy (TEM) indicates spherical nanoparticles with an average size of 5–6 nm (Fig. 1(A–C) and Fig. S4). Interestingly, the size of the particles remains stable before and after tethering the complex, only their state of aggregation increases, as discussed previously, with the organic contents. Fig. 1(B and C) displays Fast Fourier Transform (FFT) patterns and the HRTEM of TiO<sub>2</sub> nanoparticles. It shows sets of lattice fringes (Interplanar spacing  $d_{101} = 0.35$  nm) showing the presence of a highly crystalline anatase phase structure.

The XRD patterns of (I–III)-Rh are assigned to a pure tetragonal anatase phase with a high crystallization degree (JCPDS No. 21-1272). The average crystallite size (5-6 nm) estimated by the Scherrer equation is in good agreement with the TEM data (Fig. S5). It is noteworthy that the tethering of the Wilkinson complex does not influence the size and the crystalline phase of I-III. The IR spectra of (I-III)-Rh (Fig. S5) shows the presence of all bands characteristic of the parent samples (I–III) [8a], indicating that the *p*-aminobenzoate moiety was basically maintained throughout the grafting procedure on the surface of TiO<sub>2</sub> nanoparticles. The broad bands above 2500 cm<sup>-1</sup> are assigned to the stretching bands of NH<sub>2</sub> and OH groups. Bands below 1000  $\text{cm}^{-1}$ , could be assigned to the lattice vibrations of  $v_{(Ti-O)}$  [10]. New bands assigned to the phenyl fragments of the Wilkinson complex also appear at 3046 cm<sup>-1</sup>  $(v_{(Csn2-H)})$ . Simultaneously, the band at 1431 cm<sup>-1</sup> attributed to the aromatic  $v_{(C}=_{C})$  vibration of the *p*-aminobenzoate considerably increased in intensity after coordination of the complex. The band

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Surface area and total	pore volume of	(I–III)-Rh	(and I-III).

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Sample	Surface area $(m^2 g^{-1})$	Total pore volume $(cm^3 g^{-1})$	Pore size diameter (nm)		
I-Rh (I)	153 (220)	0.22 (0.26)	4 (3.7)		
II-Rh (II)	58 (216)	0.09 (0.19)	4.2 (3.8)		
III-Rh (III)	16 (153)	0.05 (0.2)	8 8 (4 9)		



Fig. 1. TEM images of III-Rh particles (A), FFT pattern (B) and HRTEM images of III-Rh particles and corresponding FFT pattern (C).

at 1119 cm<sup>-1</sup> could be assigned to the due to  $v_{(\mathbf{P}-\mathbf{Ph})}$  bond vibration [11].

Thermogravimetric analysis (TGA) of (**I–III**) presents an average organic loss of 6, 11 and 16%, respectively, while they are of 18, 27 and 40% for (**I–III**)-**Rh** (Fig. S6, the reported weight losses are those taking place above ca. 125 °C). The increase of organic content of the final materials is a clear indication of the successful tethering of the Wilkinson complex on the surface.

The fine chemical composition of (I–III)-Rh was determined by elemental analysis (Table 2). The rhodium content is respectively equal to 2.58 (0.251 mmol  $g^{-1}$ ), 4.62 (0.449 mmol  $g^{-1}$ ) and 7.00%  $(0.680 \text{ mmol g}^{-1})$ . This latter is linearly correlated to the organic loading of the corresponding I–III, even at high organic loading especially for **III** (Graph 1). This is not the case with previously reported PAMAM dendrimers materials for which the rhodium contents, less than 2% (0.2 mmol g<sup>-1</sup>), decrease while increasing the amine moiety [4a]. In the present case, approximately one rhodium per nitrogen atom and similar ratios of  $1 \pm 0.1$  Cl/Rh and  $2 \pm 0.1$  P/Rh are observed. This composition is derived from a bis(triphenylphosphino)chlororhodium moiety, given that the Wilkinson complex usually coordinates to an amine function by substitution of a triphenylphosphine group [3e,5]. These results confirmed the presence of exclusively surface accessible amine moieties on the TiO<sub>2</sub> particles. The only result which is not in line with the surface complex structure is the C/Rh ratios which are ranging from 48.1 to 52.8 and higher than the expected value (43). This is likely due to residual physisorbed toluene molecules confirmed by the <sup>13</sup>C CP/MAS spectroscopy (vide infra).

Each solid-state NMR spectrum of both (I–III) materials and (I–III)-Rh complexes collections present similarities and the cases

Elemental	content of	f the suppor	ted complexe	es (I–III)-Rh.

Table 2

	Rh	Cl	P	N	C	Rh/N	P/Rh	Cl/Rh	C/Rh
	wt % <sup>a</sup>	(th. 1) <sup>b</sup>	(th. 2) <sup>b</sup>	(th. 1) <sup>b</sup>	(th. 43) <sup>b</sup>				
I-Rh	2.58	0.90	1.36	0.35	15.88	1.0	1.8	1.0	52.8
II-Rh	4.62	1.69	2.71	0.80	27.47	0.8	1.8	1.1	51.0
III-Rh	7.00	2.58	4.24	0.84	39.28	1.1	2.0	1.1	48.1

 $^a\,$  0.05 and 0.1% error are estimated for values ranging from 0 to 1%.  $^b\,$  ±0.1.



**Graph 1.** Correlation between the organic content of (I–III) determined by TGA (wt %) and the rhodium content of (I–III)-**Rh** determined by elemental analysis (wt %).

of **III** and **III-Rh** will be discussed thereafter as an illustration (other <sup>1</sup>H, <sup>13</sup>C and <sup>31</sup>P solid-state NMR spectra in Figs. S10–S22). The <sup>13</sup>C CP/MAS spectrum of **III-Rh** shows small peaks at 114, 151 and 176 ppm respectively, attributed to m-**C**<sub>Ar</sub>, **C**<sub>Ar</sub>-NH<sub>2</sub> and **C**OO of the *p*-aminobenzoate linker (Fig. 2B) [8a,12]. Its *ipso* and *ortho* aromatic carbons signals and these of triphenylphosphine fragments range from 128 to 141 ppm. Some residual toluene is present as judged from its methyl signal at 21 ppm (confirmed by elemental analysis) and contributes to the change of the relative intensities observed for the aromatic carbon signals.

The <sup>31</sup>P MAS NMR spectrum displays two signals at 49.5 and 56.7 ppm and no peak in the – 5 ppm region from eventual uncoordinated phosphane. The absence of phosphine oxide species was confirmed when the <sup>31</sup>P MAS spectrum of **III-Rh** was in contact with air showing the appearance of one broad peak at 27.9 ppm flanked to a smaller one at 39.0 ppm. This is reasonably attributed to phosphine oxide signals (Fig. S23) [13]. Given that the <sup>31</sup>P MAS is quantitative, the integration of the two peaks from the fresh sample (1:1) supports the presence of two non-equivalent phosphorous atoms (Fig. 3). Interestingly, some groups mention the presence of one large signal centered at 29 or 32 ppm [3e,5] for the Wilkinson complex anchored through aminopropyl tethers. Their relative flexibility favors the formation of surface species in different environments which probably explains the broadening of the system



Fig. 3. <sup>31</sup>P MAS and CP/MAS NMR spectra of III-Rh. See Figs. S21 and S22 for spectra of I-Rh and II-Rh, respectively.

[Si]−NEt<sub>2</sub>RhCl(Ph<sub>3</sub>)<sub>2</sub> ([Si] =  $\equiv$ Si−O−)), reported by Petrucci et al., gives two peaks at 51.1 and 58.3 ppm [14]. The absence of any anchor in [Si]-NEt<sub>2</sub>RhCl(Ph<sub>3</sub>)<sub>2</sub> gives a rigid attached complex, more likely with a single-site character. In the present case, the aminobenzoate could be considered rigid enough to limit the sites interaction. The two peaks of **III-Rh** can be resolved into two doublets using a <sup>31</sup>P CP/MAS sequence (Fig. 3), with <sup>1</sup>J(Rh, P) coupling constants of 200 Hz for 49.5 ppm and 165 Hz for 56.7 ppm, in the same range as that of the molecular complex [15].

The mutual position of the two phosphorus atoms can be deduced from two dimensional <sup>31</sup>P NMR refocused INADEQUATE pulse sequences [16]. This method uses the homonuclear indirect <sup>31</sup>P–<sup>31</sup>P dipole–dipole *J* interaction between phosphanes species linked *via* Rh bridges for creating double quantum coherences. The <sup>31</sup>P through bound correlation spectrum obtained, using the refocused INADEQUATE pulse sequences is shown in Fig. 4. The resonance of two coupled phosphorous atoms occurs at the common double quantum frequency in the  $\omega_1$  indirect dimension correlating with the single quantum frequency of each peak in the  $\omega_2$  dimension. The P<sub>1</sub>–Rh–P<sub>2</sub> (P<sub>1</sub>  $\neq$  P<sub>2</sub>) connectivity is clearly indicated by the two intense correlations. The resonances among interconnected phosphorous atoms in *cis* position (<sup>2</sup>J(P, P)<sub>trans</sub> would have been of 365 Hz) [15].

128 C. 176 151 114 COO CARNH2 21 CH<sub>3</sub> toluene 131 120 I-CA 250 200 150 100 50 ppm

Fig. 2. <sup>13</sup>C CP/MAS NMR of III (A) and III-Rh (B); (\*: rotation bands).

In order to obtain an accurate value for  ${}^{2}J(P,P)_{cis}$ , a  ${}^{31}P$  2D *J*-resolved CP/MAS experiment was carried out [15]. The isotropic



Fig. 4. <sup>31</sup>P 2D refocused INADEQUATE NMR of III-Rh.





Scheme 1. Structure  $[({\equiv}TiO)_2(\eta^2-O_2C-C_6H_4-NH_2)RhCl-cis-(PPh_3)_2]$  proposed for the three surface complexes (I-III)-Rh.

part of the 2D *J*-resolved spectrum is shown in Fig. 5. In the <sup>31</sup>P homonuclear *J*-resolved 2D spectrum, the heteronuclear *J* coupling due to <sup>1</sup>*J*(Rh,P) remains along the F2 dimension while the homonuclear *J* coupling between <sup>31</sup>P appears along the F1 dimension. The splitting due to <sup>2</sup>*J*(P,P)<sub>cis</sub> is clearly resolved. The value of <sup>2</sup>*J*(P,P)<sub>cis</sub> is 60 ± 5 Hz from the 2D spectrum, which is similar to that observed for RhCl(PPh<sub>3</sub>)<sub>3</sub> [17].

The discrete organometallic complex structure for (**I–III**)-**Rh** denoted  $[(\equiv TiO)_2(\eta^2-O_2C-C_6H_4-NH_2)RhCl-$ *cis* $-(PPh_3)_2]$  is highly advanced (Scheme 1).

# Catalytic test

(I–III)-Rh complexes show a catalytic activity in the hydroformylation of cyclohexene into cyclohexane carboxyaldehyde and the results are summarized in Table 3. No alcohol was observed in



**Fig. 6.** TON (black) and cyclohexane carboxyaldehyde selectivity (red) of (I-III)-Rh materials. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

GC/MS. A blank test with TiO<sub>2</sub> in the same condition did not present any activity. The cyclohexene conversions start from 61% and slightly increase (61, 66 and 68% for (I-III)-Rh, respectively), however not proportionally, with the rhodium loading. Thus, the turnover numbers (TON) calculated from the number of moles of cyclohexene converted are respectively of 1436, 864 and  $592 \text{ mol mol}_{Rh}^{-1}$  while the TON of the molecular Wilkinson catalyst is of 907 mol  $mol_{Rh}^{-1}$  (Fig. 6). Although the TON of I-Rh is in the same range than the ones reported for supported Wilkinson catalysts in similar catalytic conditions [3d], the decrease of the II-Rh and III-Rh ones can be explained by surface interactions between metal centers. Blümel et al. studied the surface coverage effect on the catalytic performance in olefin hydrogenation of supported Wilkinson complex on silica and observed that reducing the Rh concentration leads to a better catalytic activity and maximal conversion can be reached faster [3b]. This can be related to a greater distance between the metal center avoiding dimerization or agglomeration deactivating the catalyst. In the present case, both TEM microscopy and BET analysis has revealed agglomerated materials when PABA loading is increased. Also, the organic and thus the metal surface coverage is sufficiently high for II-Rh and III-Rh and their surface areas sorely drop after grafting of the Wilkinson complex (vide supra BET study). Inter-granular and thus metal center interactions, as well as diffusion resistance of the substrates, seem to be favored and also support the lower TON.

#### Conclusion

In summary, the Wilkinson complex RhCl(PPh<sub>3</sub>)<sub>3</sub> has been anchored for the first time on *p*-aminobenzoate/TiO<sub>2</sub> aminated hybrid materials, by exchange of one phosphane ligand by the amine function. The crystalline phase and the morphology of the nanoparticles remain stable after the incorporation of the complex, as judged by TEM and XRD microscopies. The rhodium loading is proportional to the organic content and demonstrates the accessibility of all the surface amine functions of the non-porous parent materials. The rigidity of the *p*-aminobenzoate tether promotes the

# Table 3

Hydroformylation of cyclohexene catalyzed by (I-III)-Rh.<sup>a</sup>

Supported complex	Rh before reaction (wt %)	Rh after reaction (wt %)	Cyclohexene conversion (%)	TON <sup>b</sup>	Selectivity	
					Cyclohexane carboxy-aldehyde	Cycloh-exane
RhCl(PPh <sub>3</sub> ) <sub>3</sub> <sup>c</sup>	_	_	70	907	100	0
TiO <sub>2</sub> -PABA-Rh-I	2.58	0.43	61	1436	81	19
TiO <sub>2</sub> -PABA-Rh-II	4.62	0.47	66	864	98	2
TiO <sub>2</sub> -PABA-Rh-III (1st cycle)	7.00	1.82	68	592	100	0

<sup>a</sup> 0.100 (I-III)-Rh, 50 ml THF, 6 ml cyclohexene, 28 bar CO/H<sub>2</sub> (1:1), 100 °C, 20 h.

<sup>b</sup> TON (turnover number) = converted mol of cyclohexene/mol Rh.

 $^{c}$  m<sub>RhCl(PPh3)3</sub> = 0.042, n<sub>Rh</sub> = 0.0454 mmol.

isolation of the rhodium complex as confirmed by <sup>1</sup>H, <sup>13</sup>C, and 1D, 2D INADEQUATE refocused and *I*-resolved <sup>31</sup>P solid-state NMR suggesting the well-defined discrete structure  $[(\equiv TiO)_2(\eta^2 - \eta^2)]$ O<sub>2</sub>C-C<sub>6</sub>H<sub>4</sub>-NH<sub>2</sub>)RhCl-cis-(PPh<sub>3</sub>)<sub>2</sub>]. The three (I-III)-Rh complexes present good catalytic performances in the hydroformylation of cyclohexene. Interestingly, the activity decreases with the rhodium loading, related to local metal centers interaction but also agglomeration of the material. This unprecedented category of materials will serve as a new insight for catalysis by design.

# **Experimental section**

All manipulations were carried out under a dry argon atmosphere using glove-box and standard Schlenk techniques. Graftings were performed following the double-Schlenk procedure. Toluene was dried over Na/benzophenone, degased and freshly distilled prior to use. N<sub>2</sub> adsorption desorption isotherm were recorded on a Micromeritics ASAP 2420 apparatus. High-resolution transmission electron microscope (HR-TEM) and fast Fourier transform (FFT) pattern were obtained using FEI Titan Cryo Twin operating at 300 kV. Powder X-ray Diffractions (XRD) were recorded on a Bruker D8 Advance diffractometer with a range of  $10-90^{\circ} 2\theta$  using CuK $\alpha$ radiation as X-ray source. Thermogravimetric analysis (TGA) experiments were carried out in air within the temperature range of 27-800 °C at a temperature ramp of 10 °C using a Mettler-Toledo TGA-DSC/1. Elemental analyses (EA) were performed at the Mikroanalytisches Labor Pascher of Remagen (Germany), Fourier transform infrared (FT-IR) spectra were recorded on a Nicolet 6700 FT-IR instrument. One dimensional <sup>1</sup>H MAS. <sup>13</sup>C CP-MAS and <sup>31</sup>P CP-MAS solid state NMR spectra were recorded on a Bruker AVANCE III spectrometer operating at 400, 100 and 162 MHz resonance frequencies for <sup>1</sup>H, <sup>13</sup>C and <sup>31</sup>P respectively, with a conventional double resonance 4 mm CPMAS probe. The samples were introduced under argon into zirconia rotors, which were then tightly closed. The spinning frequency was set to 17, 10, and 15 KHz for <sup>1</sup>H, <sup>13</sup>C and <sup>31</sup>P spectra, respectively. 1H and 13C NMR chemical shifts are reported with respect to TMS as an external reference. <sup>31</sup>P chemical shifts are reported relative to H<sub>3</sub>PO<sub>4</sub>. For CP/MAS, the following sequence was used: 90° pulse on the proton (pulse length 2.4  $\mu$ s for <sup>13</sup>C and 1.8  $\mu$ s for <sup>31</sup>P), then a cross-polarization step with a contact time typically 2 ms, and finally acquisition of the <sup>13</sup>C and <sup>31</sup>P under high power proton decoupling. The delay between the scan was set to 5 s for <sup>13</sup>C and 10 s for <sup>31</sup>P, to allow the complete relaxation of the 1H nuclei and the number of scans was between 3000-5000 for carbon, 2000 scan for phosphorous and 32 for proton. An apodization function (exponential) corresponding to a line broadening of 80 Hz was applied prior to Fourier transformation. <sup>31</sup>P-<sup>31</sup>P INADEQUATE were recorded on a Bruker AVANCE III spectrometer operating at 162 MHz with a conventional double resonance 4 mm CPMAS probe according to the following general scheme. Following a short evolution time t<sub>1</sub>, during which they evolve under their combined resonance offsets, the DQ coherences are completely eliminated by phase cycling. For creating a full P-Rh-P connectivity map between the various phosphate units, 2D INADEAQUATE spectra were recorded using a spinning speed of 14 KHz, 90° pulse of 2.5 µs length. 32 data sets with 2056 scan each with delay of 1 s, under rotor-synchronized condition at t1 increments of 71.43 µs. A double coherence buildup time of  $2\tau=6$  ms was used.  $^{31}P$  J-resolved solid state NMR spectroscopy experiments were conducted on a Bruker AVANCE III spectrometer using a 4 mm MAS probe. The experiments were performed according to the following scheme pulse sequence. The first 900 pulse was replaced by the cross-polarization segment and high-power proton decoupling was performed during both the evolution (t1) and the detection  $(t_2)$ . The spectra were recorded using a spinning

speed of 14 KHz, 90° pulse of 2.5 µs length. 32 data sets with 2056 scan each with delay of 1 s the t1 increment was synchronized with the rotor t1 = 2n TR. Again, all spinning sidebands become coincident in the F1 dimension, enhancing the 2D signals.

#### Preparation of (I–III)-Rh complexes

The preparation of I-Rh is given as an example. Typically, RhCl(PPh<sub>3</sub>)<sub>3</sub> (0.359 g, 0.388 mmol, 1.1 eq./nitrogen loading) in toluene (20 ml) was stirred with I (0.800 g, 0.353 mmolN, previously dehydrated at 100 °C for 4 h under vacuum ( $10^{-5}$  Torr)), at 110 °C for 16 h. The solid was filtrated, thoroughly washed with toluene (5  $\times$  20 ml) to remove unreacted complex and dried under vacuum ( $10^{-5}$  Torr) over 5 h to provide a brick-color powder.

#### Catalytic tests

Typically, 0.100 g of (I-III)-Rh catalyst was charged in a Parr autoclave in a glove-box followed by the addition of 50 ml THF and 6 ml cyclohexene. The reactor was purged with the syngas (1:1 CO/ H<sub>2</sub>) at room temperature and then allowed to reach 100 °C. 28 bar of the syngas was charged and the reaction media stirred over 20 h under constant pressure. After cooling down the apparatus to 0 °C in an ice-bath, the pressure was released and an aliquot of the brown colored liquid phase was kept aside for GC/MS analysis. The brownish catalyst was recovered by filtration and used in the same condition for leaching study.

#### Appendix A. Supplementary data

Supplementary data related to this article can be found at http:// dx.doi.org/10.1016/i.jorganchem.2014.12.032.

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