Unexpected coordination behavior of ruthenium to a polymeric α-diimine containing the poly[*bis*(arylimino)acenaphthene] fragment

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Dedicated to Dr. Maurizio Peruzzini for his many contributions to inorganic chemistry.

Abstract

Use of homogeneous catalysts poses the problem of their recovery at the end of the reaction. A possible strategy to circumvent this problem is to make the ligand part of a polymer with limited solubility. In this work, we investigated the immobilization of complexes of Ar-BIAN ligands (Ar-BIAN = *bis*(arylimido)acenaphthene). We employed 4,4'-methylene-*bis*(aniline) as an amine able to bridge two acenaphthene moieties. However, the obtained product was a mixture of short-chain oligomers. A ruthenium complex of this mixture (Oligo-BIAN) was indeed catalytically active in the model hydrogenation of nitrobenzene to aniline by CO/H_2O but the complexes were too soluble in the reaction mixture to allow for an easy recovery. We thus further extended the molecular weight of Oligo-BIAN by polymerizing it with terephthaloyl chloride obtaining a polyamide (Poly-BIAN). The latter was insoluble in all solvents but its ruthenium complex was catalytically inactive in the model reaction. An deeper investigation, showed that coordination mode of monomeric Ar-BIAN ligands and Oligo-BIAN to $[Ru(CO)_3Cl_2(THF)]$ is differs from that of Poly-BIAN. This result was completely unexpected and constitutes a general warning not to give for granted the coordination mode of a complex to a functionalized polymer.

Keywords: N-ligands; Schiff bases; Polymeric ligands; Ruthenium; Heterogenized catalysts

1. Introduction

Transition-metal based homogeneous catalysis experienced a huge growth in the last decades. Nevertheless, it is well known that the number of homogeneous catalysts that reached commercialization is by far lower than that of heterogeneous catalysts. Indeed, the homogeneous nature of the former is a double-edged sword that enables to achieve very high activities and selectivities but is an obstacle to their recovery from the product. This is of course an issue when precious or toxic metals are used. Accordingly, many strategies have been developed to accomplish the heterogenization of homogeneous catalyst [1-7]. However, most of the times the modification of the ligand required for its immobilization and the procedure for their attachment to an insoluble support are difficult and expensive [8]. *Bis*-imine ligands of the Ar-BIAN

(*bis*(arylimino)acenaphthene) family are good candidates for overcoming these problems. In fact, Ar-BIAN synthesis is cheap and the modification of the electronic and steric properties of the ligands can be easily realized just by changing the aniline employed in their synthesis. Moreover, Ru, Ni, Pd and Pt complexes of Ar-BIAN are very active in several catalytic reactions [9-16]. In previous works by our group, we investigated the catalytic activity of polymeric membranes loaded with properly modified nitrogen ligands. We described an heterogenized system based on ruthenium/Ar-BIAN complexes embedded in modified polyether ether ketone (PEEK-WC) membranes for the catalytic reduction of nitroarenes using the CO/H_2O mixture as the reductant [17]. A major drawback of the material was its low stability in the presence of high amounts of the nitroarene (i.e. nitrobenzene), especially under the relatively forcing condition employed.

The use of transition metal complexes of insoluble polymeric ligands could have a higher economical and practical potential with respect either to their homogeneous analogues or to their heterogenized versions, specifically if easy and cheap synthetic procedures could be devised instead of tedious functionalization of preformed insoluble supports. In this context, we decided to synthesize macromolecular polyimine ligands based on the Ar-BIAN subunit and apply their ruthenium complexes in the catalytic reduction of nitrobenzene to aniline using CO as the reductant as a model reaction (equation 1) [18].

$$ArNO_2 + 2\ CO \xrightarrow[H_2O/ROH]{cat.} ArNH_2 + 2\ CO_2 \qquad \text{(eq. 1)}$$

2. Results and Discussion

2.1. Ligand and complexes synthesis

Only few examples of macromolecular Ar-BIAN have been reported in the literature so far. The synthesis of the first example was claimed in a patent in which 4,4'-methylene-*bis*(2,6-dialkylaniline) was used in combination with acenaphthenequinone (ANQ) (Figure 1A). The materials were used as ligand for Ni-catalyzed olefin polymerization. The preparation method was straightforward but, unfortunately, no characterization was reported [19]. Subsequently two different groups reported the synthesis of BIAN-polymers obtained from 1,4-phenylendiamine and ANQ (Figure 1B) [20, 21]. One of them reported a troublesome procedure based on the use of $TiCl_4$ and a sufficient characterization of the polymeric product is lacking [20]. Due to the extended π system, the polymer showed interesting properties for electronic and electrocatalytic applications. Lastly, the synthesis of phenyl-BIAN/fluorene copolymer (Figure 1C) obtained by Pd-catalyzed cross coupling reaction between an iodo-substituted Ar-BIAN and a dialkynylfluorenone was also reported [22]. The material was employed in the preparation of a graphite electrode with applications in lithium-ion batteries.

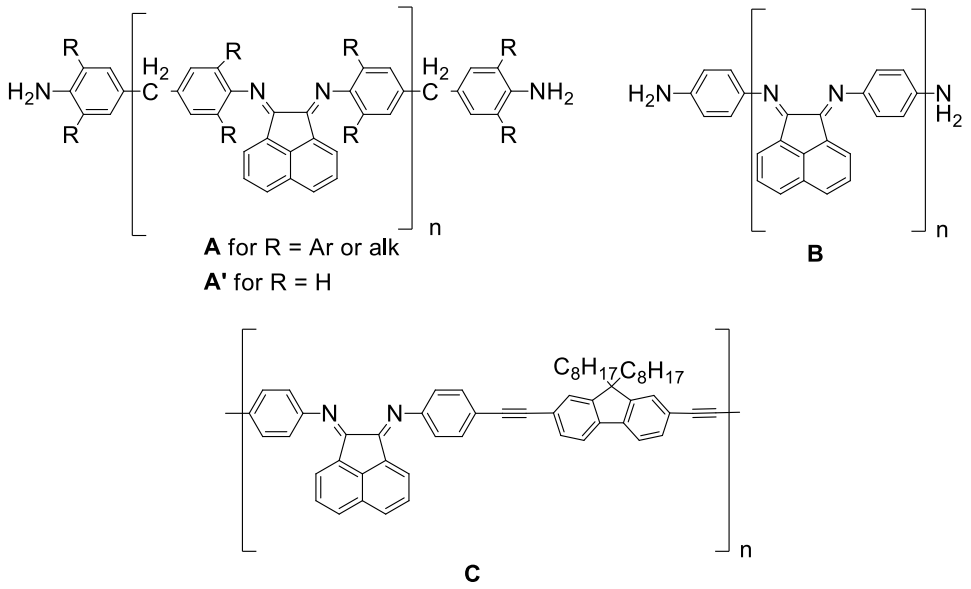


Figure 1. Polymeric materials based on an Ar-BIAN monomer

To avoid the presence of any noble metal that could remain in the polymer, we focused on the syntheses of Ar-BIAN in which only acenaphthene, a diamine and cheap and easy to handle additives were needed.

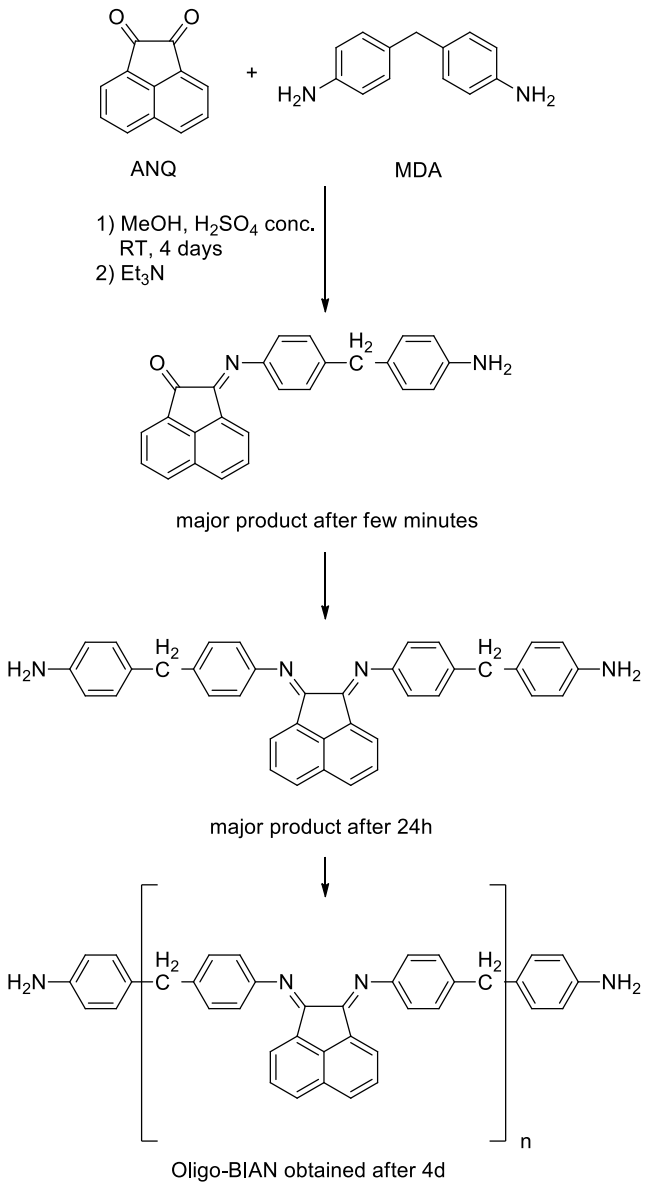
Although steric hindrance in the *ortho* positions of the aryl ring of Ar-BIAN is important to get high activities in the nickel and palladium catalyzed polymerization of olefins [23], in many other catalytic reactions, and specifically in the reductive transformation of nitroarenes, ligands with steric hinderance are almost inactive [24]. For this reason, we choose 4,4'-methylene-*bis*(aniline) (MDA) for the condensation with ANQ, to obtain a macromolecular Ar-BIAN without steric hindrance next to the *bis*-imine N-atoms and with a good flexibility (Figure 1A'). Unfortunately, while the synthesis of sterically hindered Ar-BIAN (e.g: 2,6-*i*$Pr_2C_6H_3$-BIAN) proceeds smoothly, requiring only an acid catalyst or an acid as solvent, the double condensation using unhindered anilines is less straightforward [25, 26] and most often stops at the monoimine stage.

A general synthesis of Ar-BIANs was optimized in our laboratories [27]. $ZnCl_2$ is used as condensing agent in refluxing acetic acid followed by decomplexation with potassium oxalate. Zinc chloride favors the condensation because the formed complex precipitates out the reaction mixture shifting the equilibrium. An alternative synthesis of Ar-BIANs, whose application is mainly limited to Ar-BIANs bearing alkyl or aryl groups in the *ortho* positions to the N-atom, involves acid catalyzed condensation either using or not a Dean-Stark trap for continuous removal of water. This method usually requires long reaction times and often leads to formation of side-products when unhindered anilines are employed [28].

2.1.1. Oligomeric-BIAN synthesis

In the early stage of this work, we tested both the $ZnCl_2$ mediated method and the acid catalyzed one in different solvents and for different reaction times. In the first case, we noticed a preferential complexation of MDA to the $ZnCl_2$ and fast precipitation of a mixture of complexes in which the

oligomeric BIAN was either not present or only present in minor amounts. With the second type of procedure, a partial decomposition of the product/reagents if a high temperature was maintained for long reaction times led to complex mixtures of product, often in the form of sticky tars. The reaction between MDA and ANQ was thus carried out at room temperature in dry methanol using concentrated H_2SO_4 as promoter (Scheme 1). A similar synthetic method was previously employed [29] for the preparation of Ar-DAB (DAB = diazabuta-1,3-diene) ligands, but we are not aware of its use in the synthesis of Ar-BIANs, for which the double condensation is more difficult.



Scheme 1. Synthesis of Oligo-BIAN

To avoid monomer formation, we used a molar ratio MDA/ANQ = 1.25. The reaction was carried on for four days, during which the proceeding of the reaction was constantly checked by thin-layer chromatography. The monoimine species already started to form after a few minutes. The main

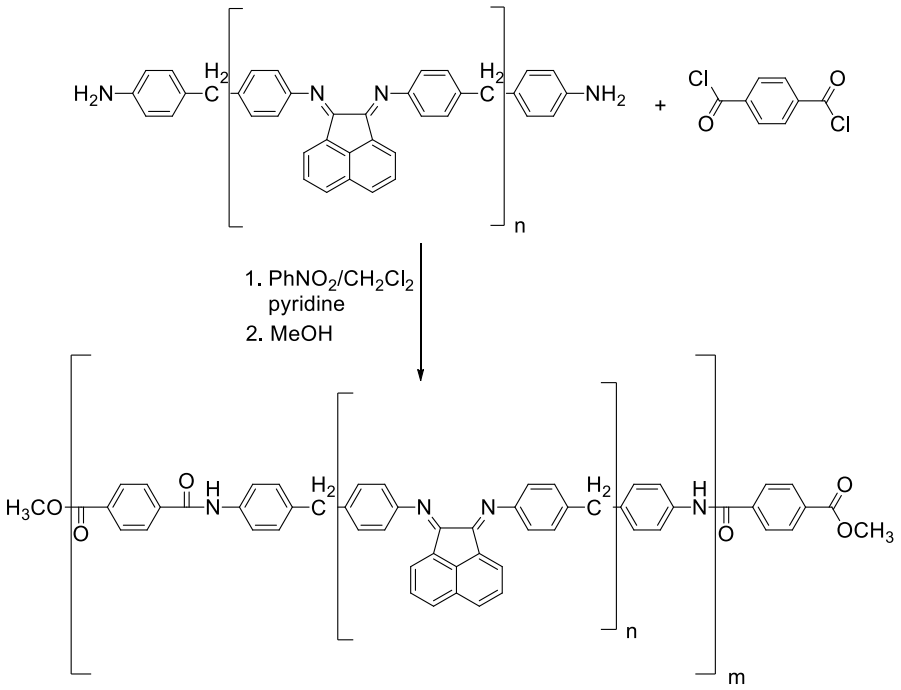
product after 24 h was the monomeric species, 4-(4-$NH_2C_6H_4$-CH_2)C_6H_4-BIAN, though it was not easily isolable from the reaction mixture. Acenaphthenequinone was completely consumed only after 48 h and, after four days, the product was composed by oligomeric species that are either insoluble or not eluted in TLC. The monomers were anyway still present and were not completely consumed even by further prolonging the reaction time, indicating that an equilibrium was reached. The insoluble fraction of the mixture of oligomers (Oligo-BIAN) was separated by filtration after basification with triethylamine. The obtained material was only slightly soluble in most of the solvents usually used in catalytic reaction, including alcohols, CH_3CN, toluene, THF and DMF.

2.1.2. Macromolecular BIAN-based ligand synthesis

Despite the low solubility of Oligo-BIAN in neat solvents, after complexation to ruthenium (vide infra), the material was partly soluble in common solvents. Among those, it was also soluble in MeOH, which is generally employed as solvent in the catalytic reduction of nitrobenzene by CO/H_2O [30], chosen as probe reaction.

Another possible strategy to obtain a polymer containing the BIAN moiety is to co-polymerize a monomeric-BIAN with another building block. However, the synthesis of monomeric-BIAN derived from MDA, proved more difficult than expected. We devised a procedure to prepare it (see Experimental section), but the yield was low, and the product could not be reproducibly obtained with a good purity.

Owing to the presence of terminal -NH_2 groups in Oligo-BIAN (vide infra) we aimed to increase the molecular weight of the oligomeric mixture, and thus to decrease its solubility, by co-polymerizing Oligo-BIAN with a co-monomer. Inspired by the structure and stability of aramid fibers (such a Kevlar and Nomex), Oligo-BIAN was reacted with terephthaloyl chloride, aiming to obtain an insoluble polymeric ligand (Poly-BIAN). Because of the incomplete solubility of Oligo-BIAN in common solvents, $PhNO_2$ was used to dissolve this starting material. The reaction with terephthaloyl chloride was thus carried out at 40 °C in the presence of excess pyridine as HCl scavenger, to prevent imine bonds hydrolysis. At the end of polymerization, MeOH was added to quench the acyl chloride groups at chains terminations (Scheme 2).



Scheme 2. Synthesis of Poly-BIAN

2.1.3. Ligands characterization

A first analysis of Oligo-BIAN was performed employing IR spectroscopy in Nujol mull. The presence of weaker bands at 1729 cm^{-1} (C=O stretching) and two very weak broad bands over 3300 cm^{-1} (-NH_2 stretching) with respect to the bands at 1657, 1625 and 1591 cm^{-1} (attributed to C=N and C=C stretchings) indicates the prevalence of polymerization products over ketonic and aminic termination. As mentioned above, Oligo-BIAN was insoluble in most common solvent used for NMR and mass analysis. We found that the material readily dissolves in nitrobenzene. Diluting the so obtained solution in acetonitrile it was possible to perform an ESI-MS analysis without precipitation of the oligomers. ESI-MS was suitable for our purpose because electron-spray ionization sources do not induce a high fragmentation degree on the molecules, thus permitting us to distinguish among the various oligomeric species present in the product mixture and their relative amounts. The relative abundance in ESI-MS analysis is not a highly precise quantitative measure of the real abundance of a certain species, since it depends also on the tendency of the molecule to be ionized. However, it was used as a semi-quantitative index of the dispersity of the oligomers. In the recorded mass spectra, we can easily assign the main peaks observed. The most intense peak was found at m/z $[M+H]^+$ = 1231.6 corresponding to the molecular mass of the trimer with two amine termination. Also very intense are the peaks at m/z $[M+H]^+$ = 1051.5 and 1395.5 attributed respectively to the trimer and tetramer with one keto and one amine terminations. Peaks with minor intensities are detected also for tetramer with two terminal -NH_2 and for pentamers with both -NH_2/-NH_2 and =O/-NH_2 terminations. Moving to higher molecular weight, the presence of peaks related to doubly charged molecular ions increases. Among these, the peak at m/z $[M+2H]^{2+}$ = 788.7, corresponding to the tetramer with two amine terminations, was the most abundant, while the molecule with the highest molecular weight detected was a hexamer (m/z $[M+2H]^{2+}$ = 1042.8). The main molecular peaks and full spectrum are reported in the SM (Table S1 and Figure S1). Neglecting the termination of the oligomer, the product

can be described as a mixture in which trimers and tetramers are the most abundant species in a ratio close to 1:1 (Figure 2).

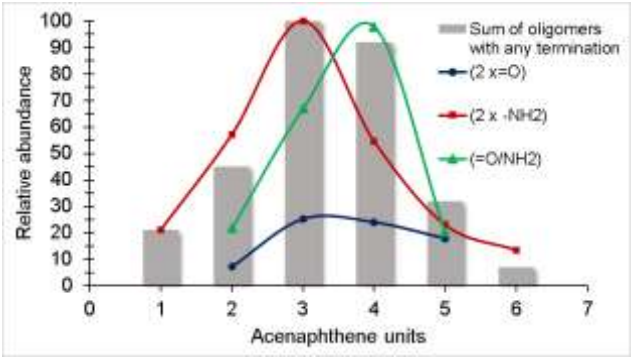


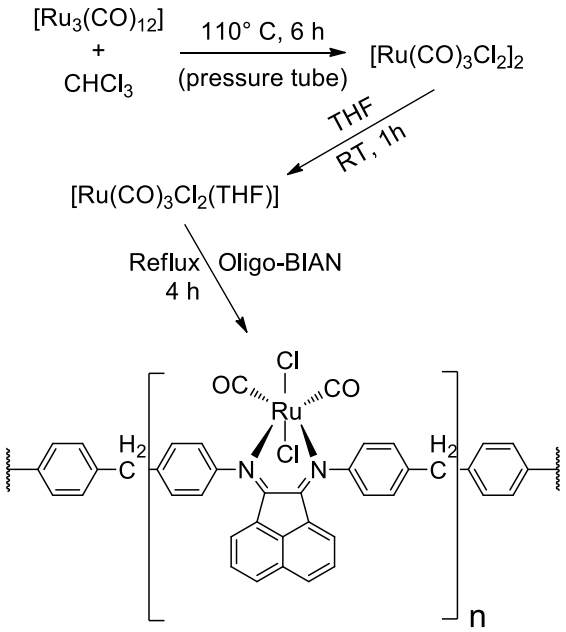
Figure 2. Oligomers distribution in Oligo-BIAN. The distinct curves refer to different chain terminations. The bar graph represents the abundance for oligomers with a given number of acenaphthene units, but with any termination. The data were obtained summing the relative abundance of all the peaks related to the same number of units and normalizing the obtained values to 100 as the largest value.

Characterization of Poly-BIAN by ESI-MS, proved to be more difficult than that of Oligo-BIAN. In fact, the material is insoluble not only in common solvents, but also in nitrobenzene. However, since we were interested in exploring the use of this heterogeneous ligand in catalytic reactions, we moved forward synthesizing its ruthenium complex without further characterization.

2.1.4. Ruthenium/macromolecular-BIAN complexes synthesis and catalytic activity

During the studies of one of us (F.R.) on Ar-BIAN-embedded catalytic membranes [17], it had been observed that the splitting of $Ru_3(CO)_{12}$ to generate $Ru(CO)_3$(Ar-BIAN) requires homogeneous conditions. A synergic action of two molecules of ligand is apparently necessary and this only efficiently occurs when the ligand is dissolved in a solvent. Therefore, the complexation of the macromolecular Ar-BIANs described above with ruthenium was performed using a monomeric ruthenium (II) carbonyl complex (Scheme 3). The procedure was adapted from a previously reported synthesis of bipyridine/ruthenium complexes [31].

Heating $Ru_3(CO)_{12}$ in chloroform at 110 °C for 6 h in a pressure tube [17, 32] afforded the dimer $[\{Ru(CO)_3Cl_2\}_2]$. The latter was then treated with THF to afford the monomeric $[Ru(CO)_3Cl_2(THF)]$, which was subsequently refluxed in THF with the BIAN ligand to accomplish the complexation. In the previous literature, $[Ru(CO)_3Cl_2(THF)]$ was prepared by recrystallization in THF at reflux temperature [31, 33, 34]. However, we found that the formation of the THF adduct takes place even at room temperature within 40 minutes, affording a purer product (see SM for kinetic of formation of the adduct and the related discussion).



Scheme 3. Synthesis of [Ru(Oligo-BIAN)$(CO)_2Cl_2$]. The same strategy was employed for other BIAN derivatives.

The synthetic strategy was used both for preparing macromolecular-BIAN complexes and complexes of 4-MeC_6H_4-BIAN and its monoimine **1** (Figure 3) subsequently used as references in IR studies. The synthesis and characterization of **1**/carbonylchlorideruthenium complexes has not previously reported, to the best of our knowledge.

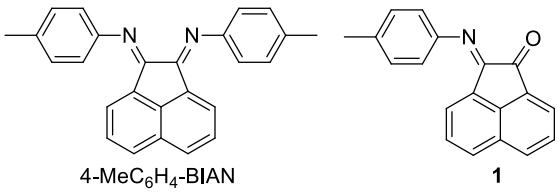


Figure 3. 4-MeC_6H_4-BIAN and monoimine **1** used in the synthesis of reference compounds.

We have previously shown [17] that membrane-embedded [Ru(Ar-BIAN)$(CO)_2Cl_2$] is reduced to [Ru(Ar-BIAN)$(CO)_3$] by CO/H_2O. The same is expected to occur for the analogous complexes in which the BIAN moiety is part of an oligomer or polymer. When [Ru(Oligo-BIAN)$(CO)_2Cl_2$] was employed as catalyst for the reduction of nitrobenzene to aniline by CO/H_2O under conditions similar to those previously reported by us [18], results close to those obtainable with the use of the monomeric [Ru(4-MeC_6H_4-BIAN)$(CO)_2Cl_2$] were obtained. However, the reaction mixture was homogeneous at the end of the reaction and the use of Oligo-BIAN was not investigated further. On the contrary, when the Poly-BIAN ruthenium complex (**2**) was employed as catalyst, the ligand remained insoluble, but only a very small nitrobenzene conversion was observed. Although a lower reactivity for an insoluble material was expected, an almost complete inactivity is hard to justify if the same kind of ruthenium

species are generated. This observation led us to investigate in more detail the nature of the ruthenium complexes formed by Oligo-BIAN and Poly-BIAN.

2.2. Characterization of ruthenium/macromolecular-BIAN coordination compounds

2.2.1. Oligo-BIAN/carbonylchlorideruthenium complex

Standard characterization techniques, such as NMR, elemental analysis, and single-crystal XRD, usually employed for coordination compounds cannot be used for macromolecular-BIAN complexes due to their low solubility and composition (i.e: dispersity of the ligand and polymeric chain termination). To understand how ruthenium coordinates to Oligo- and Poly-BIAN and explain the lack of catalytic activity of the latter, we analyzed the heterogenized catalysts using IR spectroscopy.

The spectrum of [Ru(4-MeC_6H_4-BIAN)$(CO)_2Cl_2$] synthesized as described above was used as a reference. Its IR spectrum in THF (Figure S3 in the SM) shows two main absorptions at 2061 and 2000 cm^{-1} and two weaker bands at 2055 and 1986 cm^{-1}. When the solution is evaporated in vacuo and the solid dissolved in CH_2Cl_2, only the two stronger bands are observable at 2068 and 2007 cm^{-1} (Figure S4 in the SM). These absorption are close to the ones previously observed by us for the analogous complexes *cis*(CO)-*trans*(Cl)–[Ru(4-$H_{29}C_{14}C_6H_4$-BIAN)$(CO)_2Cl_2$] for which the configuration could be unambiguously assigned by ^{1}H NMR spectroscopy [17]. In fact, the spectrum showed five aromatic signals indicating a symmetrical coordination of the BIAN ligand environment. In the previous literature, no other example on complexes of same type with Ar-BIANs is present. However, analogous complexes of Ru(II) with 2,2'-bipyridine exist in two different isomers (Figure 4) [35-37].

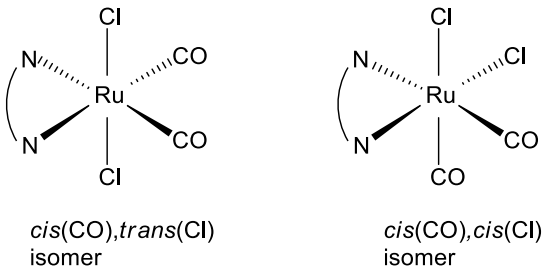


Figure 4. Geometric isomers found in [Ru(Bipy)$(CO)_2Cl_2$] complexes.

In a previous study [37], IR absorptions at 2059 and 1999 cm^{-1} (in KBr pellets) were reported for the *cis*(CO)-*trans*(Cl) and 2051 and 1986 cm^{-1} for the *cis*(CO)-*cis*(Cl) [38]. The two isomers were assigned based on NMR data. By analogy, for [Ru(4-MeC_6H_4-BIAN)$(CO)_2Cl_2$] we now assign the bands at 2061 and 2000 cm^{-1} to the *cis*(CO)-*trans*(Cl) isomer, whereas the bands at 2054 and 1985 cm^{-1} are due to the *cis*(CO)-*cis*(Cl) isomer. For the monoimine complex [Ru(**1**)$(CO)_2Cl_2$] only two IR absorptions for the carbonyls were observed in CH_2Cl_2 at 2075 and 2013 cm^{-1} (Figure S5 in the SM). The bands are shifted at higher frequencies compared to those detected for 4-MeC_6H_4-BIAN in the same solvent. This is in agreement with the general knowledge that a ketonic oxygen has a lower donating capacity than an imine nitrogen.

Complex of type [Ru(Oligo-BIAN)$(CO)_2Cl_2$] showed a pattern of absorptions for the CO stretchings similar to that observable for [Ru(4-MeC_6H_4-BIAN)$(CO)_2Cl_2$]. Two couples of absorptions are present at 2061, 1999 cm^{-1} and 2047, 1977 cm^{-1} indicating the presence of both *cis*(CO)-*trans*(Cl) and *cis*(CO)-*cis*(Cl) isomers (Figure S6 in the SM).

To gain more information on the coordination of the Oligo-BIAN to Ru, the complexation reaction was repeated at room temperature in THF. Initially, the IR analysis of the reaction mixture showed only the two CO stretching absorptions at 2046 and 1981 cm^{-1}. After several hours the absorptions related to the *cis*(CO)-*trans*(Cl) isomer were also present (Figure S7 in the SM). The initially formed *cis*(CO)-*cis*(Cl) isomer could not be observed alone at any stage of the reaction, since it started to convert into the other one before the initial THF adduct was completely consumed. Thus, it is clear that the *cis*(CO)-*cis*(Cl) isomer is initially formed, which is later transformed into the more stable *cis*(CO)-*trans*(Cl) isomer. The conversion is faster at reflux temperature and this explains why only the second isomer had been obtained in previous studies on non-polymeric ligands. It can also be surmised that a solvent such as CH_2Cl_2, able to form hydrogen bonds to chloride ligands, may accelerate the isomerization, thus explaining why only the more stable isomer is detected once all members of this family of complexes are dissolved in it.

2.2.2. Poly-BIAN/carbonylchlorideruthenium complex

As mentioned in section 2.1.4, the Poly-BIAN ruthenium complex (**2**) exhibited almost no activity of in catalytic reactions. Although different explanation are possible for this, we suspected that complexation of the polymeric ligand to [$Ru(CO)_3Cl_2$(THF)] did not occur as expected. Actually, during the complexation reaction between Poly-BIAN and [$Ru(CO)_3Cl_2$(THF)], the solid Poly-BIAN substantially changed its color thus indicating that a complexation had surely occurred. However, the catalytic behavior suggests the opposite.

IR analysis (Nujol mull) of the complex showed three absorption as for the starting THF adduct [$Ru(CO)_3Cl_2$(THF)]. The pattern is different with respect to that obtained for the complexes discussed in the previous paragraph (Figures S2-S6 in the SM). Unfortunately, direct comparison between the frequencies of absorption of **2** and [$Ru(CO)_3Cl_2$(THF)] cannot be done due to the insolubility of the first in common organic solvents and the instability of the latter in the absence of excess THF [39]. Still, the similarity between the IR patterns of the two complexes indicates that in complex **2** three CO molecules are still coordinate as in [$Ru(CO)_3Cl_2$(THF)]. This implies that the two complexes should have similar geometries around the metal (three CO ligands almost invariably adopt a *facial* arrangement in an octahedral complex). Monodentate coordination of a chelating ligand is only observed in the presence of competing strong interactions, which is not likely to occur here, even based on the behavior of the other BIAN ligand previously discusses. An alternative explanation for the observed results in the case of Poly-BIAN is that the amido groups of the chains coordinate to the metal instead of the N-atoms of the Schiff bases. It is likely that the amide substitutes THF, leaving the rest of the ligands in the same position [40]. To check the validity of this assumption, two different amido containing complexes were used as references. The adduct [$Ru(CO)_3Cl_2$(4-aminobenzamide)] (**3**), prepared from [$Ru(CO)_3Cl_2$(THF)] and 4-aminobenzamide, and the adduct [$Ru(CO)_3Cl_2$(polyamide)] (**4**), obtained from [$Ru(CO)_3Cl_2$(THF)] and a polyamide resulting from condensation of MDA and terephthaloyl chloride (see the experimental section for details on the synthetic procedures) were studied by IR. The first complex was designed considering the partial

structural similarity of 4-aminobenzamide with the amido groups in poly-BIANs chains. For the second complex, the polyamide employed resembles the Poly-BIANs structure but lacks the presence of adjacent chelating N-atoms.

The IR spectrum of the region of the carbonyl absorption of the two amide complexes **3** and **4** and of complex of Poly-BIAN **2** are reported in Figure 5.

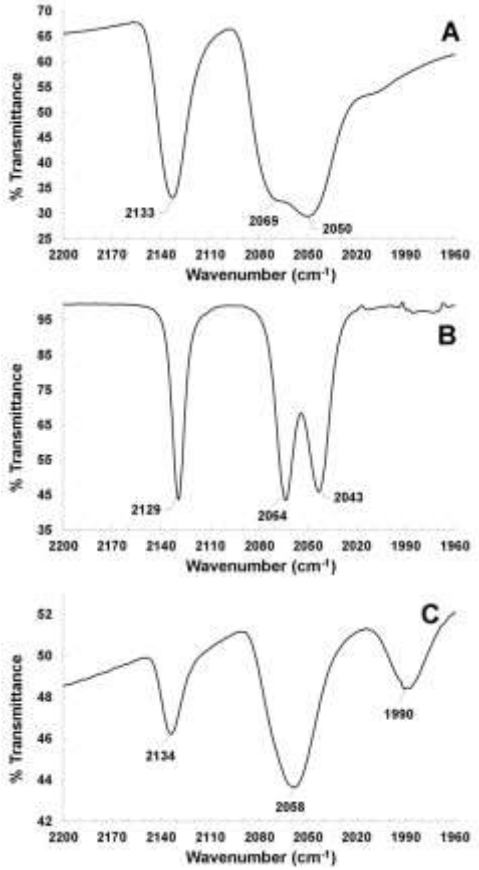


Figure 5. IR spectra in the carbonyl absorption region for: A) Poly-BIAN complex **2** in Nujol mull; B) 4-aminobenzamide complex **3** in THF; C) polyamide complex **4** in Nujol mull.

The spectrum of 4-aminobenzamide complex **3** in THF (Figure 5B) showed the same pattern of absorption and very close wavenumbers with respect to Poly-BIAN adduct **2** in Nujol (Figure 5A). The latter, in turn, closely resembles that of the polyamide adduct **4** (Figure 5C), except for the presence of an absorption at 1990 cm^{-1} in the spectrum of **4** that can be attributed to the polymeric complex $[Ru(CO)_3Cl_2]_n$ formed as a byproduct from the THF adduct [41]. Comparison of these results with the IR spectra of the Oligo-BIAN and monomeric complexes let us to conclude that while Oligo-BIAN coordinates to the ruthenium fragment through the chelating Schiff base moiety (Scheme 3), the Poly-BIAN ligand only interacts with ruthenium through the amido groups (Figure 6).

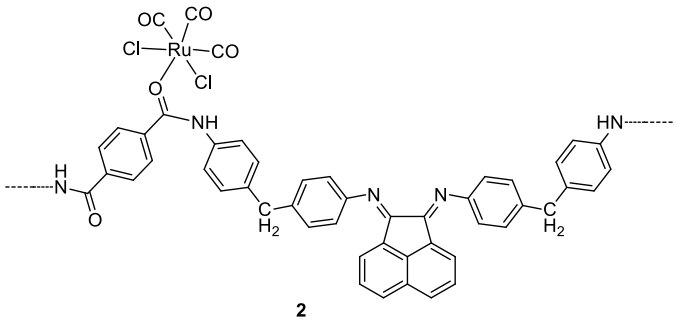


Figure 6. Coordination mode of ruthenium in [Ru(Poly-BIAN)$(CO)_3Cl_2$] (**2**).

Typically, chelating N-ligands binds much more strongly than a single amido group, thus this conclusion was completely unexpected. The odd inversion of coordination behavior could be explained considering the characteristics of the polymeric ligand. The flexibility given by the MDA monomer, the presence of aromatic rings that can give π-stacking, and the possible *intra-* and *inter-*chain hydrogen bonds in the polymer could favor a coiling of the macromolecular BIAN that hinders the access of [$Ru(CO)_3Cl_2$(THF)] to the Schiff base nitrogens. The same features may have a second effect that can impede the coordination of ruthenium to the imine N-atoms. In fact, for Ar-BIAN ligand an isomerism of the imine double bond exists. For "monomeric" Ar-BIANs the *anti-anti* isomer is the most stable and favored, thus being often the only one observable in solution. However, the packing interactions in Poly-BIAN might stabilize the usually less stable *syn-anti* isomer thus preventing the access of metalcarbonylchloride fragment (Figure 7).

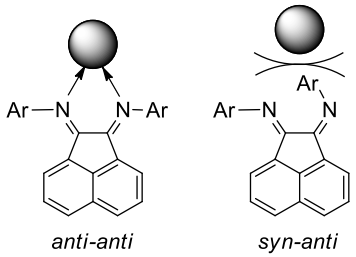


Figure 7. Isomerism and coordination behavior in Ar-BIAN ligands. The terms *trans-trans* and *cis-trans* are also employed in the literature to describe the same isomers.

The conclusions drawn from the IR characterizations explain the catalytic inactivity of the Poly-BIAN complex, since the presence of the chelating ligand is essential to boost the activity of ruthenium in the investigated reaction.

3. Conclusions

The synthetic strategies commonly used for the synthesis of Ar-BIAN were found unsuitable for the synthesis of macromolecular Ar-BIAN ligands, thus new procedures have been devised. An oligomeric ligand obtained from MDA and ANQ was used as co-monomer with terephthalic acid to yield an insoluble polymeric ligand. However, the adduct of this ligand with

carbonylchlorideruthenium fragment showed almost no activity in the reduction of nitroarenes using CO/H_2O as the reductant. We identified the reason for this result by studying the coordination mode of the metal to the polymeric ligand. Ruthenium(II) is coordinated exclusively to the amido moiety of the therephthalamide unit and not to the chelating nitrogen atoms of the Schiff base. This is a rare case in which a difference in the coordination of a metal to a polymeric ligand with respect to the monomeric and oligomeric analogues is observed. It should be noted that usually it is simply assumed that the coordination mode will be the same in all cases and different explanations are given when a lack of activity is observed. The results here reported constitute a warning not to make easy assumptions even in other cases when dealing with metal coordination to polymeric/supported ligands.

4. Experimental section

4.1.Methods and materials

Unless otherwise stated, all reactions and manipulations were performed under a dinitrogen atmosphere using standard Schlenk apparatus. All glassware and magnetic stirring bars were kept in an oven at 120 °C for at least two hours and let to cool under vacuum before use. Solvents were dried and distilled by standard procedures and stored under a dinitrogen atmosphere. THF was dried by distillation over Na/benzophenone; pyridine, CH_2Cl_2, triethylamine and 1,2-dichloroethane were dried by distillation over CaH_2. MeOH was dried by distillation over Mg. Deionized water was degassed by sonication in a cleaning bath for at least one hour under dinitrogen atmosphere. $PhNO_2$ was distilled under vacuum after having been dried over $CaCl_2$ and filtered to remove the drying agent.

Deuterated solvents were purchased by Sigma-Aldrich: DMSO-d_6 (commercially available in 0.75 mL vials under dinitrogen atmosphere) was used as purchased while $CDCl_3$ was filtered on basic alumina and stored under dinitrogen over 4 Å molecular sieves. Acenaphthenequinone (ANQ) and 4,4'-methylene-*bis*(aniline) (MDA) were purified by recrystallization from toluene and ethanol respectively. All other reagents were purchased from Sigma-Aldrich or Alfa-Aesar and used without any further purification. $[Ru_3(CO)_{12}]$ [42], $[\{Ru(CO)_3Cl_2\}_2]$ [17, 32] were prepared using literature procedures.

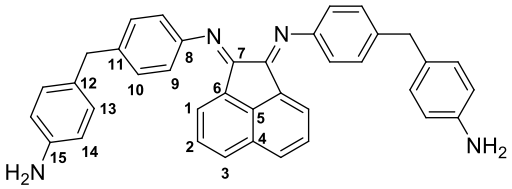
^{1}H NMR spectra were recorded on an Avance Bruker DRX 300. Chemical shifts are reported in ppm relative to TMS; data are reported as follows: proton multiplicities (s = singlet, d =doublet, t = triplet, q = quartet, m = multiplet and br = broad). When the NMR signals were assigned, the assignment was based on bidimensional experiments. For nitrobenzene carbonylation reactions quantitative analyses were performed on Shimadzu GC-2010 equipped with a SUPELCO SLB-5ms capillary column using biphenyl as an internal standard. Elemental analyses were performed on a PERKIN ELMER 2400 CHN elemental analyzer. IR spectra were registered on a Varian Scimitar FTS-1000 (s = strong, m = medium, w = weak, br = broad, sh = shoulder). Mass spectra were recorded on an ESI-MS Thermo Finnigan LCQ Advantage.

4.2.Ligand syntheses

Oligo-BIAN. In a Schlenk flask, ANQ (0.51 g, 2.8 mmol) and MDA (0.70 g, 3.5 mmol) were suspended in MeOH (100 mL) under a dinitrogen atmosphere and the mixture was stirred for 1h at room temperature. H_2SO_4 96 wt. % (50 μL, 0.94 mmol) was added while stirring. After 15-30 min the color of the mixture began to change from yellow to orange. The reaction was stirred at room temperature. The progress of the reaction was checked by TLC (neutral alumina, hexane/acetate = 1:1 + 10% Et_3N). After four days, the main product was composed by oligomeric species that are not eluted in TLC, however the monomer was still present. A separate experiment showed that the latter is not completely consumed also by further prolonging the reaction times. This indicates that an equilibrium was reached. Four days was thus chosen as the best reaction time, after which the solid was separated by filtration on a Buchner funnel. The filter cake was dried in vacuum and suspended in anhydrous CH_2Cl_2 (50 mL) under a dinitrogen atmosphere. Et_3N (5 mL, 36 mmol) was added and the mixture stirred for 2 h. The organic phase containing the oligomer suspension was then washed with water (2 × 50 mL) to remove the formed salts, and the solvent was then evaporated. The crude was refluxed in CH_2Cl_2 for 1h 30' and filtered on a Buchner funnel, affording 0.36 g of an insoluble mixture of oligomers as a dark orange to red solid. ESI-MS analysis was performed by dissolving the product in nitrobenzene and diluting the so obtained solution with HPLC grade acetonitrile (see Supplementary Material for full spectrum and assignments).

Poly-BIAN. In a Schlenk flask, Oligo-BIAN (1.00 g) and pyridine (5 mL) were dissolved in nitrobenzene (50 mL). In a separate flask, terephthaloyl chloride (212 mg, 1.0 mmol) was weighted under a dinitrogen atmosphere and suspended in dry CH_2Cl_2 (100 mL). The suspension was kept at 35 °C to favor the solubilization of the aroyl chloride and the solution was then added dropwise keeping the temperature warm with a heating gun in order to avoid re-precipitation of terephthaloyl chloride in the dropping funnel. The reaction is exothermic, thus the rate of addition was adjusted to avoid the need for cooling of the reaction mixture. After completion of the addition, the mixture was stirred overnight at RT. Methanol (25 mL) was then added and the temperature risen to 50 °C for 3h. The suspension was let to cool and the solid separated by filtration over a Buchner funnel. The obtained solid was washed repeatedly with CH_2Cl_2 and then dried under vacuum at 60 °C affording 706 mg of Poly-BIAN as a dark brown/red solid. Elem. anal. found: C, 75.79; H, 7.81; N, 5.31.

Monomeric 4-(4-Aminobenzyl)phenyl-BIAN (*N,N'*-(acenaphthylene-1,2-diylidene)*bis*(4-(4-aminobenzyl)aniline)). In a two-neck flask, acenaphthenequinone (1.04 g, 5.7 mmol) and anhydrous $ZnCl_2$ (1.94 g; 14.2 mmol) were suspended in acetic acid (40 mL) under a dinitrogen atmosphere. The mixture was heated to 60-70 °C and MDA was added as a solid in one portion while maintaining a strong magnetic stirring. The reaction was then refluxed for 45 minutes and then hot filtered on a Buchner funnel. The orange solid was washed several times with diethyl ether and then dried under vacuum. The crude zinc complex was then suspended in CH_2Cl_2 (100 mL) in the air and a saturated potassium oxalate aqueous solution (100 mL) was added. The biphasic system was vigorously stirred for 3 h. The organic layer was separated, filtered to remove undissolved side products, and dried over Na_2SO_4. The solvent was then evaporated affording a dense red sticky wax still containing unreacted MDA. The product was triturated twice in hexane (15 mL) and recrystallized twice from MeOH (25 mL). After filtration, the monomeric-BIAN was finally obtained as a dark orange solid in 29 % yield (895 mg, 1.6 mmol).



^{1}H NMR ($CDCl_3$, 300 MHz): δ = 7.87 (d, *J* = 8.3 Hz, 2H, H3), 7.36 (t, *J* = 7.8 Hz, 2H, H2), 7.26 (d, *J* = 8.1 Hz, 4H, H10), 7.06 (dd, *J* = 12.5, 8.2 Hz, 8H, H9 and H13), 6.88 (d, *J* = 7.2 Hz, 2H, H1), 6.69 (d, *J* = 8.2 Hz, 4H, H14), 3.97 (s, 4H, C*H*$_2$), 3.60 ppm (s, 4H, N*H*$_2$). ^{13}C NMR ($CDCl_3$, 75 MHz): δ = 161.7 (C), 150.1 (C), 144.9 (C), 142.1 (C), 138.4 (C), 131.8 (C), 131.6 (C), 130.2 (C3 or C13), 130.1(C3 or C13), 129.2 (C3), 129.1 (C), 128.0 (C2), 124.3 (C1), 118.7 (C9), 115.7 (C14), 41.0 ppm (*C*H$_2$).

4-MeC$_6$H$_4$-BIAN. The synthesis was performed following a procedure reported in the literature by some of us [27]. In a two-neck flask, acenaphthenequinone (500 mg, 2.7 mmol) and anhydrous $ZnCl_2$ (1.00 g; 7.3 mmol) were suspended in acetic acid (7.5 mL) under dinitrogen atmosphere. The reaction mixture was heated to 60-70 °C under stirring and *p*-toluidine (680 mg, 6.3 mmol) was then added. The mixture was heated to reflux under stirring for 45 minutes, and then hot-filtered on a Buchner funnel. The collected orange solid was washed with diethyl ether. The obtained light orange zinc complex was suspended in CH_2Cl_2 (50 mL) in the air, a saturated potassium oxalate aqueous solution (25 mL) was added and the biphasic suspension was stirred for one hour. The organic phase was then separated, dried over sodium sulfate and evaporated under vacuum affording the Schiff base as an orange powder in 83 % yield (805.0 mg, 2.2 mmol). Analytical data are in agreement with those reported in the literature [25]. ^{1}H NMR ($CDCl_3$, 400 MHz) δ = 7.88 (d, *J* = 8.3 Hz, 2H), 7.38 (pst, 2H), 7.27 (d, *J* = 8.2 Hz, 4H), 7.03 (d, *J* = 8.2 Hz, 4H), 6.94 ppm(d, *J* = 7.2 Hz, 2H). ^{13}C NMR ($CDCl_3$, 400 MHz) δ = 161.3 (C), 149.2 (C), 141.7 (C), 133.9 (C), 131.2 (C), 130.0 (CH), 128.8 (CH), 128.7 (C), 127.6 (CH), 123.9 (CH), 118.2 (CH), 21.1 ppm (CH_3).

2-(*p*-Tolylimino)acenaphthylen-1(2*H*)-one (1). The synthesis was performed following a procedure reported in the literature [43]. ANQ (820 mg, 4.5 mmol) and formic acid (0.1 mL) were mixed in ethanol (20 mL) in a Schlenk flask. An ethanol solution (15 mL) of *p*-toluidine (482 mg, 4.5 mmol) was then added dropwise over 4.5 h. The reaction was maintained at 60 °C for 6.5 h and then let to cool to room temperature. The resulting suspension was filtered on a Buchner funnel and then was purified by column chromatography on neutral alumina (elution gradient from pure hexane to hexane/ethylacetate = 8:2) affording 136 mg of monoimine as an orange solid (11 % yield). ^{1}H NMR ($CDCl_3$, 300 MHz) δ = 8.18 (d, *J* = 7.6 Hz, 2H), 8.01 (d, *J* = 8.4 Hz, 1H), 7.86 – 7.76 (m, 1H), 7.49 – 7.42 (m, 1H), 7.27 (d, *J* = 8.2 Hz, 2H), 7.12 (d, *J* = 7.2 Hz, 1H), 7.01 (d, *J* = 8.3 Hz, 1H), 2.45 ppm (s, 2H).

Poly(diphenylmethane terephthalamide). The synthesis was adapted from a literature procedure [44]. MDA (254 mg, 1.3 mmol) and pyridine (2 mL) were dissolved in dry 1.2-dichloroethane (40 mL) in a Schlenk flask under dinitrogen. Terephthaloyl chloride (270 mg, 1.3 mmol) was weighted under dinitrogen atmosphere and suspended in dry 1.2-dichloroethane (100 mL). The suspension was kept at 40 °C to favor the solubilization of the aroyl chloride and the solution was then added dropwise

keeping the temperature warm with a heating gun in order to avoid re-precipitation of terephthaloyl chloride in the dropping funnel. An off-white precipitate immediately started to form. After the end of the addition, the reaction was stirred for 1h and then MeOH (10 mL) was added. The mixture was stirred overnight, heated to 50 °C for 2h and ultimately filtered on a Buchner funnel. The so obtained solid was suspended in CH_2Cl_2 (10 mL), filtered, and dried under vacuum affording 347 mg of polyamide as a colorless solid.

4.3.Complex synthesis

General procedure for the synthesis of [RuL(CO)nCl_2] complexes at reflux. In a Schlenk flask, $[Ru(CO)_3Cl_2]_2$ (56 mg, 0.11 mmol) was stirred in THF (10 mL) for 1h at room temperature. The formation of the adduct $[Ru(CO)_2Cl_2(THF)]$ was checked by liquid cell IR analysis. The ligand (0.22 mmol) was added, and the reaction was reflux for further 4 h (the amount of ligand for oligomeric species was calculated on the amount of Schiff base moieties. Those were estimated based on the relative intensity of the peaks of the different oligomeric species as obtained in the ESI-MS analysis). Depending on the nature of the ligand, either a suspension or a solution was obtained after cooling the reaction mixture. When a precipitate was present, it was separated by filtration over a Buchner funnel. Otherwise, the solvent was evaporated, the residue dissolved in CH_2Cl_2 (20 mL) and the solution filtered through a short pad of neutral alumina. A green byproduct is only slowly eluted. The filtrate was then evaporated under vacuum affording the complex.

$[Ru(CO)_3Cl_2(THF)]$ IR (THF, ν_{max} /cm^{-1}) = 2134 (s), 2064 (s), 2056 (s).

[Ru(Oligo-BIAN)$(CO)_2Cl_2$]. Brown solid (118 mg). IR (THF) ν = 2061 (s), 2047 (w), 1999 (m), 1977 cm^{-1}(w); (Nujol mull) ν = 2061 (s), 1996 cm^{-1} (br).

[Ru(Poly-BIAN)$(CO)_2Cl_2$]. Dark red solid (167 mg). IR (Nujol mull) ν = 2133 (s), 2069 (s), 2050 (s). An additional weak shoulder at 1989 cm^{-1}(w) is due to $[Ru(CO)_3Cl_2]_n$ (see text).

[Ru(4MeC_6H_4-BIAN)$(CO)_2Cl_2$]. Violet-red solid, 73 % yield (94 mg, 0.16 mmol) IR (CH_2Cl_2) ν = 2068 (s), 2006 cm^{-1} (m); (THF) ν = 2073 (sh), 2061 (s), 2000 (m), 1985 cm^{-1} (w); (Nujol mull) ν = 2058 (s) with shoulder at 2070, 1999 (s) with shoulder at 2010, 1985 cm^{-1} (m).

[Ru(1)$(CO)_2Cl_2$]. Violet-red solid, 78 % yield (86 mg, 0.17 mmol). IR (CH_2Cl_2) ν = 2075 (s), 2013 (m); (THF) ν = 2067 (s), 2004 cm^{-1} (s); (Nujol mull) ν = 2065 (s), 2030 (w), 2001 cm^{-1} (s).

Synthesis of [Ru(Oligo-BIAN)$(CO)_2Cl_2$] at room temperature. In a Schlenk flask, $[Ru(CO)_3Cl_2]_2$ (27 mg, 5.3×10^{-2} mmol) was stirred in THF (5 mL) for 1h. The formation of the adduct $[Ru(CO)_2Cl_2(THF)]$ was checked by liquid cell IR analysis. Oligo-BIAN (100 mg) was added and the reaction was stirred at room temperature for 6h. The complex was not isolated, but IR spectra collected during the reaction were compared to those obtained for the reaction performed at reflux (see section 2.2.1).

Synthesis of complex 3. In a Schlenk flask, $[Ru(CO)_3Cl_2]_2$ (24 mg, 4.7×10^{-2} mmol) was dissolved in THF (5 mL) and the solution stirred for 1h at room temperature. 4-Aminobenzamide (35 mg, 0.26

mmol) was added and the solution was maintained under stirring at room temperature. An IR spectrum (in THF) of the complex was recorded after 1h showing the complete conversion of $[Ru(CO)_3Cl_2(THF)]$ and the formation of the corresponding mono-adduct with 4-aminobenzamide, **3** with absorption at 2129 (s), 2064 (s) and 2043 cm^{-1} (s). Extension of the reaction time to 12h did not show any change in the IR spectrum, indicating that the adduct with three coordinated CO is the most stable even in the presence of a 3-fold excess of the amide.

Synthesis of complex 4. In a Schlenk flask, $[Ru(CO)_3Cl_2]_2$ (77 mg, 0.15 mmol) was dissolved in THF 10 mL) and the solution stirred for 1h at room temperature. Poly(diphenylmethane terephthalamide) (150 mg, 0.46 mmol calculated on the monomer) was added and the suspension was refluxed for 4.5h. The suspension was let to cool and the solid separated by filtration over a Buchner funnel. The solid was suspended in THF (5 mL) for 30 min, separated by filtration again and dried under vacuum affording 98 mg of a grayish solid. IR (Nujol mull) ν = 2134 (m), 2058 (s, br). An additional absorption at 1990 cm^{-1} (m) is due to $[Ru(CO)_3Cl_2]_n$ (see text).

4.4.Catalytic reactions.

General procedure. The conditions were adapted from a previous report of our group [30]. The catalyst (1.2×10^{-2} mmol based on Ru) was weighed in a glass liner in the air. The liner was then placed inside a Schlenk tube with a wide mouth and the tube evacuated and filled with dinitrogen. Nitrobenzene (0.623 mL, 6.1 mmol), ethanol (23.5 mL), water (1.5 mL) and triethylamine (0.200 mL, 1.4 mmol) were added. The Schlenk tube was then cooled in liquid nitrogen until complete freezing of the solvent and rapidly transferred to a 200 mL stainless steel autoclave. The autoclave was then evacuated and filled with dinitrogen three times and warmed to room temperature. CO (50 bar) was then charged, and the autoclave was immersed in an oil bath preheated at 150 °C. After 3 h the autoclave was cooled in an ice bath and vented. The reaction was analyzed by GC-FID analysis using biphenyl as an internal standard.

Supplementary material

Oligomeric ligand mass spectrum, full discussion on formation $[Ru(CO)_3Cl_2(THF)]$ complex, IR spectra of ruthenium complexes, NMR spectra**.**

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