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ARTICLE

Porous Aromatic Frameworks (PAFs) as efficient supports for *N*-heterocyclic carbene catalysts

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Porous polymeric aromatic frameworks (PAFs) have high porosity, surface area, and high physicochemical stability; such characteristics are important in the design of heterogeneous catalysts with high catalytic efficiency and recyclability. This paper presents the synthesis, characterization, post functionalization and catalytic performance of resulting modified PAFs based on tetraphenyladamantane (**PAF$_{Ad}$**), tetraphenylmethane (**PAF$_{C}$**) and 9,9'-spirobisfluorene (**PAF$_{spf}$**) nodes. PAFs were obtained by the Suzuki–Miyaura cross-coupling under microwave heating, and were sequentially reacted with 1-(chloromethoxy)octane and 1-mesityl-1*H*-imidazole or 2-(1*H*-imidazol-1-yl)pyridine to yield the corresponding imidazolium chloride derivative (**PAF-Im**) which readily formed stable N-heterocyclic carbene (NHC) iridium and ruthenium complexes (**PAF-(NHC)Ir**, **PAF-(NHC)Ru**). The materials were characterized by solid-state NMR spectroscopy, FTIR spectroscopy, and textural analysis. The **PAF-(NHC)M** materials display an excellent catalytic performance in the *N*-alkylation of amines with alcohols and transfer hydrogenation of ketones over multiple catalytic cycles.

Introduction

The development of new stable, robust, and highly accessible porous materials with associated functionalities in their framework remains a key topic in material science especially for applications in adsorption, separation, catalysis, energy storage, sensors, electronic or photoluminescence devices[1] The preparation of this type of porous materials implies the use of suitable building units to create networks through appropriate synthetic procedure.[2] Thus, materials as metal-organic frameworks (MOFs)[3] or porous organic polymer (POPs),[4] with or without metals in their main structure have been reported. Within the POPs materials it is possible to find hyper-crosslinked polymers (HCPs),[5] polymers with intrinsic microporosity (PIMs),[6] or covalent organic frameworks (COFs).[7] In this group of materials, those based on totally aromatic units, named porous aromatic frameworks (PAFs), are particularly important and are more robust and stable than conventional COFs or even MOFs. The porosity, physicochemical stability and the possibility to use the rigid planar aromatic rings as reliable platform linkers are key factors to use PAFs as multi-functional catalysts to carry out catalytic reactions. In these aromatic nodes is possible to incorporate different functions, isolated, and stabilized, without blocking internal pore volume.[8]

Homogeneous catalysts play an important role in the field of modern catalysis. However, most precious organometallic catalysts have not been widely used due to their complicated synthesis, recycling problem, and thus the metal contamination of the products.[9] So far, the main method of recycling organometallic complexes is the heterogenization of the homogeneous catalysts. For instance, in the classical supporting method, the catalyst is anchored to various kinds of supports, such as silica-based materials[10] and magnetic nanoparticles.[11] POPs,[12] PAFs,[13,8] and MOFs,[14-16] have emerged as versatile materials which can be used as supports of catalysts because of its porous nature and high surface area and easily modified by post-functionalization and catalysts were loaded via covalent[8] or noncovalent interactions.[17,18]

The successful isolation and characterization of a *N*-heterocyclic carbene (NHC) in 1991[19] opened up a new class of organic compounds for research today, NHCs today rank among the most powerful tools in organic chemistry, with numerous applications in commercially important processes.[20] Transition metal complexes of NHCs have attracted great interest offering a good opportunity to tune the reactivity and selectivity of transition metal catalysts.[21] Their catalytic applications in various organic transformations, including C-C bond and C-N bond formations,[22] olefin metathesis,[23] oligomerization and polymerization of alkenes,[24] have been studied widely. Nevertheless, most of them are synthesized through multiple steps and can be used only one time in

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Electronic Supplementary Information (ESI) available: Experimental details on the preparation and characterization of the PAF materials, additional tables and figures are included. See DOI: 10.1039/x0xx00000x

homogeneous catalysis. Since NHCs and transition metals are expensive reagents, heterogenized NHC metal complexes are attractive due to their reusability and the fact that the catalyst is regenerated.[25] The strong σ-electron-donating properties of NHCs allow the formation of very strong NHC–metal bonds and preventing the decomposition of the catalyst.[26,27] The high dissociation energies of the metal–carbon bonds in NHC–metal complexes make NHCs good ligands for heterogeneous systems.[28] Various supports have been extensively used to heterogenize NHCs, which includes polymers, self-supported poly NHCs, silica and NPs.[29,30] With our continuing studies to heterogenize homogeneous catalysts on porous matrices, in particular NHC-catalysts,[31,32] herein we have chosen different **PAFs** to be used as new supports for N-heterocyclic carbene ligands. We describe a procedure for the generation of imidazolium-containing porous materials (**PAF**-Im) and the corresponding Metal-NHC compounds (**PAF**-(NHC)M) (Figure 1) and their characterization at a molecular level. Finally we used the materials as catalysts in standard transfer hydrogen reactions. They displayed activities similar to their homogeneous homologues combined with the widely recognized advantages of heterogeneous catalysts (recycling and separation of products). Heterogenized **PAF**s-NHC-complexes have great potential, and development of recyclable catalysts is highly desirable for sustainable chemistry.

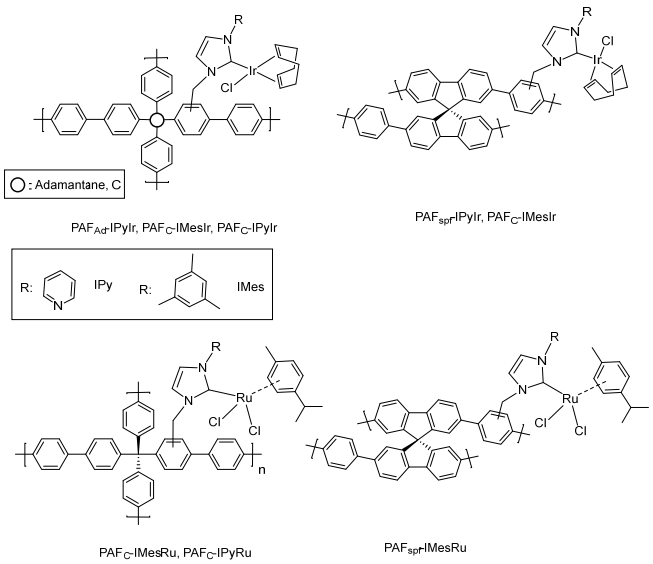

Figure 1. Schematic representation of the **PAF**-(NHC)M from this work.

Results and discussion

PAFs-Post-functionalization

Synthesis of NHC-precursors

PAFs-supported NHC-metal complexes were prepared in several steps as shown in schemes 1-2. Thus, **PAFs** were synthesized by a palladium catalyzed Suzuki-Miyaura cross-coupling reaction between *tetrakis*(4-iodophenyl)methane, 1,3,5,7-*tetrakis*(4-iodophenyl)adamantane or 2,2',7,7'-tetraiodo-9,9'-spiro*bis*fluorene and 1,4-phenylenediboronic acid under MW heating at 145 °C (the reactions were quantitative in all the cases, at least ten batches for the preparation of each material were carried out in scale of 200 mg, experimental details are included in supplementary information).[8]

PAFs-CH_2Cl (scheme 1) were obtained by reaction of the corresponding parent **PAF** materials with 1-(chloromethoxy)octane in presence of $TiCl_4$ yielding the chloromethylated derivative **(PAF-**CH_2Cl). FTIR spectra of **PAFs-**CH_2Cl display two characteristic absorption bands at 1264 cm^{-1} and 670 cm^{-1} corresponding to the C-Cl bond (Figure S1-S2).[33] ^{13}C-NMR shows the characteristic signals for the carbon atom connected with the phenyl group (Ar-C) of **PAF$_C$** and **PAF$_{spf}$** at ~67 ppm and peaks between 125 and 160 ppm (aromatic carbons) (Figure S3a-i).

In a second stage (scheme 1), a mixture of **PAF-**CH_2Cl (0.7 mmol Cl/g) and 1-mesityl-1*H*-imidazole or 2-(1*H*-imidazol-1-yl)pyridine (3 mmol) in toluene (30 mL) were stirred at reflux for 2 days. After being cooled to room temperature, the reaction mixture was filtered, and the solid washed thoroughly and dried to afford the imidazolium chloride-supported **PAF** (**PAF**-Im) with an imidazolium loading of 1.0-3.2 mmol/g depending from imidazole, as determined by the nitrogen content from elemental analysis (the analytical data of the supported imidazolium salts are listed in Table S1, it is very well known that in conjugated porous polymers lead to bad combustion and incorrect values of carbon and carbon-hydrogen ratio[34]).

PAFs-Im result porous amorphous materials and were fully characterized by N_2 adsorption/desorption, ^{13}C solid-state NMR spectroscopy, FTIR, and X-ray diffraction (see supporting Information). All data were consistent with the quantitative formation of imidazolium functionalities with no degradation of the material. FTIR showed two new absorption bands at 1546 cm^{-1} and 1155 cm^{-1} which characterize the ring vibration and the bond bending vibration of the imidazolium groups (2-C-H), respectively and provided clear evidence for the attachment of the ligands (Figures S1-S2).[33,35] ^{13}C-NMR showed a peak at ~22 ppm which corresponds to the carbon atom of the -CH_3 group, a signal at ~65 ppm assigned to the carbon atom connected with the phenyl group (Ar-C), (67 ppm for **PAF$_{spf}$**) and the peak at ~39 ppm due to the aliphatic carbons of adamantine nucleus. Signals between 120 and 160 ppm were the aromatic groups. The characteristic imidazolium (N*C*N) carbon,[36] which was overlapped with other peaks, appeared at 152 ppm (157 ppm for **PAF$_{Ad}$**, 158 ppm for **PAF$_{spf}$**) (Figures S3a-i).

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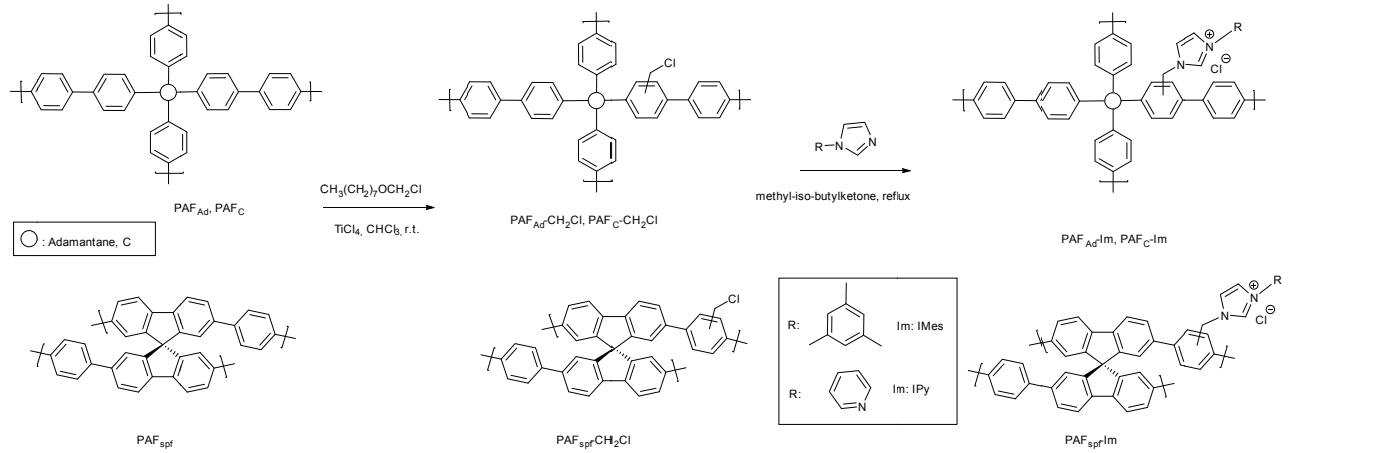
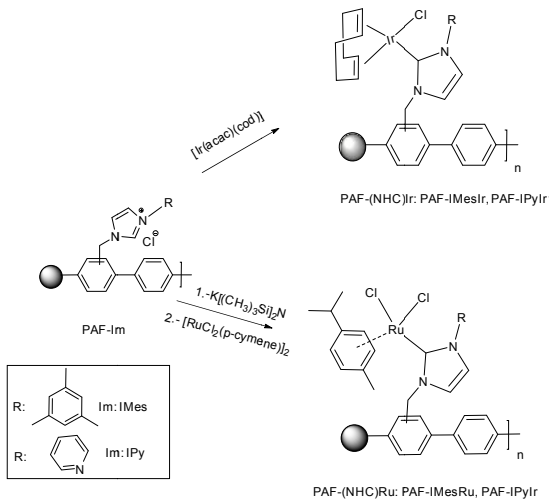


Scheme 1. Preparation of **PAF**-imidazolium chlorides: IMes, 1-mesityl-1*H*-imidazole or IPy, 2-(1*H*-imidazol-1-yl)pyridine, methyl-*iso*-butylketone, reflux, 24 h.

PAF-iridium(I) and ruthenium(II) complexes

PAF-Imidazolium were converted into corresponding **PAF–**(NHC)M-complexes (**PAF-**IMesIr**, PAF-**IPyIr**, PAF-**IMesRu**, PAF-**IPyRu) according to similar procedures reported in the literature,[36] and the preparation is shown in Scheme 2. Hereinafter, we will continue only with **PAF$_C$** and **PAF$_{spf}$** supports due to their better performance towards the metal functionalization than **PAF$_{Ad}$** materials.



Scheme 2. Preparation of **PAF-(NHC)M** (M: Ir, Ru).

PAF-(NHC)Ir were prepared by reaction of the respective PAF-imidazolium salts and [Ir(acac)(cod)][36] in dichloromethane at 40 °C (Scheme 2). The resulting **PAF**-(cod)(NHC)IrX-compounds were filtered, and washed thoroughly with dichloromethane. The iridium content determined by inductively coupled plasma-atomic emission spectrometer analysis (ICP-AES) was found 0.2 mmol/g (Table S2). Treatment of **PAF**-Im with potassium hexamethyldisilazide (in toluene at -30 °C) for 2 h, warming to room temperature and posterior addition of a solution of $[RuCl_2(p\text{-cymene})]_2$ with stirring at 100 °C overnight, led to the formation of a (NHC)Ru-supported **PAF** catalysts (**PAF**-(NHC)Ru) as brown solids containing about 0.2 mmol/g of Ru (ICP-AES) (Table S2). The comparison of elemental analysis and FTIR data indicated that only a part of imidazolium groups anchored on the polymeric supports took part in the reactions with the metal (Ir or Ru) to form the corresponding metal-carbene complexes (Table S2, Figure S1-S2).

^{13}C CP-MAS NMR spectra of resulting NHC-complexes displayed signals corresponding to aromatic carbons between 120 and 160 ppm, -CH_3 group of mesityl moiety at ~20 ppm. The metalation could be also confirmed by a weak peak for NCN carbon[36,43] at ~176 ppm for iridium and at 191 ppm for ruthenium complexes (Figures S3a-i).

The thermal stability of the supported catalysts was estimated using TG analysis. TGA curves are shown in figures S4a-d. The TGA curves of these catalysts are similar showing one important weight loss at c.a. 400 °C.

Field emission scanning electron microscopy (FE-SEM) showed no morphological changes in **PAFs** derivatives, **PAF-**CH_2Cl, **PAF-**Im and **PAF**-(NHC)M, which confirms that the shape of the materials remained intact (Figure S5a-b). **PAF**-(NHC)M are robust and stable complexes and their X-ray powder diffraction analyses revealed that these **PAFs** are amorphous solids (Figure S6). N_2 adsorption-desorption isotherms at 77 K

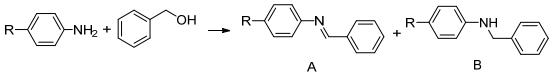
are shown in Figures S7a-g in the supporting information with BET specific surface area values of 383 m²/g for **PAF$_{spf}$**-IPyIr and 279 m²/g for **PAF$_C$-**IPyRu; IMes derivatives have lower BET values.

Catalytic activity

N-alkylation of amines with alcohols**.**

The environmentally-benign N-alkylation of primary amines with alcohols as alkylating reagents in the presence of transition metal catalysts[37] is important because secondary amines have widely been used as synthetic intermediates for pharmaceuticals, agrochemicals, bioactive compounds, polymers, and dyes.[38,39] The reaction is atom economical and the only reaction byproduct is water. Typically, iridium or ruthenium-catalyzed N-alkylation of amines and amides has become a useful way to achieve versatile amine and amide derivatives using alcohols as the greener alkylating reagents.[40] This strategy takes the hydrogen from the alcohol to form an aldehyde which can react with an amine to form an imine, and the hydrogen is then used to give a C-N bond.[41] The N-alkylation has been mainly studied with soluble homogeneous transition metals[37i,42] This prompted us to test the catalytic activities of new heterogenized-**PAFs**-(NHC)iridium and ruthenium complexes for *N*-alkylation of amines with alcohols. As a model, we studied the reaction of aniline with benzyl alcohol in toluene in the presence of 0.5 mol% of catalyst and KOH as base at 130 °C for 24 h; the reaction can be performed with a variety of different bases without large variations in reactivity. The results are summarized in Tables 1 and S3.

Table 1. Effect of support and metal on the alkylation of anilines with benzyl alcohol using **PAFs**-(NHC)M.[a]



entry	catalyst	R	Yield[b] [%]	Selec. [%] A	Selec. [%] B
1	PAF$_{spf}$-IPyIr	H	100	4.1	95.9
2	PAF$_{spf}$-IPyIr	OCH_3	100	6.0	94.0
3	PAF$_{spf}$-IPyIr	CH_3	100	20.0	80.0
4	PAF$_{spf}$-IMesIr	H	100	14.1	85.9
5	PAF$_{spf}$-IMesRu	H	91.7	33.8	66.2
6	PAF$_c$-IPyIr	H	100	22.1	77.9
7	PAF$_c$-IPyRu	CH_3	100	98.0	2.0
8	PAF$_c$-IPyRu	OCH_3	95.1	92.5	7.5
9	PAF$_c$-IMesIr	H	100	20.8	79.2
10	PAF$_c$-IMesRu	H	100	94.3	5.7
11	Ir(IPy)(cod)Cl	H	74.7	52.8	47.2
12	none	H	10	10	-

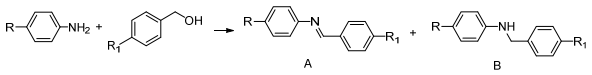
[a]Reaction conditions: aniline (0.104 mmol), benzyl alcohol (0.208 mmol), KOH (0.13 mmol), toluene (0.3 mL), 130 °C, 24 h, 0.5 mol % catalyst based on metal. [b]Determined by GC and GC-MS.

When the reaction was carried out without a base, only imine was formed (Table S3, entry 1) and *N*-benzylaniline was obtained in an excellent yield when the reaction was carried out in the presence of KOH (Table S3, entries 2-5). Generally, the imine formation readily proceeds upon heating. The reaction was also performed in the absence of the catalyst to estimate the contribution of **PAF-(NHC)M-**catalyst to imine formation, and this was not reached to obtain neither amine nor imine (Table 1, entry 12). For comparison purposes the reaction was also tested in the presence of Ir(IPy)(cod)Cl (as homogeneous reference catalyst), and we found a lesser activity and selectivity than the corresponding supported PAF catalyst (Table 1, entry 11). Comparing the structure of parent PAF-supports we also observed that spirobifluorene-derivatives resulted better catalysts that tetraphenylmethane-ones (see table 1). By tracing the reactions by using GC-MS, amine was observed as the major product in all of the **PAFs**-(NHC)Ir-catalyzed-reactions. Reactions follow the general accepted reaction pathways where the intermediate aldehyde stays coordinated to the Ir-complex and reacts with the amine to give the hemiaminal which is also bound to the catalyst; dehydration to the imine and reduction to the product amine would also takes place without breaking the coordination to the catalyst, as it has been previously proposed.[43] In the case of **PAFs**-(NHC)Ru-catalysts last reduction step don't takes place and mainly lead to the imine products.

For preparative purposes, an experiment between aniline and benzyl alcohol was scaled up by a factor of 10 and a conversion of 100% and a selectivity of 50% towards the amine were reached at 24 h; being necessary additional 48 h to obtain a 80% selectivity.

The scope of the **PAF$_{spf}$**-IPyIr-catalyzed *N*-alkylation was examined after optimization of the reaction conditions (Table 2). Various amines and alcohols were then chosen to explore the activity and all reactions efficiently proceeded to give the corresponding secondary amines in moderate to excellent yields.

Table 2. Effect of substrates on the alkylation of anilines with benzyl alcohols using **PAF$_{spf}$**-IPyIr.[a]



entry	R	R_1	Selec. [%] A	Selec. [%] B
1	H	H	4.1	95.9
2	OCH_3	H	6.0	94.0
3	Cl	H	14.7	85.3
4	CH_3	H	20.0	80.0
5	Br	H	59.9	-[b]
6	H	OCH_3	30.4	69.6
7	H	CH_3	26.6	68.3
8	H	Cl	21.9[c]	55.2[b]

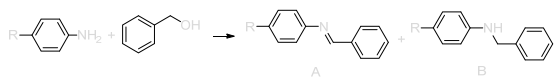
[a]Reaction conditions: aniline (0.104 mmol), benzyl alcohol (0.208 mmol), KOH (0.13 mmol), 0.5 mol % based on iridium, toluene (0.3 mL), 130 °C, 24 h, 100% yield was determined via GC and GC-MS. [b]N-benzylaniline. [c]N-benzylideneaniline.

First, different amines were studied in the reaction with benzyl alcohol; *p*-substituted anilines with methyl, methoxy, and

chloro substituents participated in an efficient way in the secondary amines formation (entries 1-4). *p*-bromoaniline was a poor substrate due to considerable dehalogenation as a side reaction (entry 5). *p*-Methoxy and *p*-methyl substituted benzyl alcohols (entries 6 and 7) reacted well with aniline to lead the corresponding amine and *p*-chloro substituents reacted with good yields although dehalogenation also occurs (entry 8). An experiment with four times of reactants and catalyst was also performed and reaction was completed in 24 h.

In organic synthesis, there are many advantages of replacing organic solvents with water (an inexpensive, safe and environmentally friendly solvent); in this context, the development of water-tolerant catalysts has become an active area of research. We studied the efficiency of PAF-system for the N-alkylation of amines with a benzyl alcohol in water under air. The results are summarized in Table 3. The reaction proceeds smoothly using water as solvent with KOH as base (table S5) and resulted in the selective formation of N-benzylideneanilines, except when *p*-anisidine was the substrate (Table 3, entry 4). In addition, the reuse of the water-tolerant **PAF**-(NHC)Ir catalyst has also been demonstrated (Table S6).

Table 3. Alkylation of anilines with benzyl alcohol using **PAFc-**IMesIr in water.[a]



entry	R	Conv. (%)[c]	Selec. [%] A	Selec. [%] B
1	H	67.5	94.9	5.0
2	CH_3	91.3	100	-
3	Cl	95.6	100	-
4	OCH_3	100	62.3	37.7

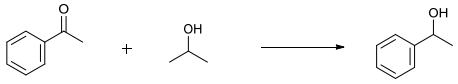
[a]Reaction conditions: aniline (0.104 mmol), benzyl alcohol (0.208 mmol), 3.0 mol% catalyst based on iridium, KOH (0.13 mmol), water (0.3 mL), 100 °C, 24h. Yields determined by GC and GC-MS. [d]TON: [conv.]/[cat] (for a single run).

Recycling of **PAF$_{spf}$-**IPyIr was carried out for the N-alkylation of *p*-methoxyaniline with benzyl alcohol finding that the activity was maintained for at least eight cycles although selectivity to the imine decreased after the fifth run (Figure S8). In order to verify whether the observed catalysis is derived from solid **PAF$_{spf}$-**IPyIr or leached iridium species, the N-alkylation of aniline with benzylic alcohol was carried out and the Ir-catalyst was removed from the reaction mixture by filtration at ca. 40% conversion of aniline. After removal of the catalyst, the reaction was again carried out with the filtrate under the same conditions. In this case, the reaction was stopped. It was confirmed by ICP-AES analysis that no iridium was detected in the filtrate (below detection limit). All these facts can rule out any contribution to the observed catalysis from iridium species that leached into the reaction solution and the observed catalysis is intrinsically heterogeneous. Analysis for the recovered catalyst shows that the structure was maintained without important degradation (see ESI).

Transfer Hydrogenation Catalysis.

Catalytic transfer hydrogenation is one of the most important applications of (NHC)-Ir(I) and Ru(II) complexes.[36,44] In this work, the reduction of acetophenone to 1-phenylethanol, with isopropanol as hydrogen donor in the presence of KO*t*Bu as the base, was chosen as a model reaction to test the performance of **PAFs**-(NHC)Ir and Ru as catalysts for transfer hydrogen reactions. Several catalytic runs have been carried out at different catalyst concentrations using 0.5, 1.0, 2.0, 2.5 mol%. The catalytic activity of **PAFs**-(NHC)iridium was similar to that of the comparable ruthenium catalyst (Table 4), several bases were also employed being KO*t*Bu the most effective.

Table 4. Catalytic hydrogen transfer from 2-Propanol to acetophenone using **PAFs**-(NHC)Ir and **PAFs**-(NHC)Ru.[a]



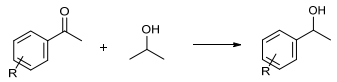
entry	catalyst	catalyst[b] [mol %]	yield[c] [%]	TON[d]
1	PAF_{spf}-IPyIr	2.5	94.6	37.8
2	PAF_{spf}-IPyIr	1.0	99.0	99.0
3	PAF_{spf}-IPyIr	0.5	85.0	170.0
4	PAF_{spf}-IMesIr	0.5	69.1	138.2
5	PAF_c-IPyIr	0.5	41.6	83.2
6	PAF_c-IMesIr	0.5	42.3	84.6
7	PAF_c-IMesIr	5.0	98.2	19.6
8	PAF_c-IMesRu	5.0	98.7	19.7
9	PAF_c-IMesRu	2.5	49.7	19.9
10	PAF_c-IPyRu	2.5	99.0	39.6
11	PAF_c-IPyRu	2.0	92.0	46.0
12	PAF_c-IPyRu	0.5	53.0	106
13	IPyRu	2.0	94.6	47.3
14	PAF_c-IPyCl	5.0	2.0	-

[a]Reaction conditions: acetophenone (0.043 mmol), KO*t*Bu (0.12 mmol, *i*PrOH (0.5 mL), 82 °C, 24 h. [b]Based on Metal. [c]Yields determined via GC and GC-MS. [d]TON is defined as [1-phenylethanol]/[cat] (for a single catalysis run).

The scope of the reaction was studied with different ketones in the presence of **PAF$_C$-**IPyRu or **PAF$_{spf}$-**IPyIr catalysts, KO*t*Bu as the base, and *i*PrOH as the solvent as well as hydrogen source, as shown in Table 5. Benzophenone and *p*-chloroacetophenone exhibited almost quantitative yields at the S/C ratio of 50. The position of substitution on the phenyl ring of aniline affected to the reaction yield. Interestingly, moderately activating groups i.e. methyl at the *o*-position furnished higher yield compared to the para position.

After the end of reaction **PAF$_C$**-IPyRu was filtered and recycled at least six runs without loss of reactivity (Figure S9).

Table 5. PAF_C-IPyRu-catalyzed hydrogen transfer from 2-Propanol to ketones.[a]



entry	Ketone	Yield[c] [%]	
		PAFc-IPyRu	PAFspf-IPylr
1	H	92.0	99.0
2	4-Cl	95.8	98.6
3	2-CH_3	99.0	99.2
4	4-CH_3	93.0	94.0

[a]Reaction conditions: ketone (0.043 mmol), KO*t*Bu (0.12 mmol, *i*PrOH (0.5 mL), 82 °C, 2.0 mol% catalyst (based on Ru), 24 h. [c]Yields determined via GC and GC-MS.

Conclusions

This paper demonstrates that polymeric aromatic frameworks are easily obtained with high physicochemical stability and can be used as supports to obtain robust heterogenized catalysts. Here, we have shown that N-heterocyclic carbene complexes can be supported onto PAFs maintaining the integrity of both the organometallic moiety and the organic support. These catalysts were superior to iridium catalyzed homogeneous system for the transfer hydrogen reactions and *N*-alkylation of amines with alcohols in the same conditions. The catalyst could be recovered by simple filtration and reused without significant loss of its catalytic activity. These unique characteristics clearly indicate that PAF catalysts based on covalently and homogeneously active sites could provide new potential in the exploration of heterogeneous catalysts and their applications in sustainable catalysis.

Experimental

A detailed synthesis for parent **PAFs** materials and postfuncionalized materials **PAF**-CH_2Cl and **PAF**-Im was described in supplementary material.

Functionalization of PAFS

Synthesis of PAFs-(NHC)Ir(I). **PAF**-Im (200 mg) (see details in Supplementary Information), [Ir(acac)(cod)] (636 mg, 2.74 mmol) and CH_2Cl_2 (25 mL) were added to a Schlenk flask and the resulting suspension was stirred at 40 °C for 24 h. The solution was then filtered and the solid washed with CH_2Cl_2 and diethyl ether and dried under vacuum at 60 °C overnight. The **PAFs**-NHC-Ir(I) catalyst was obtained as a light yellow solid containing 0.20 mmol/g of iridium determined by ICP-AES analysis.

Synthesis of PAFs-(NHC)Ru(II). A solution of potassium *bis*(trimethylsilyl)amide ($[K(CH_3)_3Si]_2N$, 20 mg, 0.10 mmol) in toluene (50 mL) was dropwised into a suspension of **PAF**-Im (0.10 mmol) in toluene (2.0 mL) at 0 °C under N_2, and the mixture was warmed to at room temperature and stirred for 1 h. Then, a solution of $[Ru(p\text{-cymene})Cl_2]_2$ (45 mg, 0.07 mmol) in toluene (2.0 mL) was added. After stirring for 48 h at 60 °C, the reaction mixture was filtered, and the solid was washed several times with dichloromethane and THF until the filtrate was colorless and finally dried under vacuum (95 %). The ruthenium amount was found to be 0.10-0.20 mmol/g based on ICP-AES analysis.

Catalytic activity

N-alkylation of amines with alcohols. Alcohol (1.5 mmol) and amine (1.0 mmol), were weighed into a micro reactor vessel. KOH (8 mg, 0.13 mmol) was added, followed by solvent (0.30 mL). The mixture was put under an atmosphere of nitrogen, and catalyst (2.70 mg, Ir: 0.5 mol%) was added before stoppering the flask and immersing it in a preheated oil bath (130 °C) for 24 h. The reaction mixture was cooled and filtered. Aliquots were analyzed by GC-MS.

Hydrogen transfer from 2-Propanol to ketones. Ketone (1.0 mmol), KO*t*Bu (4.0 mmol), catalyst (3.68 mg, Ru: 2.0 mol%) and *i*PrOH (0.5 mL) were added to a micro reactor vessel, and the mixture was refluxed for 24 h. The reaction was cooled, and an aliquot was filtered and analyzed by GC-MS.

Recycling experiments. According to the general procedure for the *N*-alkylation of amines with alcohols or transfer hydrogen reactions, the first run reaction was carried out. After completion of the reaction, the catalyst was filtered off, washed with CH_2Cl_2, and then vacuum-dried. The recovered catalyst was used for consecutive reactions under the same conditions.

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Polymeric aromatic frameworks (PAFs), easily obtained from organic platforms, result excellent supports to yield robust well-defined organometallic heterogenized catalysts.