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Polymer-Supported, Carbon Dioxide-Protected N-Heterocyclic Carbenes: Synthesis and Application in Organo- and Organometallic Catalysis

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Abstract: The synthesis of a resin-supported, carbon dioxide-protected N-heterocyclic carbene (NHC) and its use in organocatalysis and organometallic catalysis are described. The resin-bound carbon dioxide-protected NHC-based catalyst was prepared *via* ring-opening metathesis copolymerization of 1,4,4a,5,8,8a-hexahydro-1,4,5,8-*exo,endo*-dimethanonaphthalene (**DMNH6**) with 3-(bicyclo[2.2.1]hept-5-en-2-ylmethyl)-1-(2-propyl)-3,4,5,6-tetrahydropyrimidin-1-ium-2-carboxylate (**M1**), using the well-defined Schrock catalyst Mo[*N*-2,6-(2-Pr)$_2$-C$_6$H$_3$](CHCMe$_2$Ph)(OCMe$_3$)$_2$ and was used for a series of organocatalytic reactions, i.e., for the trimerization reaction of isocyanates, as well as for the cyanosilylation of carbonyl compounds. In the latter reaction, turn-over numbers (TON) up to 5000 were achieved. In addition, the polymer-supported, carbon dioxide-protected N-heterocyclic carbene served as an excellent progenitor for various polymer-supported metal complexes. It was loaded with a series of rhodium(I), iridium(I), and palladium(II) precursors and the resulting Rh-, Ir-, and Pd-loaded resins were successfully used in the polymerization of phenylacetylene, in the hydrogen transfer reaction to benzaldehyde, as well as in Heck-type coupling reactions. In the latter reaction, TONs up to 100,000 were achieved. **M1**, as a non-supported analogue of **poly-M1-*b*-DMNH6**, as well as the complexes PdCl$_2$[1,3-bis(2-Pr)tetrahydropyrimidin-2-ylidene]$_2$ (**Pd-1**) and IrBr[1-(norborn-5-ene-2-ylmethyl)-3-(2-Pr)-3,4,5,6-tetrahydropyrimidin-2-ylidine](COD) (**Ir-1**) were used as homogeneous analogues and their reactivity in the above-mentioned reactions was compared with that of the supported catalytic systems. In all reactions investigated, the TONs achieved with the supported systems were very similar to the ones obtained with the unsupported, homogeneous ones, the turn-over frequencies (TOFs), however, were lower by up to a factor of three.

Keywords: Heck reaction; heterogeneous catalysis; metathesis; organocatalysis; polymerization

Introduction

The chemistry of N-heterocyclic carbenes (NHCs) has attracted attention because of the rapid development of general synthetic methods and wide applications in the field of molecular catalysis. The close analogy of NHCs to trialkylphosphanes and their excellent *s*-donating properties make them ligands for transition metals[1–7] and potent nucleophilic organic catalysts for a wide variety of organic transformations.[8–21] Metal-free catalyzed processes are interesting alternatives to classical organic transformations since they are often more economical and environmentally friendly. Within that context, NHCs have been reported to be active organocatalysts for a number of reactions, such as transesterifications/amidations,[22] the living ring-opening polymerization of cyclic esters,[23] the trimerization of isocyanates,[7] as well as for benzoin condensation,[24] sila-Stetter,[25] trifluoromethylation,[26] and cyanosilylation reactions.[27]

It is worth noting that the manipulation of the free carbenes is often difficult due to their highly reactive nature as well as air and moisture sensitivity. Recently, the use of CO$_2$ adducts of NHCs attracted much attention in organocatalysis as well as in synthesis of the corresponding NHC-metal complexes.[6,7,28] In this article, we describe the synthesis and application of a polymer-supported, CO_2-protected N-heterocyclic carbene. It was prepared *via* ring-opening metathesis copolymerization of 1,4,4a,5,8,8a-hexahydro-1,4,5,8-*exo,endo*-dimethanonaphthalene with 3-(bicyclo[2.2.1]hept-5-en-2-ylmethyl)-1-(2-propyl)-3,4,5,6-tetrahydropyrimidin-1-ium-2-carboxylate, using the well-defined Schrock catalyst $Mo[N\text{-}2,6\text{-}(2\text{-}Pr)_2\text{-}C_6H_3](CHCMe_2Ph)(OCMe_3)_2$. The resin-bound, NHC-based catalyst was then used for a series of organocatalytic reactions, namely, for the trimerization reaction of isocyanates, as well as for the cyanosilylation of carbonyl compounds. Heating of polymer-supported CO_2-protected, N-heterocyclic carbene in presence of Rh(I), Ir(I), and Pd(II) precursors resulted in the release of CO_2 and formation of the polymer-supported Rh(I), Ir(I), and Pd(II) catalysts. These were used for series of catalytic reactions such as polymerization of phenylacetylene, hydrogen transfer to benzaldehyde, and Heck coupling reactions, respectively.

Results and Discussion

Synthesis of Monomer M1

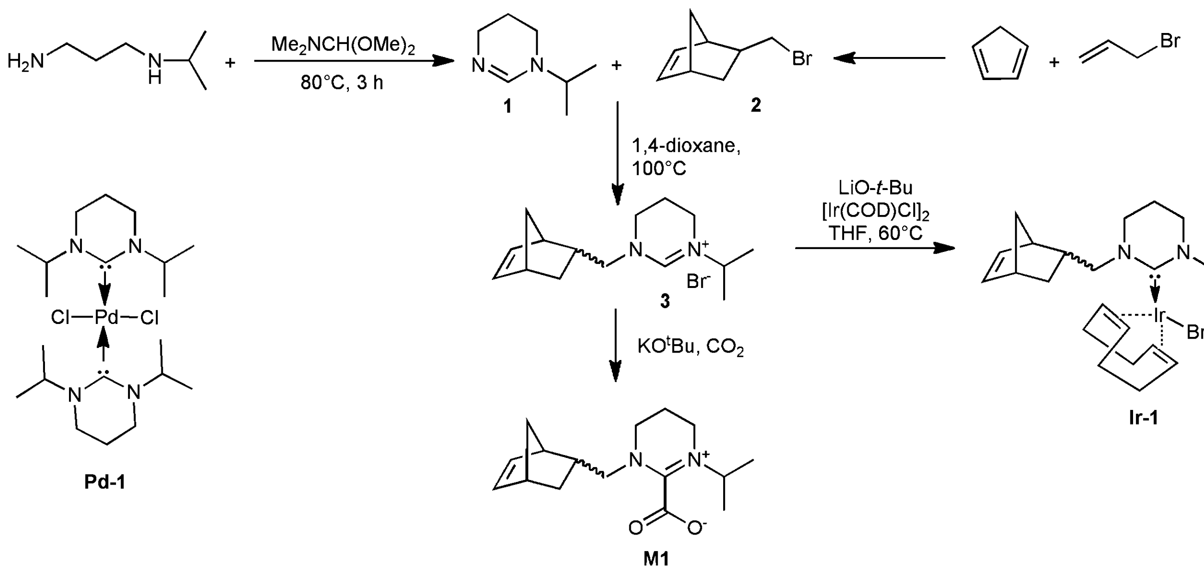
The synthesis of CO_2-protected N-heterocyclic carbene-based monomer is outlined in Scheme 1. 1-(2-Propyl)-1,4,5,6-tetrahydropyrimidine(**1**) was synthesized *via* reaction of *N*-(2-propyl)propane-1,3-diamine with 1,1-dimethoxy-*N,N*-dimethylmethanamine.[29] 5-(Bromomethyl)bicyclo[2.2.1]hept-2-ene (**2**) was synthesized from cyclopentadiene and allyl bromide.[30] The corresponding NHC precursor 3-bicyclo[2.2.1]hept-5-en-2-ylmethyl-1-(2-propyl)-3,4,5,6-tetrahydropyrimidin-1-ium bromide (**3**) was accessible by the reaction of **1** with **2** in 90% yield (Scheme 1). Compound **3** was finally converted into the corresponding CO_2-protected monomer **M1** by treatment with potassium *tert*-butoxide followed by the reaction with dry CO_2.

Homopolymerization

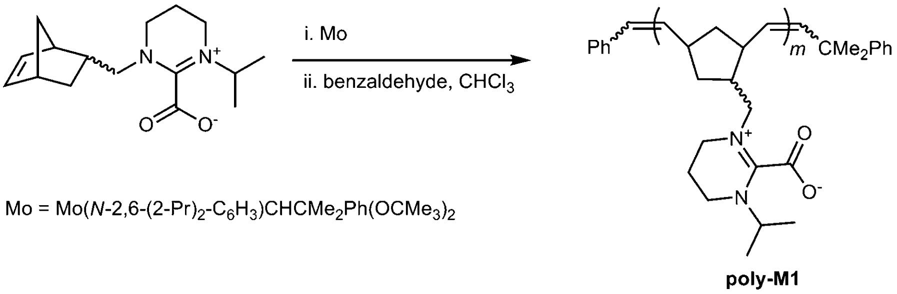
In order to determine the ring-opening metathesis polymerization (ROMP) propensity of **M1** with the Schrock initiator $Mo[N\text{-}2,6\text{-}(2\text{-}Pr)_2\text{-}C_6H_3](CHCMe_2Ph)(OCMe_3)_2$, the corresponding homopolymerization was carried out in $CHCl_3$ at room temperature. The homopolymer **poly(M1)** was isolated in 95% yield (Scheme 2). The number average molecular weight (*Mn*) as determined by ^1H NMR-based end group analysis was 4100 $g\,mol^{-1}$ $[Mn_{(calc)}=5500\ g\,mol^{-1}]$ and the polydispersity index (PDI) as determined by GPC of **poly(M1)** was PDI = 1.26. In addition, the polymerization kinetics of **M1** were determined (Figure S1, Supporting Information). As can be seen, the polymerization of **M1** followed 1st order kinetics, suggesting a living polymerization setup. Within 20 min a degree of polymerization (DP) of 12 could be realized.

Synthesis of Polymer-Supported CO_2-Protected N-Heterocyclic Carbenes

The conventional protocol for the preparation of polymer-supported ligands usually entails the surface modification of commercially available polymer sup-



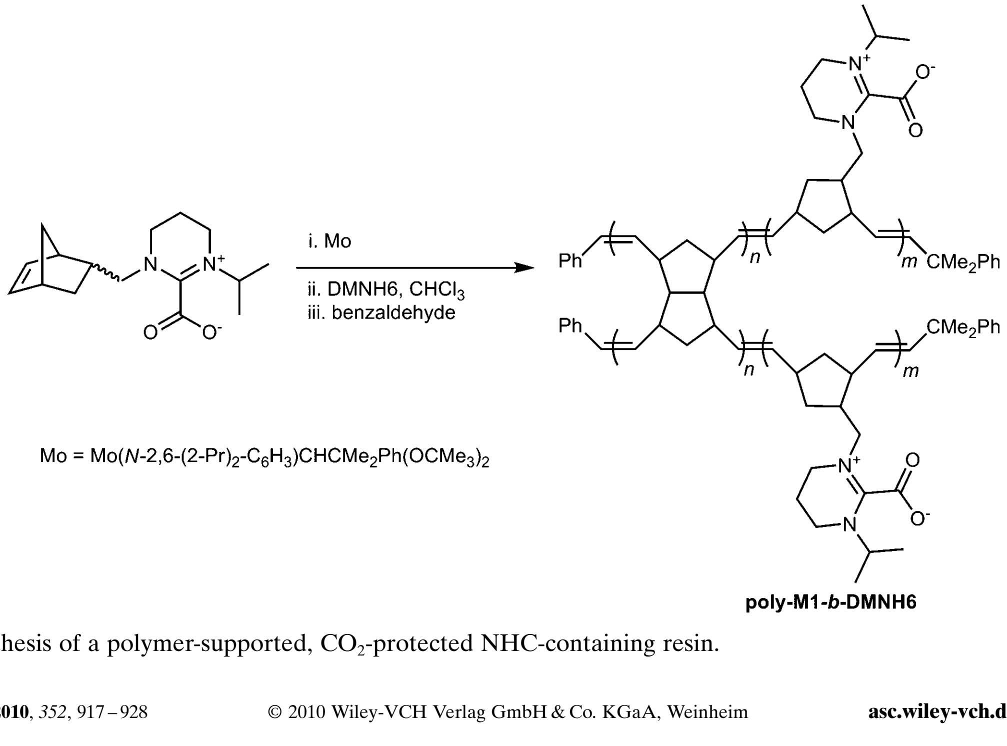
Scheme 1. Synthesis of monomer **M1** and **Ir-1** and structure of **Pd-1**.



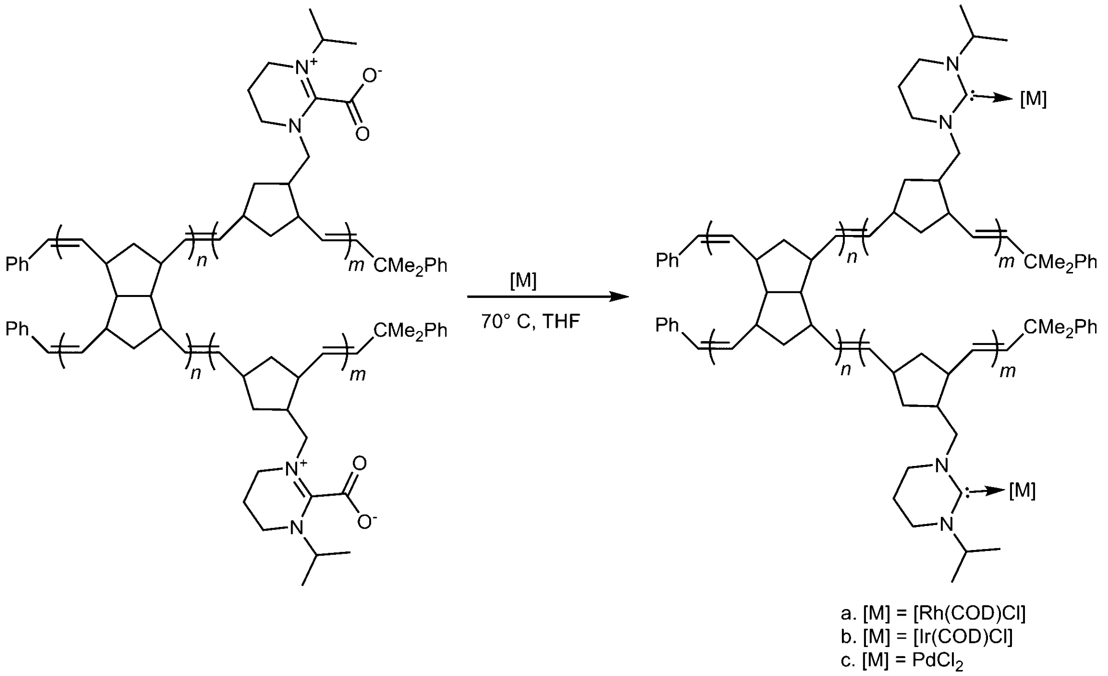
Scheme 2. Polymerization of monomer **M1**.

ports, for example, polystyrene-divinylbenzene (PS-DVB) or chloromethylated PS-DVB (Merrifield polymer).[31] These synthetic routes, however, are characterized by some disadvantages. To achieve a maximum derivatization capacity (usually expressed in mmol of functional group/g of resin), porous materials with high surface areas have to be chosen. As a major part of the specific surface area (σ) results from small pores, large amounts of the desired ligand are located inside the particle. This leads to a diffusion-controlled reaction during catalysis which usually significantly reduces the overall reaction rate constant.[32] In addition, the synthetic protocol consists of at least two or three steps. Since it is difficult to achieve each step in a quantitative way, ill-defined supports are obtained.

Some years ago, we described a powerful tool for the preparation of functionalized polymeric supports *via* ROMP.[33–42] Following this concept, we prepared polymer-supported, CO_2-protected N-heterocyclic carbenes from the CO_2-protected, NHC based monomer **M1** and a cross-linker, i.e., 1,4,4a,5,8,8a-hexahydro-1,4,5,8-*exo*-*endo*-dimethanonaphthalene **DMNH6** (Scheme 3). Monomer **M1** was polymerized in a living manner by the Schrock catalyst Mo[N-2,6-(2-Pr)$_2$-C_6H_3](CHCMe$_2$Ph)(OCMe$_3$)$_2$ (*vide supra*). In a second step, the living polymer chains were cross-linked using **DMNH6**. Based on the kinetic measurements, a time span of 20 min was chosen that ensured for a complete polymerization of **M1** prior to the addition of the cross-linker. As a consequence of the polymerization order, the linear polymer chains bearing the CO_2-protected NHC groups form tentacles which are attached to the surface of the cross-linked carrier. The polymeric resin that was obtained had a mean particle diameter of 40 ± 10 μm. The particles consisted of agglomerates of smaller particles 5–10 μm in diameter. The cross-linked material showed significant swelling propensity, which amounted to 20 and 30% in THF and CH_2Cl_2, respectively. Used in heterogeneous catalysis, the resin is best used in stirred reactors and can easily be removed by filtration.



Scheme 3. Synthesis of a polymer-supported, CO_2-protected NHC-containing resin.



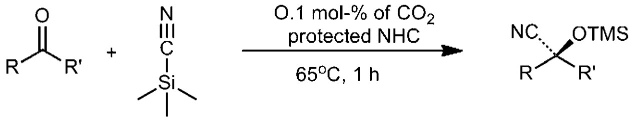
Scheme 4. Synthesis of resin-bound Rh, Ir and Pd catalysts.

Synthesis of Rh-, Ir-, and Pd-Loaded Resins

Rh-, Ir-, and Pd-loaded resins were synthesized by the reaction of $[Rh(COD)Cl]_2$, $[Ir(COD)Cl]_2$ and $PdCl_2$ with the polymer-supported, CO_2-protected N-heterocyclic carbene (Scheme 4). The Rh, Ir and Pd contents were determined by ICP-OES after dissolving samples in aqua regia and were found to be 22 mg/g (0.21 mmol/g), 46 mg/g (0.24 mmol/g) and 85 mg/g (0.80 mmol/g) polymer, respectively.

Cyanosilylation of Carbonyl Compounds

The cyanosilylation of carbonyl compounds is an efficient method for the synthesis of cyanohydrins (Scheme 5), which can be readily converted into other useful compounds such as α-hydroxy acids, α-hydroxy aldehydes, α-amino alcohols and 1,2-diols.[43,44] It is known that Lewis acids catalyze the cyanosilylation of aldehydes *via* activation of the aldeydes,[45,46] while Lewis bases catalyze the reaction *via* activation of the reagent, i.e., TMS-CN.[47,48] Here, we used the polymer-supported, CO_2-protected NHC for these purposes. Upon heating, CO_2 evolves and the free NHC is formed which then catalyzes the cyanosilylation[27] of carbonyl compounds .



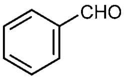
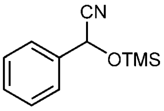
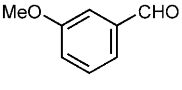
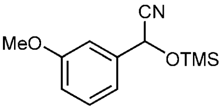
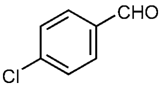
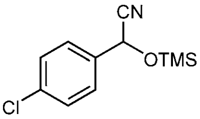
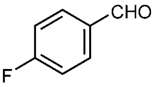
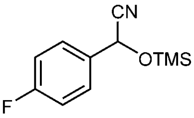
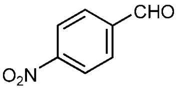
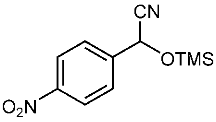
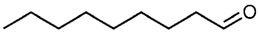
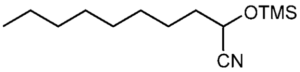
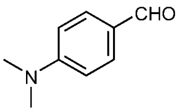
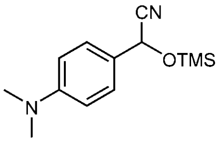
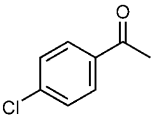
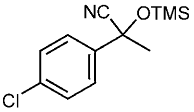
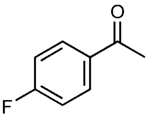
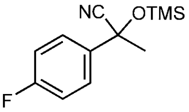
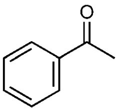
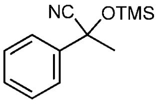
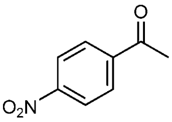
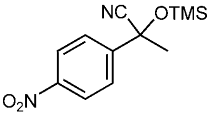
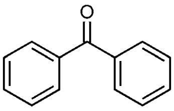
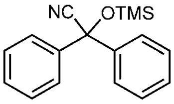
Scheme 5. Cyanosilylation of carbonyl compounds catalyzed by a polymer-supported, CO_2-protected NHC catalyst.

To examine the catalytic performance of the polymer-supported, CO_2-protected NHC for cyanosilylation, reactions between various carbonyl compounds including aldehydes and ketones with TMSCN were carried out in THF at 65 °C. Product quantification was accomplished by GC-MS. A summary of the results is given in Table 1. As can be seen, the catalyst showed excellent reactivity in these reactions. Thus, using a catalyst loading of 0.1–0.02 mol% of NHC with respect to the corresponding carbonyl compound, turn-over numbers (TONs) in the range of 1000–5000 were achieved. Yields were in the 95–100% range within 20–90 min. All cyanohydrins were isolated with high purity after simple filtration. In case the reactions were run with the soluble (monomeric) analogue, i.e., with **M1**, similar TONs were obtained, however, reactions were faster by up to a factor of three.

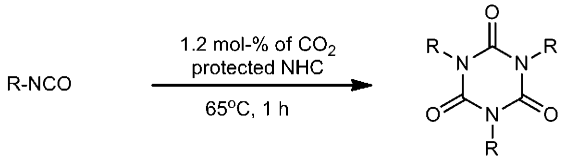
Trimerization of Isocyanates

The polymer-supported, CO_2-protected N-heterocyclic carbenes were also used in the trimerization of isocyanates. For this purpose, a variety of aromatic isocyanates were used (Scheme 6). A summary of the results is given in Table 2. The CO_2-protected, NHC-containing resin showed excellent catalytic performance allowing for the synthesis of the corresponding

Table 1. Results of the cyanosilylation of carbonyl compounds catalyzed by the polymer-supported, CO_2-protected NHC catalyst.

			Poly(M1-*b*-DMNH6)			**M1**		
Entry	Carbonyl compound	Product	Time [min]	Conversion [%][b]	TON/ TOF [h^{-1}]	Time [min]	Conversion [%][b]	TON/ TOF [h^{-1}]
1			20	100[c]	5000/ 15000	15	96[c]	4800/ 19200
2			20	100[c]	5000	–	–	–
3			60	99[c]	4950	–	–	–
4			20	100[c]	5000/ 15000	15	97[c]	4850/ 19400
5			30	100[c]	5000	–	–	–
6			40	98[c]	4900	–	–	–
7			40	100[a]	1000/ 1500	30	99[a]	990/1980
8			90	100[a]	1000/670	30	96	960/1920
9			90	100[a]	1000/670	30	99[a]	990/1980
10			60	100[a]	1000	–	–	–
11			40	100[a]	1000	–	–	–
12			90	100[a]	1000/670	30	99[a]	990/1980

[a] 0.1 mol% of CO_2-protected NHC with respect to the carbonyl compounds. Reactions were run at 65 °C temperature.
[b] GC-MS conversions.
[c] 0.02 mol% of CO_2-protected NHC with respect to the carbonyl compounds.



Scheme 6. Trimerization of isocyanates catalyzed by the polymer-supported, CO_2-protected NHC catalyst.

isocyanurates. Using a catalyst loading of 1.2 mol% of NHC with respect to the isocyanate, pure products were isolated in the range of 75–92% within 60–90 min. Purification of the isocyanurates was accomplished by simply dissolving the reaction mixture in CH_2Cl_2, followed by filtration and washing. No by-products were observed by ^1H and ^{13}C NMR. Again, similar TONs were obtained in cases where the reactions were run with the soluble (monomeric) analogue, i.e., with **M1**.

Heck Reactions

The Heck reaction of aryl halides with terminal olefins is among the most important Pd-catalyzed transformations in organic synthesis and a favorite test re-

Table 2. Results of the trimerization of isocyanates catalyzed by the polymer-supported, CO_2-protected NHC catalyst.

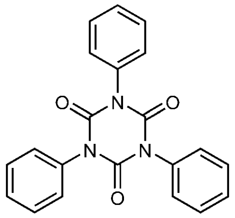
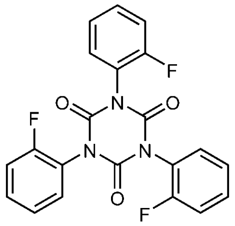
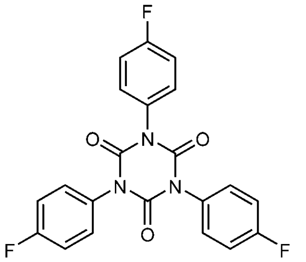
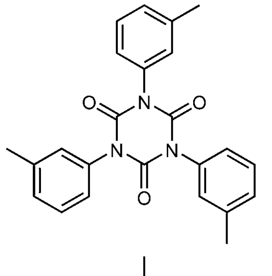
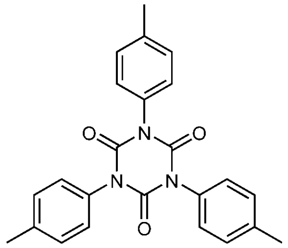
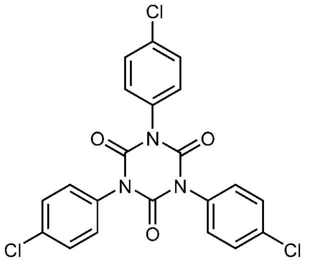
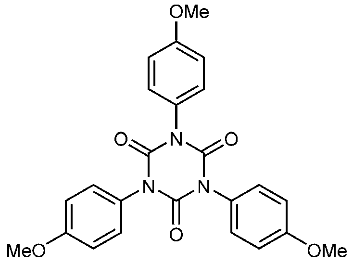
			Poly(M1-*b*-DMNH6)		**M1**	
Entry	Ar in Ar-NCO	Product	Time [min]	Yield [%][b]	Time [min]	Yield [%][b]
1	phenyl		60	92[a]	20	98[a]
2	2-F-C_6H_4		90	85[a]	–	–
3	4-F-C_6H_4		60	83[a]	60	85[a]
4	3-Me-C_6H_4		60	87[a]	–	–
5	4-Me-C_6H_4		60	91[a]	–	–

Table 2. (Continued)

			Poly(M1-*b*-DMNH6)		M1	
Entry	Ar in Ar-NCO	Product	Time [min]	Yield [%][b]	Time [min]	Yield [%][b]
6	4-Cl-C_6H_4		90	75[c]	90	72[c]
7	4-MeO-C_6H_4		90	78[c]	90	65[c]

[a] 1.2 mol% of CO_2-protected NHC with respect to the isocyanate were used. Reactions were run at 65 °C.
[b] Isolated yields.
[c] 1.3 mol% of CO_2-protected NHC with respect to the isocyanate were used.

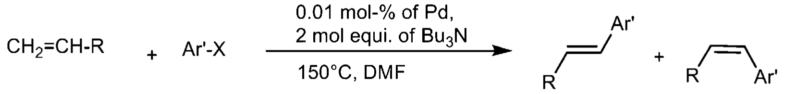
action for new palladium pre-catalysts (Scheme 7).[49] For checking the efficiency of the resin-bound Pd-NHC catalysts, we carried out a series of test reactions of styrene and butyl acrylate with various aryl bromides in DMF at 150 °C. A summary of the results is given in Table 3. As can be seen, the Pd-loaded resin showed excellent reactivity for these kinds of reactions and turn-over numbers (TONs) up to 100,000 were achieved without any optimization of the reaction conditions. Pd-leaching to the products was checked by means of ICP-OES and was found to be <0.1 ppm, that is, below the limit of detection. For purposes of comparison, reactions were run in the presence of **Pd-1** (Scheme 1). Similar TONs were obtained, however, the reaction proceeded faster with **Pd-1** by up to a factor of three.

Hydrogen Transfer to Benzaldehyde

The catalytic efficiency of the Ir-loaded resin was studied in the hydrogen transfer reaction to benzaldehyde (Scheme 8). Benzadehyde, K_2CO_3 were mixed with 2-propanol and the reaction mixture was refluxed in the presence of the Ir-loaded resin. Product conversion was monitored by GC-MS. The Ir-loaded catalyst showed excellent reactivity. Thus, using a catalyst loading of 0.1 mol% of Ir with respect to benzaldehyde, a TON of 980 as well as a TOF of 250 h^{-1} were achieved within four hours. Iridium leaching was determined by means of ICP-OES and was found to be <50 ppm, which translates into an Ir-leaching of $<3\%$. For comparison, the same amount of Ir present in a soluble catalyst, i.e., in **Ir-1**, gave a TON of 800 and a TOF of 200 h^{-1}.

Polymerization of Phenylacetylene

The use of the Rh-loaded heterogeneous catalyst also allowed for the quantitative polymerization of phenylacetylene to form poly(phenylacetylene) (**PPA**, Scheme 9). For this purpose, the Rh-loaded resin was added to the solution of phenylacetylene in $CHCl_3$ and stirred for 2 hour. Then, the reaction mixture was passed through a small bed of celite to remove the catalyst and polymer was precipitated by the addition of pentane. The number average molecular weights (*Mn)* and polydispersity indices (PDI) observed for **PPA** were 8400 g mol^{-1} [$Mn_{(calc)=}$10200 g mol^{-1}], PDI = 2.45. According to the ^1H and ^{13}C NMR spectra, a *cis*-transoidal **PPA** was obtained. Rh-leaching to the



Scheme 7. Heck coupling reactions catalyzed by a resin-bound Pd catalyst.

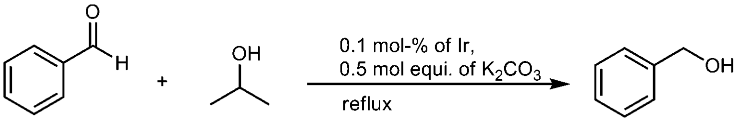
Table 3. Results of the Heck type reaction catalyzed by resin-bound Pd catalyst.[a]

			Resin-Bound Pd Caatalyst				**Pd-1**		
Entry	CH_2= CH–R	Ar-Br	Pd [mol%]	Time [h]	Conversion [%][b]	TON/TOF [h^{-1}]	Time [h]	Conversion [%][b]	TON/TOF [h^{-1}]
1	styrene	bromobenzene	0.02	36	45	2260	–	–	–
2	styrene	4-Br-acetophenone	0.01	20	100	10000	5	100	50000/10000
			0.002	14	100[d]	10000[c]			
					100	50000			
3	styrene	4-Br-nitrobenzene	0.01	20	100	10000	–	–	–
4	styrene	4-Br-benzonitrile	0.001	24	87	87000/3630	7	94	94000/13400
5	butyl acrylate	4-Br-acetophenone	0.001	4	100	100000/ 25000	2	100	100000/ 50000
6	butyl acrylate	4-Br-benzonitrile	0.001	4	100	100000/ 25000	2	98	98000/49000
7	styrene	4-Br-toluene	0.01	27	18	1800	–	–	–
8	styrene	1-bromo-4-methoxybenzene	0.01	29	17	1700	–	–	–

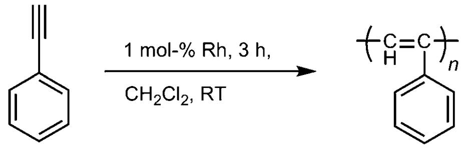
[a] Reactions were run at 150 °C in DMF.

[b] Conversion was determined by GC-MS.

[c] Reuse of catalyst.



Scheme 8. Hydrogen transfer reaction to benzaldehyde catalyzed by a resin-bound Ir catalyst.



Scheme 9. Polymerization of phenylacetylene catalyzed by a resin-bound Rh catalyst.

products was determined by means of ICP-OES and was found to be 715 ppm, which translates into a rhodium leaching of 4.5%.

Conclusions

In conclusion, a polymer-supported, CO_2-protected N-heterocyclic carbene has been successfully synthesized *via* ring-opening metathesis copolymerization of a CO_2-protected NHC containing monomer (**M1**) and the cross-linker **DMNH6**. The resin-bound NHC catalyst was found to be a highly efficient catalyst in the cyanosilylation of carbonyl compounds allowing for TONs of 1000–5000 within 20–90 min. The resin-bound NHC catalyst was also successfully used in the cyclotrimerization of isocyanates. Rh-, Ir-, and Pd-loaded resins were synthesized *via* immobilization of Rh, Ir, and Pd precursors to the polymer-supported, CO_2 protected N-heterocyclic carbene. These metal-loaded resins were found to be excellent catalysts for Heck coupling reactions, the hydrogen transfer reaction to benzaldehyde, and for the polymerization of phenylacetylene. However, it has to be stated that there was significant metal leaching from the supported Ir and in particular from the supported Rh catalyst.

Experimental Section

General Methods

All manipulations were performed under an N_2 atmosphere in a glove box (MBraun LabMaster 130, MBraun, Garching, Germany) or by standard Schlenk techniques unless stated otherwise. Purchased starting materials were used without any further purification. Pentane, diethyl ether, toluene, CH_2Cl_2 and tetrahydrofuran (THF) were dried using a solvent drying system (SPS, MBraun, Garching, Germany). Benzene, *n*-hexane and dimethoxyethane (DME) were dried and distilled from Na/benzophenone ketyl under argon. NMR spectra were recorded on a Bruker Avence 600 (600.25 MHz for proton and 150.93 MHz for carbon) and Bruker Avence 250 (250.13 MHz for proton and 62.90 MHz for carbon) spectrometer, respectively, at room temperature unless stated otherwise. Proton and carbon spectra were referenced to the internal solvent resonance and are reported in ppm relative to tetramethylsilane. Deuterated NMR solvents (C_6D_6 and THF-d_8) were dried and distilled from Na/benzophenone ketyl, dichloromethane-d_2 and chloroform-d_1 were dried and distilled from CaH_2. Phenyl isocyanate, 4-methoxyphenyl isocyanate, 2-fluorophenyl isocyanate, *p*-toluyl isocyanate, *o*-toluyl isocyanate, 4-chlorophenyl isocyanate and 4-fluorophenyl isocyanate were purchased from Aldrich (Germany), dried over P_2O_5, and degassed prior to use. $[Rh(COD)Cl]_2$, $[Ir(COD)Cl]_2$, $PdCl_2$ were purchased from Aldrich. Molecular weights and polydispersity indexes (PDIs) of **poly(M1)** were determined by gel permeation chromatography (GPC) on three consecutive 4.6×300 mm Waters Styragel HR4 columns in *N,N*-dimethylformamide (DMF) at 30 °C using an isocratic pump (model 1515), an 1717 autosampler and a 2415 refractive index detector (all Waters Co, USA). The flow rate was set to 1 mL min^{-1}. Narrow poly(styrene) standards in the range $162 < M_n < 5{,}500{,}000$ g mol^{-1} (Easi Vial-red, yellow and green) were purchased from Polymer Labs. FT-IR spectra were recorded on a Bruker Vector22 spectrometer using ATR technology. GC-MS investigations were carried out on a Shimadzu GCMS-QP5050 with an AOC-20i autosampler, using an SPB fused silica (Rxi-5MS) column (30 m×0.25 mm×0.25 μm film thickness) and on a Shimadzu GCMS-QP2010S equipped with an AOC-20i autosampler using a SPB fused silica (Rxi-5MS) column (30 m×0.25 mm×0.25 μm film thickness), respectively. The injection temperature was 150 °C, the initial column temperature was set to 70 °C and then increased to 120 °C within 7.3 min. The column flow was 1.12 mL min^{-1}. Mo[*N*-2,6-(2-Pr)$_2$-C_6H_3](CHCMe$_2$Ph)(OCMe$_3$)$_2$,[50] 5-(bromomethyl)bicyclo[2.2.1]hept-2-ene,[30] 1,4,4a,5,8,8a-hexahydro-1,4,5,8-*exo,endo*-dimethanonaphthalene (**M2**),[51] 1-(2-propyl)-1,4,5,6-tetrahydropyrimidine[29] and $PdCl_2$(1,3-bis(2-Pr)tetrahydropyrimidin-2-ylidene)$_2$[52] were synthesized according to the literature methods.

3-Bicyclo[2.2.1]hept-5-en-2-ylmethyl)-1-(2-propyl)-3,4,5,6-tetrahydropyrimidin-1-ium Bromide

1-(2-Propyl)-1,4,5,6-tetrahydropyrimidine (5.0 g, 39.62) was dissolved in a minimum amount of 1,4 dioxane, and 5-(bromomethyl)bicyclo[2.2.1]hept-2-ene (7.4 g, 39.62 mmol) was added slowly to the solution. The reaction mixture was stirred for 4 h at 100 °C. The solvent was removed under vacuum and pure product was obtained as a white colored solid; yield: 11.2 g (90%). ^{1}H NMR ($CDCl_3$): $\delta = 0.57$ and 1.24 (m, 2H, NBE), 1.30 (d, 6H, CH_3), 1.41 and 1.86 (m, 2H, NBE), 2.1 (m, 2H, CH_2), 2.43 and 2.73 (m, 3H, NBE), 3.20–3.50 (m, 6H, CH_2), 4.36 (sep, 1H, CH), 6.00 and 6.19 (m, 2H, NBE), 9.16 and 9.58 (s, 1H, CH); ^{13}C NMR ($CDCl_3$): $\delta = 19.5$, 20.7 (d), 30.3, 38.3 (d), 42.6, 44.6 (d), 49.9, 56.5, 59.5, 131.8, 139.1, 152.6. FT-IR (ATR mode): $\tilde{\nu} = 2961$ (w), 1673 (s), 1437 (m), 1375 (w), 1324 (m), 1252 (w), 1210 (w), 1131 (m), 1004, 825 (w), 738 cm^{-1} (m); ESI-MS: *m/z* = 313.14, calcd. for $C_{15}H_{25}BrN_2$ $(M+H)^+$: 312.12.

3-(Bicyclo[2.2.1]hept-5-en-2-ylmethyl)-1-(2-propyl)-3,4,5,6-tetrahydropyrimidin-1-ium 2-Carboxylate (M1)

3-Bicyclo[2.2.1]hept-5-en-2-ylmethyl-1-(2-propyl)-3,4,5,6-tetrahydropyrimidin-1-ium bromide (5.0, 15.95 mmol) was suspended in 130 mL of THF. Potassium *tert*-butoxide (2.3 g, 20.74 mmol) was dissolved in THF (8.0 mL) and added to this suspension. The reaction mixture was stirred for 14 h and then filtered through celite to remove residual salts. The filtrate was transferred to a 250-mL Schlenk flask and removed from the glove box. CO_2 was bubbled through the solution at 0 °C for 60 min, during this time a white precipitate formed. The solvent was removed under vacuum, and the residue was washed with diethyl ether and dried; yield: 3.3 g (75%). ^{1}H NMR ($CDCl_3$): $\delta = 0.64$ (m, 1H, NBE), 1.12–1.56 (m, 8H, CH_3+NBE), 1.91 and 2.05 (m, 3H, NBE), 2.45–2.93 (m, 3H, CH_2+NBE), 3.02–3.64 (m, 6H, CH_2), 4.45 (sept, 1H, CH), 6.00 and 6.19 (m, 2H, NBE); ^{13}C NMR ($CDCl_3$): $\delta = 19.4$ (d), 19.8 (d), 20.4 (d), 30.0, 30.5, 36.6, 37.7, 38.0, 38.4, 42.3 (d), 44.0, 44.5, 45.0, 45.4, 49.7 (d), 54.2, 56.2, 58.5, 59.2, 131.6 (d), 138.7 (d), 159.1, 161.6. FT-IR (ATR mode): $\tilde{\nu} = 2958$, 2867, 1656 (s), 1596 (s), 1459, 1327 (s), 1212 (w), 1149 (w), 1090 (w), 1046 (w), 921(w), 862 (w), 761 (w), 722 cm^{-1} (m); ESI-MS: *m/z* = 277.19, calcd. for $C_{16}H_{24}N_2O_2$ $(M+H)^+$: *m/z* = 276.18.

Homopolymerization of M1

M1 (100 mg, 0.36 mmol) and Mo[*N*-2,6-(2-Pr)$_2$-C_6H_3](CHCMe$_2$Ph)(OCMe$_3$)$_2$ (10 mg, $18.0{\cdot}10^{-3}$ mmol) were separately dissolved in $CHCl_3$ (2 mL each). The monomer solution was added to the catalyst solution and the resulting mixture was vigorously stirred for 2 h. Then the polymerization was terminated by the addition of benzaldehyde (10 mol equiv. with respect to catalyst). The polymer was then precipitated by addition of diethyl ether, filtered off and dried; yield of **Poly(M1)**: 87 mg (87%). $Mn_{(found)} = 1550$ g mol^{-1} (PDI = 1.26), $Mn_{(calc)} = 5500$ g mol^{-1}. $M_n = 4100$ g mol^{-1} *via* ^{1}H NMR end group analysis; ^{1}H NMR ($CDCl_3$): $\delta = 0.80$–1.68 (br m, CH_3+NBE), 2.06 (br s, NHC), 2.43 and 2.66 (br s, CH_2+NBE), 3.29 (br m, CH_2), 4.36 (br s, CH), 5.32 (br s, NBE); ^{13}C NMR ($CDCl_3$): $\delta = 19.6$, 20.5, 22.6, 34.4, 37.1, 38.6, 42.3, 43.4, 44.6, 125.1, 126.3, 128.6, 129.7, 132.2, 133.5, 135.3, 154.1, 159.5, 161.8; FT-IR (ATR mode): $\tilde{\nu} = 3390$ (w), 2973 (w), 2935 (w), 2866 (w), 1653 (s), 1604 (s), 1451 (w), 1326 (m), 1214 (w), 1118 (w), 756 , cm^{-1} (w).

Kinetics

M1 (70 mg, 0.25 mmol) and Mo[*N*-2,6-(2-Pr)$_2$-C_6H_3)(CHCMe$_2$Ph)(OCMe$_3$]$_2$ (9.2 mg, $16.90{\cdot}10^{-3}$ mmol) were separately dissolved in $CDCl_3$ (3 mL each). The monomer solution was added to the catalyst solution and the resulting mixture was stirred at room temperature. Aliquots (0.5 mL) were taken at fixed times, quenched with benzaldehyde (10 mol equiv. with respect to catalyst) and product conversion was monitored by ^{1}H NMR at defined time intervals. Proton signals of the monomer and those of the double bonds of the polymer double were used for calculations.

Preparation of the CO_2-Protected NHC-Containing Resin

Mo[*N*-2,6-(2-Pr)$_2$-C_6H_3](CHCMe$_2$Ph)(OCMe$_3$)$_2$ (10 mg, $18.0{\cdot}10^{-3}$ mmol) was added to a stirred solution of **M1** (100 mg, 0.36 mmol) in 5 mL of $CHCl_3$. After 20 min, **DMNH-6** (115 mg, 0.72 mmol) was added to the solution and stirring was continued for 2 h. Finally, benzaldehyde (10 mol equiv. with respect to the catalyst) was added in order to ensure quantitative termination of the reaction. After 1 h, the polymer was filtered off, washed with CH_2Cl_2 and diethyl ether, and dried under vacuum; yield: 180 mg (85%). FT-IR (ATR mode): $\tilde{\nu}=3384$ (w), 2927 (s), 2863 (m), 1669 (s), 1604 (s), 1449 (w), 1325 (s), 1213 (w), 966 (s), 730 cm^{-1} (s); elemental anal. (%) calcd. for the resin assuming 100% incorporation of **M1**: C 77.88, H 9.15, N 6.05; found: C 72.82, H 8.51, N 3.47. This corresponds to 57.3% monomer incorporation.

Synthesis of a Resin-Bound Pd Catalyst

The CO_2-protected NHC-containing resin (100 mg) was suspended in 5 mL of THF, then H_2PdCl_4 (35 mg, 0.19 mmol)[32] was added. The mixture was heated to 70 °C. After 3 h of stirring, the reaction mixture was cooled to room temperature. The mixture was filtered off and washed with CH_2Cl_2 and diethyl ether and dried. The Pd content was determined by ICP-OES after dissolving a 23.7 mg sample in aqua regia and found to be 31.1 mg g^{-1}(0.29 mmol g^{-1}). In view of the amount of NHC present in the polymer (1.23 mmol g^{-1}), this corresponds to a Pd loading of 24% assuming the formation of a mono-NHC-Pd complex.

Synthesis of a Resin-Bound Ir Catalyst

The CO_2-protected NHC-containing resin (100 mg) was suspended in 5 mL of THF, then $[Ir(COD)Cl]_2$ (27 mg, 0.04 mmol) was added. The mixture was heated to 70 °C. After 3 h of stirring, the reaction mixture was cooled to room temperature. The mixture was filtered off and washed with CH_2Cl_2 and diethyl ether and dried. The Ir content was determined by ICP-OES after dissolving a 17.9 mg sample in aqua regia and found to be 45.5 mg g^{-1}(0.23 mmol g^{-1}). In view of the amount of NHC present in the polymer (1.23 mmol g^{-1}), this corresponds to an Ir loading of 19% assuming the formation of a mono-NHC-Ir complex.

Synthesis of a Resin-Bound Rh Catalyst

The CO_2-protected, NHC-containing resin (100 mg) was suspended in 5 mL of THF, then $[Rh(COD)Cl]_2$ (15 mg, 0.03 mmol) was added. The mixture was heated to 70 °C. After 3 h of stirring, the reaction mixture was cooled to room temperature. The mixture was filtered off and washed with CH_2Cl_2 and diethyl ether and dried. The Rh content was determined by ICP-OES after dissolving a 13.2 mg sample in aqua regia and found to be 21.6 mg g^{-1}(0.21 mmol g^{-1}). In view of the amount of NHC present in the polymer (1.23 mmol g^{-1}), this corresponds to an Ir loading of 17% assuming the formation of a mono-NHC-Rh complex.

IrBr(3-bicyclo[2.2.1]hept-5-en-2-ylmethyl)-1-(2-propyl)-3,4,5,6-tetrahydropyrimidin-1-ium)COD (Ir-1)

$[Ir(COD)Cl]_2$ (214 mg, 0.31 mmol) was dissolved in THF (5 mL), and lithium *tert*-butoxide (128 mg, 1.59 mmol) was added under vigorous stirring. The mixture was stirred for a further 30 min at room temperature, then 3-bicyclo[2.2.1]hept-5-en-2-ylmethyl)-1-(2-propyl)-3,4,5,6-tetrahydropyrimidin-1-ium bromide (200 mg, 0.64 mmol) was added. The reaction mixture was stirred overnight at 65 °C, after this time TLC showed no further conversion. The solvent was removed under vacuum and the product was purified by column chromatography (silica gel) using CH_2Cl_2:ethanol (250:4) as a mobile phase. The product eluted as a yellow band in the second fraction. The product fractions were pooled and evaporated to dryness to furnish a yellow solid; yield: 0.176 g (45%). Yellow crystals were obtained by layering pentane over a dilute solution of **Ir-1** in CH_2Cl_2 at −30 °C. ^{1}H NMR ($CDCl_3$): $\delta=0.95$ (m, 1H, NBE), 1.18–1.28 (m, 8H, CH_3+NBE), 1.42 (m, 2H, NBE), 1.52–2.12 (m, 7H, COD+NBE), 2.18 (m, 2H, CH_2), 2.40–2.92 (m, 4H, NBE+COD), 3.01, 3.09 and 3.31 (m, 5H, NCH_2+NBE), 3.50, 3.84, 4.26, 4.36, 4.57 and 4.75 (m, 4H, COD), 5.81 (hept, 1H, NCH, $J=6.0$ Hz) 6.02, 6.10, 6.19, and 6.25 (m, 2H, NBE); ^{13}C NMR ($CDCl_3$): $\delta=19.5$, 20.4, 21.4, 28.0, 30.8, 31.4, 37.8, 42.3,45.7, 49.9, 52.2, 56.5, 61.9, 62.8, 80.7, 131.5, 132.3, 137.8, 138.4, 199.5 (C-Ir); FT-IR (ATR mode): $\tilde{\nu}=3055$ (w), 2959 (s), 2924 (s), 2869 (s), 2832 (m), 2532, 1507 (s), 1448 (m), 1368 (w), 1335 (m), 1307 (s), 1207 (m), 1160 (m), 1080 (w), 1005 (w), 753 (s), 718 cm^{-1} (m); ESI-MS: *m/z* = 533.25, calcd. for $C_{23}H_{36}BrIrN_2$ (M-Br$^-$): 613.177.

Typical Cyanosilylation Procedure

In a 10-mL Schlenk tube, the CO_2-protected NHC-containing resin (0.10 mol% of NHC with respect to the carbonyl compound), acetophenone (1.2 g, 10.00 mmol) and trimethylsilyl cyanide (1.5 g, 15.00 mmol) were dissolved in 5 mL of THF. The reaction mixture was heated to 65 °C. Product conversion was monitored by GC-MS at defined time intervals. Compounds were identified by GC-MS. Educt and product peaks were used for calculation.

Typical Procedure for the Trimerization of Isocyanates

In a 10-mL Schlenk tube, phenylisocyanate (120 mg, 1.0 mmol) and the CO_2-protected NHC-containing resin (1.20 mol% NHC with respect to the isocyanate) were added. The reaction mixture was heated to 65 °C for 1 hour. After the reaction was completed, CH_2Cl_2 (5 mL) was added, the slurry was stirred and then filtered through a short silica column. The solvent was evaporated under vacuum and a white solid was obtained. The crude product was washed with pentane and dried; yield: 98 mg (82%).

1,3,5-Tris(2-fluorophenyl)-1,3,5-triazinane-2,4,6-trione: ^{1}H NMR ($CDCl_3$): $\delta=7.06$, 7.25, 7.46 and 8.10 (m, Ph); ^{13}C NMR ($CDCl_3$): $\delta=116.6$ (d, $J=180$ Hz), 124.9, 130.5 (d, $J=330$ Hz), 131.8, 147.3, 157.3, 159.0; FTIR (ATR mode): $\tilde{\nu}=1712$ (s), 1595 (w), 1496 (s), 1411 (s), 1255 (m), 1209 (m), 1102 (w), 1029 (w), 904 (w), 853 (w), 745 cm^{-1} (s); ESI-MS: *m/z* = 412.1, calcd. for $C_{21}H_{12}F_3N_3O_3$ $(M+H)^+$: 411.083.

Typical Procedure for a Heck Coupling Reaction

In a 25-mL Schlenk tube, the resin-bound Pd-catalyst (0.01 mol% of Pd with respect to styrene), 4-bromoacetophenone (5.2 g, 26.12 mmol), styrene (2.7 g, 25.96 mmol), tributylamine (9.6 g, 51.79 mmol) and *tert*-butylbenzene (800 mg, internal standard) were dissolved on 10 mL of DMF. The reaction mixture was heated to 150 °C. Product conversion was monitored by GC-MS at defined time intervals. Compounds were identified by GC-MS.

Hydrogen Transfer to Benzaldehyde

The resin-bound Ir-catalyst (0.10 mol% of Ir with respect to aldehyde), K_2CO_3 (130 mg, 0.94 mmol) and benzaldehyde (200 mg, 1.88 mmol) were added to the 10 mL of 2-propanol. The reaction mixture was heated under reflux. Aliquots (0.5 mL) were taken at fixed times, quenched in *n*-hexane (10 mL) and filtered through a short path column of SiO_2. The filtrate was subject to GC-MS analysis. Product identification and conversion was monitored by GC-MS.

Polymerization of Phenylacetylene

The resin-bound Rh-catalyst (1.00 mol% of Rh with respect to phenylacetylene) was added to a solution of phenylacetylene (102 mg, 1.0 mmol) in 4 mL of $CHCl_3$. The reaction mixture was stirred at room temperature for 2 h. The polymer was then precipitated by the addition of pentane, filtered off and dried. Yield of Poly(phenylacetylene): 67 mg (67%). $Mn_{(found)} = 8400\ \mathrm{g\,mol^{-1}}$ (PDI = 2.45), $Mn_{(calc)} = 22400\ \mathrm{g\,mol^{-1}}$; ^{1}H NMR ($CDCl_3$): $\delta = 5.85$ (br s, 1H, CH), 6.65 and 6.96 (br s, 5H, Ph); ^{13}C NMR ($CDCl_3$): $\delta = 126.8$, 127.7, 127.9, 131.9, 139.4, 143.0.

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