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Polyoxometalate-Based N-Heterocyclic Carbene (NHC) Complexes for Palladium-Mediated C−C Coupling and Chloroaryl Dehalogenation Catalysis

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Molecular hybrids are of particular interest in catalysis, due to the interplay of joint organic–inorganic domains with very diverse functional environments. The hybrid strategy is expected to allow for fine-tuning of the stereo-electronic properties of the catalyst through a tailored choice of the interacting organic–inorganic moieties. Such a hybrid upgrade of the catalytic system can be readily accessed, through the covalent functionalization of molecular polyoxometalates (POMs).[1] Indeed, covalent POM hybrids are characterized by discrete, nanosized, multi-metal oxides as polyanionic scaffolds, which allow for anchoring on-surface organic pendants, including chiral residues.[1,2] The hybrid structures display a remarkable stability, and resist harsh catalytic conditions, enabling a multi-turnover performance and sequential recycling in ionic-liquid media exposed to MW irradiation.[3] Interestingly, the hybrid modification of the POM framework has been successfully used to expand the coordination potential by introduction of tailored organic domains. In this respect, polydentate salen-type or thiol/phosphine-terminated ligands have been immobilized on the POM surface to bind Mn, Pd or Rh ions, or to implement the stabilization of Pd^0 colloids.[4–6] We present herein the synthesis, characterization, and catalytic applications of new POM-appended N-heterocyclic carbene (NHC) palladium complexes and their remarkable performance in catalyzing C−C cross-coupling and aromatic dehalogenation reactions.[7] To this end, imidazolium moieties have been successfully grafted on the defect site of the divacant Keggin polyanion [γ-$SiW_{10}O_{36}]^{8-}$.[8] These organic domains are useful precursors of N-heterocyclic (NHC) carbenes, which are known to provide strong M−NHC bonds, thus imparting high thermal robustness and stability to organometallic intermediates in multi-turnover palladium catalysis.[9]

In addition to the specifically designed Pd binding site, such POM-based hybrids display an extended polyanionic surface. This setup is expected to contribute sterically and by virtue of electrostatic repulsions to prevent agglomeration of incipient Pd^0, which generally deteriorates the turnover efficiency of the system.[4c] The molecular nature of such composite structures is a further point of interest, offering a single-site model for extended materials. Specifically, the molecularly defined structure of the hybrid allows for selective tailoring of the active site as well as for detecting subtle changes by solution characterization techniques, including heteronuclear NMR spectroscopy and ESI-MS.

The synthetic route to Keggin-type hybrids involves the reaction of organosilane reagents with the nucleophilic oxygen atoms that border a defect site on the POM surface. Grafting strategies have been optimized in acetonitrile in which the presence of excess $n\mathrm{Bu}_4\mathrm{NBr}$ promotes the solubilization of the POM by counterion metathesis (Scheme 1). Under these conditions, decoration of the lacunary POM is known to yield hybrids with two surface-anchored organosilyl (RSi-) groups, each one linked to two oxygen atoms of two edge-shared WO_6 octahedra.[4,10]

A first attempt focused on a divergent approach, including the covalent attachment of the triethoxysilyl-functionalized 4,5-dihydro-imidazolium bromide (**1**) to the divacant decatungstosilicate. The hybrid POM (**2**) was isolated and displayed spectroscopic data (^1H, ^{13}C, ^{29}Si and ^{183}W NMR, FT-IR) that are in agreement with the expected bis-functionalized structure. However, palladation of **2** met with little success (Scheme 1). Neither direct metalation using $Pd(OAc)_2$ nor transmetalation using Ag_2O resulted in the

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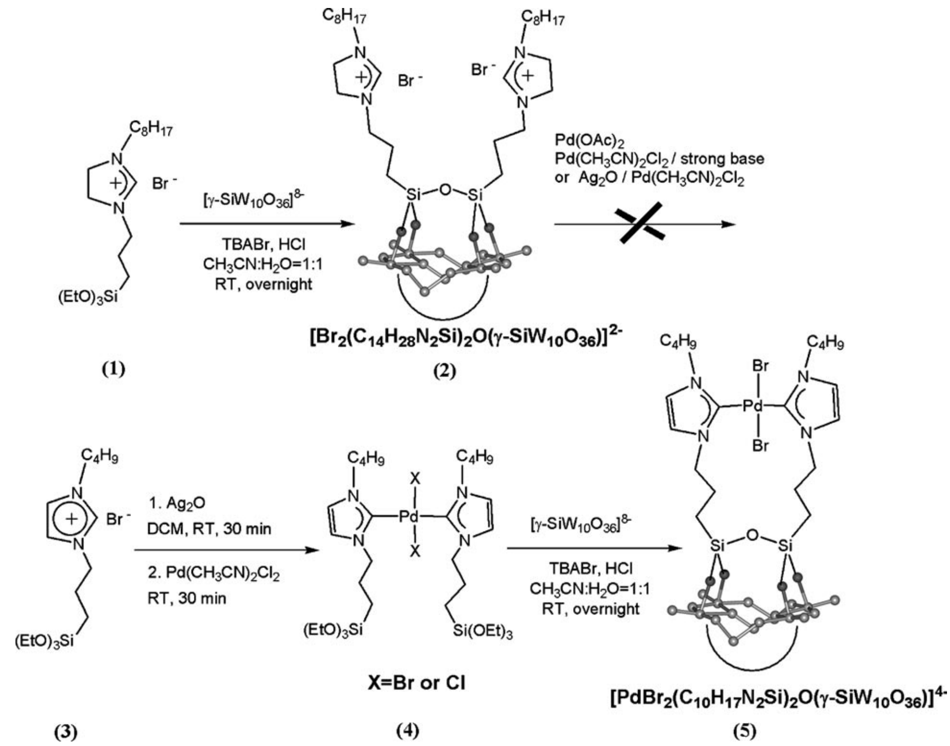


Scheme 1. Synthetic strategies to the hybrid POMs **2** and **5**.

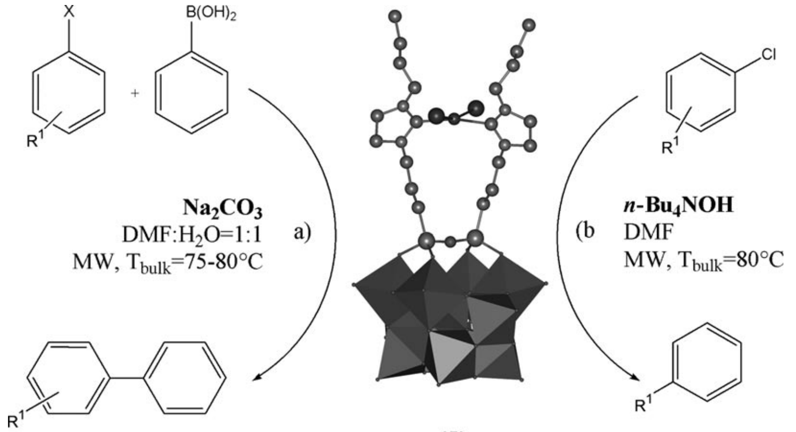
formation of the desired palladium NHC complex.[11–13] Similarly, base-mediated palladation with $[PdCl_2(CH_3CN)_2]$ in the presence of potassium bis(trimethylsilyl)amide (KHMDS) or NaH failed, as evidenced by the persistence of the ^1H NMR resonance of the C2-bound protons on the dihydroimidazolium ring ($\delta_H = 8.1$ ppm). Analysis of the reaction by UV/Vis spectrophotomeric titration suggests a possible electrostatic association of Pd^{2+} ions to the anionic POM surface.[14] To avoid such complications, we concentrated on a convergent approach involving the immobilization of preformed palladium complexes on the POM. Hence, the trialkoxysilyl-tagged imidazolium precursor **3**, containing an unsaturated heterocycle and a less hindered *n*-butyl substituent at the nitrogen atom,[9,15] was synthesized under strictly anhydrous conditions, from (3-chloropropyl)-triethoxysilane and 1-butylimidazole. Reaction of **3** with Ag_2O followed by transmetallation with $[PdCl_2(CH_3CN)_2]$[13] afforded the Pd–biscarbene complex **4**, as confirmed by ESI-MS, ^1H and ^{13}C NMR analyses. The absence of a resonance due to the C2-bound imidazolium proton ($\delta_H =$ 10.3 ppm) is corroborated by the appearance of a new signal at $\delta_C = 170.6$ ppm, which is characteristic of a palladium-bound carbene carbon (see the Supporting Information, Figures S16 and S15). ESI-MS (positive mode) shows signals centered at $m/z = 799.3$ and 843.3, corresponding to the monochloride and monobromide cationic fragments $[\{C_{10}H_{17}N_2Si(OEt)_3\}_2PdCl]^+$ and $[\{C_{10}H_{17}N_2Si(OEt)_3\}_2PdBr]^+$, respectively (Supporting Information, Figure S17). Complex **4** was finally reacted with the divacant Keggin POM $[\gamma\text{-}SiW_{10}O_{36}]^{8-}$ in acetonitrile under phase transfer conditions (Scheme 1), leading to the functionalized hybrid **5** in 75 % yield.[10]

Complex **5** was characterized both in the solid state (by FT-IR spectroscopy and elemental analysis) and in solution (^1H, ^{13}C, ^{29}Si and ^{183}W NMR spectroscopy and ESI-MS). All spectroscopic results confirmed the proposed structure (Supporting Information, Figures S18–S23).[10] The ^{183}W NMR spectrum shows three resonances at −107.4, −135.8, and −142.1 ppm in 2:1:2 ratio, in agreement with the expected C_{2v} symmetry. The ^{29}Si NMR spectrum reveals two signals at −62.8 and −88.4 ppm with integration ratio 2:1. These results are consistent with a double substitution of the POM surface. Coordination of Pd^{II} has been confirmed by X-ray photoelectron spectroscopy (XPS) of a solid sample of **5**, for which the expected Pd 3d 5/2 peaks centered at 338 and 343 eV in binding energy were observed (Supporting Information, Figures S24–S26). The DFT optimized structure of **5** suggests a planar distorted coordination for Pd, with *trans* halide ligands and bond lengths around 2.07–2.11 (Pd−C) and 2.59 Å (Pd−Br) (Scheme 2).

Complex **5** has been tested in the palladium-catalyzed cross-coupling of aryl halides with phenylboronic acids, according to established Suzuki–Miyaura protocols (Scheme 2, path a).[16] This reaction represents one of the key tools for selective C−C bond formation. The performance of catalyst **5** in this chemistry has been screened in 1:1 DMF/H_2O mixtures and under microwave (MW)-induced dielectric heating (Table 1).[17,18] This method is particularly efficient for polycharged catalysts, which behave as MW-activated molecular heat-carriers.[19] Indeed, hybrid POMs, are known to display a remarkable thermal stability and high catalytic efficiency in MW-assisted processes.[3]

The cross-coupling catalytic activity of **5** was initially evaluated using a representative range of aryl halides as substrates and MW irradiation at 10 W for 10–30 min (Table 1).

Under these conditions, both activated and deactivated aryl iodides react smoothly with 0.05 mol % catalyst loading, leading to the corresponding substituted biphenyl products with up to 99 % yield, 1980 turnover numbers (TON), and frequencies (TOF) up to 11 880 h^{-1} (entries 1–4, Table 1, comparison with literature benchmarks in Tables S1 and S2 in the Supporting Information). In all reactions, the bulk temperature is kept at about 80 °C by simultaneous cooling



(5)

Scheme 2. Cross-coupling (path a) and dehalogenation reactions (path b) catalyzed by **5** under MW irradiation. DFT optimized geometry is presented for the proposed structure of **5**.

Table 1. Suzuki coupling catalyzed by **5** under MW-irradiation (Scheme 2, path a). In all reactions: aryl halide, ArX (0.25 mmol), phenylboronic acid, $PhB(OH)_2$ (1.1 equiv, 0.275 mmol), Na_2CO_3 (2 equiv, 0.5 mmol), $DMF:H_2O = 1:1$ (0.45:0.45 mL); MW irradiation: 10 W, compressed air at 30–40 psi; $T_{bulk} = 75\text{-}85\,°C$.

Entry	X	R_1	**5** loading [%]	product [%]	*t* [min]
1[a]	I	*p*-$COCH_3$	0.05	99	10
2	I	H	0.05	85	30
3	I	*p*-CH_3	0.05	80[c]	20
4	I	*p*-OCH_3	0.05	95[c]	20
5	Br	*p*-$COCH_3$	0.1	99	10
6	Br	*p*-NO_2	0.1	93[c]	10
7[b]	Br	H	0.1	94	35
8[b]	Br	*p*-CH_3	0.1	87[c]	30
9[b]	Cl	*p*-$COCH_3$	1	98[c]	30
10[b]	Cl	*o*-$COCH_3$	1	10[d]	150
11[b]	Cl	*p*-CHO	1	20[c]	30
12	Cl	*p*-NO_2	1	38[e]	30
13[b]	Cl	H	1	57	60
14[b]	Cl	*p*-CH_3	1	33[f]	60

[a] Under analogous conditions, the coupling reaction catalyzed by **4** proceeds with 32 % yield. [b] ArX (0.25 mmol), $PhB(OH)_2$ (1.3 equiv, 0.32 mmol), Na_2CO_3 (3 equiv, 0.75 mmol). [c] Biphenyl (1–7 %) and dehalogenation products observed in traces. [d] Biphenyl (4 %) and acetophenone (14 %) were detected. [e] Biphenyl (18 %) was detected. [f] Biphenyl (9 %) and toluene (6 %) were detected.

with compressed air. Control experiments performed with iodobenzene and phenylboronic acid indicate no coupling products in the Pd-free reaction, nor in the presence of the imidazolium-functionalized POM **2**. It is worth noting that the POM-free NHC complex **4** deactivates rapidly under analogous catalytic regime, thus yielding poor conversion and turnover efficiency (see note [a] in Table 1). Addition of Na_2CO_3 (2 or 3 equivalents) is an essential prerequisite of the catalytic protocol, in agreement with the generally accepted mechanism involving a reactive borate anion for the transmetallation step.[20] Coupling of aryl bromides is readily achieved by increasing the catalyst loading to 0.1 mol %, with similar yields and reaction time (yield up to 99 %, TON = 990, TOF = 5940 h^{-1}, entry 5, Table 1). A remarkable 87 % yield of 4-methylbiphenyl was obtained after 30 min irradiation when using the unactivated 4-bromotoluene as substrate (TOF = 1740 h^{-1}, entry 8, Table 1).[21]

The POM-based system was also effective in coupling aryl chlorides, which are known to be poorly reactive but synthetically highly appealing.[22,23] An increased catalyst loading (1.0 mol %), and a larger excess of phenylboronic acid and Na_2CO_3 (1.3 and 3 equivalents with respect to aryl chloride), were pivotal for ensuring reactivity. Under such conditions, 4-chloroacetophenone gave the corresponding coupling product in 98 % yield when subjected to MW irradiation for 30 min (TON = 98, TOF = 196 h^{-1}, entry 9, Table 1).[24] *ortho*-Substituted 2-chloroacetophenone was converted only sluggishly, presumably due to steric factors (entry 10, Table 1). The POM residue may be sufficiently bulky to hamper the oxidative addition and/or transmetallation step of the catalytic cycle.[25] Other activated aryl chlorides reacted with less success, as for 4-chloronitrobenzene, affording a significant amount (18 %) of biphenyl originating from homo-coupling together with 38 % of cross-coupled 4-nitrobiphenyl (entry 12, Table 1). In this case, the selectivity of the process did not improve upon increasing the amount of base.[26]

Interestingly, the reaction of the unactivated 4-chlorotoluene turned out to yield 33 % of the desired product, with concurrent homocoupling (< 9 %) and dehalogenation to toluene (< 10 %).[27] Catalytic dehalogenation was previously reported as a parallel reaction in Suzuki coupling; however, few papers provide details on this topic.[28] Such reaction is of major importance from an environmental point of view, in particular with regards to the degradation of highly toxic halogenated organic compounds.[29]

The proposed mechanism of palladium-catalyzed dehalogenation involves the oxidative addition of the aryl halide to the Pd^0–NHC intermediate, and the formation of a Pd^{II}–hydride species, generated by a strong base such as an alkoxide.[29,30] In line with this proposal, the dehalogenation reaction is strongly promoted upon changing the base from Na_2CO_3 to nBu_4NOH.[31] Under conditions that are otherwise identical to the Suzuki protocol, catalytic dehalogenation of aryl chlorides was readily accomplished (Scheme 2, path b). In the presence of nBu_4NOH as the base, 4-chloroacetophenone and phenyl boronic acid, dehalogenated acetophenone was formed as the major product (63 % yield), together with 4-acetylbiphenyl in 35 % yield. The competitive dehalogenation reaction has thus been investigated in more detail. Highest selectivities were achieved when using two equivalents of $n\mathrm{Bu_4NOH}$ in DMF, under MW irradiation (Table 2). Under these conditions, a formate ion is surmised to be generated from DMF and hydroxide, as the hydrogen donor.[32] Dehalogenation of activated aryl chlorides occurs smoothly and quantitative yields were reached within 30–40 min (entries 1 and 4, Table 2).[33] Sterically hindered 2-chloroacetophenone was converted at a slower rate and afforded 57 % acetophenone after 2 h (entry 2, Table 2). Aryl chlorides with electron-donating substituents were dehalogenated less efficiently (entries 5 and 6, Table 2). Nevertheless, 4-chlorotoluene yielded appreciable 43 % of toluene after irradiation for 1 h (entry 6, Table 2).

Table 2. Dehalogenation of aryl chlorides (ArCl), catalyzed by **5** under MW-irradiation (Scheme 2, path b).[a]

Entry	ArCl	ArH Yield [%]	t [min]
1	4-chloroacetophenone	>99	30
2	2-chloroacetophenone	57	120[b]
3	3-chloroacetophenone	86	60
4	4-chloronitrobenzene	>99	40
5	4-chlorophenol	12	60
6	4-chlorotoluene	43	60
7	1-chloronaphtalene	87	60

[a] ArCl (0.25 mmol), $n\mathrm{Bu_4NOH\ 30H_2O}$ (2 equiv, 0.5 mmol), **5** (1 mol %, 0.0025 mmol), DMF (0.5 mL); MW irradiation: 10 W, compressed air at 30 psi; $T_{\mathrm{bulk}} = 80–95$ °C. [b] After 3 cycles (2×30 min + 1×60 min).

In conclusion, a novel synthetic route to hybrid Pd catalysts has been developed through decoration of a POM surface with imidazolium-based NHC palladium complexes. The interplay of the Pd binding domains with the inorganic scaffold provides new opportunities to access multi-turnover catalysis with good to excellent performance under MW-assisted protocols. Depending on the reaction conditions, both cross-coupling and dechlorination of aromatic compounds are efficiently accomplished. Future studies will concentrate on optimizing the carbene domain, in particular with respect to steric effects and the Pd/carbene ratio. The introduction of the POM platform is potentially amenable to nanofiltration techniques for catalyst recovery and product purification, while being instrumental for heterogeneization strategies on charged surfaces/supports.[34] In this respect, a straightforward upgrade of the system in ionic-liquid phases can be envisaged due to the implemented affinity of such POM-based hybrids for these media.[35]

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[1] a) M. Carraro, A. Sartorel, G. Scorrano, C. Maccato, M. H. Dickman, U. Kortz, M. Bonchio, *Angew. Chem.* **2008**, *120*, 7385–7389; *Angew. Chem. Int. Ed.* **2008**, *47*, 7275–7279; b) M. Carraro, G. Modugno, A. Sartorel, G. Scorrano, M. Bonchio, *Eur. J. Inorg. Chem.* **2009**, 5164–5174.

[2] a) M. T. Pope, A. Müller in *Polyoxometalate Chemistry: From Topology via Self-Assembly to Applications*, Kluwer, Dordrecht, **2002**; b) C. Sanchez, G. J. de Soler-Illia, F. Ribot, T. Lalot, C. R. Mayer, V. Cabuil, *Chem. Mater.* **2001**, *13*, 3061–3083; c) D. L. Long, E. Burkholder, L. Cronin, *Chem. Soc. Rev.* **2007**, *36*, 105–121.

[3] a) S. Berardi, M. Bonchio, M. Carraro, V. Conte, A. Sartorel, G. Scorrano, *J. Org. Chem.* **2007**, *72*, 8954–8957; b) M. Carraro, L. Sandei, A. Sartorel, G. Scorrano, M. Bonchio, *Org. Lett.* **2006**, *8*, 3671–3674; c) M. Bonchio, M. Carraro, A. Bagno, G. Scorrano, *Adv. Synth. Catal.* **2004**, *346*, 648–654.

[4] a) I. Bar-Nahum, R. Neumann, *Chem. Commun.* **2003**, 2690–2691; b) I. Bar-Nahum, H. Cohen, R. Neumann, *Inorg. Chem.* **2003**, *42*, 3677–3684; c) M. De Bruyn, R. Neumann, *Adv. Synth. Catal.* **2007**, *349*, 1624–1628.

[5] S. Favette, B. Hasenknopf, J. Vaissermann, P. Gouzerh, C. Roux, *Chem. Commun.* **2003**, 2664–2665.

[6] a) V. Kogan, Z. Aizenshtat, R. Popovitz-Biro, R. Neumann, *Org. Lett.* **2002**, *4*, 3529–3532; b) V. Kogan, Z. Aizenshtata, R. Neumann, *New J. Chem.* **2002**, *26*, 272–274.

[7] J. Tsuji in *Palladium Reagents and Catalysts*, Wiley, New York, **1995**.

[8] J. Canny, A. Tézé, R. Thouvenot, G. Hervé, *Inorg. Chem.* **1986**, *25*, 2114–2119.

[9] a) W. A. Herrmann, *Angew. Chem.* **2002**, *114*, 1342–1363; *Angew. Chem. Int. Ed.* **2002**, *41*, 1290–1309; b) O. Schuster, L. Yang, H. G. Raubenheimer, M. Albrecht, *Chem. Rev.* **2009**, *109*, 3445–3478; c) S. Nolan in *N-Heterocyclic Carbenes in Synthesis*, Wiley-VCH, Weinheim, **2006**; d) E. A. B. Kantchev, C. J. O'Brien, M. G. Organ, *Angew. Chem.* **2007**, *119*, 2824–2870; *Angew. Chem. Int. Ed.* **2007**, *46*, 2768–2813.

[10] C. R. Mayer, I. Fournier, R. Thouvenot, *Chem. Eur. J.* **2000**, *6*, 105–110.

[11] I. Özdemir, M. Yiğit, E. Çetinkaya, B. Çetinkaya, *Appl. Organomet. Chem.* **2006**, *20*, 187–192.

[12] T. Weskamp, V. P. W. Bölm, W. A. Herrmann, *J. Organomet. Chem.* **2000**, *600*, 12–22, and references therein.

[13] a) C. K. Lee, J. C. C. Chen, K. M. Lee, C. W. Liu, I. J. B. Lin, *Chem. Mater.* **1999**, *11*, 1237–1242; b) D. S. McGuinness, K. J. Cavell, *Organometallics* **2000**, *19*, 741–748; c) M. C. Perry, X. Cui, K. Burgess, *Tetrahedron: Asymmetry* **2002**, *13*, 1969–1972.

[14] UV/Vis spectrophotometric titration ($\lambda < 450$ nm), of **2** upon addition of $[\mathrm{Pd(OAc)_2}]$ in DMSO and incubation at 50 °C for 4 h and at 100 °C for 30 min indicates a 1:1 $\mathrm{Pd^{2+}}$/**2** association stoichiometry.

[15] M. B. Andrus, C. Song, *Org. Lett.* **2001**, *3*, 3761–3764.

[16] a) N. Miyaura, A. Suzuki, *Chem. Rev.* **1995**, *95*, 2457–2483; b) F. Alonso, I. P. Beletskaya, M. Yus, *Tetrahedron* **2008**, *64*, 3047–3101.

[17] H. Qiu, S. M. Sarkar, D.-H. Lee, M.-J. Jin, *Green Chem.* **2008**, *10*, 37–40.

[18] a) R. K. Arvela, N. E. Leadbeater, *Org. Lett.* **2005**, *7*, 2101–2104; b) M. Marco, N. E. Leadbeater, *J. Org. Chem.* **2003**, *68*, 888–892; c) R. K. Arvela, N. E. Leadbeater, M. S. Sangi, V. A. Williams, P. Granados, R. D. Singer, *J. Org. Chem.* **2005**, *70*, 161–168.

[19] a) I. Guryanov, F. M. Toma, A. Montellano Lopez, M. Carraro, T. Da Ros, G. Angelini, E. D'Aurizio, A. Fontana, M. Maggini, M. Prato, M. Bonchio, *Chem. Eur. J.* **2009**, *15*, 12837–12845; b) I. Guryanov, A. Montellano Lopez, M. Carraro, T. Da Ros, G. Scorrano, M. Maggini, M. Prato, M. Bonchio, *Chem. Commun.* **2009**, 3940–3942.

[20] A. de Meijere, F. Diederich in *Metal Catalyzed Cross-Coupling Reactions*, Wiley-VCH Weinheim, **2004**.

[21] Average TON and TOF values in the range 1100–1900 and 314–543 h^{-1}, respectively, have been reported for classic NHC ligands employed in the homogeneous Suzuki coupling of deactivated aryl bromides: N. Marion, O. Navarro, J. Mei, E. D. Stevens, N. M. Scott, S. P. Nolan, *J. Am. Chem. Soc.* **2006**, *128*, 4101–4111.

[22] A. F. Littke, G. C. Fu, *Angew. Chem.* **2002**, *114*, 4350–4386; *Angew. Chem. Int. Ed.* **2002**, *41*, 4176–4211.

[23] Ligand **2** in combination with $[Pd(Ac)_2]$ (1 equiv) was found to be inactive with chloroaryl substrates, thus confirming the superior performance of the POM-based NHC ligand in this chemistry.

[24] Literature TON and TOF values, for Suzuki coupling of aryl chlorides by Pd–NHC catalysts are in the range 40–100 h^{-1}; see, for example: a) Z. Jin, S.-X. Guo, X.-P. Gu, L.-L. Qiu, H.-B. Song, J.-X. Fang, *Adv. Synth. Catal.* **2009**, *351*, 1575–1585; b) R. Singh, M. S. Viciu, N. Kramareva, O. Navarro, S. P. Nolan, *Org. Lett.* **2005**, *7*, 1829–1832.

[25] a) O. Diebolt, P. Braunstein, S. P. Nolan, C. S. J. Cazin, *Chem. Commun.* **2008**, 3190–3192; b) G. Altenhoff, R. Goddard, C. W. Lehmann, F. Glorius, *Angew. Chem.* **2003**, *115*, 3818–3821; *Angew. Chem. Int. Ed.* **2003**, *42*, 3690–3693.

[26] a) M. J. Burns, I. J. S. Fairlamb, A. R. Kapdi, P. Sehnal, R. J. K. Taylor, *Org. Lett.* **2007**, *9*, 5397–5400; b) R. Rodríguez González, L. Liguori, A. Martinez Carrillo, H.-R. Bjørsvik, *J. Org. Chem.* **2005**, *70*, 9591–9594; c) G. Dyker, A. Kellner, *J. Organomet. Chem.* **1998**, *555*, 141–144.

[27] M. Moreno-Mañas, M. Pérez, R. Pleixats, *J. Org. Chem.* **1996**, *61*, 2346–2351.

[28] S. T. Handy, H. Bregman, J. Lewis, X. Zhang, Y. Zhang, *Tetrahedron Lett.* **2003**, *44*, 427–430.

[29] O. Navarro, H. Kaur, P. Mahjoor, S. P. Nolan, *J. Org. Chem.* **2004**, *69*, 3173–3180.

[30] F. Alonso, I. P. Beletskaya, M. Yus, *Chem. Rev.* **2002**, *102*, 4009–4091.

[31] FT-IR analysis of pre-catalyst **5** (5 mM in DMF) after incubation with $n\mathrm{Bu_4NOH{\cdot}30\,H_2O}$ (5 equiv) under microwave irradiation for 1 h and subsequent precipitation with water shows retention of the main spectral features associated to the POM scaffold, with bands at $\tilde{\nu}=946$ (w), 883 (s), 825 (w), 741 cm^{-1} (s), indicating that the POM support is stable under catalytically relevant reaction conditions.

[32] a) E. Buncel, E. A. Symons, *J. Chem. Soc. Chem. Commun.* **1970**, 164–165; b) Y. Ben-David, M. Gozin, M. Portnoy, D. Milstein, *J. Mol. Catal.* **1992**, *73*, 173–180.

[33] Thermal and photoredox carbon−halogen bond cleavage by POM catalysts has been reported to proceed by radical mechanisms (D. Sattari, C. L. Hill, *J. Am. Chem. Soc.* **1993**, *115*, 4649–4657); under the condition explored, no reaction was observed with the Pd-free complex **2**.

[34] a) P. T. Witte, S. R. Chowdhury, J. E. ten Elshof, D. Sloboda-Rozner, R. Neumann, P. L. Alsters, *Chem. Commun.* **2005**, 1206–1208; b) S. R. Chowdhury, J. E. ten Elshof, N. E. Benes, K. Keizer, *Desalination* **2002**, *144*, 41–46.

[35] a) H. Hagiwara, K. H. Ko, T. Hoshi, T. Suzuki, *Chem. Commun.* **2007**, 2838–2840; b) A. Bordoloi, S. Sahoo, F. Lefebvre, S. B. Halligudi, *J. Catal.* **2008**, *259*, 232–239.

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