

Supporting Information for:

Polyoxometalate-based N-heterocyclic carbene (NHC) complexes for palladium-mediated C-C coupling and chloroaryl dehalogenation catalysis

Serena Berardi,^[a] Mauro Carraro,^[a] Manuel Iglesias,^[b] Andrea Sartorel,^[a] Gianfranco Scorrano,^[a]
Martin Albrecht*,^[b] and Marcella Bonchio*,^[a]

^[a] ITM-CNR and Department of Chemical Sciences, University of Padova via Marzolo 1, 35131 Padova (Italy) Tel./ Fax: (+39) 0498275670 / (+39) 0498275239 E-mail: marcella.bonchio@unipd.it

^[b] Department of Chemistry, University of Fribourg (Switzerland). Current address: School of Chemistry and Chemical Biology, University College Dublin, Belfield, Dublin 4, (Ireland) Tel./ Fax: (+353) 17162504 / (+353) 17162501 E-mail: martin.albrecht@ucd.ie

Content

Experimental Section and Spectra	S2
General	S2
Synthesis of 1-octyl-3-(3-triethoxysilylpropyl)-4,5-dihydroimidazolium bromide (1)	S4
Synthesis of (<i>n</i> -Bu ₄ N) ₂ K ₂ [Br ₂ (C ₁₄ H ₂₈ N ₂ Si) ₂ O(γ-SiW ₁₀ O ₃₆)] (2)	S7
Synthesis of 1-butyl-3-(3-triethoxysilylpropyl)-imidazolium bromide (3)	S11
Synthesis of dichloro- <i>bis</i> -(1-butyl-3-(3-triethoxysilylpropyl)-imidazol-2-ylidene)-palladium(II) (4)	S13
Synthesis of (<i>n</i> -Bu ₄ N) _{3.5} H _{0.5} [PdBr ₂ (C ₁₀ H ₁₇ N ₂ Si) ₂ O(γ-SiW ₁₀ O ₃₆)] (5)	S16
Representative Procedures for the Reactions	S22
Suzuki Coupling Reaction of Aryl Halides with Phenylboronic acid catalyzed by complex 5 under conventional heating	S22
Microwave-Assisted Suzuki Coupling Reaction of Aryl Halides with Phenylboronic acid catalyzed by complex 5	S22
Microwave-Assisted Dehalogenation of Aryl Chlorides catalyzed by complex 5	S22
Literature benchmark values for Pd-carbene catalyzed Suzuki-Miyaura and dehalogenation protocols	S23
Computational details	S24
Cartesian coordinates (in Å) of the DFT optimized structure for (5).	S25
References	S27

Experimental Section and Spectra

General: All reagents were purchased from commercial sources and used as received, without further purification.

^1H -NMR spectra were recorded using Bruker AC250, AV300 and AV360 instruments operating, respectively, at 250.18 MHz, 300.13 MHz and 360.13 MHz; ^{13}C -NMR spectra were recorded with Bruker AC250 and AV300 spectrometers operating, respectively, at 62.5 MHz and 75.4 MHz. ^{183}W -NMR and ^{29}Si -NMR spectra have been recorded with a Bruker Avance DRX 400 instrument operating respectively, at 16.67 MHz and 79.50 MHz and using a 2 M solution of Na_2WO_4 in D_2O and $\text{Si}(\text{CH}_3)_4$ in CDCl_3 as external references.

FT-IR (KBr) spectra were collected on a Thermo Quest Nicolet 5700 instrument.

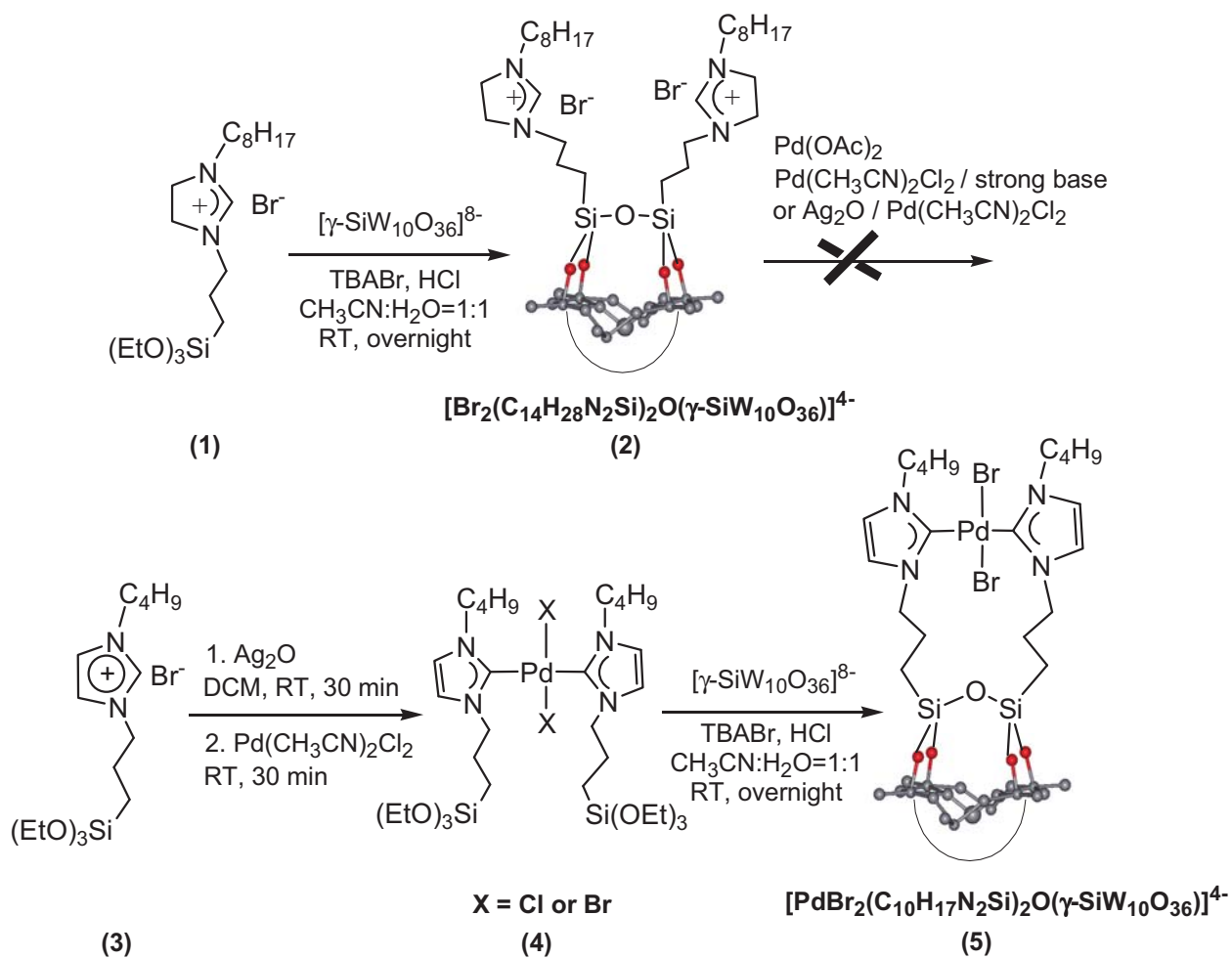
ESI-MS spectra of polyoxometalates were recorded on a Agilent 1100-LC/MSD Trap SL spectrometer, using capillary potential = + 4500 V, skimmer potential = - 35 V and cap. exit. potential = - 100 V.

ESI-MS spectra of compound **4** was recorded on a Bruker FTMS 4.7T BioAPEX II spectrometer.

Gas-chromatographic analyses were performed using a Shimadzu GC-2010 instrument, equipped with a EquityTM-5 capillary column (length = 15 m, internal diameter = 0.10 mm, film thickness = 0.10 μm).

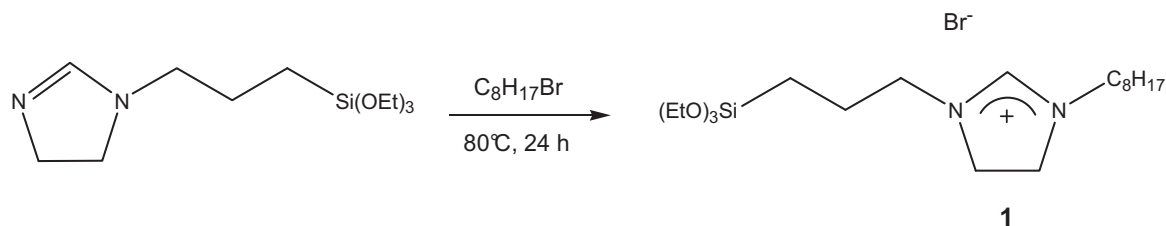
Microwave experiments were performed using a monomodal CEM-Discover microwave apparatus operating at 2.45 GHz with continuous irradiation power.

Vacant polyoxotungstate $[\gamma\text{-SiW}_{10}\text{O}_{36}]^{8-}$ was prepared as described in the literature.^[1]



Scheme S1

Synthesis of 1-octyl-3-(3-triethoxysilylpropyl)-4,5-dihydroimidazolium bromide (**1**)^[2]



A mixture of 3-(2-imidazolin-1-yl)propyltriethoxysilane (0.5 mL, 1.8 mmol) and 1-bromooctane (1 mL, 5.8 mmol) was stirred and heated at 80°C for 24 h in a Schlenk tube, under a nitrogen atmosphere. After the reaction, the mixture was cooled to room temperature and the volatile compounds were removed by the evaporation under reduced pressure. The orange viscous liquid was washed with anhydrous pentane (2 x 3 mL) and evaporated to dryness. The product was redissolved in anhydrous dichloromethane (ca. 5 mL) and filtered with activated carbon. The product, 1-octyl-3-(3-triethoxysilylpropyl)-4,5-dihydroimidazolium bromide (**1**), was dried under vacuum to give a sticky yellow solid. Yield: 0.82 g (98%).

²⁹Si-NMR (59.6 MHz, CDCl₃, 25°C): δ -47.4 ppm. **¹³C{¹H}-NMR** (75.5 MHz, CDCl₃, 25°C): δ 158.4 (NCHN), 58.6 (OCH₂), 53.5 (CH₃(CH₂)₆CH₂N), 50.5 (SiCH₂CH₂CH₂N), 48.5 (SiCH₂CH₂CH₂NCH₂CH₂N), 48.2 (SiCH₂CH₂CH₂NCH₂CH₂N), 31.7, 29.1, 29.0, 27.5, 26.4, 22.6, 21.2 (methylene groups), 18.3 (OCH₂CH₃), 14.0 (methyl), 7.2 (SiCH₂) ppm. **¹H-NMR** (300 MHz, CDCl₃, 25°C): δ 9.54 (1H, s, NCHN), 3.95-3.88 (4H, m, CH₂ dihydroimidazole), 3.77 (6H, q, *J* = 7.14 Hz, CH₃CH₂O), 3.65-3.54 (4H, m, SiCH₂CH₂CH₂N, NCH₂(CH₂)₆CH₃), 1.76-1.58 (4H, m, SiCH₂CH₂CH₂N, NCH₂CH₂(CH₂)₅CH₃), 1.27-1.13 (19H, m, methylene, CH₃CH₂O), 0.83 (3H, t, *J* = 6.98 Hz, CH₃(CH₂)₆CH₂N), 0.61-0.52 (2H, m, SiCH₂CH₂) ppm. **ESI-MS(+)** (CH₃CN): *m/z* 387.3, calcd. for [C₂₀H₄₃N₂O₃Si]⁺ = 387.3.

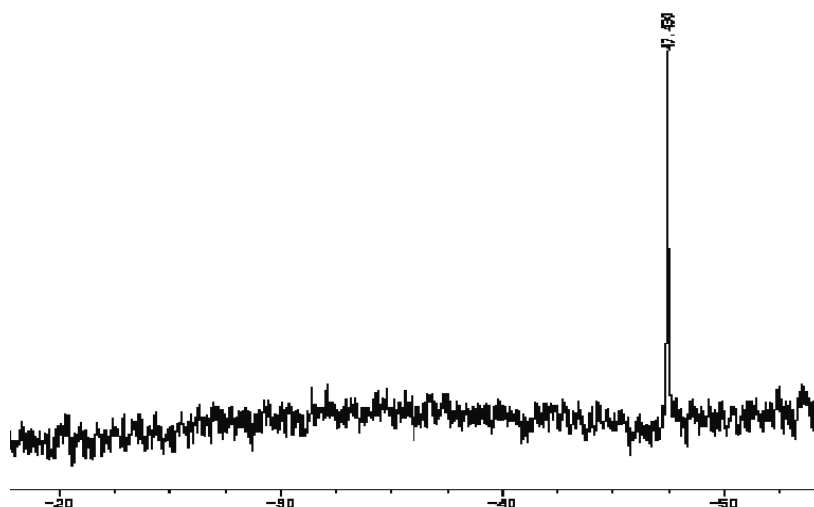


Figure S1. ²⁹Si-NMR spectrum of compound **1**.

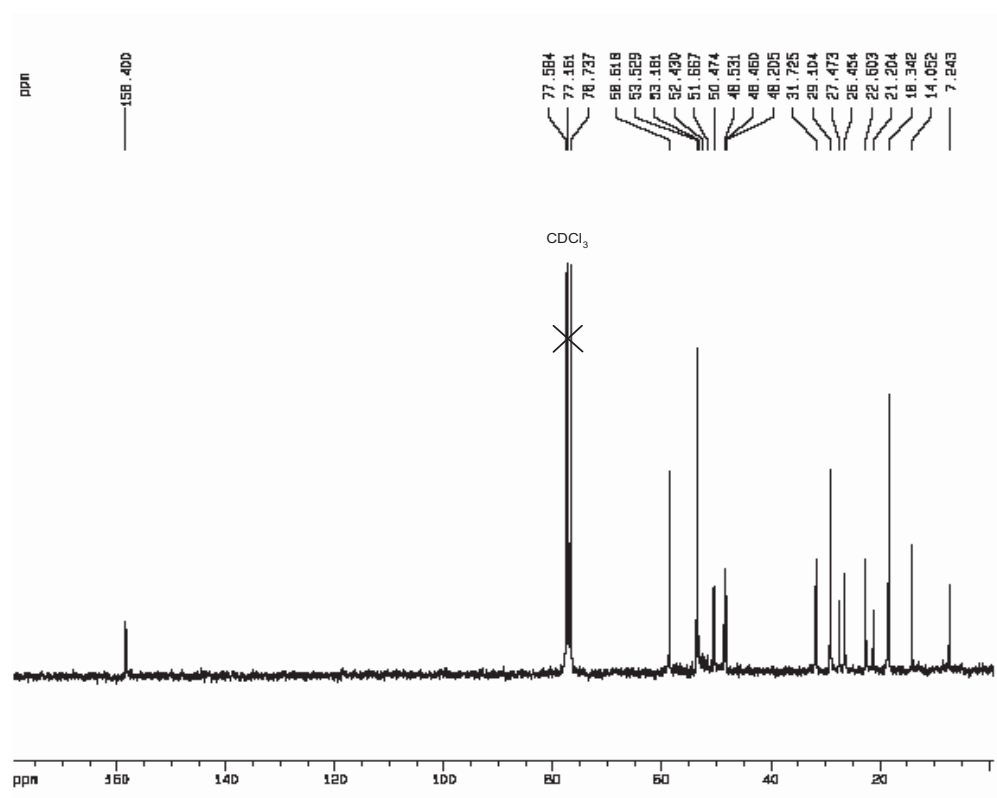


Figure S2. $^{13}\text{C}\{^1\text{H}\}$ -NMR spectrum of compound **1**.

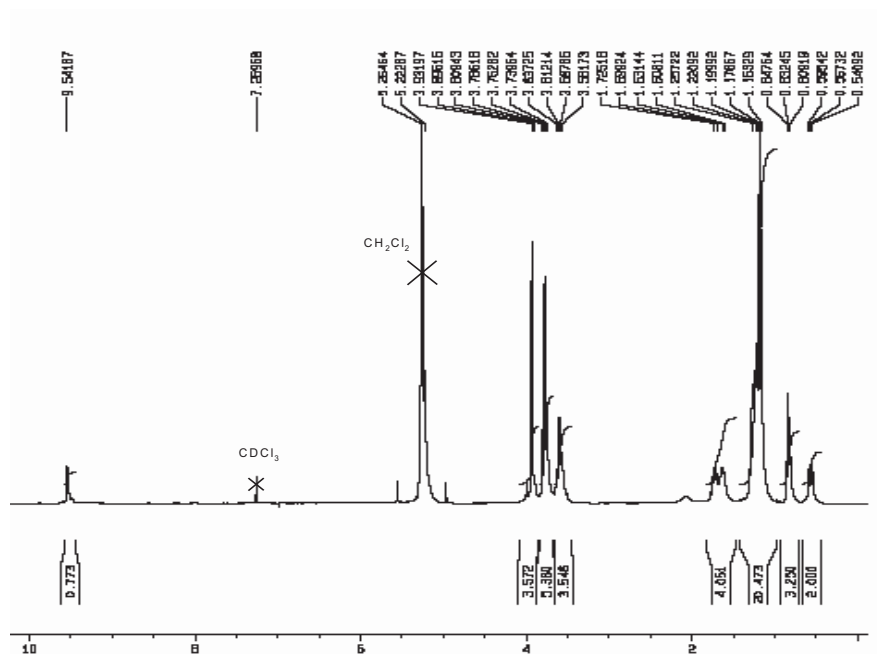


Figure S3. ^1H -NMR spectrum of compound **1**.

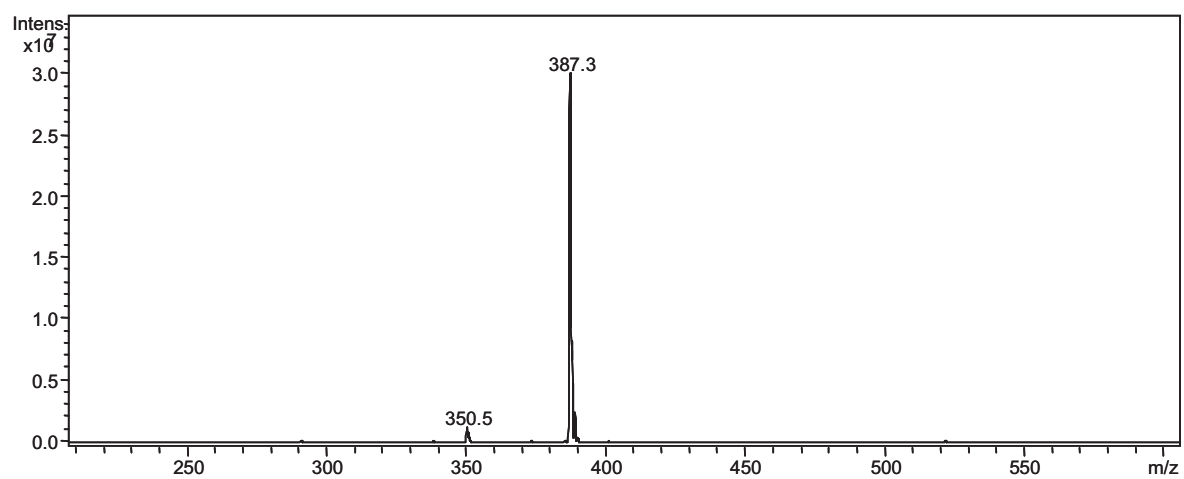
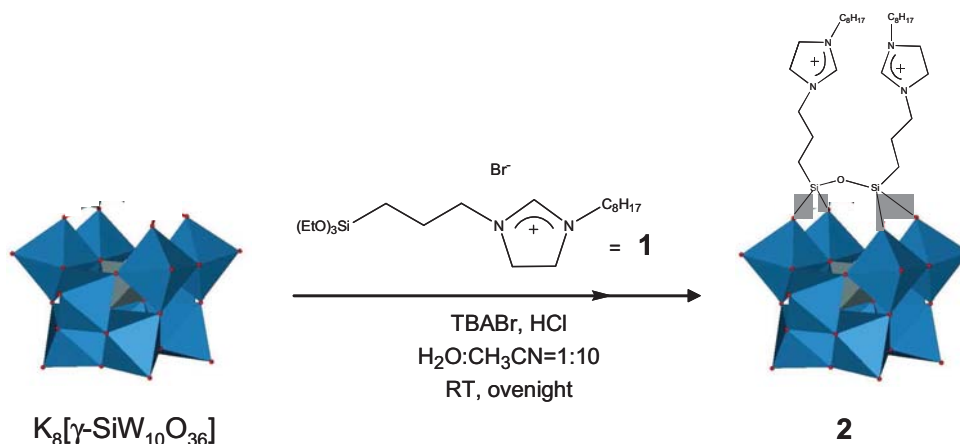


Figure S4. ESI-MS spectrum of compound **1**.

Synthesis of $(n\text{-Bu}_4\text{N})_2\text{K}_2[\text{Br}_2(\text{C}_{14}\text{H}_{28}\text{N}_2\text{Si})_2\text{O}(\gamma\text{-SiW}_{10}\text{O}_{36})]$ (**2**)^[3]



$\text{K}_8[\gamma\text{-SiW}_{10}\text{O}_{36}]$ (1.2 g, 0.44 mmol) was suspended in H_2O (2 mL). $(n\text{-Bu}_4\text{N})\text{Br}$ (0.57 g, 1.8 mmol, 4 eq) and CH_3CN (15 mL) were added and the mixture was stirred at room temperature for 20 minutes. 1-octyl-3-(3-triethoxysilylpropyl)-4,5-dihydroimidazolium bromide **1** (0.41 g, 0.88 mmol, 2 eq), dissolved in 5 mL of anhydrous CH_3CN , and HCl 4 M (2.6 mmol, 6 eq) were successively added under vigorous stirring. The mixture was stirred overnight at room temperature. The product was obtained after filtration of the insoluble portion and evaporation of the organic solvent. The crude compound was thoroughly washed with water. Yield: 0.501 g (31 %).

FT-IR (KBr) 3067, 2960, 2931, 2872, 1653, 1483, 1465, 1380, 1304, 1250, 1173, 1154, 1103, 1043, 1004, 965, 903, 886, 818, 781, 734, 668, 545, 511, 482 cm^{-1} . **^{29}Si -NMR** (79.5 MHz, CD_3CN , 25°C) δ -62.1 (2 Si), -88.0 (1 Si) ppm. **^{183}W -NMR** (16.7 MHz, CD_3CN , 25°C) δ -107.0 (4 W), -134.2 (2 W), -141.6 (4 W) ppm. **$^{13}\text{C}\{^1\text{H}\}$ -NMR** (75.5 MHz, CD_3CN , 25°C) δ 158.3 (NCHN), 59.3 ($(\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2)_4\text{N}^+$), 58.2 ($\text{CH}_3(\text{CH}_2)_6\text{CH}_2\text{N}$), 50.9 ($\text{SiCH}_2\text{CH}_2\text{CH}_2\text{N}$), 49.5 ($\text{SiCH}_2\text{CH}_2\text{CH}_2\text{NCH}_2\text{CH}_2\text{N}$), 49.0 ($\text{SiCH}_2\text{CH}_2\text{CH}_2\text{NCH}_2\text{CH}_2\text{N}$), 32.6, 29.9, 28.0, 27.1, 23.4, 22.5, 14.5 (methylene groups), 24.4 ($(\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2)_4\text{N}^+$), 20.4 ($(\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2)_4\text{N}^+$), 14.1 ($(\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2)_4\text{N}^+$), 12.4 (SiCH_2) ppm. **^1H -NMR** (300 MHz, CD_3CN , 25°C) δ 8.14 (2H, s, NCHN), 4.22-3.87 (8 H, m, $\text{SiCH}_2\text{CH}_2\text{CH}_2\text{NCH}_2\text{CH}_2\text{N}$, $\text{SiCH}_2\text{CH}_2\text{CH}_2\text{NCH}_2\text{CH}_2\text{N}$), 3.76-3.57 (4H, m, $\text{SiCH}_2\text{CH}_2\text{CH}_2\text{N}$), 3.56-3.38 (4H, m, $\text{CH}_3(\text{CH}_2)_6\text{CH}_2\text{N}$), 3.23-3.15 (16H, m, $(\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2)_4\text{N}^+$), 1.81-1.54 (16H, m, $(\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2)_4\text{N}^+$), 1.38 (16H, sextet, $J = 7.1$ Hz, $(\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2)_4\text{N}^+$), 1.34-1.17 (28H, m, methylene), 0.98 (24H, t, $J = 7.1$ Hz, $(\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2)_4\text{N}^+$), 0.91-0.85 (6 H, m, CH_3), 0.71-0.39 (4 H, m, SiCH_2) ppm. **ESI-MS(-)** (CH_3CN) $m/z = 1482$, calcd. for $\{[(\text{C}_{14}\text{H}_{28}\text{N}_2\text{Si})_2\text{O}(\gamma\text{-SiW}_{10}\text{O}_{36})]\}^{2-} = 1481$. **Elemental Analysis** calcd (%) for $\text{C}_{60}\text{H}_{128}\text{Br}_2\text{K}_2\text{N}_6\text{O}_{37}\text{Si}_3\text{W}_{10}$: C 19.55, H 3.50, N 2.28; found: C 19.43, H 3.42, N 2.07.

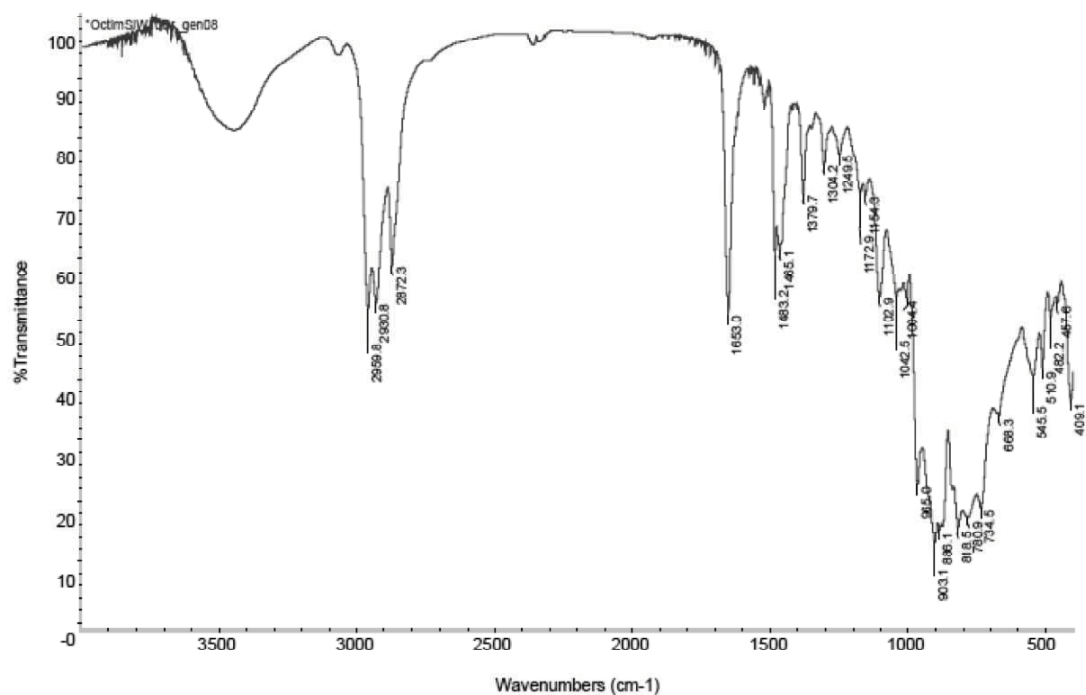


Figure S5. FT-IR spectrum of compound **2**.

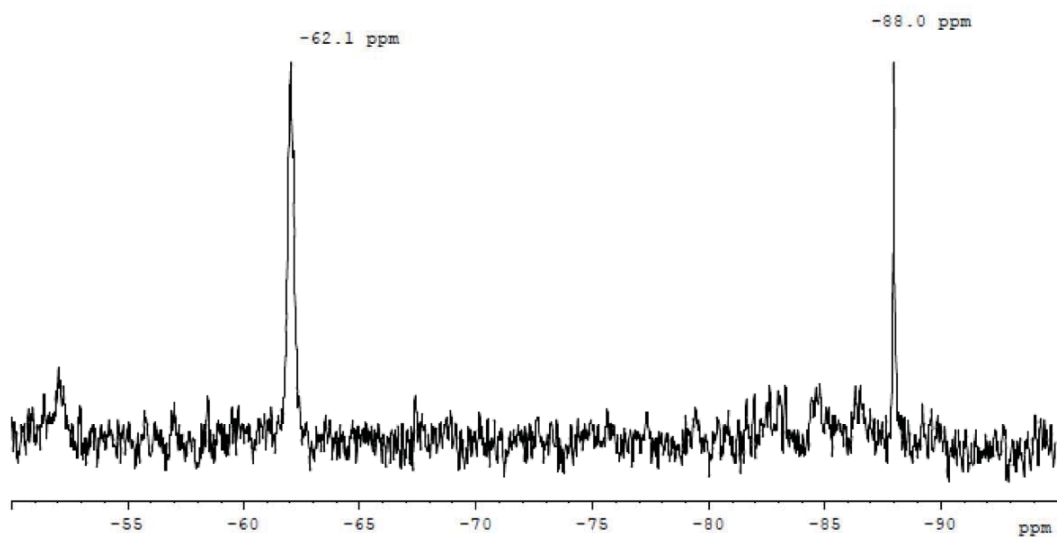


Figure S6. ²⁹Si-NMR spectrum of compound **2**.

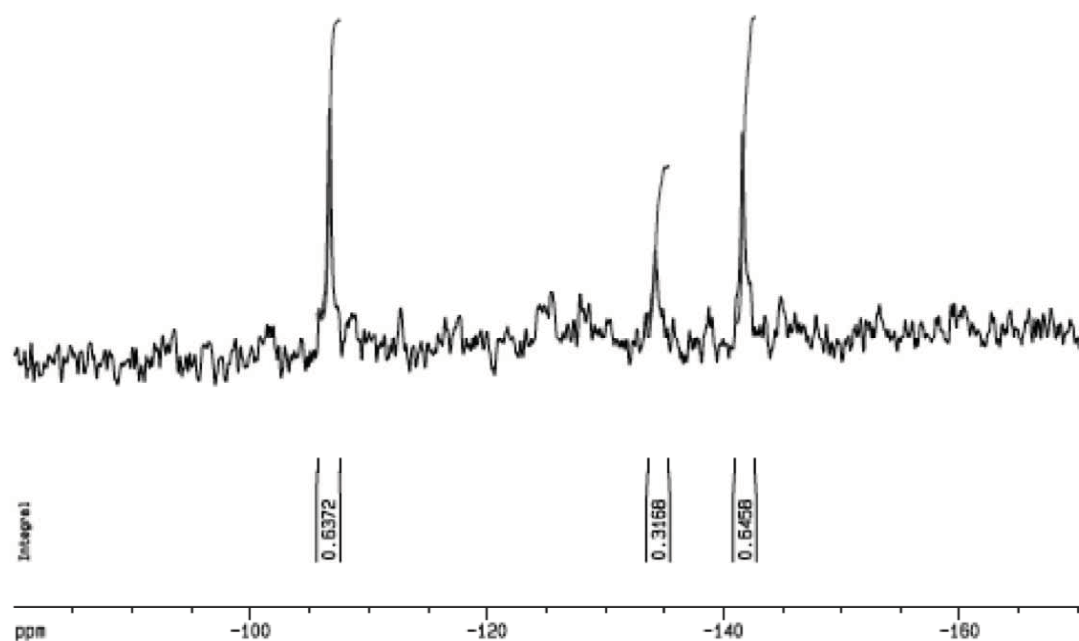


Figure S7. ^{183}W -NMR spectrum of compound 2.

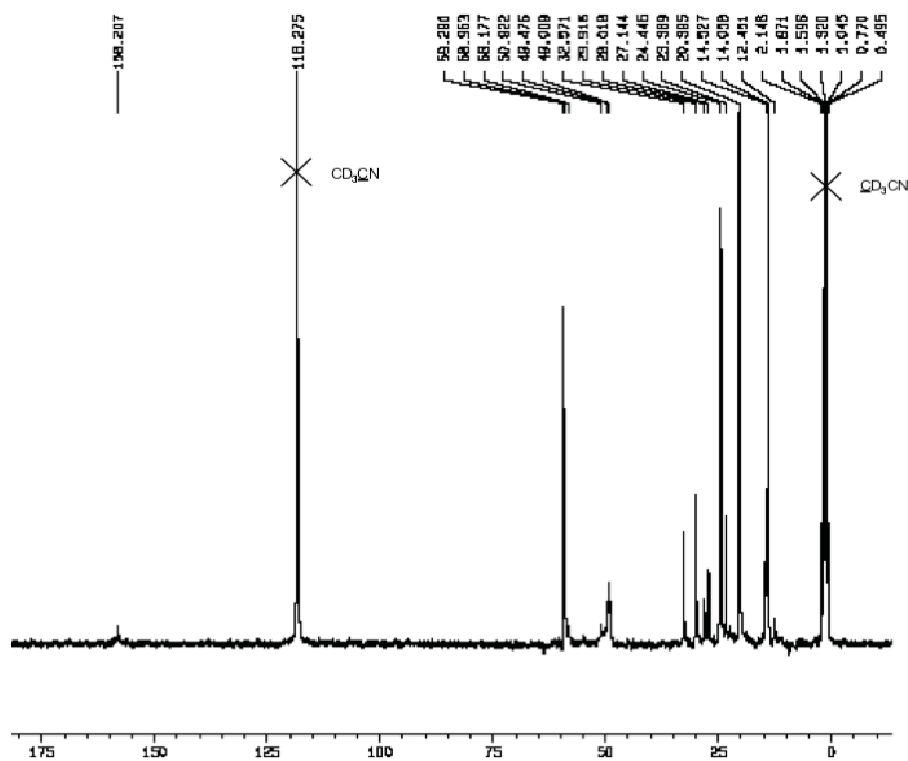


Figure S8. $^{13}\text{C}\{^1\text{H}\}$ -NMR spectrum of compound 2.

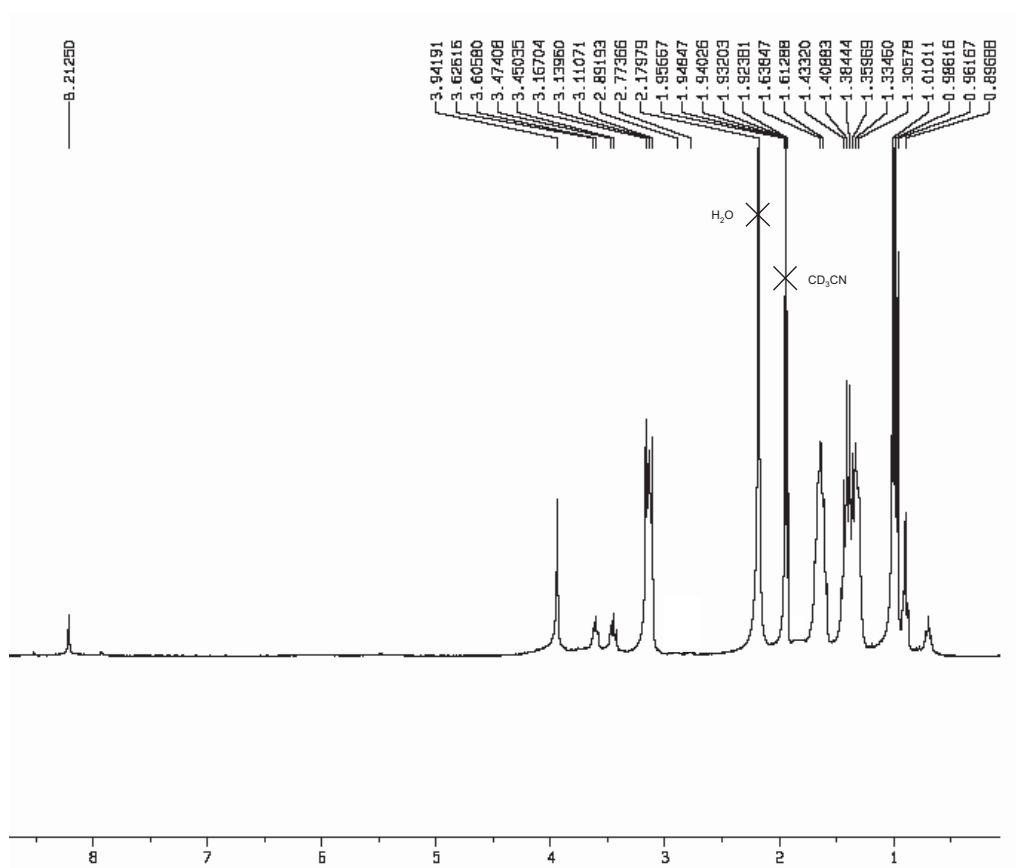


Figure S9. ^1H -NMR spectrum of compound **2**.

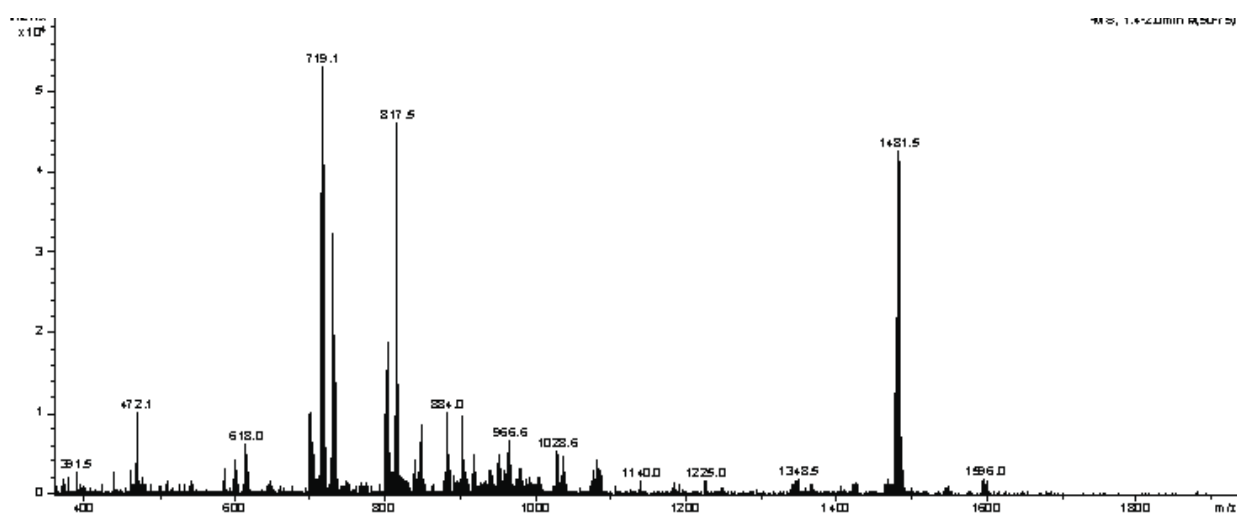
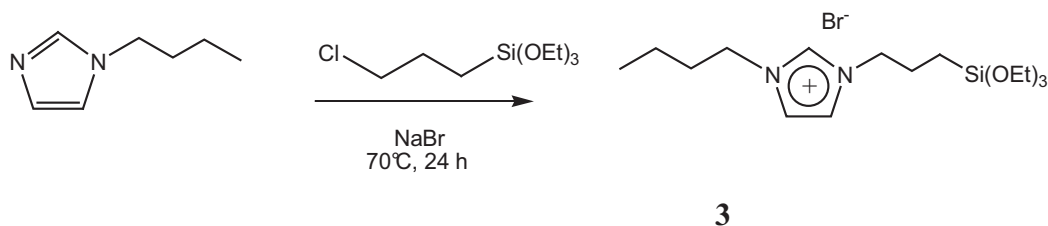


Figure S10. ESI-MS spectrum of compound **2**.

Synthesis of 1-butyl-3-(3-triethoxysilylpropyl)-imidazolium bromide (**3**)^[4]



1-butylimidazole (0.7 mL, 5 mmol), (3-chloropropyl)triethoxysilane (1.3 mL, 5.5 mmol, 1.1 eq) and sodium bromide (1.0 g, 15 mmol, 3 eq) were added to a well-dried Schlenk tube and allowed to react at 70°C under nitrogen for 3 days. The reaction mixture was washed twice with anhydrous Et₂O. The product was then redissolved in anhydrous CH₂Cl₂ and filtered through celite. Evaporation of the solvent gives the desired product as a yellow solid. Yield: 1.64 g (80%).

²⁹Si-NMR (59.6 MHz, CD₂Cl₂, 25°C): δ -47.3 ppm. **¹³C{¹H}-NMR** (62.5 MHz, CD₂Cl₂, 25°C): δ 136.5 (NCHN imidazolium), 122.5, 122.1 (C4 and C5, imidazolium ring), 58.1 (OCH₂), 51.2 (CH₃(CH₂)₂CH₂N), 49.1 (SiCH₂CH₂CH₂N), 31.9, 24.1, 19.1 (methylene groups), 17.9 (OCH₂CH₃), 13.0 (methyl), 6.7 (SiCH₂) ppm. **¹H-NMR** (360 MHz, CD₂Cl₂, 25°C) δ 10.34 (1H, s, NCHN), 7.62 (1H, s, CH imidazolium), 7.48 (1H, s, CH imidazolium), 4.38-4.24 (4H, m, Si(CH₂)₂CH₂N, NCH₂(CH₂)₂CH₃), 3.74 (6H, q, *J* = 7.20 Hz, CH₃CH₂O), 2.01-1.78 (4H, m, NCH₂CH₂CH₂CH₃, NCH₂CH₂CH₂Si), 1.31 (2H, sextet, *J* = 7.20 Hz, NCH₂CH₂CH₂CH₃), 1.13 (9H, t, *J* = 7.20 Hz, CH₃CH₂O), 0.89 (3H, t, *J* = 7.20 Hz, CH₃(CH₂)₃N), 0.60-0.48 (2H, m, SiCH₂) ppm. **Elemental Analysis** calcd (%) for **3**·(0.5 CH₂Cl₂), C_{16.5}H₃₄ClBrN₂O₃Si: C 43.85, H 7.58, N 6.20; found: C 43.85, H 8.06, N 6.03.

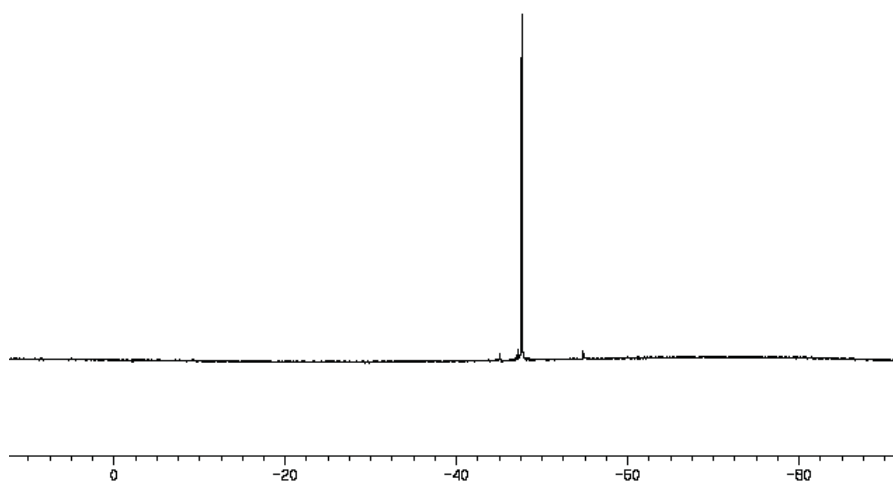


Figure S11. ²⁹Si-NMR spectrum of compound **3**.

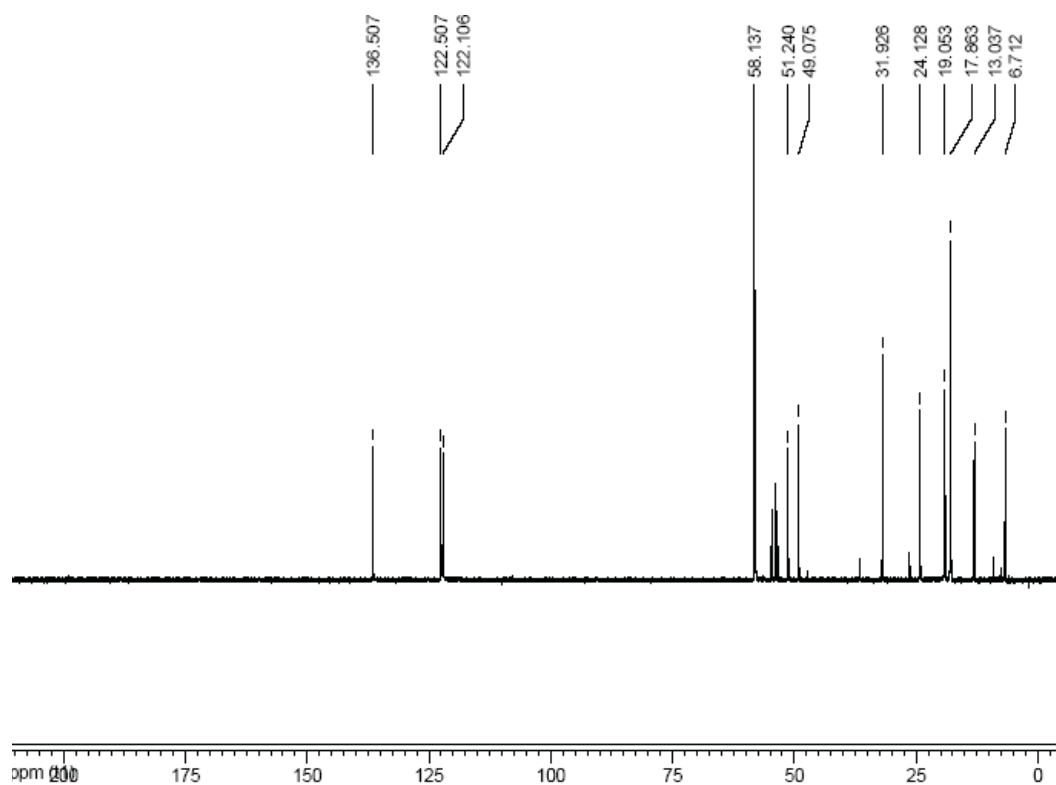


Figure S12. $^{13}\text{C}\{^1\text{H}\}$ -NMR spectrum of compound **3**.

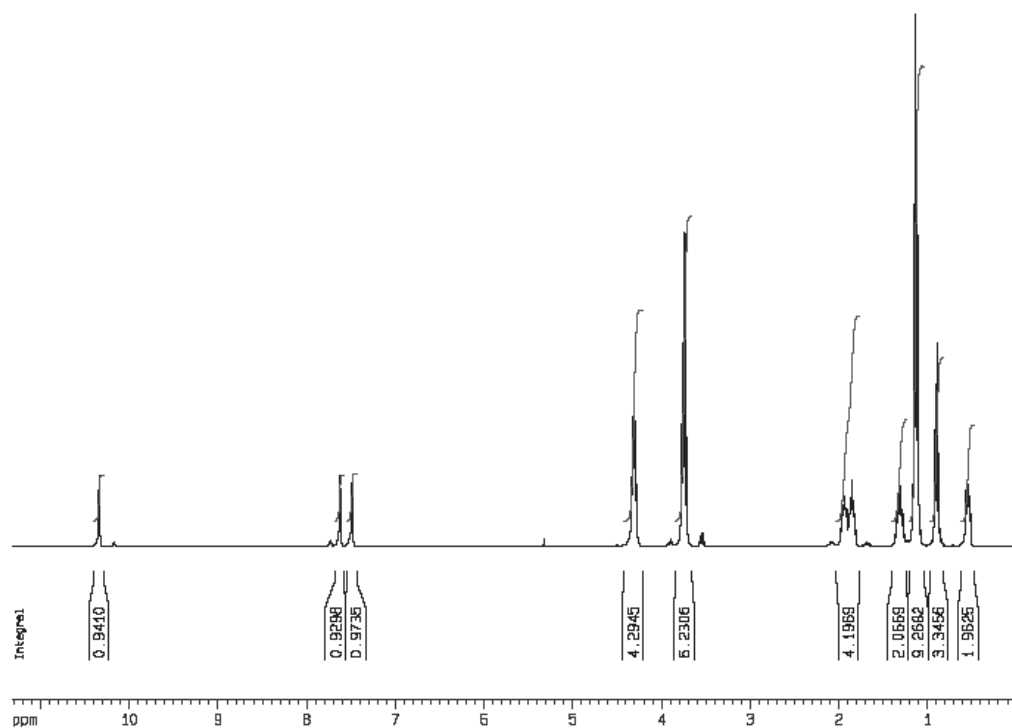
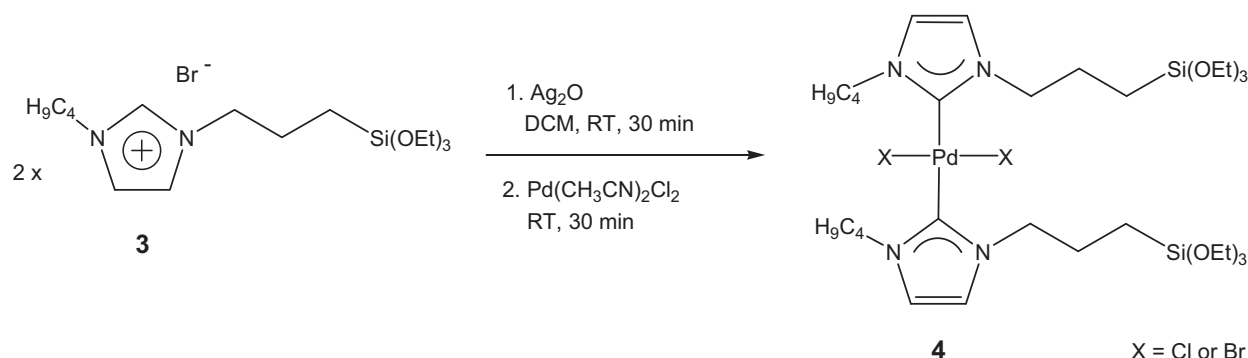


Figure S13. ^1H -NMR spectrum of compound **3**.

Synthesis of dichloro-*bis*-(1-butyl-3-(3-triethoxysilylpropyl)-imidazol-2-ylidene) palladium(II)

(4) ^[5]



1-butyl-3-(3-triethoxysilylpropyl)-imidazolium bromide **3** (0.61 g, 1.5 mmol) was introduced in a well-dried Schlenk tube. Anhydrous CH_2Cl_2 (40 mL) and Ag_2O (0.209 g, 0.90 mmol) were then added. The reaction mixture, vigorously stirred, was allowed to react at room temperature, under nitrogen. After 30 min $\text{Pd}(\text{CH}_3\text{CN})_2\text{Cl}_2$ ^[6] (0.197 g, 0.77 mmol) was added and the mixture was stirred for other 30 min, then filtered through celite. Evaporation of the solvent gives the desired product as a yellow solid. Yield: 0.55 g (88%).

FT-IR (KBr disk) 3119, 2973, 2930, 2884, 1465, 1426, 1389, 1365, 1315, 1293, 1256, 1231, 1191, 1166, 1100, 1074, 1017, 982, 953, 879, 779, 745, 704 cm^{-1} . **$^{13}\text{C}\{^1\text{H}\}$ -NMR** (62.5 MHz, CD_2Cl_2 , 25°C): δ 170.6 (C-Pd), 121.1, 120.9 (C4 and C5, imidazol-2-ylidene), 58.9 (OCH_2), 51.1, 50.9 ($\text{CH}_3(\text{CH}_2)_2\text{CH}_2\text{N}$ and $\text{SiCH}_2\text{CH}_2\text{CH}_2\text{N}$), 33.7, 25.2, 20.7 (methylene groups), 18.7 (OCH_2CH_3), 14.2 (methyl), 8.2 (SiCH_2) ppm. **^1H -NMR** (360 MHz, CD_2Cl_2 , 25°C) δ 6.92 (2H, s, CH imidazol-2-ylidene), 6.87 (2H, s, CH imidazol-2-ylidene), 4.47 (8H, t, $\text{Si}(\text{CH}_2)_2\text{CH}_2\text{N}$, $\text{NCH}_2(\text{CH}_2)_2\text{CH}_3$), 3.79 (12H, q, J = 7.20 Hz, $\text{CH}_3\text{CH}_2\text{O}$), 2.24-1.98 (8H, m, $\text{NCH}_2\text{CH}_2\text{CH}_2\text{CH}_3$, $\text{SiCH}_2\text{CH}_2\text{CH}_2\text{N}$), 1.51-1.37 (4H, m, $\text{NCH}_2\text{CH}_2\text{CH}_2\text{CH}_3$), 1.19 (18H, t, J = 7.20 Hz, $\text{CH}_3\text{CH}_2\text{O}$), 1.04-0.94 (6H, m, $\text{N}(\text{CH}_2)_3\text{CH}_3$), 0.73-0.63 (4H, m, SiCH_2) ppm. **ESI-MS(+)** (CH_3CN) m/z = 799.3, calcd. for $\{[\text{C}_{10}\text{H}_{17}\text{N}_2\text{Si}(\text{OC}_2\text{H}_5)_3]_2\text{PdCl}\}^+$ = 799.9; 843.3, calcd. for $\{[\text{C}_{10}\text{H}_{17}\text{N}_2\text{Si}(\text{OC}_2\text{H}_5)_3]_2\text{PdBr}\}^+$ = 844.4. **Elemental Analysis** calcd (%) for $\text{C}_{32}\text{H}_{64}\text{Cl}_2\text{N}_4\text{O}_6\text{PdSi}_2$: C 46.06, H 7.73, N 6.71; calcd (%) for $\text{C}_{32}\text{H}_{64}\text{Br}_2\text{N}_4\text{O}_6\text{PdSi}_2$: C 41.63, H 6.99, N 6.07; found: C 42.42, H 7.18, N 6.00, ascribed to the dibromo complex, with a small impurity of the dichloro analogue (as confirmed by ESI-MS analysis).

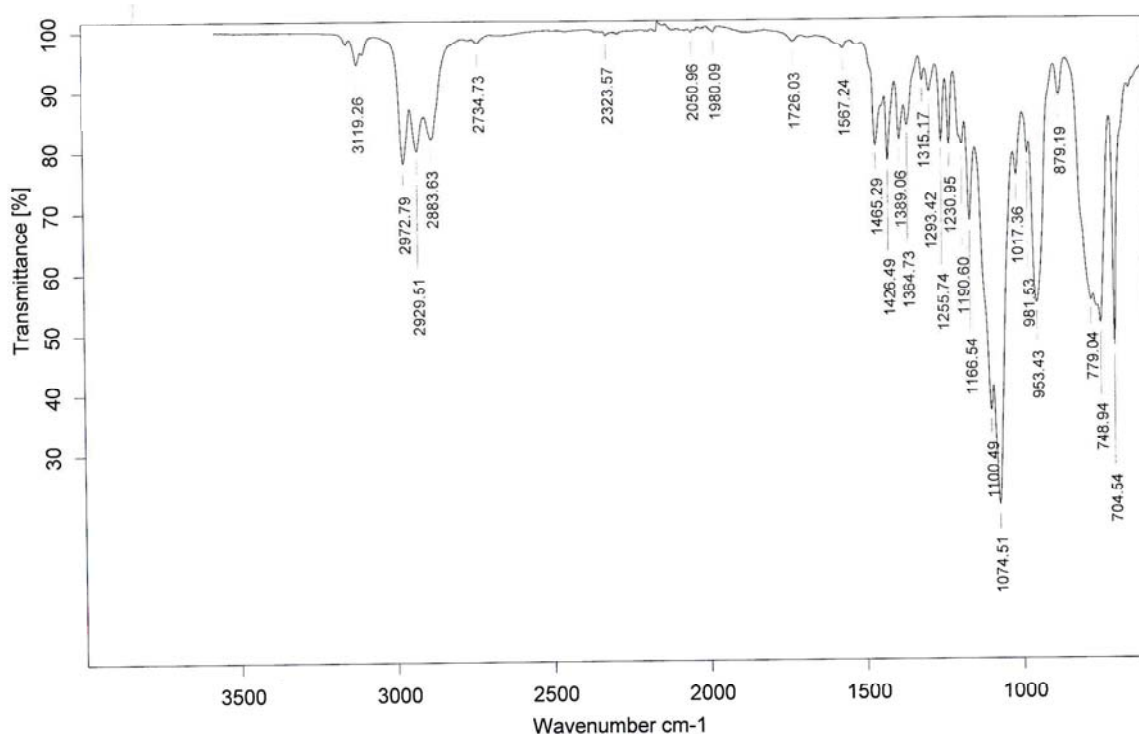


Figure S14. FT-IR spectrum of compound **4**.

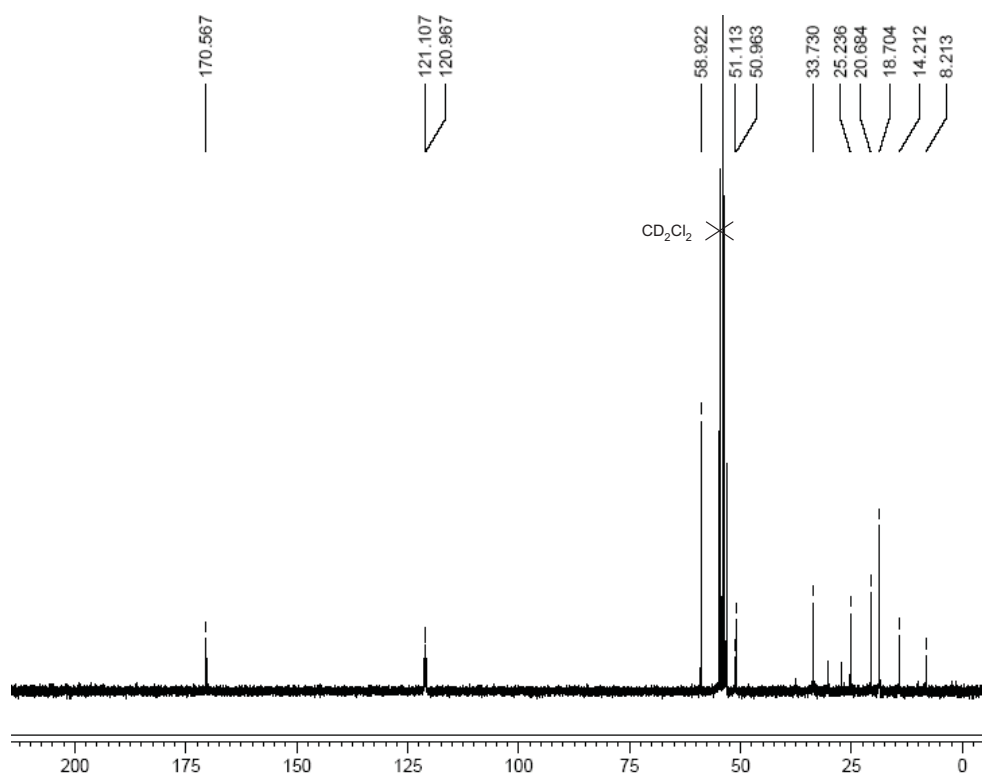


Figure S15. ¹³C{¹H}-NMR spectrum of compound **4**.

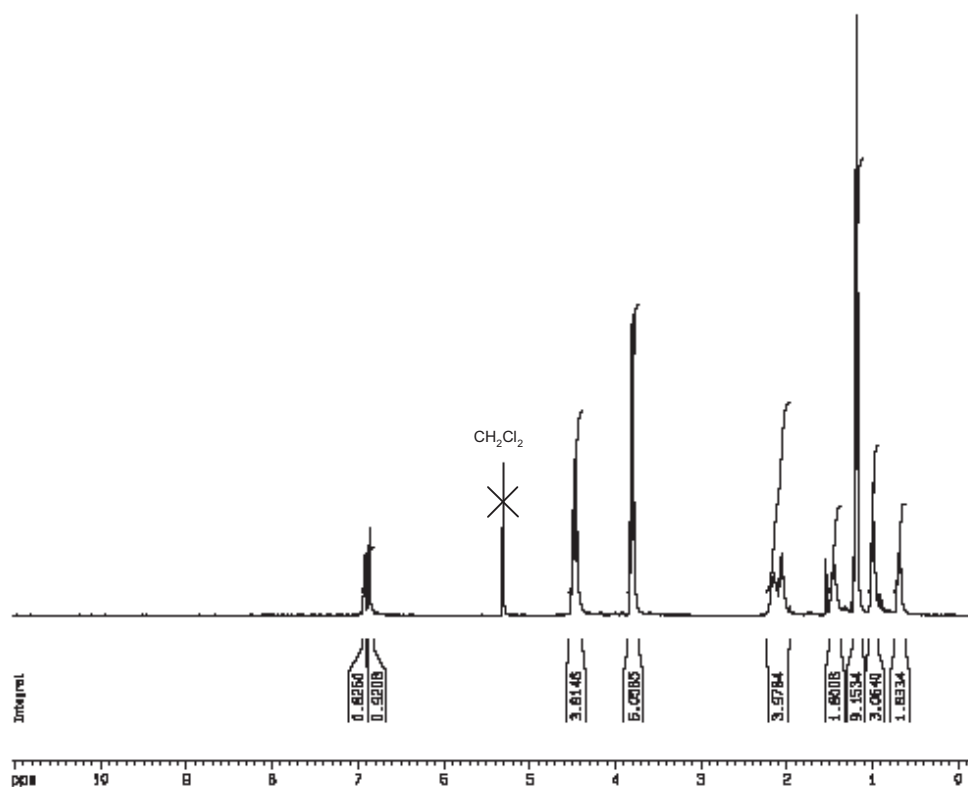


Figure S16. ^1H -NMR spectrum of compound 4.

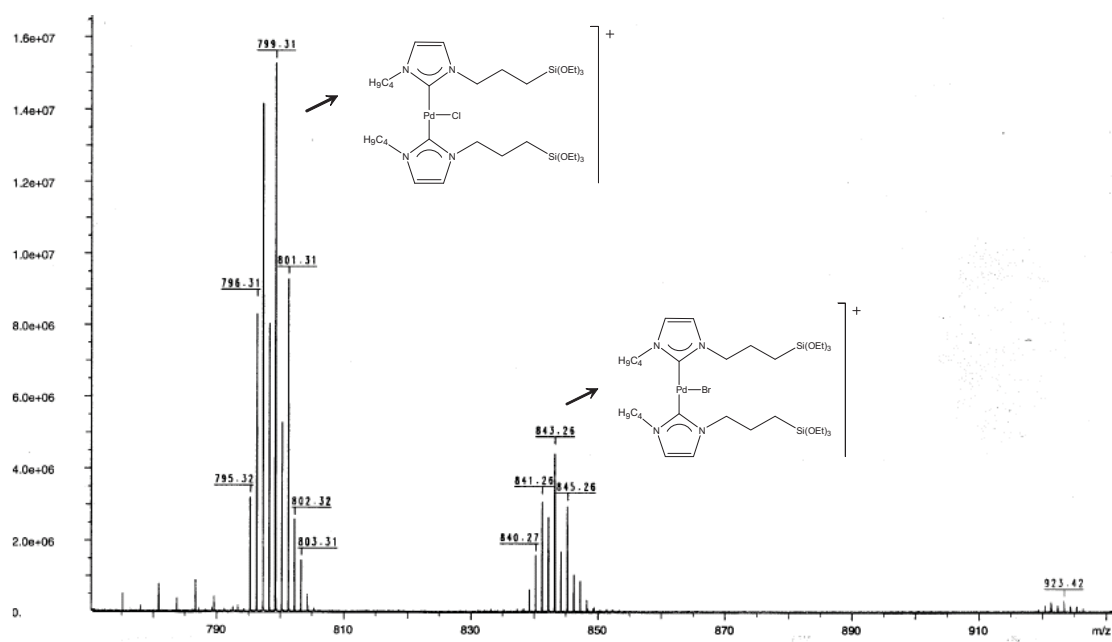
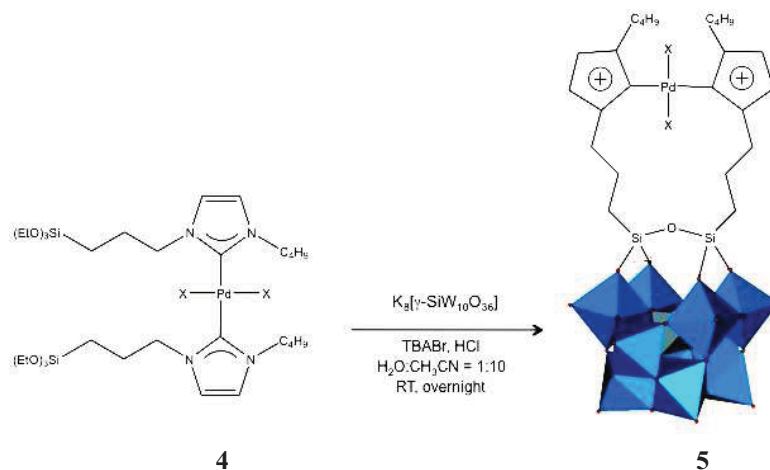


Figure S17. ESI-MS spectrum of compound 4.

Synthesis of $(n\text{-Bu}_4\text{N})_3.5\text{H}_{0.5}[\text{PdBr}_2(\text{C}_{10}\text{H}_{17}\text{N}_2\text{Si})_2\text{O}(\gamma\text{-SiW}_{10}\text{O}_{36})]$ (**5**)^[3]



$\text{K}_8[\gamma\text{-SiW}_{10}\text{O}_{36}]$ (0.826 g, 0.3 mmol) was suspended in H_2O (1.4 mL). $(n\text{-Bu}_4\text{N})\text{Br}$ (0.484 g, 1.5 mmol, 5 eq) and CH_3CN (9 mL) were added and the mixture was stirred at room temperature for 20 minutes. The compound **5** (0.25 g, 0.3 mmol), dissolved in 5 mL of anhydrous CH_3CN , and HCl 4 M (1.8 mmol, 6 eq) were successively added under vigorous stirring. The mixture was stirred overnight at room temperature. The product was obtained after filtration of the insoluble portion and evaporation of the organic solution. The crude compound was thoroughly washed with water. Yield: 0.89 g (75 %).

FT-IR (KBr disk) 3165, 3128, 2961, 2934, 2873, 1635, 1483, 1466, 1425, 1380, 1152, 1097, 1055, 1043, 1003, 963, 946, 902, 886, 839, 820, 735, 602, 546, 509 cm^{-1} . **^{29}Si -NMR** (79.5 MHz, CD_3CN , 25°C) δ -62.8 (2 Si), -88.4 (1 Si) ppm. **^{183}W -NMR** (16.7 MHz, CD_3CN , 25°C) δ -107.4 (4 W), -135.8 (2 W), -142.1 (4 W) ppm. **$^{13}\text{C}\{^1\text{H}\}$ -NMR** (62.5 MHz, CD_3CN , 25°C) δ 169.3 ($\underline{\text{C}}\text{-Pd}$), 122.2, 121.8 (C4 and C5, imidazol-2-ylidene), 59.1 ($((\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2)_4\text{N}^+)$), 54.5, 51.1 ($\text{CH}_3(\text{CH}_2)_2\text{CH}_2\text{N}$ and $\text{SiCH}_2\text{CH}_2\text{CH}_2\text{N}$), 33.6, 25.8, 20.6 (methylene groups), 24.3 ($((\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2)_4\text{N}^+)$), 20.3 ($((\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2)_4\text{N}^+)$), 14.2 (methyl), 14.0 ($((\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2)_4\text{N}^+)$), 7.8 (SiCH_2) ppm. **^1H -NMR** (300 MHz, CD_3CN , 25°C) δ 7.05 (2H, s, $\underline{\text{CH}}$ imidazol-2-ylidene), 7.01 (2H, s, $\underline{\text{CH}}$ imidazol-2-ylidene), 4.71-4.19 (8H, m, $\text{Si}(\text{CH}_2)_2\text{CH}_2\text{N}$, $\text{NCH}_2(\text{CH}_2)_2\text{CH}_3$), 3.17 (32H, t, $(\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2)_4\text{N}^+$), 2.60-2.21 (8H, m, $\text{NCH}_2\text{CH}_2\text{CH}_2\text{CH}_3$, $\text{SiCH}_2\text{CH}_2\text{CH}_2\text{N}$), 2.20-1.98 (4H, m, $\text{NCH}_2\text{CH}_2\text{CH}_2\text{CH}_3$), 1.89-1.77 (6H, m, $\text{N}(\text{CH}_2)_3\text{CH}_3$), 1.78-1.52 (32H, m, $(\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2)_4\text{N}^+$), 1.40 (32H, q, $(\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2)_4\text{N}^+$), 0.97 (48H, t, $(\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2)_4\text{N}^+$), 0.71-0.44 (4H, m, SiCH_2) ppm. **ESI-MS(-)** (CH_3CN) m/z = 1007, calcd. for $\{[(\text{C}_{10}\text{H}_{17}\text{N}_2\text{Si})_2\text{O}(\gamma\text{-SiW}_{10}\text{O}_{36})\text{PdBr}]\}^{3-}$ = 1009; 1470, calcd. for $\{[(\text{C}_{10}\text{H}_{17}\text{N}_2\text{Si})_2\text{O}(\gamma\text{-SiW}_{10}\text{O}_{36})\text{Pd}]\}^{2-}$ = 1474. **Elemental Analysis** calcd (%) for $\text{C}_{76}\text{H}_{160.5}\text{Br}_2\text{N}_{7.5}\text{O}_{37}\text{PdSi}_3\text{W}_{10}$: C 23.05, H 4.08, N 2.65; found: C 23.94, H 4.19, N 2.61.

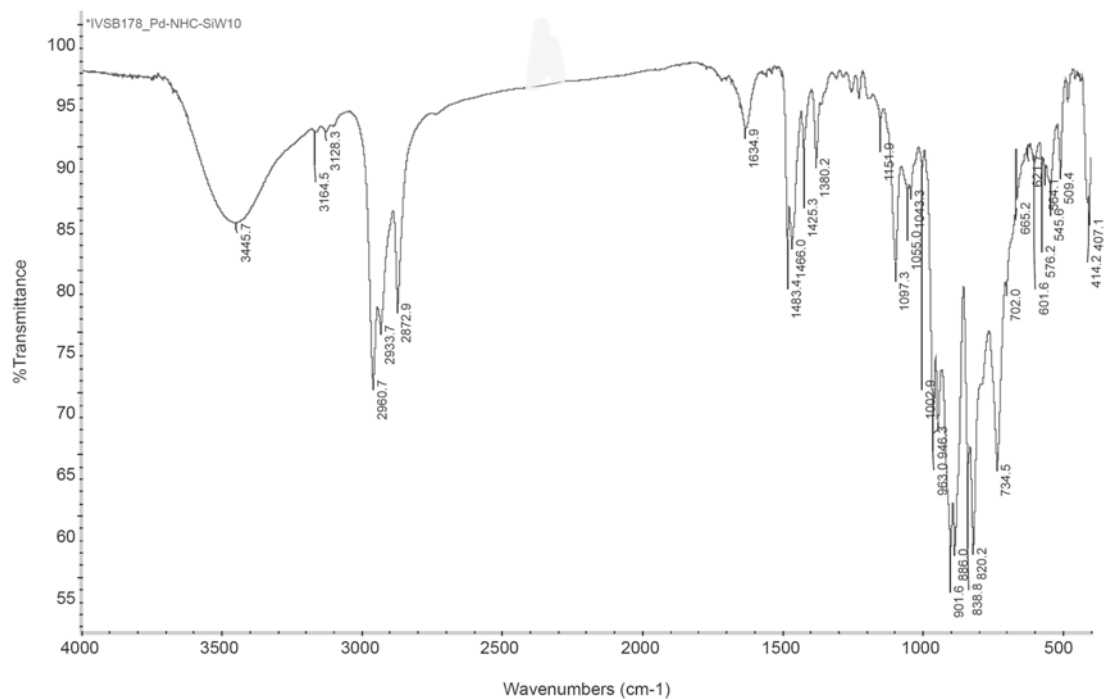


Figure S18. FT-IR spectrum of compound **5**.

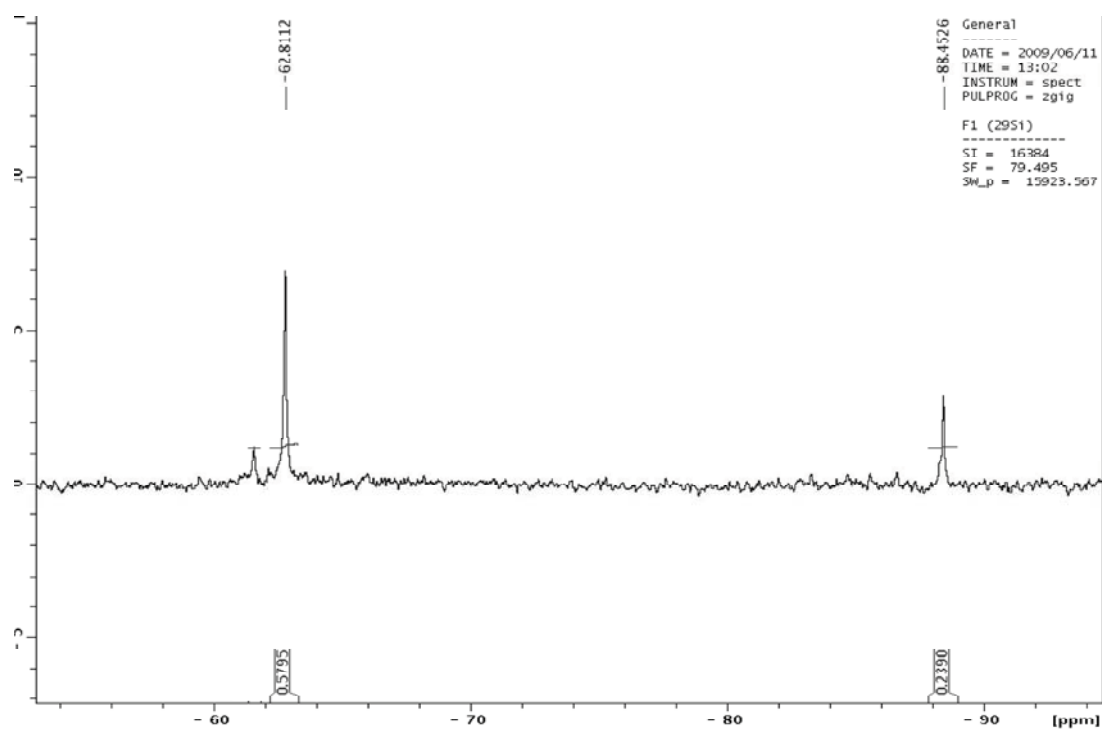


Figure S19. ²⁹Si-NMR spectrum of compound **5**.

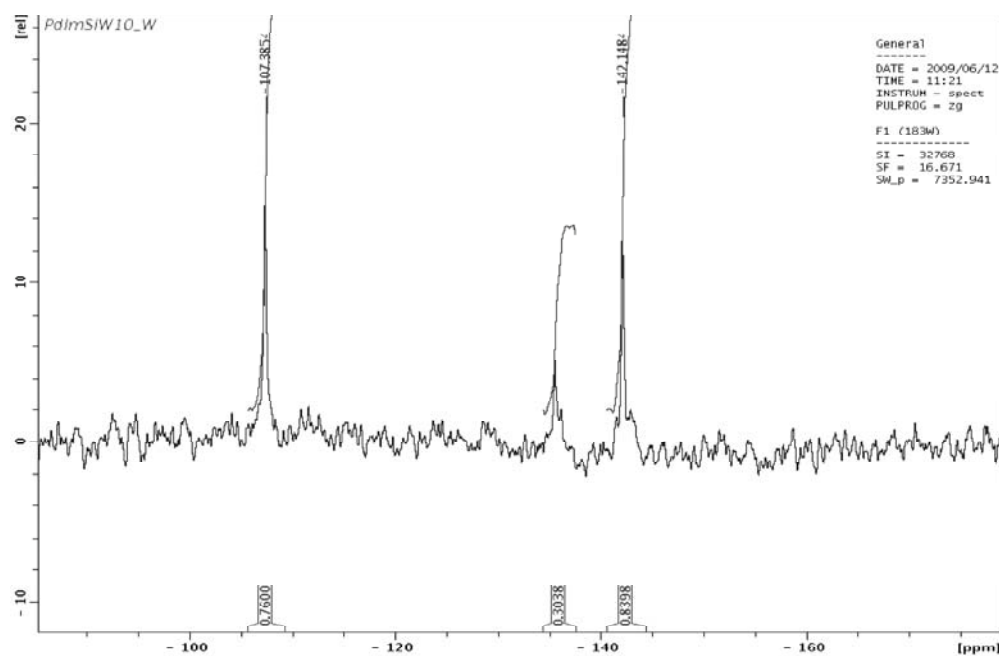


Figure S20. ^{183}W -NMR spectrum of compound **5**.

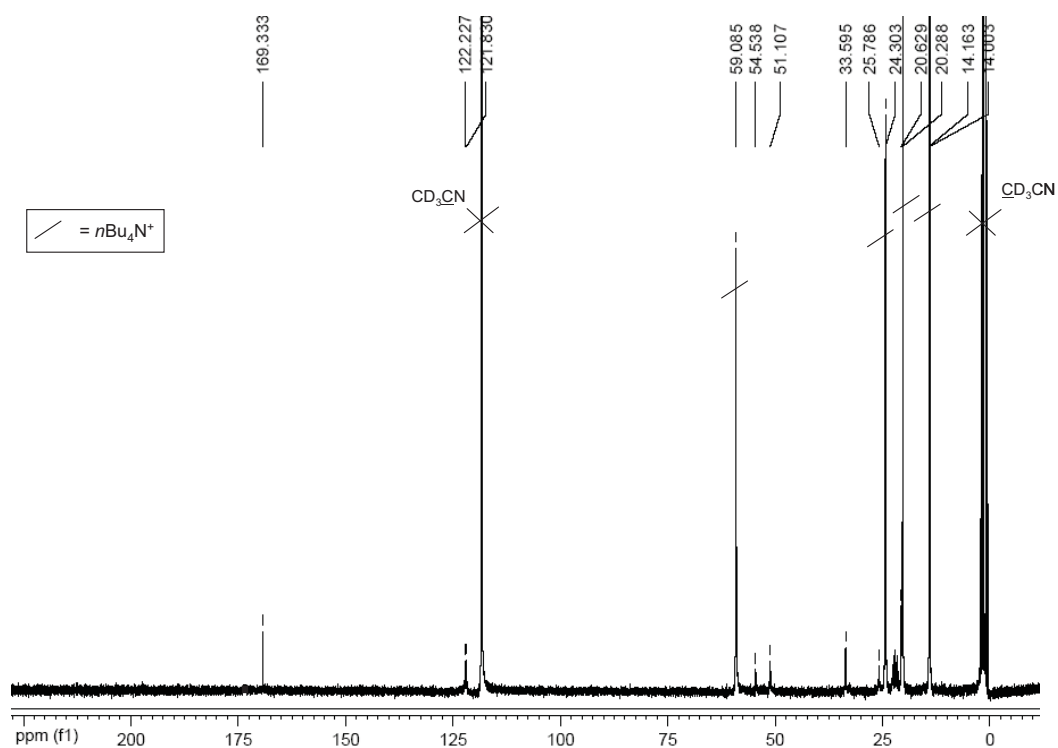


Figure S21. $^{13}\text{C}\{^1\text{H}\}$ -NMR spectrum of compound **5**.

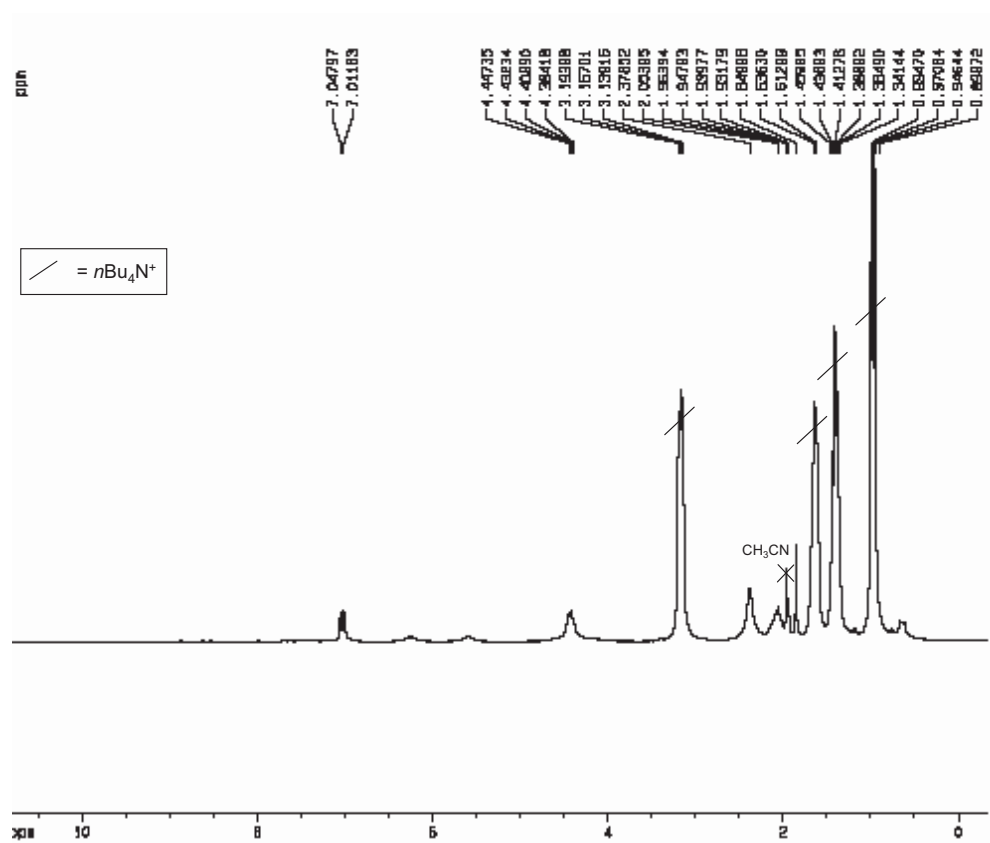


Figure S22. ^1H -NMR spectrum of compound **5**.

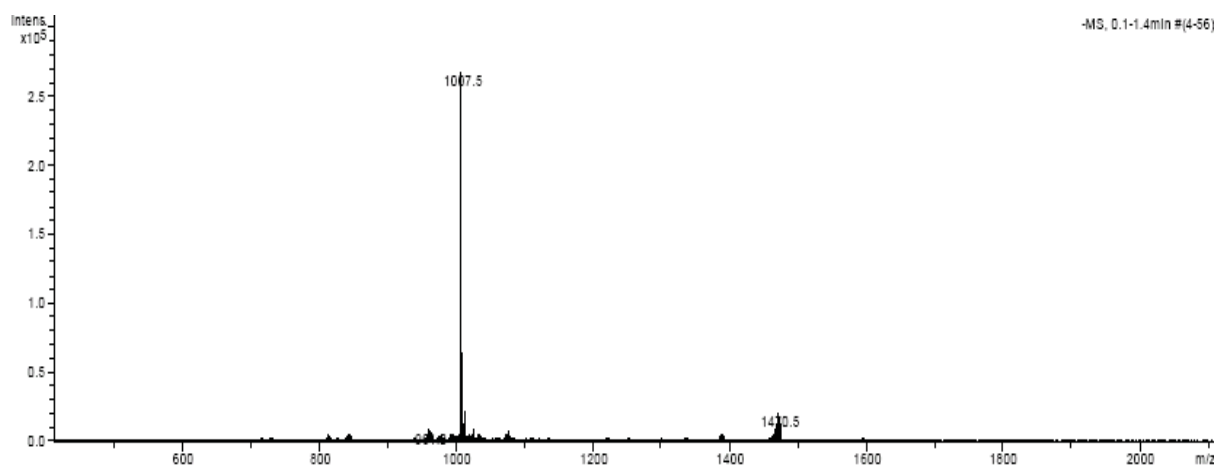


Figure S23. ESI-MS spectrum of compound **5**.

XPS analysis of 5. XPS spectra were recorded using a Perkin-Elmer PHI 5600 ci spectrometer with a standard Al-K α source (1486.6 eV) working at 350 W. The working pressure was less than 1×10^{-8} Pa. The spectrometer was calibrated by assuming the binding energy (BE) of the Au 4f_{7/2} line to lie at 84.0 eV with respect to the Fermi level. Extended spectra (survey) were collected in the range 0-1350 eV (187.85 eV pass energy, 0.5 eV step, 0.025 s step⁻¹). Detailed spectra were recorded for the following regions: Pd 3d, W 4f, Si 2p, Br 3d, N 1s, O 1s, C 1s (11.75 eV pass energy, 0.1 eV step, 0.2 s step⁻¹). The standard deviation in the BE values of the XPS line is 0.10 eV. To take into account charging problems the C 1s peak at 285.0 eV was considered and the peaks BE differences were evaluated. The atomic percentage, after a Shirley type background subtraction, was evaluated by using the PHI sensitivity factors.^[7,8] The samples for the XPS analysis were mounted on steel sample holders and then evacuated for 12 h at ca. 1×10^3 Pa before measurement.

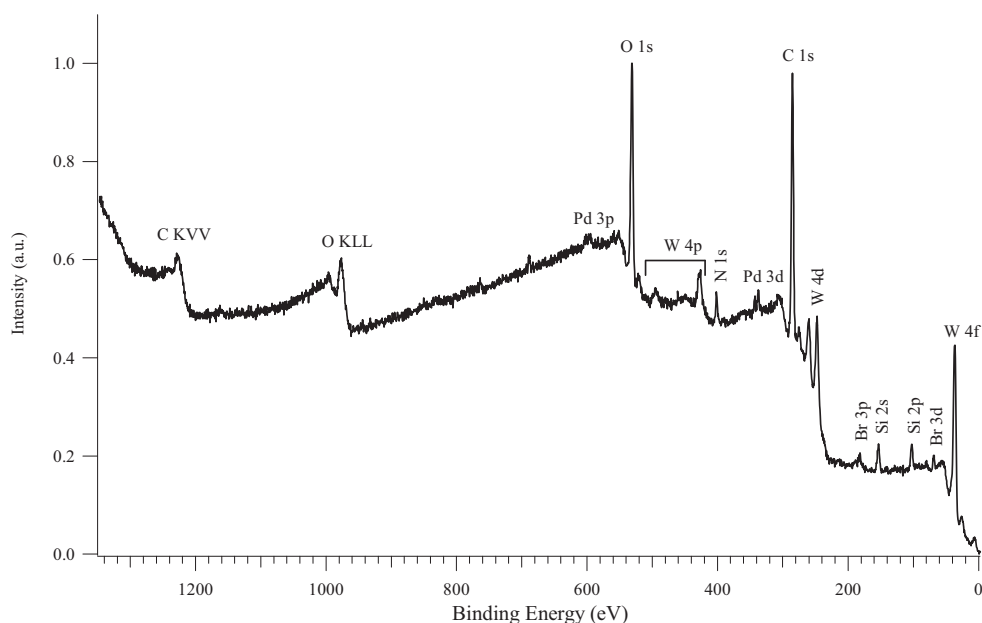


Figure S24. XPS spectrum of **5** (powder).

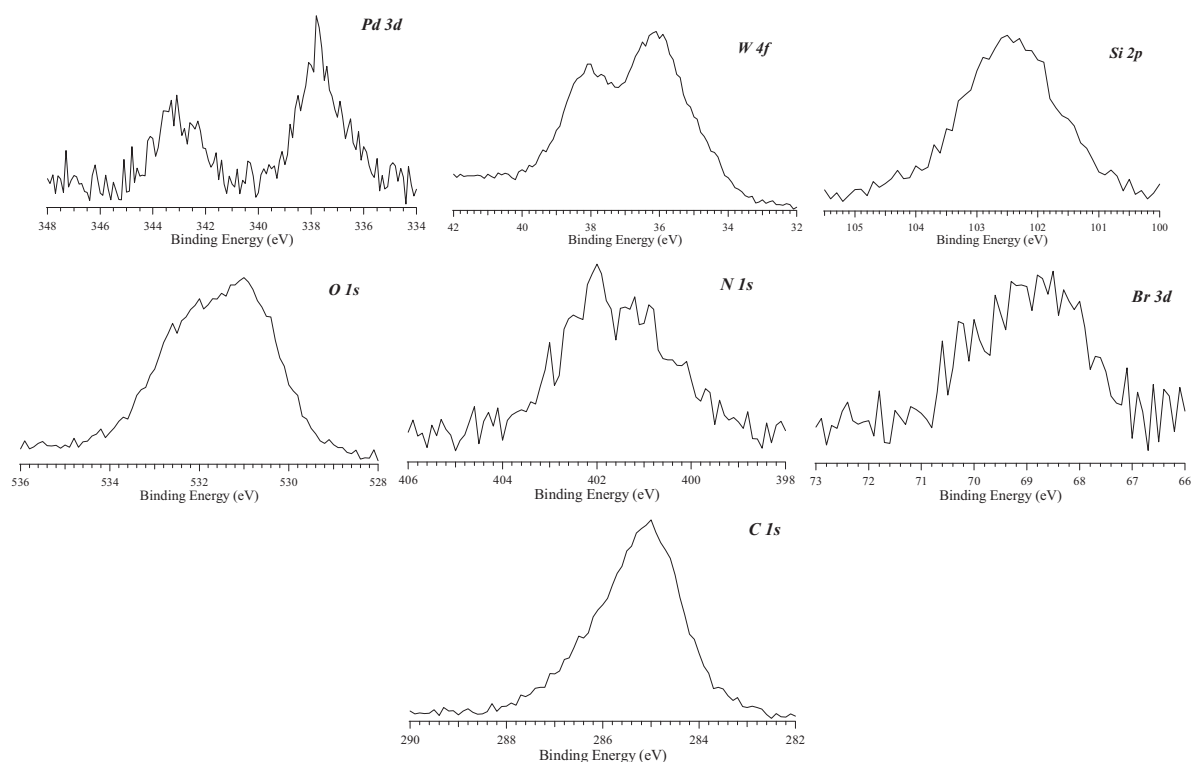


Figure S25. XPS details for the elements found for sample **5**. Pd presents two peaks at 337.8 and 342.9 eV as expected for a Pd(II) complex

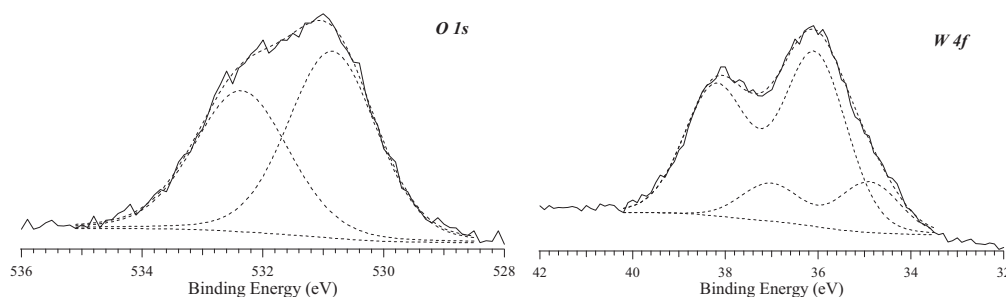


Figure S26. Top: Fitting of the O1s peak, showing two components due to different oxygen environments (530.9 eV (W-O) and 532.4 eV (Si-O)). Bottom: Fitting of W 4f peak, showing the contribution of W(VI) (W 4f_{7/2} at 36.1 eV) and of reduced W species (W4f_{7/2} at 34.9 eV). Reduction results on X-ray irradiation: the sample was blue after the analysis and returned to the initial colour after air exposure.

Representative Procedures for the Reactions

Suzuki Coupling Reaction of Aryl Halides with Phenylboronic acid catalyzed by complex **5** under conventional heating ^[9]

The appropriate amount of a 0.025 M solution of catalyst **5** in DMF was placed in a closed vessel. PhB(OH)₂ (0.275 mmol, 1.1 eq.) in DMF (0.2 mL), Na₂CO₃ (0.5 mmol, 2 eq.) in H₂O (0.45 mL) and the aryl halide (0.25 mmol) were then added, followed by the addition of the appropriate amount of DMF, in order to match the volume of water. The reaction mixture was stirred in a oil bath (T = 80°C) for the appropriate amount of time, then cooled to room temperature. After the addition of water (2 mL ca.), the mixture was extracted with diethylether (3 x 3 mL ca.). The organic solutions were collected and dried over MgSO₄. The resulting solution was analyzed by gas-chromatography.

Microwave-Assisted Suzuki Coupling Reaction of Aryl Halides with Phenylboronic acid catalyzed by complex **5** ^[9]

We followed the same procedure described in the previous paragraph. The reaction vessel was placed in the single-mode cavity of the instrument and irradiated with power at 10 watt under simultaneous stirring and cooling by a stream of compressed air (pressure = 20-40 psi). The registered T_{bulk} are reported in Table 1. At the end of the reaction, the mixture was cooled to room temperature, then, after the addition of water (2 mL ca.), extracted with diethylether (3 x 3 mL ca.). The organic portions were collected and dried over MgSO₄. The resulting solution was analyzed by gas-chromatography.

Microwave-Assisted Dehalogenation of Aryl Chlorides catalyzed by complex **5**

0.1 mL (0.0025 mmol, 1 mol%) of a 0.025 M stock solution of catalyst **5** in DMF were placed in a closed vessel. *n*-Bu₄NOH · 30 H₂O (0.5 mmol, 2 eq., 0.4 mL), DMF (0.4 mL) and the aryl chloride (0.25 mmol) were then added. The reaction vessel was placed in the single-mode cavity of the instrument and irradiated with power at 10 watt under simultaneous stirring and cooling by a stream of compressed air (pressure = 20-40 psi). The registered T_{bulk} are reported in Table 2.

At the end of the reaction, the mixture was cooled to room temperature and extracted with diethylether (3 x 3 mL ca.). The organic phase was collected, dried over MgSO₄ and analyzed by gas-chromatography.

Literature benchmark values for Pd-carbene catalyzed Suzuki-Miyaura and dehalogenation protocols

Table S1: NHC-based ligands for Palladium, selected examples of Suzuki-Miyaura coupling

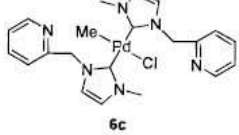
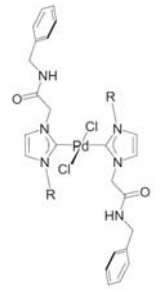
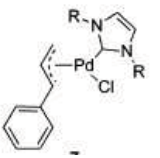
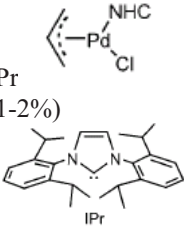
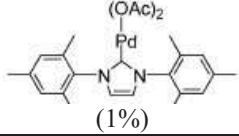
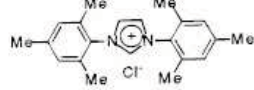
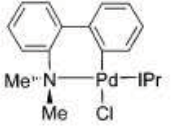
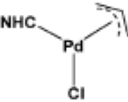
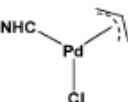
Catalyst (loading, mol%)	substrate	Reaction conditions	Yield, % (time, h)	TOF, h ⁻¹	TON	Reference
 6c (4 x 10 ⁻⁴ %)	4-bromo acetophenone	toluene K ₂ CO ₃ , 110 °C	51 (48)	2656	127500	D. S. McGuinness, K. J. Cavell <i>Organometallics</i> 2000 , <i>19</i> , 741-748
 R= i-Pr, CH ₂ Ph (0.35 %)	aryl bromides	CH ₃ CN, K ₂ CO ₃ , 90 °C	78-99 (12)	19-24	223-283	S. Kumar, M. M. Shaikh, P. Ghosh <i>J. Organomet. Chem.</i> 2009 , <i>694</i> , 4162-4169
	aryl iodides		42-96 (12)	10-23	120-274	
 R=i-Pr(0.05%)	aryl bromides	iPrOH, ^t BuOK, RT	55-95 (3.5)	314- 543	1100- 1900	N. Marion, O. Navarro, J. Mei, E. D. Stevens, N. M. Scott, S. P. Nolan <i>J. Am. Chem. Soc.</i> 2006 , <i>128</i> , 4101-4111
	aryl chlorides		83-96 (15)	111- 128	1660- 1920	
NHC =  IPr (1-2%)	4-chloro toluene	Dioxane, ^t BuONa, 80 °C	97 (1.5)	32	49	M. S. Viciu, R. F. Germaneau, O. Navarro-Fernandez, E. D. Stevens, S. P. Nolan <i>Organometallics</i> 2002 , <i>21</i> , 5470-5472
	4-chloro anisole	iPrOH, ^t BuOK, RT	99 (2)	50	99	Z. Jin, S.-X. Guo, X.-P. Gu, L.-L. Qiu, H.-B. Song, J.-X. Fang <i>Adv. Synth. Catal.</i> 2009 , <i>351</i> , 1575-1585
 (1%)	aryl chlorides	iPrOH ^t BuOK RT	65-100 (1-24)	4-97	65-100	R. Singh, M. S. Viciu, N. Kramareva, O. Navarro, S. P. Nolan <i>Org. Lett.</i> 2005 , <i>7</i> , 1829-1832
Pd ₂ (dba) ₃ (1.5%) +  (2 eq)	4-chloro toluene	Dioxane, Cs ₂ CO ₃ , 80°C	96 (1.5)	43	64	C. Zhang, J. Huang, M. L. Trudell, S. P. Nolan <i>J. Org. Chem.</i> 1999 , <i>64</i> , 3804-3805

Table S2: NHC-based ligands for Palladium, selected examples of catalytic dehalogenation

Catalyst (loading, mol%)	Substrate	Reaction conditions	Yield, % (time)	TOF, h ⁻¹	TON	Reference
 (2 %)	aryl chlorides	iPrOH, ^t BuONa, RT	84-95 (0.75-2 h)	24-57	42-48	O. Navarro, N. Marion, Y. Oonishi, R. A. Kelly III, S. P. Nolan <i>J. Org. Chem.</i> 2006 , <i>71</i> , 685-692
 NHC = IPr (0.025 %)	aryl chlorides	iPrOH, ^t BuONa, 120 °C (MW)	95-100 (120 sec)	~10 ⁵	3800-4000	O. Navarro, H. Kaur, P. Mahjoor, S. P. Nolan <i>J. Org. Chem.</i> 2004 , <i>69</i> , 3173-3180
 NHC = IPr (0.5 %)	aryl chlorides	iPrOH, ^t BuONa, 60 °C	91-100 (1.75 h)	104-114	182-200	O. Navarro, H. Kaur, P. Mahjoor, S. P. Nolan <i>J. Org. Chem.</i> 2004 , <i>69</i> , 3173-3180

Computational details

Computational resources and assistance were provided by the Laboratorio Interdipartimentale di Chimica Computazionale (LICC) at the Department of Chemical Sciences of the University of Padova. DFT calculations have been carried out using the Amsterdam density functional (ADF) code,^[10] scalar relativistic effects were taken into account by means of the two-component zero-order regular approximation (ZORA) method,^[11] adopting the Becke 88 exchange plus the Perdew 86 correlation (BP) functional.^[12] The basis functions for describing the valence electrons are triple-zeta quality doubly polarized (TZ2P), specially optimized for ZORA calculations. Due to the large size of the molecule under investigation, the internal or core electrons (C, N, O: 1s; Si: 1s to 2sp; Br: 1s to 3d; Pd: 1s to 4sp; W: 1s to 4spdf) were kept frozen. The solvent effect was modeled by means of the ADF implementation^[13] of the COSMO method.^[14] This method requires a prior definition of atomic radii, which were set at their following recommended values (in Å): H: 1.3500; C: 1.7000; N: 1.6083; O: 1.5167; Si: 1.9083; Br: 1.850; Pd: 1.9750; W: 1.9917. In addition to the dielectric permittivity ϵ , the solvent is modeled also by an empirical parametrization of non-electrostatic solvation terms derived from the solvation of alkanes.^[15] Since these parameters are currently available only for water, energies and gradients can be reliably calculated only for this solvent.^[16] Therefore, all calculations assumed water as solvent.

Cartesian coordinates (in Å) of the DFT optimized structure for (5).

Atom	X	Y	Z (Angstrom)
1.Si	0.102645	1.612465	3.487004
2.O	-1.243099	2.326873	2.803858
3.W	-1.597374	2.883956	0.951413
4.O	-2.678957	4.235665	1.254699
5.O	0.048936	-0.033817	3.406587
6.Si	0.003837	-1.678385	3.471850
7.O	1.330727	-2.396599	2.752628
8.W	1.640957	-2.919530	0.882454
9.O	2.731391	-4.276427	1.139888
10.O	-0.004219	-1.386512	0.647107
11.Si	0.010164	-0.010126	-0.215760
12.O	1.384076	-0.029895	-1.153231
13.W	1.866565	-1.751339	-2.647276
14.O	2.031825	-0.031368	-3.619555
15.W	1.931791	1.674382	-2.648204
16.O	0.012640	1.766590	-2.930248
17.W	-1.899533	1.755621	-2.592923
18.O	-2.087579	0.055071	-3.571296
19.W	-1.964276	-1.671007	-2.615931
20.O	-0.052504	-1.764806	-2.947827
21.W	-1.703038	-2.873835	0.899972
22.O	-2.829216	-4.196256	1.180629
23.O	2.951760	-1.456391	0.760304
24.W	3.691840	-0.071473	-0.350637
25.O	3.598377	-1.360936	-1.834175
26.O	1.610757	-2.892401	-1.082063
27.O	-0.045779	-3.917299	0.890837
28.O	-1.357286	-2.341980	2.759913
29.O	1.447085	2.272614	2.749591
30.W	1.748686	2.840478	0.893475
31.O	1.711929	2.812082	-1.058438
32.O	2.876333	4.160826	1.167341
33.O	0.043516	1.347084	0.672907
34.O	0.090773	3.877130	0.940666
35.O	3.020473	1.333764	0.763213
36.O	-2.913691	1.422783	0.842943
37.W	-3.674470	0.054504	-0.269699
38.O	-3.610734	1.357360	-1.737856
39.O	-1.608402	2.871023	-1.007499
40.O	-5.372357	0.086429	0.176516
41.O	-2.971427	-1.366279	0.812317
42.O	-1.382884	0.018579	-1.123652
43.O	-3.662023	-1.230484	-1.761531
44.O	-2.450713	2.915045	-3.787827
45.O	5.399557	-0.106995	0.056848
46.O	3.644405	1.226386	-1.827834
47.O	2.489721	2.812289	-3.860826

48.O	2.391504	-2.886492	-3.883777
49.O	-1.712831	-2.833832	-1.057608
50.O	-2.550485	-2.776900	-3.850948
51.C	0.010660	-2.238298	5.262610
52.H	0.989136	-1.968107	5.694744
53.H	-0.010959	-3.340815	5.243269
54.C	0.136718	2.193044	5.269251
55.H	-0.810871	1.901014	5.751841
56.H	0.101890	3.295291	5.203330
57.C	1.318746	1.772736	6.163343
58.H	2.279010	1.950121	5.656790
59.H	1.265461	0.698882	6.394173
60.C	-1.118227	-1.711569	6.168654
61.H	-2.102845	-1.963506	5.747597
62.H	-1.070137	-0.616286	6.246396
63.C	1.247497	2.571976	7.468227
64.H	1.462236	3.631200	7.270661
65.H	0.236842	2.515513	7.879219
66.C	-0.962290	-2.319086	7.565569
67.H	-1.065840	-3.411366	7.512078
68.H	0.036213	-2.107160	7.954515
69.N	-1.920317	-1.841849	8.573787
70.N	2.159395	2.143023	8.538697
71.C	1.855188	1.290366	9.569489
72.C	-3.201313	0.135091	11.296421
73.H	-2.264222	0.624911	11.572418
74.H	-3.836696	0.902426	10.834955
75.C	-3.894081	-0.438055	12.531828
76.H	-4.296623	0.433088	13.073977
77.H	-4.773911	-1.037328	12.248085
78.C	-2.988594	-1.232958	13.479965
79.H	-2.693944	-2.184682	13.011084
80.H	-2.056938	-0.666030	13.637058
81.C	-3.658195	-1.497198	14.833353
82.H	-4.591565	-2.066724	14.714350
83.H	-3.000641	-2.065380	15.504858
84.H	-3.911352	-0.550435	15.334319
85.N	-2.866428	-0.839174	10.240764
86.C	3.211970	0.436282	11.530721
87.H	2.247399	-0.019038	11.770947
88.H	3.892292	-0.378973	11.251734
89.C	3.768514	1.202948	12.730310
90.H	4.034813	0.443990	13.483429
91.H	4.715232	1.699827	12.463418
92.N	2.991106	1.261923	10.329761
93.C	2.794822	2.214415	13.343813
94.H	2.539359	2.979913	12.595510
95.H	1.852559	1.695885	13.584243
96.C	3.354219	2.882638	14.603502
97.H	4.290271	3.418904	14.388378
98.H	2.642137	3.606543	15.021846
99.H	3.571526	2.136797	15.381768

100.C	-1.689586	-0.898639	9.543916
101.Pd	0.079387	0.205302	9.709759
102.Br	1.385649	-1.982826	10.046795
103.Br	-1.225011	2.412734	9.853875
104.C	-3.805140	-1.709438	9.705409
105.C	-3.209426	-2.341370	8.663503
106.C	3.977267	2.067709	9.780428
107.C	3.453352	2.622450	8.658517
108.H	4.954727	2.183990	10.226905
109.H	3.880760	3.318483	7.949467
110.H	-4.803003	-1.810211	10.106819
111.H	-3.582439	-3.102410	7.991379

References

-
- [1] J. Canny, A. Tézé, R. Thouvenot, G. Hervé *Inorg. Chem.* **1986**, 25, 2114-2119.
- [2] K. Yamaguchi, C. Yoshida, S. Uchida, N. Mizuno *J. Am. Chem. Soc.* **2005**, 127, 530-531.
- [3] C. R. Mayer, I. Fournier, R. Thouvenot *Chem. Eur. J.* **2000**, 6, 105-110.
- [4] a) L.-F. Xiao, F.-W. Li, J.-J. Peng, C.-G. Xia *J. Mol. Catal. A: Chem.* **2006**, 253, 265-269. b) S. Udayakumar, V. Raman, H.-L. Shim, D.-W. Park *Appl. Catal., A* **2009**, 368, 97-104.
- [5] C. K. Lee, J. C. C. Chen, K. M. Lee, C. W. Liu, I. J. B. Lin *Chem. Mater.* **1999**, 11, 1237-1242.
- [6] Prepared following literature procedures, in particular: I. Abrunhosa, L. Delain-Bioton, A.-C. Gaumont, M. Gulea, S. Masson *Tetrahedron* **2004**, 60, 9263-9272.
- [7] Shirley, D. A. *Phys. Rev. B* **1972**, 5, 4709.
- [8] J. F. Moulder, W. F. Stickle, P. E. Sobol, K. D. Bomben, In *Handbook of X-ray Photoelectron Spectroscopy*; Chastain, J., Ed.; Physical Electronics: Eden Prairie, MN, **1992**.
- [9] H. Qiu, S. M. Sarkar, D.-H. Lee, M.-J. Jin *Green Chem.* **2008**, 10, 37-40.
- [10] G. te Velde, F.M. Bickelhaupt, E.J. Baerends, C. Fonseca Guerra, S.J.A. van Gisbergen, J.G. Snijders, T. Ziegler, *J. Comput. Chem.* **2001**, 22, 931-967.
- [11] a) S.K. Wolff, T. Ziegler, E. van Lenthe, E.J. Baerends, *J. Chem. Phys.* **1999**, 110, 7689-7698. b) J. Autschbach, *Calculation of NMR and EPR Parameters*; Eds.: Kaupp, M.; Bühl, M.; Malkin, V.G.; Wiley-VCH: Weinheim, 2004, chapter 14. c) E. van Lenthe, E.J. Baerends, J.G. Snijders, *J. Chem. Phys.* **1993**, 99, 4597-4610. (d) E. van Lenthe, PhD. Thesis, Vrije Universiteit, Amsterdam, the Netherlands, **1996**.
- [12] a) A.D. Becke, *Phys. Rev. A* **1988**, 38, 3098-3100. b) J.P. Perdew, *Phys. Rev. B* **1986**, 33, 8822-8824.
- [13] C.C. Pye, T. Ziegler, *Theor. Chem. Acc.* **1999**, 101, 396-408.
- [14] a) A. Klamt, G. Schüürmann, *J. Chem. Soc., Perkin Trans. 2* **1993**, 799-805. b) A. Klamt, V. Jones, *J. Chem. Phys.* **1996**, 105, 9972-9981. (c) A. Klamt, *J. Phys. Chem.* **1995**, 99, 2224-2235.
- [15] T.N. Truong, E.V. Stefanovich, *Chem. Phys. Lett.* **1995**, 240, 253-260.

- [16] It is worth noting that the thermodynamics of solvation of hydrocarbons is profoundly different according to whether the solvent is water or any other liquid. W. Blokzijl, J.B.F.N. Engberts, *Angew. Chem. Int. Ed. Engl.* **1993**, 32, 1545-1579.