Molecular Adsorbates Switch on Heterogeneous Catalysis: Induction of Reactivity by N-Heterocyclic Carbenes

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Supporting Information

1. General Information

Unless otherwise noted, all reactions were carried out under an atmosphere of argon in oven-dried Schlenk tubes. Reaction temperatures are reported as the temperature of the heat transfer medium surrounding the vessel unless otherwise stated. Dry solvents (<50 ppm H_2O) were purchased from Acros Organics, Sigma-Aldrich or Carl Roth and stored over molecular sieves under argon atmosphere and were transferred under argon.

Commercially available chemicals were obtained from Acros Organics, Aldrich Chemical Co., Combi-Blocks, Alfa Aesar, ABCR and TCI Europe and used as received unless otherwise stated.

Analytical thin layer chromatography (TLC) was performed on silica gel 60 F254 aluminum plates (Merck). TLC plates were visualized by exposure to short wave ultraviolet light (254 nm, 366 nm). Flash chromatography was performed on Merck silica gel (40-63 mesh) by standard techniques. Solvents used for flash column chromatography were distilled before use.

^{1}H- and ^{13}C-NMR spectra were recorded on a Bruker AV 300 or Bruker AV 400 in solvents as indicated. Chemical shifts (δ) for ^{1}H- and ^{13}C-NMR spectra are given in ppm relative to TMS. The residual solvent signals were used as references for ^{1}H- and ^{13}C-NMR spectra and the chemical shifts converted to the TMS scale (CDCl$_3$: $\delta H = 7.26$ ppm, $\delta C = 77.2$ ppm). Coupling constants (J) are quoted in Hz. To describe the multiplicities of the signals, the following abbreviations were used: s: singlet, bs: broad signal, d: doublet, t: triplet, q: quartet, hept: heptet, m: multiplet.

Exact ESI mass spectra were recorded on a Bruker Daltonics MicroTof. High resolution ESI mass spectra were recorded on a Thermo-Fisher Scientific Orbitrap LTQ XL.

2. Optimization of reaction conditions

General procedure

Unless otherwise noted, toluene (1 mL) was added to a mixture of the corresponding Pd-catalyst, NHC and base. After one minute of stirring, bromobenzene (21 μL, 0.2 mmol, 1.0 equiv) was added and the reaction mixture was stirred for an additional minute at room temperature. Aniline (1.0 equiv) was added and the reaction mixture was stirred for the given time at the given temperature. After the reaction mixture was cooled down to room temperature, the reaction mixture was analyzed by GC-FID analysis with mesitylene as internal standard.

Table S1. Screening of different catalyst, supplier in parenthesis.

Pd-catalyst	Yield
Pd/Al$_2$O$_3$ (ABCR)	2%
Pd/Al$_2$O$_3$ (ABCR, Escat 1241)	22%
Pd/Al$_2$O$_3$ (ABCR)	**12%**
Pd/Al$_2$O$_3$ (Johnson Matthey)	16%
Pd/C (Evonik, Type 1)	2%
Pd/C (Evonik, Type 2)	2%
Pd/CaCO$_3$ (Johnson Matthey)	18%
Pd/SiO$_2$ (ABCR, Escat 1351)	2%
Pd/BaSO$_4$ (Johnson Matthey)	21%

Reactions were performed according to the general procedure with 20 mol% IPr•HBF$_4$, 10 mol% corresponding Pd-catalyst, and 1.5 equiv KOtBu at 80 °C for 16 h.

Table S2. Screening of different NHCs.

NHC	Yield
IPr	**22%**
ICy	1%
IAd	1%
IMes	0%
SIPr	17%
ItBu	1%

Reactions were performed with 20 mol% IPr•HBF$_4$, 10 mol% Pd/Al$_2$O$_3$ (ABCR, Escat 1241), and 1.5 equiv KOtBu at 80 °C for 16 h.

Table S3. Screening of NHC-loading.

NHC	Yield
5 mol%	**48%**
7.5 mol%	42%
10 mol%	39%
15 mol%	22%
20 mol%	22%
25 mol%	22%
30 mol%	0%

Reactions were performed with 10 mol% Pd/Al$_2$O$_3$ (ABCR, Escat 1241), and 1.5 equiv KOtBu at 80 °C for 16 h.

Table S4. Screening of different bases.

Base	Yield
KO*t*Bu	**48%**
NaO*t*Bu	0%
LiO*t*Bu	0%
NaOMe	0%
Cs$_2$CO$_3$	0%
K$_2$CO$_3$	0%
K$_3$PO$_4$	0%
KHMDS	0%
LiHMDS	0%

Reactions were performed with 10 mol% Pd/Al$_2$O$_3$ (ABCR, Escat 1241), 5 mol% IPr•HBF$_4$ and 1.5 equiv base at 80 °C for 16 h.

Table S5. Screening of equivalents of KO*t*Bu.

Equivalents KOtBu	Yield
1.0 equivalents	13%
1.5 equivalents	48%
2.0 equivalents	60%
2.5 equivalents	**72%**
3.0 equivalents	8%

Reactions were performed with 10 mol% Pd/Al$_2$O$_3$ (ABCR, Escat 1241), 5 mol% IPr•HBF$_4$ and KOtBu at 80 °C for 16 h.

Table S6. Screening of solvent.

Solvent	Yield
toluene	**72%**
trifluorotoluene	32%
1,4-dioxane	36%
THF	51%
DME	15%
*t*AmOH	6%

Reactions were performed with 10 mol% Pd/Al$_2$O$_3$ (ABCR, Escat 1241), 5 mol% IPr•HBF$_4$ and 2.5 equiv KO*t*Bu at 80 °C for 16 h.

Table S7. Screening of reaction temperature.

Temperature	Yield
80 °C	72%
110 °C	**82%**

Reactions were performed with 10 mol% Pd/Al$_2$O$_3$ (ABCR, Escat 1241), 5 mol% IPr•HBF$_4$ and 2.5 equiv KO*t*Bu for 16 h.

Table S8. Screening of catalyst loading.

Catalyst loading	Yield
2.5 mol%	65%
5.0 mol%	**82%**
10 mol%	82%

Reactions were performed with Pd/Al$_2$O$_3$ (ABCR, Escat 1241), 5 mol% IPr•HBF$_4$ and 2.5 equiv KO*t*Bu at 110 °C for 16 h.

Table S9. Screening of aniline equivalents.

Equivalents aniline	Yield
1.0	82%
1.2	**95%**
1.5	67%

Reactions were performed with 5 mol% Pd/Al$_2$O$_3$ (ABCR, Escat 1241), 2.5 mol% IPr•HBF$_4$ and 2.5 equiv KO*t*Bu at 110 °C for 16 h.

Table S10. Screening of reaction time.

Reaction time	*Yield*
4 h	**95% (93%)**
10 h	95%
16 h	95%

Reactions were performed with 5 mol% Pd/Al$_2$O$_3$ (ABCR, Escat 1241), 2.5 mol% IPr•HBF$_4$ and 2.5 equiv KOtBu at 110 °C. Isolated yield in parenthesis.

Table S11. Control experiments.

Note	*Yield*
no Pd, only Al$_2$O$_3$	0%
no IPr•HBF$_4$	0%
no KOtBu	0%
2.5 mol% PPh$_3$ (instead of IPr•HBF$_4$)	0%

Reactions were performed with 5 mol% Pd/Al$_2$O$_3$ (ABCR, Escat 1241), 2.5 mol% IPr•HBF$_4$ and 2.5 equiv KOtBu at 110 °C.

3. Isolation of products

General procedure

Unless otherwise noted, toluene (2 mL) was added to a mixture of Pd/Al$_2$O$_3$ (44 mg, 0.02 mmol, 5.0 mol%), IPr•HBF$_4$ (4.8 mg, 0.01 mmol, 2.5 mol%) and KO^{t}Bu (112 mg, 1.0 mmol, 2.5 equiv). After one minute of stirring, the corresponding aryl halide (0.40 mmol, 1.0 equiv) was added and the reaction mixture was stirred for an additional minute at room temperature. The corresponding amine (0.44 mmol, 1.2 equiv) was added and the reaction mixture was stirred for 4 h at 110 °C. After the reaction mixture was cooled down to room temperature, the reaction mixture was filtered over silica (EtOAc rinse) and concentrated. Purification by flash column chromatography afforded the corresponding product.

Diphenylamine (5a)
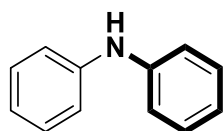
The desired product **5a** was synthesized according to the general procedure starting from bromobenzene (42 μL, 0.40 mmol, 1.0 equiv), chlorobenzene (40.5 μL, 0.40 mmol, 1.0 equiv) or iodobenzene (44.5 μL, 0.40 mmol, 1.0 equiv) and aniline (43 μL, 0.44 mmol, 1.2 equiv) respectively. The desired product **5a** was obtained after flash column chromatography eluting with 4% EtOAc in *n*-pentane as a white solid (for bromobenzene: 63 mg, 0.37 mmol, 93%; for chlorobenzene: 53 mg, 0.31 mmol, 78%; for iodobenzene 65 mg, 0.38 mmol, 96%).
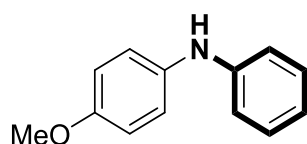
R$_f$: 0.29 (4% EtOAc in *n*-pentane).

^{1}H-NMR (400 MHz, CDCl$_3$): δ = 7.33 – 7.27 (m, 4H), 7.13 – 7.08 (m, 4H), 6.99 – 6.93 (m, 2H), 5.72 (bs, 1H).

^{13}C-NMR (101 MHz, CDCl$_3$): δ = 143.2, 129.5, 121.1, 117.9.

HR-MS (ESI): Found (M+H$^+$) 170.0972. C$_{12}$H$_{11}$NH$^+$ requires 170.0964.

4-Methoxy-*N*-phenylaniline (5b)

The desired product **5b** was synthesized according to the general procedure starting from bromoanisole (50.5 μL, 0.40 mmol, 1.0 equiv) and aniline (43 μL, 0.44 mmol, 1.2 equiv). The desired product **5b** was obtained after flash column chromatography eluting with 5% EtOAc in *n*-pentane as a white solid (68 mg, 0.34 mmol, 85%).
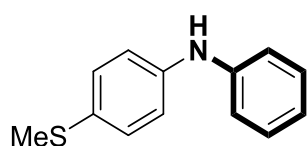
*R*f: 0.27 (5% EtOAc in *n*-pentane).

^{1}H-NMR (400 MHz, CDCl$_3$): δ = 7.16 – 7.08 (m, 2H), 7.01 – 6.95 (m, 2H), 6.84 – 6.80 (m, 2H), 6.79 – 6.71 (m, 3H), 5.33 (bs, 1H), 3.70 (s, 3H).

^{13}C-NMR (101 MHz, CDCl$_3$): δ = 155.4, 145.2, 135.8, 129.4, 122.3, 119.7, 115.8, 114.8, 55.7.

HR-MS (ESI): Found (M+H$^+$) 200.1071. C$_{13}$H$_{13}$NOH$^+$ requires 200.1070.

4-(Methylthio)-*N*-phenylaniline (5c)

The desired product **5c** was synthesized according to the general procedure starting from (4-bromophenyl)-(methyl)sulfane (81.2 mg, 0.40 mmol, 1.0 equiv) and aniline (43 μL, 0.44 mmol, 1.2 equiv). The desired product **5c** was obtained after flash column chromatography eluting with 2% EtOAc in *n*-pentane as an off-white solid (58 mg, 0.27 mmol, 67%).
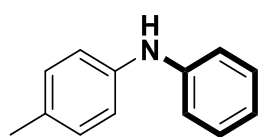
*R*f: 0.35 (5% EtOAc in *n*-pentane).

^{1}H-NMR (300 MHz, CDCl$_3$): δ = 7.35 – 7.24 (m, 4H), 7.13 – 7.02 (m, 4H), 7.02 – 6.93 (m, 1H), 5.72 (bs, 1H), 2.50 (s, 3H).

^{13}C-NMR (75 MHz, CDCl$_3$): δ = 143.1, 141.4, 129.9, 129.5, 129.1, 121.2, 118.6, 117.8, 17.9.

HR-MS (ESI): Found (M$^+$) 215.0757. C$_{13}$H$_{13}$NS$^+$ requires 215.0763.

4-Methyl-*N*-phenylaniline (5d)

The desired product **5d** was synthesized according to the general procedure starting from 1-bromo-4-methylbenzene (49.5 μL, 0.40 mmol, 1.0 equiv) and aniline (43 μL, 0.44 mmol, 1.2 equiv). The desired product **5d** was obtained after flash column chromatography eluting with 2% EtOAc in *n*-pentane as a white solid (67 mg, 0.37 mmol, 91%).
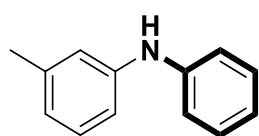
*R*f: 0.26 (2% EtOAc in *n*-pentane).

^{1}H-NMR (300 MHz, CDCl$_3$): δ = 7.19 – 7.10 (m, 2H), 7.02 – 6.96 (m, 2H), 6.94 – 6.87 (m, 4H), 6.83 – 6.74 (m, 1H), 5.48 (bs, 1H), 2.21 (s, 3H).

^{13}C-NMR (75 MHz, CDCl$_3$): δ = 144.0, 140.3, 131.0, 129.9, 129.4, 120.3, 118.9, 116.9, 20.8.

HR-MS (ESI): Found (M+H$^+$) 184.1124. C$_{13}$H$_{13}$NH$^+$ requires 184.1121.

3-Methyl-*N*-phenylaniline (5e)

The desired product **5e** was synthesized according to the general procedure starting from 1-bromo-3-methylbenzene (48.5 μL, 0.40 mmol, 1.0 equiv) and aniline (43 μL, 0.44 mmol, 1.2 equiv). The desired product **5e** was obtained after flash column chromatography eluting with 1% EtOAc in *n*-pentane as a colorless oil (70 mg, 0.38 mmol, 95%).
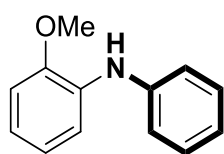
R$_f$: 0.22 (1% EtOAc in *n*-pentane).

^{1}H-NMR (300 MHz, CDCl$_3$): δ = 7.37 – 7.27 (m, 2H), 7.24 – 7.17 (m, 1H), 7.14 – 7.08 (m, 2H), 7.03 – 6.90 (m, 3H), 6.85 – 6.77 (m, 1H), 5.68 (bs, 1H), 2.36 (s, 3H).

^{13}C-NMR (75 MHz, CDCl$_3$): δ = 143.3, 143.1, 139.3, 129.4, 129.3, 122.0, 121.0, 118.6, 117.9, 115.0, 21.7.

HR-MS (ESI): Found (M+H$^+$) 184.1123. C$_{13}$H$_{13}$NH$^+$ requires 184.1121.

2-Methoxy-*N*-phenylaniline (5f)

The desired product **5f** was synthesized according to the general procedure starting from 1-bromo-2-methoxybenzene (50.0 μL, 0.40 mmol, 1.0 equiv) and aniline (43 μL, 0.44 mmol, 1.2 equiv). The desired product **5f** was obtained after flash column chromatography eluting with 2% EtOAc in *n*-pentane as a yellow (65 mg, 0.33 mmol, 82%).
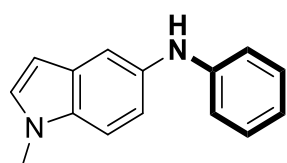
R$_f$: 0.28 (5% EtOAc in *n*-pentane).

^{1}H-NMR (300 MHz, CDCl$_3$): δ = 7.38 – 7.28 (m, 3H), 7.23 – 7.17 (m, 2H), 7.02 – 6.95 (m, 1H), 6.94 – 6.87 (m, 3H), 6.20 (bs, 1H), 3.92 (s, 3H).

^{13}C-NMR (75 MHz, CDCl$_3$): δ = 148.3, 142.8, 133.0, 129.4, 121.2, 120.9, 120.0, 118.6, 114.7, 110.6, 55.7.

HR-MS (ESI): Found (M+Na$^+$) 222.0892. C$_{13}$H$_{13}$NONa$^+$ requires 222.0889.

1-Methyl-N-phenyl-1*H*-indol-5-amine (5g)

The desired product **5g** was synthesized according to the general procedure starting from 5-bromo-1-methyl-1*H*-indole (84 mg, 0.40 mmol, 1.0 equiv) and aniline (43 μL, 0.44 mmol, 1.2 equiv). The desired product **5g** was obtained after flash

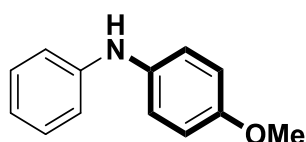column chromatography eluting with 10% EtOAc in *n*-pentane as an off-white solid (45 mg, 0.20 mmol, 51%).

R$_f$: 0.28 (10% EtOAc in *n*-pentane).

^{1}H-NMR (300 MHz, CDCl$_3$): δ = 7.43 (d, *J* = 2.1 Hz, 1H), 7.33 – 7.18 (m, 3H), 7.13 – 7.03 (m, 2H), 7.00 – 6.92 (m, 2H), 6.87 – 6.79 (m, 1H), 6.46 – 6.39 (m, 1H), 5.65 (bs, 1H), 3.80 (s, 3H).

^{13}C-NMR (75 MHz, CDCl$_3$): δ = 146.5, 134.7, 133.9, 129.6, 129.3, 129.2, 119.0, 118.1, 115.2, 113.6, 109.9, 100.6, 33.1.

HR-MS (ESI): Found (M+H$^+$) 223.1227. C$_{15}$H$_{14}$N$_2$H$^+$ requires 223.1230.

4-Methoxy-*N*-phenylaniline (5h)

The desired product **5h** was synthesized according to the general procedure starting from bromobenzene (42 μL, 0.40 mmol, 1.0 equiv) and 4-methoxyaniline (49.3 mg, 0.44 mmol, 1.2 equiv). The desired product **5h** was obtained after flash column chromatography eluting with 2% EtOAc in *n*-pentane as a white solid (65 mg, 0.33 mmol, 82%).
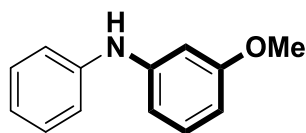
R$_f$: 0.10 (2% EtOAc in *n*-pentane).

^{1}H-NMR (300 MHz, CDCl$_3$): δ = 7.17 – 7.08 (m, 2H), 7.02 – 6.93 (m, 2H), 6.86 – 6.70 (m, 5H), 5.40 (bs, 1H), 3.70 (s, 3H).

^{13}C-NMR (75 MHz, CDCl$_3$): δ = 155.3, 145.2, 135.8, 129.4, 122.3, 119.6, 115.7, 114.8, 55.7.

HR-MS (ESI): Found (M+H$^+$) 200.1074. C$_{13}$H$_{13}$NOH$^+$ requires 200.1070.

3-Methoxy-*N*-phenylaniline (5i)

The desired product **5i** was synthesized according to the general procedure starting from bromobenzene (42 μL, 0.40 mmol, 1.0 equiv) and 3-methoxyaniline (45 μL, 0.44 mmol, 1.2 equiv). The desired product **5i** was obtained after flash column chromatography eluting with 2% EtOAc in *n*-pentane as a colorless oil (56 mg, 0.28 mmol, 70%).
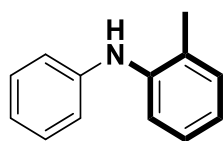
R$_f$: 0.14 (2% EtOAc in *n*-pentane).

^{1}H-NMR (300 MHz, CDCl$_3$): δ = 7.34 – 7.26 (m, 2H), 7.23 – 7.16 (m, 1H), 7.14 – 7.09 (m, 2H), 7.00 – 6.94 (m, 1H), 6.71 – 6.55 (m, 2H), 6.54 – 6.49 (m, 1H), 5.74 (bs, 1H), 3.80 (s, 3H).

^{13}C-NMR (75 MHz, CDCl$_3$): δ = 160.8, 144.7, 142.9, 130.2, 129.4, 121.3, 118.4, 110.3, 106.2, 103.3, 55.3.

HR-MS (ESI): Found (M+H$^+$) 200.1077. C$_{13}$H$_{13}$NOH$^+$ requires 200.1070.

2-Methyl-*N*-phenylaniline (5j)

The desired product **5j** was synthesized according to the general procedure starting from bromobenzene (42 μL, 0.40 mmol, 1.0 equiv) and 2-methylaniline (53 μL, 0.44 mmol, 1.2 equiv). The desired product **5j** was obtained after flash column chromatography eluting with 2% EtOAc in *n*-pentane as a yellow oil (50 mg, 0.27 mmol, 68%).
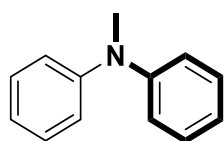
R$_f$: 0.24 (2% EtOAc in *n*-pentane).

^{1}H-NMR (300 MHz, CDCl$_3$): δ = 7.27 – 7.08 (m, 5H), 6.97 – 6.85 (m, 4H), 5.36 (bs, 1H), 2.24 (s, 3H).

^{13}C-NMR (75 MHz, CDCl$_3$): δ = 144.0, 141.2, 131.0, 129.3, 128.3, 126.8, 122.0, 120.5, 118.8, 117.5, 18.0.

HR-MS (ESI): Found (M+H$^+$) 184.1122. C$_{13}$H$_{13}$NH$^+$ requires 184.1121.

N-Methyl-*N*-phenylaniline (5k)

The desired product **5k** was synthesized according to the general procedure starting from bromobenzene (42 μL, 0.40 mmol, 1.0 equiv) and *N*-methylaniline (52 μL, 0.44 mmol, 1.2 equiv). The desired product **5k** was obtained after flash column chromatography eluting with 1% EtOAc in *n*-pentane as a yellow oil (38 mg, 0.21 mmol, 52%).
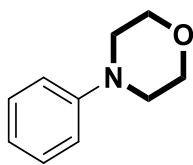
R$_f$: 0.32 (1% EtOAc in *n*-pentane).

^{1}H-NMR (300 MHz, CDCl$_3$): δ = 7.33 – 7.26 (m, 4H), 7.07 – 7.02 (m, 4H), 7.00 – 6.93 (m, 2H), 3.33 (s, 3H).

^{13}C-NMR (75 MHz, CDCl$_3$): δ = 149.1, 129.3, 121.4, 120.6, 40.4.

HR-MS (ESI): Found (M+H$^+$) 184.1119. C$_{13}$H$_{13}$NH$^+$ requires 184.1121.

4-Phenylmorpholine (5l)

The desired product **5l** was synthesized according to the general procedure starting from bromobenzene (42 μL, 0.40 mmol, 1.0 equiv) and morpholine (41.5 μL, 0.44 mmol, 1.2 equiv). The desired product **5l** was obtained after flash column chromatography eluting with 4% EtOAc in *n*-pentane as a white solid (56 mg, 0.28 mmol, 70%).

R_f: 0.16 (4% EtOAc in *n*-pentane).

^{1}H-NMR (300 MHz, CDCl$_3$): δ = 7.34 – 7.7.25 (m, 2H), 6.96 – 6.86 (m, 3H), 3.88 (t, J = 4.8 Hz, 4H), 3.17 (t, J = 4.8 Hz, 4H).

^{13}C-NMR (75 MHz, CDCl$_3$): δ = 51.4, 129.3, 120.2, 115.8, 67.1, 49.5.

HR-MS (ESI): Found (M+H$^+$) 164.1079. C$_{10}$H$_{13}$NOH$^+$ requires 164.1070.

4. Mechanistic investigations

4.1 Reaction kinetics

The reaction was performed according to the general procedure on a 0.2 mmol scale starting from bromobenzene and aniline. Yields of **5a** were determined by GC-FID analysis using mesitylene as standard.

Table S12. Kinetics of the Buchwald-Hartwig amination depending on the NHC-loading.

t/min	1.25 mol% IPr	2.5 mol% IPr	5.0 mol% IPr	7.5 mol% IPr	10.0 mol% IPr
20	5%	6%	3%	6%	6%
40	25%	29%	15%	18%	14%
60	58%	65%	37%	31%	26%
80	80%	88%	62%	58%	46%
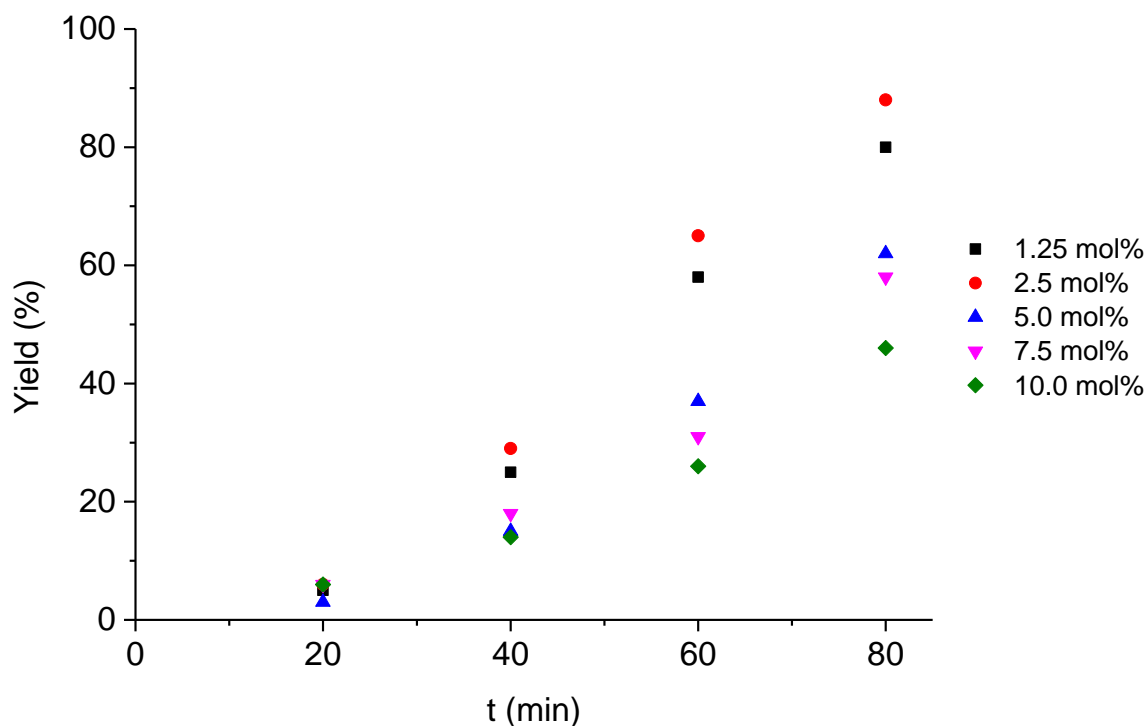
Figure S1. Kinetic profile of the Buchwald-Hartwig amination depending on the NHC-loading.

4.2 Mercury drop test

The mercury drop test is a widely applied method to investigate the nature of the catalytically active species. After addition of mercury to the reaction mixture the reaction should not continue if the catalytically active species is heterogeneous in nature as palladium forms catalytically inactive amalgams rapidly.

The reaction was performed according to the general procedure on a 0.2 mmol scale starting from bromobenzene and aniline. After 25 minutes at 110 °C, mercury (25 μL, 1.63 mmol, 163 equiv Pd) was added to the reaction mixture and the reaction was heated for 215 min at 110 °C. Yields of **5a** were determined by GC-FID analysis using mesitylene as standard.

Table S13. Mercury drop test.

t / min	Hg-addition reaction	Control reaction
25 min - before Hg-addition	10%	12%
240 min	14%	85%

The result that the reaction is stopped by adding mercury to the reaction mixtures though the control reaction without mercury continues indicate that the catalytically active species is heterogeneous in nature. Furthermore, we added mercury to the corresponding homogeneous catalyst system and the reaction was not inhibited by the addition of mercury.

4.3 Hot filtration test

The hot filtration test is a widely applied method to investigate the nature of the catalytically active species. After filtration of the reaction mixture to remove the heterogeneous catalyst, the reaction should not continue if the catalytically active species is heterogeneous in nature.

The reaction was performed according to the general procedure on a 0.2 mmol scale starting from bromobenzene and aniline. After 25 min at 110 °C, the reaction mixture was filtered over Celite and the filtrate was heated for 215 min at 110 °C. Yields of **5a** were determined by GC-FID analysis using mesitylene as standard.

Table S14. Hot filtration experiments.

t / min	Filtered reaction	Control reaction
20 min - before filtration	8%	12%
240 min	8%	85%

The result that the reaction is stopped by removing the heterogeneous catalysts though the control reaction continues indicate that the catalytically active species is heterogeneous in nature.

4.4 3-Phase test

Synthesis of immobilized substrate
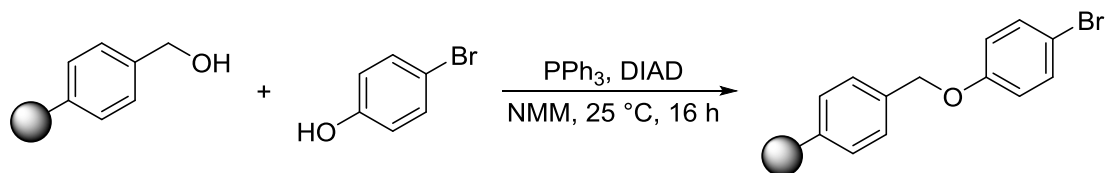
Commercially available Wang-resin (100-200 mesh, 1.0-1.5 mmol/g OH loading, 1% crosslinked with divinylbenzene) was washed with CH_2Cl_2 and EtOH and dried *in vacuo* prior to use. To a suspension of Wang-resin (650 mg, 0.98 mmol, 1.0 equiv), PPh_3 (768 mg, 2.93 mmol, 3.0 equiv) and 4-bromophenol (507 mg, 2.93 mmol, 3.0 equiv) in NMM (2.6 ml) DIAD (580 μL, 2.93 mmol, 3.0 equiv) was added dropwise at room temperature. The reaction mixture was sonicated for 1 h prior to stirring at room temperature for 16 h. The reaction mixture was filtered, the residue washed with THF, CH_2Cl_2, MeOH, H_2O, MeOH, CH_2Cl_2 (30 mL each) and dried *in vacuo*.

To determine the loading of the substrate, 50 mg of the Wang-resin were stirred in a TFA/CH_2Cl_2-mixture (4 mL, 3:1) at room temperature for 2 h. The reaction mixture was filtered, the residue washed with CH_2Cl_2 (20 mL) and the filtrate was washed with sat. aqueous $NaHCO_3$-solution (2 x 30 mL). The combined aqueous layer was extracted with CH_2Cl_2 (2 x 30 mL) and the combined organic layer was dried over Na_2SO_4 and concentrated under reduced pressure. The mass of the isolated material allowed for the determination of the loading of the Wang resin (0.80 mmol/g). The obtained material was analyzed by GC-MS and ^{1}H-NMR.

3-Phase test
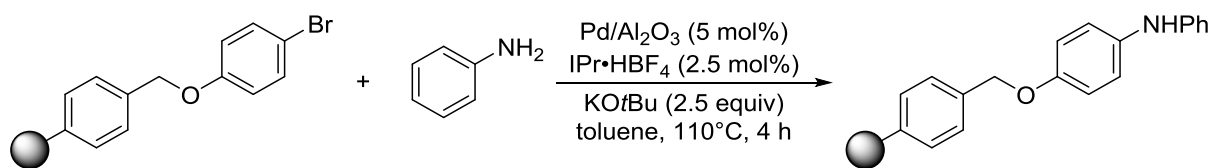
The reactions were performed according to the general procedure on a 0.2 mmol scale substituting bromobenzene with the immobilized 4-bromophenol (127 mg). To the determine whether the immobilized substrate reacted under the reaction conditions, the reaction mixture was filtered and the residue was stirred in a TFA/ CH_2Cl_2-mixture (4 mL, 3:1) at room temperature for 2 h. The reaction mixture was filtered, the residue washed with CH_2Cl_2 (20 mL) and the filtrate was washed with sat. aqueous $NaHCO_3$-solution (2 x 30 mL). The combined aqueous layer was extracted

with CH_2Cl_2 (2 x 30 mL) and the combined organic layer was dried over Na_2SO_4 and concentrated under reduced pressure. The obtained material was analyzed by GC-MS and ESI-MS.

Different scenarios were tested to determine whether the catalytically active species is heterogeneous in nature.

1) *The standard reaction was undertaken in the presence of unmodified Wang-resin and bromobenzene (1.0 equiv) to determine whether the resin poisons the reaction.*
Result: The reaction was not poisoned by the resin as product formation could be observed.

2) *The reaction was undertaken with the immobilized substrate.*
Result: No product formation in solution and on the solid support could be observed. Furthermore, no cleavage of the immobilized substrate could be observed proving the stability of the immobilization under reaction conditions. These observations strongly suggest that no homogeneous catalytically active species is present under the reaction conditions.

3) *The reaction was performed using less reactive 4-bromoanisole and the immobilized substrate to determine whether the activity of the catalyst is preserved in the presence of the immobilized substrate.*
Result: Only the formation of 4-methoxy-*N*-phenylaniline in solution was observed. No product formation on the solid support could be observed. These observations strongly support that the catalytically active species is heterogeneous in nature.

4) *The reaction was performed using the corresponding homogeneous catalyst system to determine whether this is able to perform the reaction with the immobilized substrate.*
Result: Product formation on the solid support could be observed. This clearly supports that the catalytically active species is heterogeneous in nature as, in the case of a homogeneous catalytically active species, the reaction of the immobilized substrate with aniline is possible.

4.5 Poisoning experiments

The reaction was performed according to the general procedure on a 0.1 mmol scale starting from bromobenzene and aniline in the presence of different catalyst poisons. Yields of **5a** were determined by GC-FID analysis using mesitylene as standard.

Table S15. Effect of catalyst poisons on the reaction.

Catalyst poison	Yield **4a**
PPh$_3$ (1.0 equiv)	4%
benzyl mercaptan (1.0 equiv)	traces

Strongly coordinating catalyst poisons, represented by PPh$_3$ and benzyl mercaptan, significantly inhibit the reaction.

4.6 NHC-modified catalyst

In a flame-dried Schlenk flask, IPr•HBF$_4$ (112 mg, 0.24 mmol, 1.0 equiv) and KO*t*Bu (31.6 mg, 0.28 mmol, 1.2 equiv) were stirred for 4 h at room temperature in toluene. The reaction mixture was filtered over Celite. The filtrate was added to Pd/Al$_2$O$_3$ (1000 mg, 0.47 mmol Pd, 2.0 equiv) and the catalyst was impregnated with the IPr-solution for 1 h at room temperature. The catalyst was allowed to settle and the supernatant was removed by syringe. The catalyst was dried *in vacuo*. ICy@Pd/Al$_2$O$_3$ was prepared according to this procedure. For the preparation of ^{13}C-labelled samples, the corresponding ^{13}C-labelled imidazolium salt (labelling in the C1-position) was applied.

The reaction with the NHC-modified catalyst was performed according to the general procedure on a 0.4 mmol using bromobenzene and aniline as starting materials. Product **5a** was isolated after column chromatography eluting with 4% EtOAc in *n*-pentante as a white solid (62 mg, 0.37 mmol, 92%).

4.7 Determination of metal amount in solution by TXRF

The reactions were performed according to the general procedure on a 0.2 mmol scale starting from bromobenzene and aniline. After the corresponding reaction time, the reaction solution was filtered hot over glass wool to remove insoluble material and to prevent precipitation or readsorption of soluble species at lower temperatures. The samples were subsequently analyzed by TXRF spectroscopy.

Table S16. Pd-concentration at different times during the reaction determined by TXRF spectroscopy.

t / h	*Pd-concentration*
1	<0.41 ppm
2	<0.41 ppm
3	0.76 ppm
4	4.17 ppm

According to the low amount of palladium in solution during the first three hours and the fact that the reaction of bromobenzene and aniline reaches full conversion within two hours, the TXRF-results support the fact that the catalytically active species is heterogeneous in nature.

4.8 Mass spectrometry experiments

The reactions were performed according to the general procedure on 0.1 mmol scale starting from bromobenzene and aniline. After the corresponding reaction time, the reaction solution was analyzed by mass spectrometry (ESI).

Table S17. Mass spectrometry results of the reaction mixture at different reaction times.

t / h	*Mass spectrometry results*
1	no Pd-complex observed
2	traces of catalytically inactive Pd(IPr)$_2$H$^+$ observed (m/z = 883.4860)
3	traces of catalytically inactive Pd(IPr)$_2$H$^+$ observed (m/z = 883.4860)

The observation of only catalytically inactive Pd-species by mass spectrometry in the reaction solution after two and three hours and the fact that already 65% of product are formed within one hour suggest that the catalytically active species is heterogeneous in nature.

4.9 Hydrogenolysis of bromobenzene

Toluene (0.8 mL) was added to a mixture of Pd/Al$_2$O$_3$ (22 mg, 0.01 mmol, 5.0 mol%), corresponding NHC•HBF$_4$ (0.005 mmol, 2.5 mol%) and KO^{t}Bu (56 mg, 0.5 mmol, 2.5 equiv). After one minute of stirring, the bromobenzene (21 µL, 0.2 mmol, 1.0

equiv) was added and the reaction mixture was stirred for an additional minute at room temperature. Ethanol (0.2 mL) was added and the reaction mixture was stirred at 80 °C. Yields of product **2** were determined by GC-FID analysis using mesitylene as standard.

Table S18. Kinetics of the hydrogenolysis of bromobenzene depending on the applied.

t/min	no NHC	IMes	IPr	ICy	IMe
10	17%	34%	34%	19%	26%
20	41%	65%	63%	39%	50%
30	45%	77%	75%	50%	57%
40	47%	85%	83%	56%	61%
50	47%	88%	87%	58%	61%
60	48%	88%	91%	61%	61%

4.10 Recycling experiments

The reactions were performed according to the general procedure on 0.1 mmol scale starting from bromobenzene and aniline. After the corresponding reaction time, the reaction mixture was allowed to settle and the supernatant was removed. The remaining catalyst was washed with various different solvents (water, EtOH, toluene, THF, CH_2Cl_2) and subsequently dried *in vacuo*. The second cycle was performed according to the general procedure with KOtBu (2.5 equiv), bromobenzene (1.0 equiv) and aniline (1.5) though no remaining catalytic activity could be observed in all cases. This is likely due to poisoning of the catalyst surface by KBr which could be observed *via* STEM-EDS analysis of the catalyst after the reaction. Additionally, morphological changes of the catalyst could lead to the loss of activity.
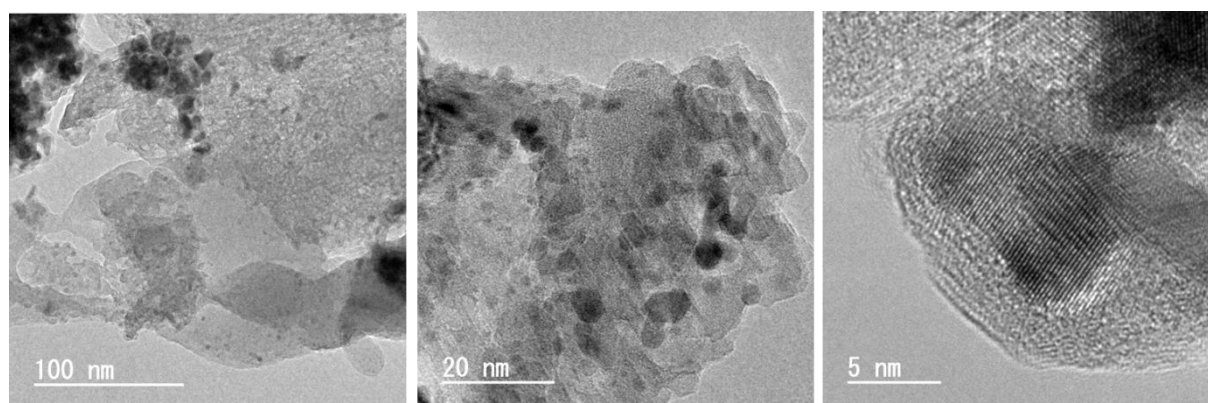

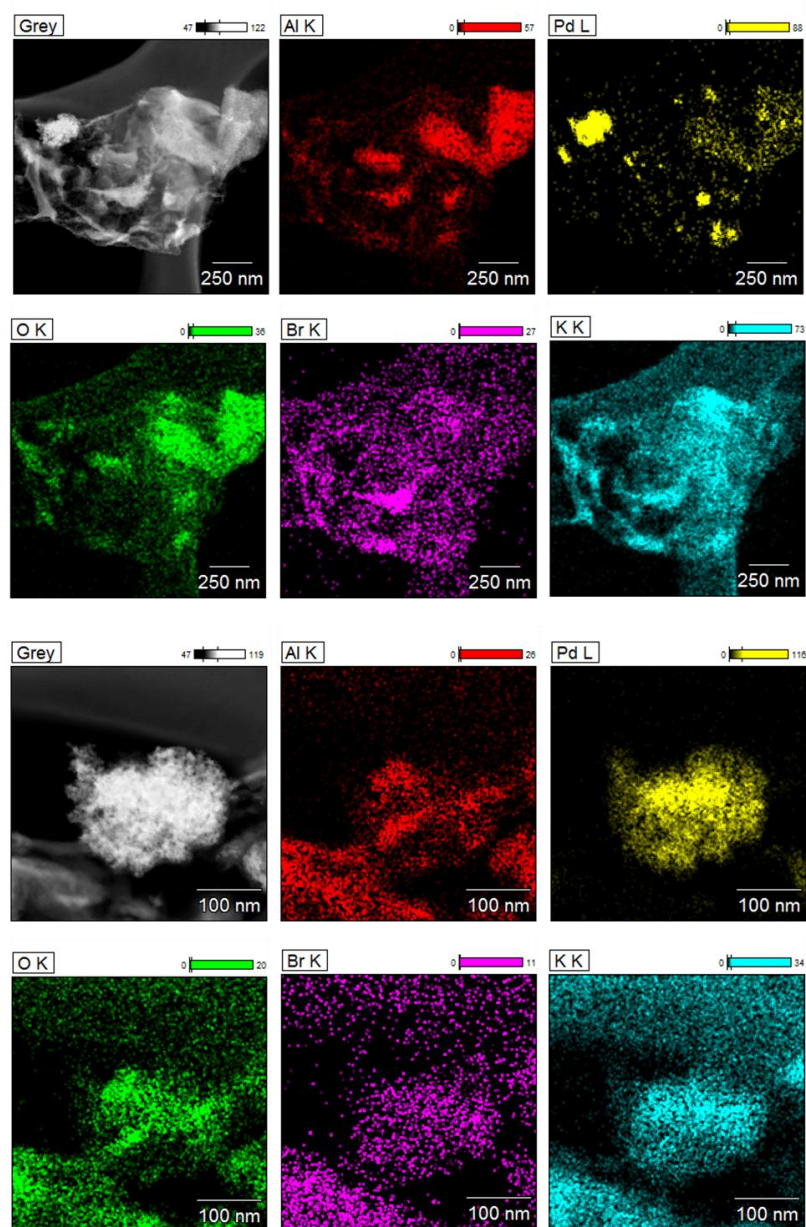**Figure S2:** TEM images of IPr@Pd/Al_2O_3 after the reaction

Figure S3: STEM-EDS images of IPr@Pd/Al$_2$O$_3$ after the reaction.

5. Structural analysis of the catalyst

NMR spectroscopy

The ^{13}C solid-state (SS) magic angle spinning (MAS) NMR spectra of solid samples (^{13}C-labelled IPr@Pd/Al$_2$O$_3$, unlabeled IPr@Pd/Al$_2$O$_3$, and ^{13}C-labelled IPr@Al$_2$O$_3$) were recorded on an NMR spectrometer (ECX-400, JEOL) using a cross-polarization (CP) method. The magic angle spinning rates were 10 kHz and 8 kHz for distinguishing genuine signals from side-band signals. The relaxation decay, the contact time, and the scan number were 0.5 s, 5 ms, and 1,000,000, respectively. Hexamethylbenzene (^{13}C: 17.17 ppm) was used as an external standard for calibrating chemical shifts.

X-ray photoelectron spectroscopy (XPS)

XPS spectra of IPr@Pd/Al$_2$O$_3$, ICy@Pd/Al$_2$O$_3$, IPr@Al$_2$O$_3$, and Pd/Al$_2$O$_3$ were recorded with an ECSA3057, (ULVAC Phi.) using an Al Kα X-ray source (1486.7 eV). Narrow multiplex scans were recorded with 11.75 eV pass energy and 0.1 eV step size. A charge neutralization function was employed to compensate for charge built up on solid samples by X-ray irradiation. Binding energies were referenced to that of Al 2p as 74.0 eV.

Thermogravimetric analysis (TGA)

TGA measurements were conducted on a TGA550 (TA instrument Inc.). For TGA measurements, each sample (17~20 mg) was placed on a platinum pan, and was kept at 298 K for 10 min before measurements and heated under air at a rate of 10 K min^{-1}.

FT-IR spectroscopy

The FT-IR spectra of IPr@Pd/Al$_2$O$_3$ and Pd/Al$_2$O$_3$ were recorded on an FT-IR spectrometer in a diffuse reflectance mode (4 cm^{-1} resolution, FT/IR-4200, JASCO).

Transmission electron microscopy (TEM) and scanning transmission electron microscopy (STEM) with energy dispersive spectroscopy (EDS)

TEM and STEM-EDS images of IPr@Pd/Al$_2$O$_3$ and Pd/Al$_2$O$_3$ were taken on a JEM-2100F/HK transmission electron microscope (JEOL) using an accelerating voltage of 200 kV. Cu grids were directly mixed with samples, and the Cu grids were collected and mounted on a stage.
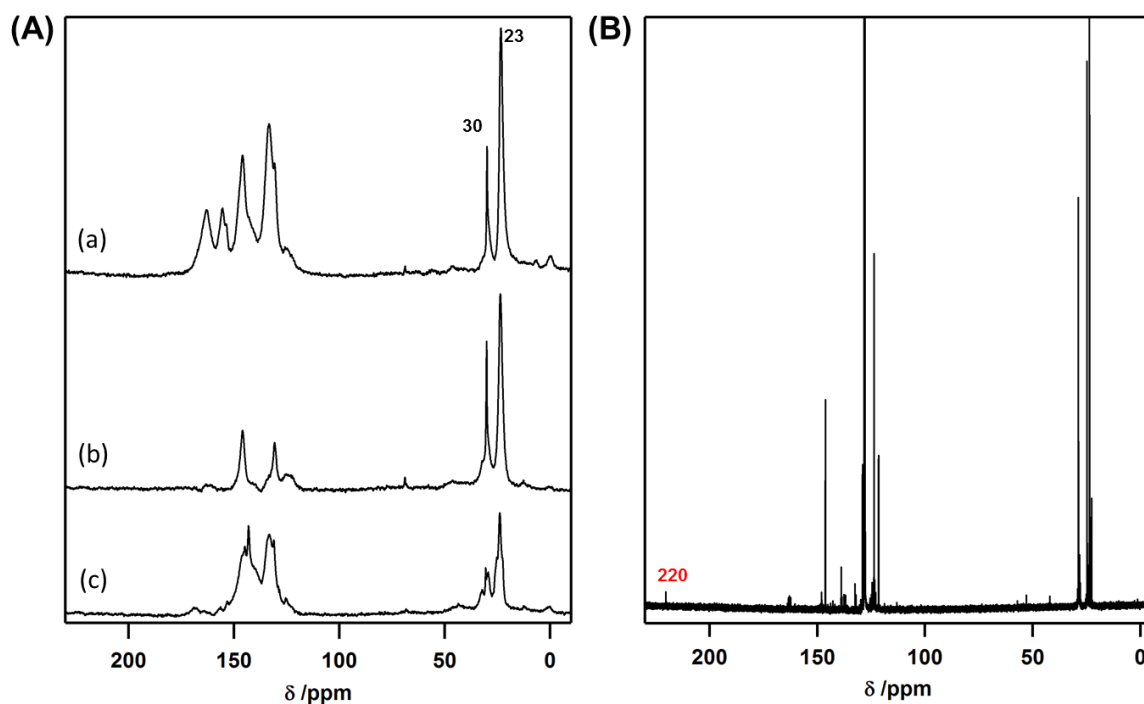
Figure S4: (A) ^{13}C-SS CP-MAS NMR spectra of (a) ^{13}C-labelled IPr@Pd/Al$_2$O$_3$, (b) unlabelled IPr@Pd/Al$_2$O$_3$, and (c) ^{13}C-labelled IPr@Al$_2$O$_3$. (B) ^{13}C LS NMR spectra of IPr (in d^6-benzene).
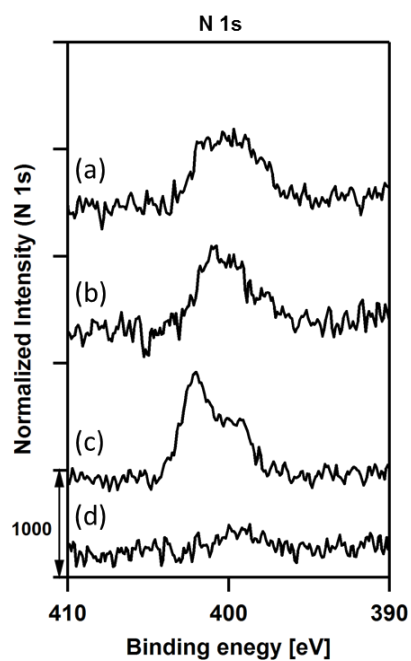
Figure S5: N 1s XPS spectra of NHC-modified Pd/Al$_2$O$_3$ and Al$_2$O$_3$. XPS spectra of (a) IPr@Pd/Al$_2$O$_3$, (b) ICy@Pd/Al$_2$O$_3$, (c) IPr@Al$_2$O$_3$ and (d) Pd/Al$_2$O$_3$.
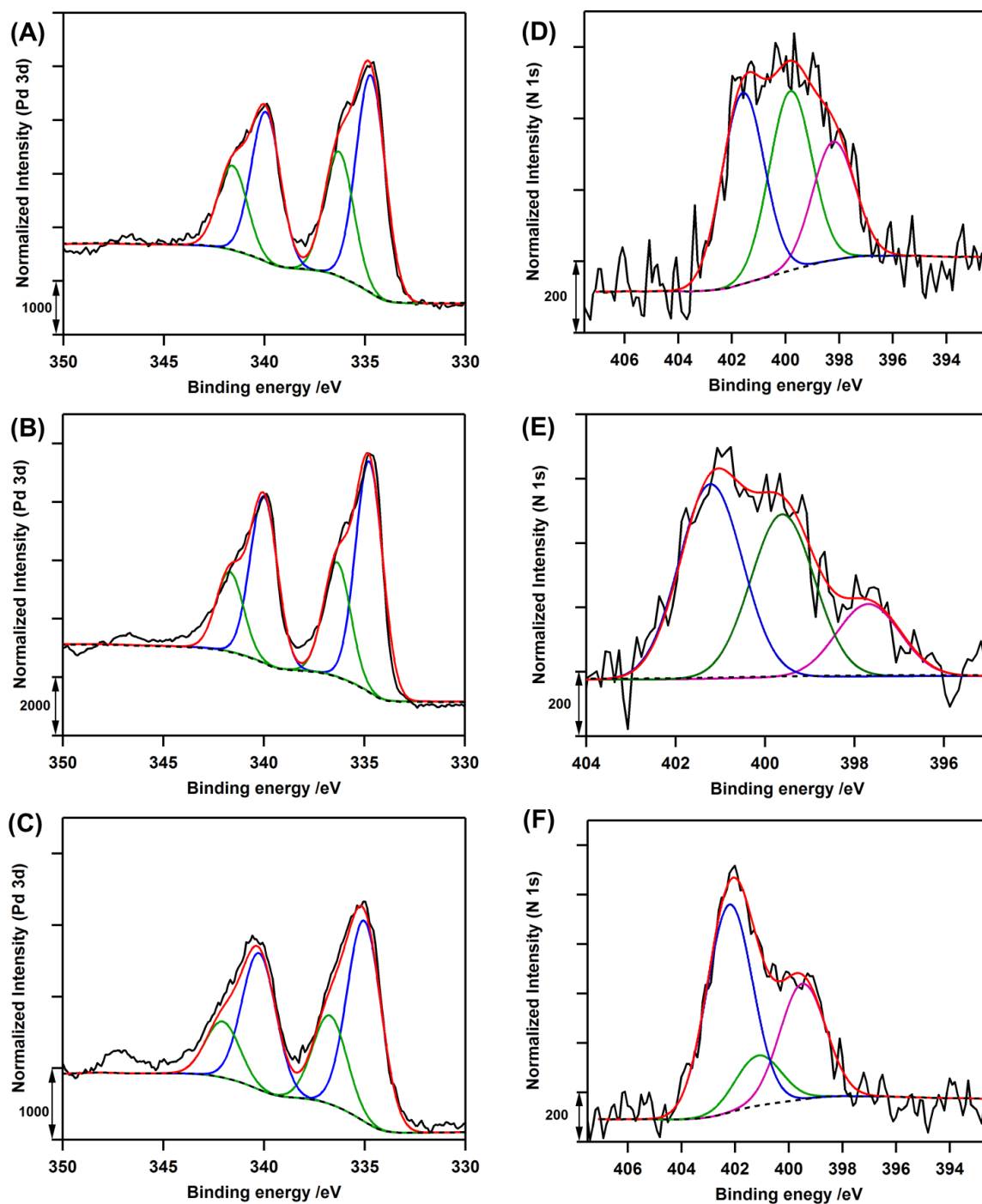
Figure S6: Curve fitting analyses of Pd 3d and N 1s XPS spectra of NHC-modified Pd/Al$_2$O$_3$. (A) A normalized Pd 3d (3d$_{3/2}$ and 3d$_{5/2}$) XPS spectrum of IPr@Pd/Al$_2$O$_3$ and its curve-fitting results, (B) A normalized Pd 3d (3d$_{3/2}$ and 3d$_{5/2}$) XPS spectrum of ICy@Pd/Al$_2$O$_3$ and its curve-fitting results, (C) A normalized Pd 3d (3d$_{3/2}$ and 3d$_{5/2}$) XPS spectrum of Pd/Al$_2$O$_3$ and its curve-fitting results, (D) A normalized N 1s XPS spectrum of IPr@Pd/Al$_2$O$_3$ and its curve-fitting results, (E) A normalized N 1s XPS spectrum of ICy@Pd/Al$_2$O$_3$ and its curve-fitting results, and (F) A normalized N 1s XPS spectrum of IPr@Al$_2$O$_3$ and its curve-fitting results.
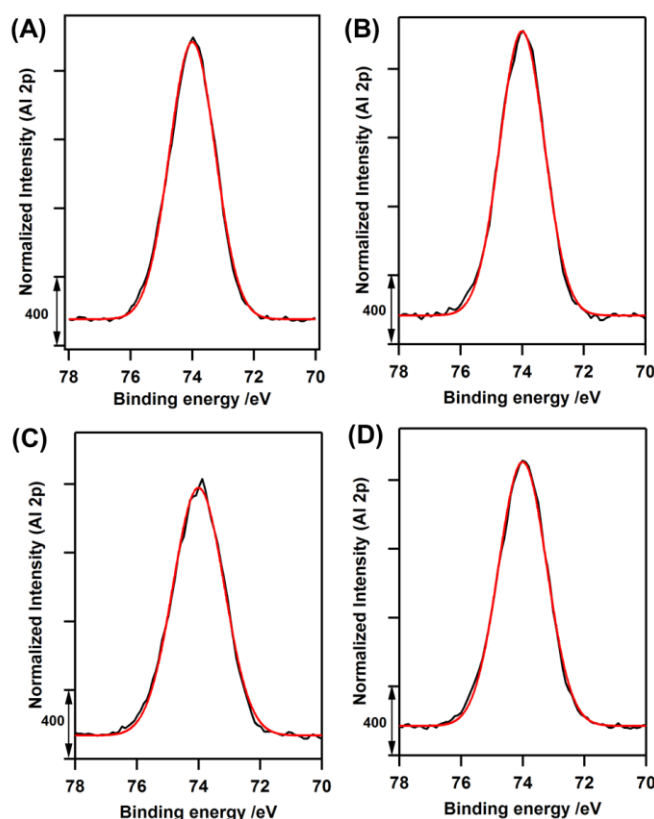
Figure S7: Curve fitting analyses of Al 2p of NHC-modified Pd/Al$_2$O$_3$. A normalized Al 2p XPS spectra of (A) IPr@Pd/Al$_2$O$_3$, (B) ICy@Pd/Al$_2$O$_3$, (C) Pd/ Al$_2$O$_3$, and (D) IPr@Al$_2$O$_3$, and their curve-fitting results.

Table S19. Curve-fitting data for Pd 3d, N 1s, and Al 2p XPS spectra.[a]

	Pd 3d $_{5/2}$				Pd 3d $_{3/2}$			
	Binding energy /eV	Area	Binding energy /eV	Area	Binding energy /eV	Area	Binding energy /eV	Area
IPr@Pd/Al$_2$O$_3$	334.7	7201	336.3	4157	339.9	5063	341.6	2910
ICy@Pd/Al$_2$O$_3$	334.8	6983	336.4	3462	340.0	5044	341.7	2414
Pd/Al$_2$O$_3$	335.0	5941	336.7	2621	340.3	4038	342.1	1659
IPr@Al$_2$O$_3$	---	---	---	---	---	---	---	---
	N 1s (1st)		N 1s (2nd)		N 1s (3rd)		Al 2p	
	Binding energy /eV	Area	Binding energy /eV	Area	Binding energy /eV	Area	Binding energy /eV	Area
IPr@Pd/Al$_2$O$_3$	398.2	657	399.8	996	401.6	1060	74.0	3000
ICy@Pd/Al$_2$O$_3$	397.7	203	399.6	450	401.2	535	74.0	3000
Pd/Al$_2$O$_3$	---	---	---	---	---	---	74.0	3000
IPr@Al$_2$O$_3$	399.5	1001	401.1	433	402.2	1797	74.0	3000

[a] Binding energies were referenced to that of Al 2p as 74.0 eV, and peak areas were normalized to that of Al 2p.
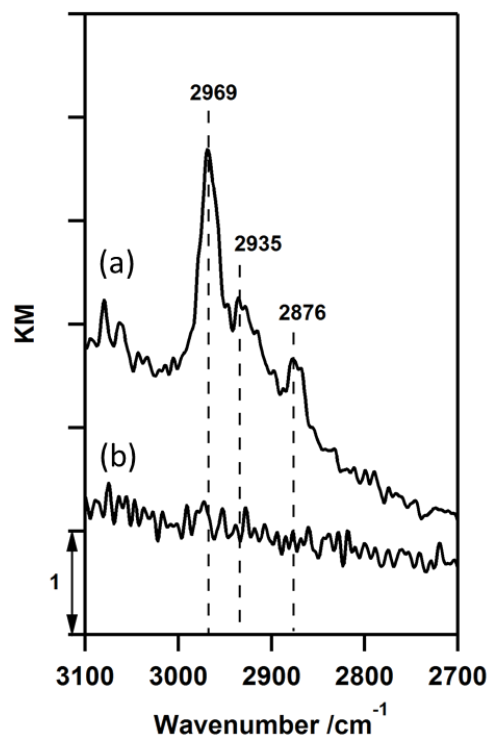
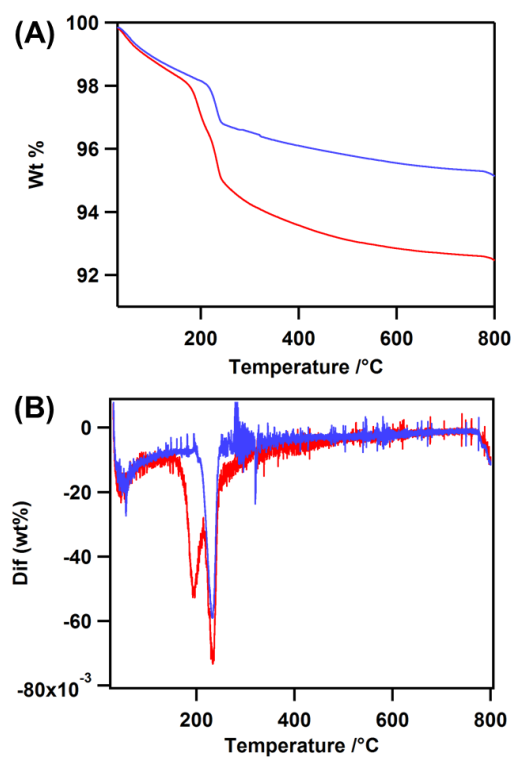**Figure S8:** FT-IR spectra of (a) IPr@Pd/Al$_2$O$_3$ and (b) Pd/Al$_2$O$_3$.

Figure S9: (A) TGA curves and (B) their differential plots for IPr@Pd/Al$_2$O$_3$ (red) and Pd/Al$_2$O$_3$ (blue).
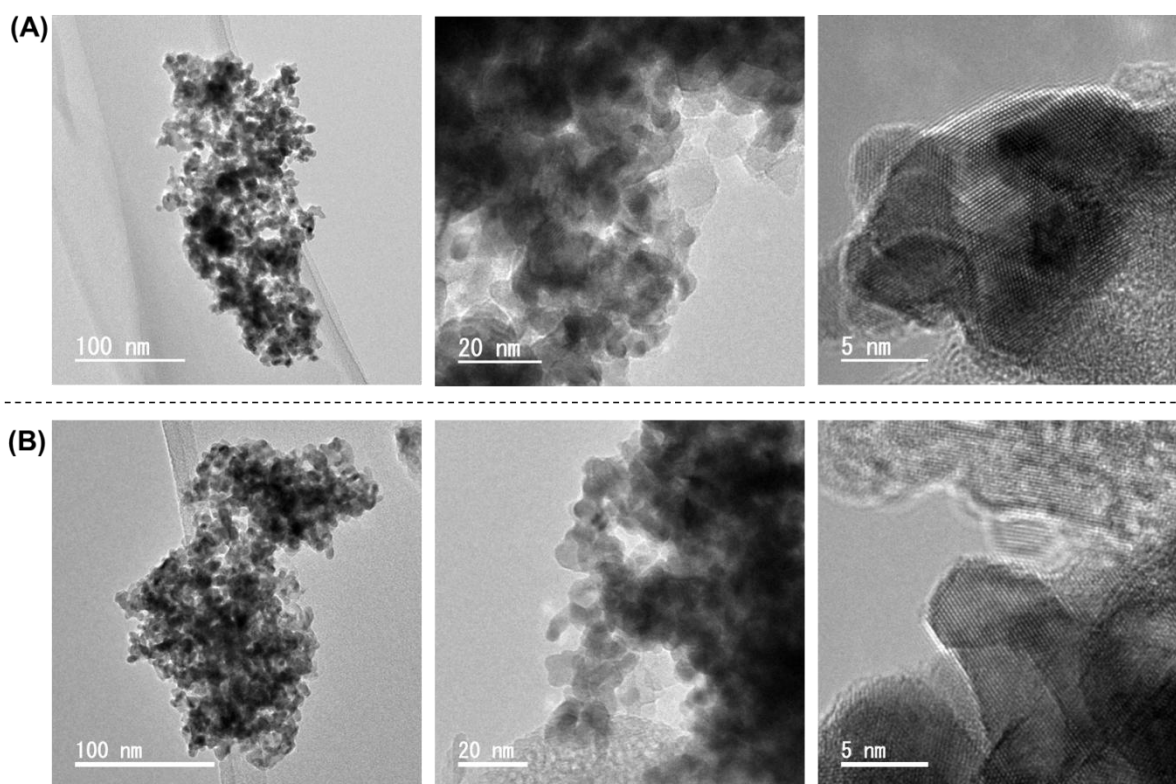
Figure S10: TEM images of (A) IPr@Pd/Al$_2$O$_3$ and (B) Pd/Al$_2$O$_3$.
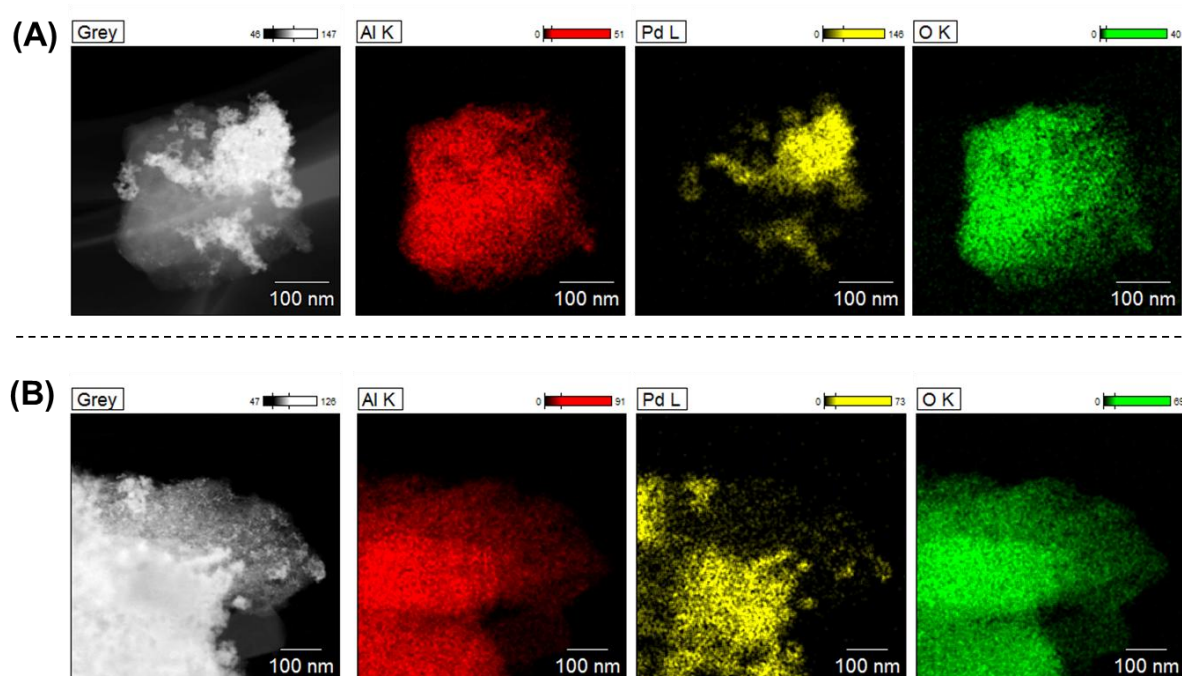

Figure S11: STEM-EDS images of (A) IPr@Pd/Al$_2$O$_3$ and (B) Pd/Al$_2$O$_3$.

6. *Ab initio* calculations

Computational Details

All DFT calculations were performed with the ORCA program package[1] using the PBE GGA density functional[2] and the def2SVP basis set of Ahlrichs and coworkers.[3] Quasi-relativistic Stuttgart-Dresden ECPs[4] replacing 28 core electrons were used for Pd atoms. The RI-J approximation[5] for Coulomb integrals was employed using the corresponding def2SVP/J auxiliary basis set.[6] No empirical dispersion corrections were used to avoid overestimations of bonding interactions between ligands and metal surfaces. Structures and orbitals were visualized using VMD 1.9.2 with the internal Tachyon renderer.[7]

To attain a consistent description of all spin states, all calculations were performed using the unrestricted Kohn-Sham formalism. Since the beta-spin orbitals of the Pd_{13} model system tend to have a very small band gap, Fermi smearing with a temperature of T=300 K was applied to the occupation numbers, to make the calculations feasible and to appropriately model an extended metal system. For all model systems geometry optimizations with standard convergence criteria were performed. Ionization potentials were obtained via a ΔSCF procedure, i.e. taking the energy difference of the neutral and the singly positively charged system. Since for most cases two singly positively charged spin states were possible, the one lowest in energy was used. Dissociation barriers were calculated by performing a relaxed potential hypersurface scan along the C-Br bond of an adsorbed bromobenzene molecule. The maxima were confirmed by transition state optimizations. Localized orbitals were calculated using the implementation of the Pipek-Mezey[8] localization procedure in ORCA.

Spin States

Table S20. Relative energies for optimized geometries of relevant spin states for the pure Pd_{13} cluster and with different adsorbates.

Spin	Energy relative to ground state E / eV						
2s+1	Pd_{13}	IMe	ICy	IMes	IPr	IPrCl	IPrMe
1	0.414	0.257	0.265	0.103	0.000	0.000	0.000
3	0.357	0.226	0.234	0.044	0.015	0.005	0.016
5	0.275	0.122	0.134	0.000	0.150	0.141	0.149
7	0.161	0.000	0.000	0.218	0.433	0.427	0.434
9	0.000	0.198	0.205	0.535	1.102	1.075	1.107

The spin states for the pure cluster follow the same trend already observed by Köster *et al.*[9] The overall lower relative energies obtained here result from the additional degree of freedom introduced by fractional occupation numbers.

The adsorption of a NHC lowers the energy of lower spin states, thus making the septet the ground state for IMe- and ICy-modified Pd_{13}. Interactions with aromatic N-substituents further stabilize low spin states, resulting in a minimum for the quintet of IMes-Pd_{13} and the singlet for IPr-Pd_{13} and its derivatives.

Partial charges

Table S21. Löwdin and ChelpG partial charges, summed over all Pd atoms.

	Pd_{13}	IMe	ICy	IMes	IPr	IPrCl	IPrMe
Löwdin / |e|	0.000	-0.698	-0.912	-1.638	-1.887	-1.872	-1.907
CHelpG / |e|	0.000	-0.298	-0.479	-0.586	-0.975	-1.127	-1.131

The calculated partial charges show that the adsorption of a NHC indeed increases the electron density of the Pd nanoparticle. Additionally a correlation between charges and ionization potentials (see table 21) can be observed.

Orbital energies and Ionization potentials (IPs)

Table S22. HOMO energies and IPs for the Pd_{13} cluster with various adsorbates. Calculated with the PBE GGA-functional.

	ε_{HOMO} / eV	IP / eV
Pd_{13}	-4.781	6.386
IMe	-4.315	5.781
ICy	-4.241	5.646
IMes	-3.958	5.389
IPr	-3.741	5.162
IPrCl	-3.855	5.206
IPrMe	-3.739	5.126

Table S23. HOMO energies and IPs for the Pd_{13} cluster with various adsorbates. Calculated with the PBE0 hybrid-functional.

	ε_{HOMO} / eV	IP / eV
Pd_{13}	-5.348	6.310
IMe	-4.831	5.752
ICy	-4.780	5.572
IMes	-4.548	5.356
IPr	-4.305	5.074
IPrCl	-4.413	5.143
IPrMe	-4.274	4.999

Since Koopmans' Theorem does not hold for DFT, the negative of the HOMO energy is not equal to the IP. However, for all model systems they are correlated. Additional evaluations using the PBE0 hybrid density functional[2,10] show significantly lower HOMO energies, but within the expected accuracy of DFT practically no change in ΔSCF-Ionization potentials, thus justifying the use of the computationally less expensive GGA functional PBE.
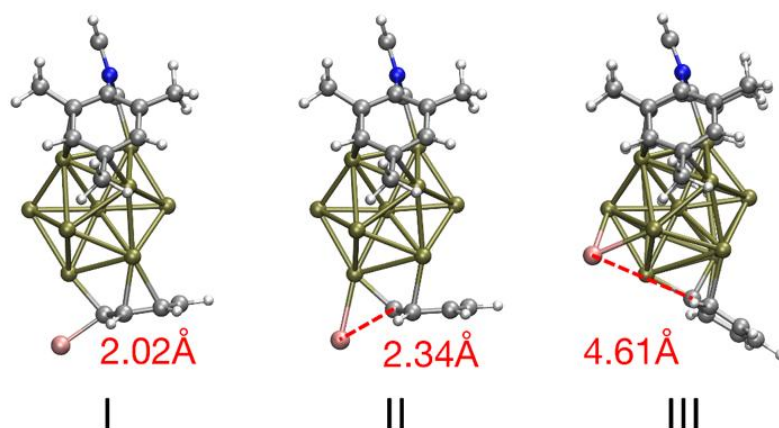
Reaction energetics

Figure S12. Calculated dissociation path of bromobenzene on IMes-stabilized Pd$_{13}$. I) Optimized geometry. II) Transition state. III) Optimized dissociated geometry.
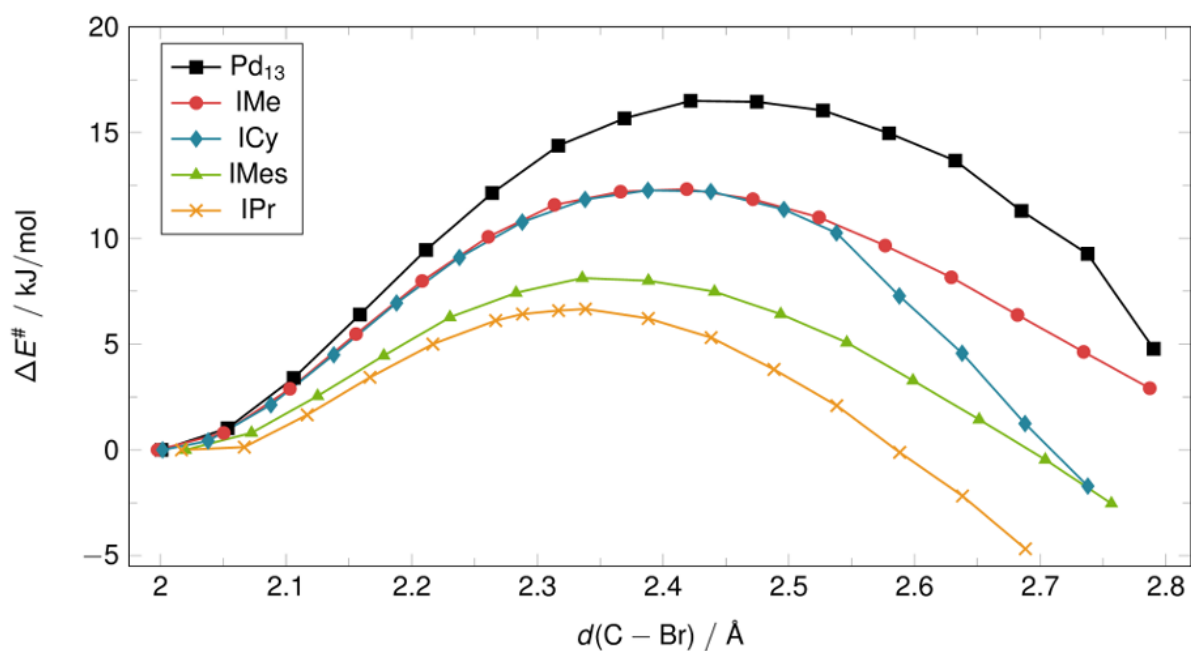

Figure S13. Dissociation barriers for bromobenzene on Pd$_{13}$ clusters with various adsorbates. The energies were normalized to the ground state energy of the initial, non-dissociated structure. E_r is obtained by performing geometry optimizations starting from the structure with largest distance d, i.e. the rightmost point. The resulting points are not shown in the graph.

Table S24. Barrier height $\Delta E^{\#}$, reaction energy E_r obtained by geometry optimization of dissociated geometries and C-Br distance d for the transition state. The numbers in parentheses were obtained by transition state optimization.

	Pd$_{13}$	IMe	ICy	IMes	IPr
$\Delta E^{\#}$ / kJ/mol	16.50 (16.75)	12.32 (12.39)	12.27 (12.31)	8.12 (8.46)	6.66 (6.65)
E_r / kJ/mol	64.27	82.15	82.31	67.61	48.77
d / Å	2.42 (2.49)	2.42 (2.43)	2.39 (2.42)	2.34 (2.37)	2.34 (2.36)

The dissociation barriers decrease in correlation with experimental reaction speeds. Furthermore, the C-Br distance at the transition state geometry and the barrier width decrease with barrier height. Geometry optimizations beyond the barrier show a decreasing stabilization of dissociated geometries, implying a weaker bonding interaction between the Br atom or the phenyl group and the cluster.

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7. NMR spectra of isolated products

7.19 7.10 7.02 6.96 6.94 6.87 6.83 6.74
5.48
2.21

2.25 2.20 4.18 1.07
1.03
3.00

f1 (ppm)

144.0 140.3 131.0 129.9 129.4 120.3 118.9 116.9
20.8

f1 (ppm)

S33

S34

¹H NMR spectrum peaks: 7.38, 7.28, 7.23, 7.17, 7.02, 6.95, 6.94, 6.87, 6.20, 3.92

Integration: 3.12, 2.09, 1.13, 2.98, 0.93, 3.00

¹³C NMR spectrum peaks: 148.3, 142.8, 133.0, 129.4, 121.2, 120.9, 120.0, 118.6, 114.7, 110.6, 55.7

S35

S37

S38

S39

S40