Synthesis of NHC Complexes by Oxidative Addition of 2-Chloro-N-methylbenzimidazole

Tim Kösterke, Tania Pape and F. Ekkehardt Hahn*

Institut für Anorganische und Analytische Chemie, Westfälische Wilhelms-Universität Münster, Corrensstrasse 30, D-48149 Münster, Germany

Supporting Information

Description of Synthetic Procedures. All manipulations were performed under an argon atmosphere using standard Schlenk techniques or in a glove box. Glassware was oven dried at 130° C prior to use. Solvents were freshly distilled by standard procedures prior to use. ^{1}H, $^{13}C\{^{1}H\}$ and $^{31}P\{^{1}H\}$ NMR spectra were recorded on Bruker AVANCE I 400 or Bruker AVANCE III 400 spectrometers. Chemical shifts (δ) are expressed in ppm using the residual protonated solvent as an internal standard. Coupling constants are expressed in Hertz. Mass spectra were obtained with Orbitrap LTQ XL (Thermo Scientific) or Varian MAT 212 spectrometers. 2-Chlorobenzimidazole, $[Pd(PPh_3)_4]$ and $[Pt(PPh_3)_4]$ were purchased from commercial sources and used as received. Consistent microanalytical data for the metal compelexes were difficult to obtain due to the large fluorine content (BF_4^- anions)

For assignment of NMR spectra see Figure 1.

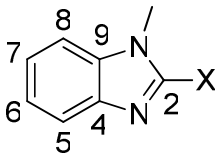


Figure S1. Assignment of NMR resonances.

Synthesis of 2-Chloro-N-methylbenzimidazole 1. A sample of 2-chlorobenzimidazole (500 mg, 3.3 mmol) was dissolved in acetonitrile (10 mL).

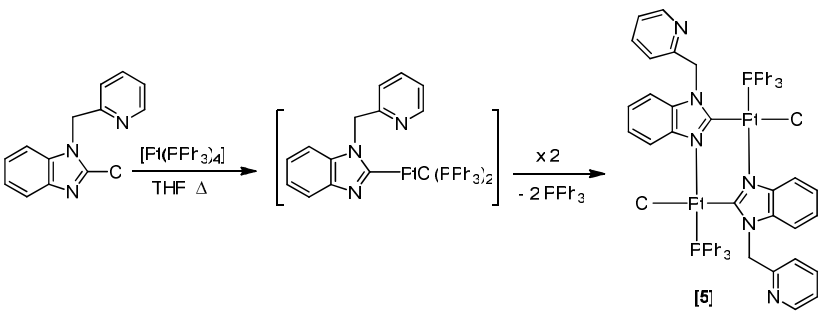
Aqueous NaOH (5 mL of a 25 % solution) was added and the solution was cooled to 0 °C. Then, a solution of iodomethane (488 mg, 3.4 mmol, 0.22 mL) dissolved in acetonitrile (10 mL) was added slowly. The mixture was stirred for 3 d at ambient temperature. Subsequently, all solvents were removed *in vacuo* and the colorless residue was extracted three times with chloroform (20 mL each). The organic layer was dried with $MgSO_4$ and filtered. Removal of the solvent gave **1** as colorless solid. Yield: 0.478 g (2.87 mmol, 88%). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.70–7.67 (m, 1H, H5), 7.30–7.25 (m, 3H, H6, H7, H8), 3.77 (s, 3H, NCH_3). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ = 141.5 (C4), 140.9 (C2), 135.6 (C9), 123.1 (C7), 122.7 (C6), 119.3 (C5), 109.2 (C8), 30.5 (NCH_3). MS (EI, 20 eV): *m/z* (%) = 168 ([**1**]$^+$ 30.2), 166 ([**1**]$^+$ 100). Anal. Calcd (%): C, 57.67; H, 4.23; N, 16.81. Found: C, 57.47; H, 4.22; N, 16.90.

Synthesis of *trans*-[3]BF_4. Samples of 2-chloro-N-methylbenzimidazole **1** (4 mg, 0.026 mmol) and $[Pd(PPh_3)_4]$ (30 mg, 0.026 mmol) together with an excess of NH_4BF_4 (0.1 mmol, 10 mg) were heated under reflux for 6 d in toluene (10 mL). After removal of the solvent *in vacuo* the residue was dissolved in dichloromethane and insoluble material was separated by filtration. The remaining solid was dried *in vacuo*. Colorless crystals of *trans*-[**3**]$BF_4 \cdot CH_2Cl_2$ were obtained by slow diffusion of diethyl ether into a saturated solution of *trans*-[**3**]BF_4 in dichloromethane. Yield: 17 mg (0.019 mmol, 73% of the solvent-free compound). ^{1}H NMR (400 MHz, DMSO-d_6/$CDCl_3$): δ = 12.84 (s, 1H, NH), 7.53–7.46 (m, 12H, Ph-H_{ortho}), 7.30 (t, $^3J_{HH}$ = 7.4 Hz, 6H, Ph-H_{para}), 7.21 (t, $^3J_{HH}$ = 7.4 Hz, 12H, Ph-H_{meta}), 7.08–7.02 (m, 2H, H6, H7), 6.93 (dd, $^3J_{HH}$ = 6.1 Hz, $^4J_{HH}$ = 2.6 Hz, 1H, H5), 6.79 (dd, $^3J_{HH}$ = 6.3 Hz, $^4J_{HH}$ = 2.3 Hz, 1H, H8), 3.31 (s, 3H, NCH_3). $^{13}C\{^1H\}$ NMR (100 MHz, DMSO-d_6/$CDCl_3$): δ = 169.7 (t, $^2J_{CP}$ = 9.2 Hz, C2), 133.6 (C4), 133.3 (t, $^{2/4}J_{CP}$ = 6.3 Hz, Ph-C_{ortho}), 133.0 (C9), 130.8 (Ph-C_{para}), 128.0 (t, $^{3/5}J_{CP}$ = 5.2 Hz, Ph-C_{meta}), 127.9 (t, $^{1/3}J_{CP}$ = 25.3 Hz, Ph-C_{ipso}), 122.9 (C6), 122.5 (C7), 110.9 (C5), 109.0 (C8), 33.6 (NCH_3). $^{31}P\{^1H\}$ NMR (162 MHz, DMSO-d_6/$CDCl_3$): δ = 21.4 (s). HRMS (ESI, positive ions): *m/z* = 797.1234 (calcd for *trans*-[**3**]$^+$ 797.1241).

Synthesis of the Mixture *cis*-[4]BF_4/*trans*-[4]BF_4. Samples of 2-chloro-N-methylbenzimidazole **1** (4 mg, 0.024 mmol) and $[Pt(PPh_3)_4]$ (30 mg, 0.024 mmol) together with an excess of NH_4BF_4 (0.1 mmol, 10 mg) were heated under reflux for 6

d in toluene (10 mL). After removal of the solvent *in vacuo* the residue was dissolved in dichloromethane insoluble material was separated by filtration. Removal of the solvent gave a mixture of compounds *cis*-[**4**]BF_4/*trans*-[**4**]BF_4. The compounds could not be separated by chromatography. Slow diffusion of diethyl ether into a saturated dichloromethane solution of the mixture *cis*-[**4**]BF_4/*trans*-[**4**]BF_4 led to precipitation of colorless crystals. The two isomeric compounds (*cis*-[**4**](BF_4) thin plates and *trans*-[**4**](BF_4) needles) could be separated manually after crystallization The *cis* isomer is the major component (95%) in the mixture with only a small amount of the *trans* isomer (5%) present. Both isomers of the mixture could be identified together in solution by different resonances in the $^{13}C\{^1H\}$ and $^{31}P\{^1H\}$ NMR spectra. Yield: 8 mg (0.008 mmol, 34% of the solvent-free mixture *cis*-[**4**]BF_4/*trans*-[**4**]BF_4. The NMR spectra are dominated by the resonances of the major compound *cis*-[**4**]BF_4 and only few resonances for the *trans* isomer could be identified in the $^{13}C\{^1H\}$ NMR spectrum. ^1H NMR (400 MHz, DMSO-d_6/$CDCl_3$): δ = 12.98 (s, 1H, NH), 7.50–7.39 (m, 15H, Ph-H), 7.33 (d, $^3J_{HH}$ = 5.3 Hz, 1H, H8), 7.29–7.23 (m, 12H, H5, H6, H7 and Ph-H), 7.15 (t, $^3J_{HH}$ = 6.5 Hz, 6H, PPh_3-H*meta trans* to NHC), 4.00 (s, 3H, NCH_3). ^{13}C NMR (100 MHz, DMSO-d_6/$CDCl_3$, *cis* isomer): δ = 170.7 (dd, $^2J_{CP(cis)}$ = 10.3 Hz, $^2J_{CP(trans)}$ = 142.4 Hz, C2), 134.6 (PPh_3-C*ortho trans* to NHC), 133.3 (PPh_3-C*ortho cis* to NHC), 133.0 (C4 and C9), 131.6 (PPh_3-C*para cis* to NHC), 130.9 (PPh_3-C*para trans* to NHC), 128.7 (PPh_3-C*ipso trans* to NHC), 128.4 (PPh_3-C*meta cis* to NHC), 128.2 (PPh_3-C*meta trans* to NHC), 127.5 (PPh_3-C*ipso cis* to NHC), 123.6 (C6), 123.2 (C7), 111.8 (C5), 110.5 (C8), 34.0 (NCH_3). Resonances for the *trans* isomer: δ = 166.9 (C2), 133.3 (PPh_3-C*ortho*), 133.0 (C4 and C9), 131.6 (PPh_3-C*para*), 128.4 (PPh_3-C*meta*), 127.5 (PPh_3-C*ipso*), 123.6 (C6), 123.2 (C7), 111.8 (C5), 110.5 (C8), 34.0 (NCH_3). $^{31}P\{^1H\}$ NMR (162 MHz, DMSO-d_6/$CDCl_3$): δ = 15.7 (d, Pt satellites, $^1J_{PtP}$ = 2223 Hz, $^2J_{PP}$ = 19.2 Hz, PPh_3 *trans* to NHC, *cis* isomer), 11.1 (d, Pt satellites, $^1J_{PtP}$ = 3702 Hz, $^2J_{PP}$ = 19.2 Hz, PPh_3 *cis* to NHC, *cis* isomer), 18.2 (s, Pt satellites, $^1J_{PtP}$ = 2524 Hz, *trans* isomer). HRMS (ESI, positive ions): *m/z* = 887.1823 (calcd for [*cis*/*trans*-[**4**]–BF_4]$^+$ 887.1845).

Synthesis of [5].



Samples of 2-chloro-N-picolylbenzimidazole (5.9 mg, 0.024 mmol) and [$Pt(PPh_3)_4$] (30 mg, 0.024 mmol) were heated under reflux for 6 d in tetrahydrofuran (10 mL). After removal of the solvent *in vacuo* the residue was dissolved in dichloromethane and insoluble material was separated by filtration. The remaining solid was dried *in vacuo*. Colorless crystals of the dinuclear complex [**5**]·H_2O·0.5Et_2O were obtained by slow diffusion of diethyl ether into a saturated solution of [**5**] in dichloromethane. Yield: 7 mg (0.010 mmol, 42% of the solvent-free compound). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.23 (d, $^3J_{HH}$ = 5.1 Hz, 2H, pyridine-H$_\varepsilon$), 7.90 (dd, $^3J_{HP}$ = 11.8 Hz, $^3J_{HH}$ = 7.4 Hz, 12H, PPh-H$_{ortho}$), 7.78 (d, $^3J_{HH}$ = 8.2 Hz, 2H, Ar-H), 7.28 (dt, $^3J_{HH}$ = 7.4 Hz, $^5J_{HP}$ = 3.6 Hz, 6H, PPh-H$_{para}$), 7.19 (td, $^3J_{HH}$ = 7.4 Hz, $^4J_{HP}$ = 2.4 Hz, 12H, PPh-H$_{meta}$), 6.93 (t, $^3J_{HH}$ = 8.2 Hz, 2H, Ar-H), 6.76 (t, $^3J_{HH}$ = 8.2 Hz, 2H, Ar-H), 6.71 (dd, $^3J_{HH}$ = 7.8 Hz, $^3J_{HH}$ = 5.1 Hz, 2H, pyridine-H$_\delta$), 6.56 (d, $^3J_{HH}$ = 8.2 Hz, 2H, Ar-H), 6.03 (dd, $^3J_{HH}$ = 7.8 Hz, $^4J_{HH}$ = 1.8 Hz, 2H, pyridine-H$_\gamma$), 5.64 (d, $^3J_{HH}$ = 7.8 Hz, 2H, pyridine-H$_\beta$), 5.52 (d, $^2J_{HH}$ = 16.2 Hz, 2H, NC*H*H), 4.15 (d, $^2J_{HH}$ = 16.2 Hz, 2H, NCH*H*). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ = 159.8 (d, $^2J_{CP}$ = 8.8 Hz, NCN), 156.5 (pyridine-C$_\alpha$), 148.6 (pyridine-C$_\varepsilon$), 141.5 (Ar-C), 136.3 (pyridine-C$_\gamma$), 134.6 (d, $^2J_{CP}$ = 10.7 Hz, PPh-C$_{ortho}$), 134.0 (Ar-C), 130.6 (d, $^4J_{CP}$ = 2.4 Hz, PPh-C$_{para}$), 130.0 (d, $^1J_{CP}$ = 61.6 Hz, PPh-C$_{ipso}$), 128.3 (d, $^2J_{CP}$ = 11.0 Hz, PPh-C$_{meta}$), 122.0 (pyridine-C$_\delta$), 121.3 (Ar-C), 120.6 (Ar-C), 119.9 (pyridine-C$_\beta$), 116.5 (Ar-C), 109.3 (Ar-C), 51.5 (NCH_2). ^{31}P{^{1}H} NMR (162 MHz, $CDCl_3$): δ = 5.45 (s, Pt satellites, $^1J_{PPt}$ = 1814 Hz). HRMS (ESI, positive ions): *m/z* = 1402.2331 (30%, calcd for [**5**] 1402.2314), 1424.2128 (100%, calcd for [**5**+Na^+] 1424.2131).

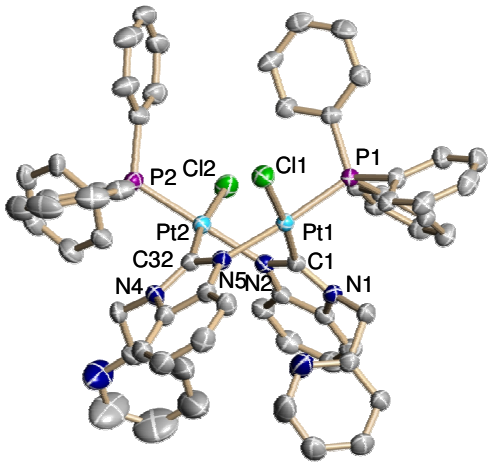


Figure S2. Molecular structure of complex [**5**] in [**5**]·H_2O·0.5Et_2O.

Alkylation of *trans*-[3]BF_4 to *trans*-[6]X. To a solution of *trans*-[**3**]BF_4 (5 mg, 0.006 mmol) in dichloromethane (5 mL) was added KO*t*Bu (0.7 mg, 0.006 mmol) and MeOTf (0.8 mg, 0.006 mmol). The reaction mixture was stirred for 2 h. The solvent was removed *in vacuo* and the residue was washed with diethylether giving *trans*-[**5**]BF_4 as a yellow solid. HRMS (ESI, positive ions): *m/z* = 811.1423 (calcd for $[[\mathbf{5}]-BF_4]^+$ 811.1394). Consisten micronanalytical data for *trans*-[**5**]X could not be obtained due to the possible presence of two different anions (BF_4^- and OTf^-).

X-ray Crystallography. Diffraction data were collected at T = 153(2) K (*trans*-[**3**]$BF_4 \cdot CH_2Cl_2$, *cis*-[**4**]BF_4 and [**5**]$\cdot H_2O \cdot 0.5Et_2O$) and at T = 223(2) K (*trans*-[**4**]$BF_4 \cdot 0.5CH_2Cl_2$) with a Bruker AXS APEX CCD diffractometer equipped with a rotation anode using graphite-monochromated Mo-Kα radiation (λ = 0.71073 Å). Diffraction data were collected over the full sphere and were corrected for absorption. Structure solutions were found with the SHELXS-97[1] package using direct methods and were refined with SHELXL-97[1] against $|F^2|$ using first isotropic and later anisotropic thermal parameters (for exceptions see description of the individual molecular structures). Hydrogen atoms were added to the structure models in calculated positions.

***Trans*-[3](BF$_4$)·CH$_2$Cl$_2$.** Crystals suitable for an X-ray diffraction study were obtained by diffusion of diethyl ether into a saturated dichloromethane solution of [**3**](BF_4). $C_{45}H_{40}N_2BCl_3F_4P_2Pd$, M = 970.29, colorless crystal, 0.21 × 0.06 × 0.02 mm^3, monoclinic, space group $P2_1/c$, Z = 4, a = 12.7079(4), b = 10.4589(4), c = 33.0698(12) Å, β = 94.4330(10)°, V = 4382.2(3) Å^3, ρ_{calc} = 1.471 g·cm^{-3}, μ = 0.731 mm^{-1}, ω- and φ-scans, 51827 measured intensities (2.5° ≤ 2θ ≤ 61.0°), MoKα radiation, λ = 0.71073 Å, semiempirical absorption correction (0.862 ≤ T ≤ 0.986), 13321 independent (R_{int} = 0.0405) and 10283 observed intensities ($I \geq 2\sigma(I)$), refinement of 534 parameters against $|F^2|$ of all measured intensities with hydrogen atoms on calculated positions. R = 0.0487, wR = 0.1272, R_{all} = 0.0672, wR_{all} = 0.1398. The asymmetric unit contains one formula unit.

***Trans*-[4]BF$_4$·0.5CH$_2$Cl$_2$ and *cis*-[4]BF$_4$.** Crystals of both compounds, suitable for X-ray diffraction studies, precipitated simultaneously by slow diffusion of diethyl ether into a saturated dichloromethane solution of a mixture of *trans*-[**4**]BF_4/*cis*-[**4**]BF_4. Compound *trans*-[**4**](BF_4)$\cdot 0.5CH_2Cl_2$ crystallized as needles while crystals of *cis*-

[**4**](BF_4) crystallized as prisms.

Trans-[**4**]$BF_4 \cdot 0.5CH_2Cl_2$: $C_{44.50}H_{39}N_2BCl_2F_4P_2Pt$, M = 1016.52, colorless crystal, 0.15 × 0.03 × 0.03 mm^3, monoclinic, space group $P2_1/c$, Z = 4, a = 12.7733(6), b = 10.5578(5), c = 33.0376(15) Å, β = 94.4420(10)°, V = 4442.0(4) $Å^3$, ρ_{calc} = 1.520 $g \cdot cm^{-3}$, μ = 3.401 mm^{-1}, ω- and φ-scans, 50985 measured intensities (3.2° ≤ 2θ ≤ 60.2°), MoKα radiation, λ = 0.71073 Å, semiempirical absorption correction (0.629 ≤ T ≤ 0.905), 12992 independent (R_{int} = 0.0397) and 9929 observed intensities ($I \geq 2\sigma(I)$), refinement of 514 parameters against $|F^2|$ of all measured intensities with hydrogen atoms on calculated positions. R = 0.0445, wR = 0.1243, R_{all} = 0.0638, wR_{all} = 0.1350. The asymmetric unit contains one formula unit.

Cis-[**4**]BF_4: $C_{44}H_{38}N_2BClF_4P_2Pt$, M = 974.05, colorless crystal, 0.13 × 0.08 × 0.07 mm^3, triclinic, space group $P\bar{1}$, Z = 2, a = 10.4079(3), b = 12.9817(4), c = 16.6774(10) Å, α = 102.085(1)°, β = 104.508(1)°, γ = 106.140(1)°, V = 1998.97(10) $Å^3$, ρ_{calc} = 1.618 $g \cdot cm^{-3}$, μ = 3.710 mm^{-1}, ω- and φ-scans, 23672 measured intensities (3.4° ≤ 2θ ≤ 60.0°), MoKα radiation, λ = 0.71073 Å, semiempirical absorption correction (0.644 ≤ T ≤ 0.781), 11585 independent (R_{int} = 0.0146) and 10834 observed intensities ($I \geq 2\sigma(I)$), refinement of 497 parameters against $|F^2|$ of all measured intensities with hydrogen atoms on calculated positions. R = 0.0244, wR = 0.0619, R_{all} = 0.0268, wR_{all} = 0.0629. The asymmetric unit contains one formula unit.

[**5**]$\cdot H_2O \cdot 0.5Et_2O$: $C_{64}H_{56}N_6Cl_2O_{1.5}P_2Pt$, M = 1456.17, colorless crystal, 0.18 × 0.06 × 0.02 mm^3, monoclinic, space group $P2_1/c$, Z = 4, a = 20.6422(7), b = 12.4704(4), c = 24.1515(8) Å, β = 106.3130(10)°, V = 5966.7(3) $Å^3$, ρ_{calc} = 1.621 $g \cdot cm^{-3}$, μ = 4.875 mm^{-1}, ω- and φ-scans, 57985 measured intensities (2.1° ≤ 2θ ≤ 60.0°), MoKα radiation, λ = 0.71073 Å, semiempirical absorption correction (0.474 ≤ T ≤ 0.909), 17351 independent (R_{int} = 0.0453) and 13450 observed intensities ($I \geq 2\sigma(I)$), refinement of 725 parameters against $|F^2|$ of all measured intensities with hydrogen atoms on calculated positions. R = 0.0348, wR = 0.0867, R_{all} = 0.0544, wR_{all} = 0.0974. The asymmetric unit contains one formula unit. The water molecule is disordered over two position.

References

(1) *SHELXS-97*, *SHELXL-97*, G. M. Sheldrick, *Acta Crystallogr.*, *Sect. A* **2008**, *64*, 112–122.