Synthesis of complexes bearing NH,NMe-substituted NHCs by oxidative addition of 2-halogenato-N-methylbenzimidazoles to Ni$^0$

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Supporting Information

General: 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-Chloro-N-methylbenzimidazole was synthesized using a method previously published.$^1$ [Ni(cod)$_2$], dppe and PEt$_3$ were purchased from commercial sources and were used as received. Consistent micro analytical data for the metal complexes were difficult to obtain due to the large fluorine content (BF$_4^-$ and PF$_6^-$ anions).

For assignment of NMR spectra see Fig. 1.

Fig. 1 Assignment of NMR resonances.
Synthesis of 2-iodo-N-methylbenzimidazole 1: A sample of N-methylbenzimidazole (500 mg, 3.78 mmol) was dissolved in tetrahydrofuran (10 mL). The solution was cooled to −78 °C and 2.4 equiv of 1.7 M t-BuLi (5.35 mL, 9.10 mmol) were added dropwise. After stirring for 1 h a solution of 1.5 equiv N-iodosuccinimide (1.28 g, 5.67 mmol) in tetrahydrofuran (10 mL) was added slowly and the stirring was continued for an additional hour at ambient temperature. The reaction was quenched with a saturated solution of ammonium chloride and diluted with dichloromethane. The aqueous layer was extracted three times with dichloromethane (50 mL each). The combined organic phases were dried with MgSO4 and filtered. After removal of the solvent in vacuo, the residual solid was purified by column chromatography (SiO2, CH2Cl2/MeOH). Removal of the solvent gave 1 as lightly brown solid. Yield: 0.372 g (1.44 mmol, 37%). 1H NMR (400 MHz, CDCl3): δ = 7.74–7.70 (m, 1H, H5), 7.36–7.33 (m, 1H, H8), 7.28–7.20 (m, 2H, H6, H7), 3.78 (s, 3H, NCH3); 13C{1H} NMR (100 MHz, CDCl3): δ = 145.4 (C4), 136.3 (C9), 123.1 (C7), 122.3 (C6), 119.2 (C5), 109.4 (C8), 104.2 (C2), 33.7 (NCH3). HRMS (ESI, positive ions): m/z = 258.9717 (calcd for [1+H]+ 258.9727). Anal. calcd for C8H7N2I (%): C, 37.23; H, 2.73; N, 10.86. Found: C, 37.31; H, 2.74; N, 10.80.

Synthesis of [2]BF4: Samples of [Ni(cod)2] (10 mg, 0.036 mmol) and dppe (14.5 mg, 0.036 mmol) were dissolved in THF (10 mL). The reaction mixture was stirred at ambient temperature for 15 min until the solution turned bright orange. After the colour change 2-iodo-N-methylbenzimidazole 1 (9.4 mg, 0.036 mmol) and an excess of NH4BF4 (10 mg, 0.1 mmol) were added and the resulting suspension was heated to 60 °C for 1 h. Subsequently, the solvent was removed in vacuo and the residue was washed twice with hexane (5 mL each) and diethyl ether (5 mL each) and then dissolved in a small amount of dichloromethane. Insoluble material was separated by filtration. Removal of the solvent from the liquid phase gave 1 as red-brown solid. Yield: 23 mg (0.023 mmol, 79%). It is possible that compound [2]BF4 at this point was contaminated with chloro counterions. These were also found after recrystallization. The source of the chloride is not known at this time. It could result from a NH4Cl impurity in the proton source NH4BF4. Due to the impossibility to obtain consistent microanalytical data (presence of BF4−) the exact amount of chloride is not known but it is also insignificant for the composition of the cation [2]+. Crystals of [2](BF4)0.5Cl0.5·0.5C7H8 were obtained by slow evaporation of the solvents from an acetone/toluene solution of (possible chloride contaminated) [2]BF4. 1H NMR (400 MHz, CD2Cl2): δ = 11.35 (s, 1H, NH), 8.02–7.21 (m, 21H, Ph-H, H5), 7.20–7.04 (m, 3H, H6, H7, H8), 3.55 (s, 3H, NCH3), 2.61–2.38 (m, 2H, CH2P(trans to NHC)), 2.31–2.13 (m, 2H, CH2P(cis to NHC)); 13C{1H} NMR (100 MHz, CD2Cl2): δ = 179.6 (dd, 2JCP(cis) = 97.0 Hz, 2JCP(trans) = 29.3 Hz, C2), 135.7 (C4), 135.5 (C9), 134.6–124.1 (m, Ph-C), 123.7 (C6), 123.2 (C7), 112.7 (C5), 109.2 (C8), 35.0 (NCH3), 28.0 (dd, 1JCP(trans) = 31.6 Hz, 2JCP(cis) = 15.0 Hz,
CH$_2$P$_{\text{trans}}$ to NHC), 26.2 (dd, $^1J_{\text{CP(cis)}} = 29.8$ Hz, $^2J_{\text{CP(trans)}} = 13.8$ Hz, CH$_2$P$_{\text{cis}}$ to NHC); $^{31}$P$_{\text{H}}$ NMR (162 MHz, CD$_2$Cl$_2$): $\delta = 66.5$ (d, $^2J_{\text{PP}} = 47.7$ Hz), 54.3 (d, $^2J_{\text{PP}} = 47.7$ Hz). The resonances of the NHC ligand were assigned by 2D NMR spectroscopy. HRMS (ESI, positive ions): $m/z = 715.0422$ (calcd for [2]$^+ 715.0433$).

Synthesis of [3]BF$_4$: Samples of [Ni(cod)$_2$] (20 mg, 0.072 mmol) and triethylphosphine (17.2 mg, 0.146 mmol) were stirred in hexane (10 mL) at ambient temperature for 15 min after which time the solution turned orange-red. After the colour change, 2-chloro-N-methylbenzimidazole (12 mg, 0.072 mmol) and an excess of NH$_4$BF$_4$ (20 mg, 0.2 mmol) were added. The suspension was stirred for additional 2 h during which a yellow participate formed. The precipitate was isolated by filtration and washed twice with hexane (10 mL each). The solid residue was dissolved in a small amount of dichloromethane and insoluble material was separated by filtration. Removal of the solvent gave [3]BF$_4$ as a yellow solid. Yield: 31 mg (0.056 mmol, 76%). Brown-orange crystals of [3]BF$_4$ were obtained by slow diffusion of diethyl ether into a saturated dichloromethane solution of [3]BF$_4$. $^1$H NMR (400 MHz, CD$_2$Cl$_2$): $\delta = 11.86$ (s, 1H, NH), 7.87–7.82 (m, 1H, H5), 7.46–7.40 (m, 1H, H8), 7.39–7.31 (m, 2H, H6, H7), 4.30 (s, 3H, NCH$_3$), 4.30–4.28 (m, 6H, PCH$_2$), 1.64–1.51 (m, 6H, PCH$_2$), 1.23–1.12 (m, 18H, PCH$_2$C$_3$); $^{13}$C$_{\text{H}}$ NMR (100 MHz, CD$_2$Cl$_2$): $\delta = 176.4$ (t, $^2J_{\text{CP}} = 34.9$ Hz, C2), 135.8 (C4), 134.6 (C9), 124.7 (C6), 124.0 (C7), 113.7 (C5), 109.4 (C8), 35.5 (NCH$_3$), 14.7 (t, $^1J_{\text{CP}} = 13.7$ Hz, PCH$_2$), 8.4 (PCH$_2$C$_3$); $^{31}$P$_{\text{H}}$ NMR (162 MHz, CD$_2$Cl$_2$): $\delta = 19.4$ (s). HRMS (ESI, positive ions): 461.1536 (calcd for [3]$^+ 461.1547$), 343.0626 (calcd for [3–PEt$_3$]$^+ 343.0635$).

Synthesis of [3]PF$_6$: Samples of [Ni(cod)$_2$] (10 mg, 0.036 mmol) and triethylphosphine (8.6 mg, 0.073 mmol) were stirred in hexane (10 mL) at ambient temperature for 15 min after which time the solution turned orange-red. After the color change, 2-chloro-N-methylbenzimidazole (6 mg, 0.036 mmol) and an excess of NH$_4$PF$_6$ (16 mg, 0.1 mmol) were added. The suspension was stirred for an additional 2 h. During this time a yellow participate formed. The precipitate was isolated by filtration and washed twice with hexane (10 mL each). The solid residue was dissolved in a small amount of dichloromethane and insoluble material was separated by filtration. Removal of the solvent yielded [3]PF$_6$ as a yellow solid. Yield: 14 mg (0.023 mmol, 63%). Yellow-orange crystals of [3]PF$_6$ were obtained by slow diffusion of diethyl ether into a saturated dichloromethane solution of [3]PF$_6$. $^1$H NMR (400 MHz, CD$_2$Cl$_2$): $\delta = 10.79$ (s, 1H, NH), 7.87–7.81 (m, 1H, H5), 7.46–7.41 (m, 1H, H8), 7.40–7.34 (m, 2H, H6, H7), 4.31 (s, 3H, NCH$_3$), 1.64–1.52 (m, 6H, PCH$_2$), 1.51–1.40 (m, 6H, PCH$_2$), 1.23–1.12 (m, 18H, PCH$_2$C$_3$); $^{13}$C$_{\text{H}}$ NMR (100 MHz, CD$_2$Cl$_2$): $\delta = 177.0$ (t, $^2J_{\text{CP}} = 34.5$ Hz, C2), 135.5 (C4), 134.4 (C9), 125.0 (C7), 124.2 (C6), 113.6 (C5), 109.5 (C8), 35.6 (NCH$_3$), 14.7 (t, $^1J_{\text{CP}} = 13.8$ Hz, PCH$_2$), 8.4 (PCH$_2$C$_3$); $^{31}$P$_{\text{H}}$ NMR (162 MHz, CD$_2$Cl$_2$): $\delta = 19.4$ (s). HRMS (ESI, positive ions): 461.1536 (calcd for [3]$^+ 461.1547$), 343.0626 (calcd for [3–PEt$_3$]$^+ 343.0635$).

**X-ray Crystallography:** Diffraction data were collected at T = 153(2) K 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-97² package using direct methods and were refined with SHELXL-97² against |F²| 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 if not noted otherwise.

[2](BF₄)₀.₅Cl₀.₅·₀.₅C₇H₈: Crystals of [2](BF₄)₀.₅Cl₀.₅·₀.₅C₇H₈ were obtained by slow evaporation of the solvents from an acetone/toluene solution of (possible chloride contaminated) [2]BF₄. C₃₇.₅H₃₆N₂B₀.₅Cl₀.₅F₂P₂INi, M = 823.36, red-brown crystal, 0.06 × 0.05 × 0.03 mm³, triclinic, space group P₁, Z = 2, a = 9.5503(3), b = 10.1764(3), c = 20.2212(6) Å, α = 84.7210(10), β = 81.8170(10), γ = 69.2620(10)°, V = 1817.37(10) Å³, ρcalc = 1.505 g·cm⁻³, μ = 1.547 mm⁻¹, ω- and φ-scans, 21343 measured intensities (2.0° ≤ 2θ ≤ 60.0°), Mo-Kα radiation, λ = 0.71073 Å, semi-empirical absorption correction (0.9129 ≤ T ≤ 0.9551), 10447 independent (Rint = 0.0243) and 8065 observed intensities (I ≥ 2σ(I)), refinement of 423 parameters against |F²| of all measured intensities with hydrogen atoms on calculated positions. R = 0.0605, wR = 0.1739, Rall = 0.0795, wRall = 0.1899. The asymmetric unit contains one formula unit. One toluene molecule is distributed over two asymmetric units. The asymmetric unit contains ½ each of the anions BF₄⁻ and Cl⁻.

[3]BF₄: Brown-orange crystals of [3]BF₄ were obtained by slow diffusion of diethyl ether into a saturated dichloromethane solution of [3]BF₄. C₂₀H₃₈N₂BClF₄P₂Ni, M = 549.43, brown-orange crystal, 0.13 × 0.07 × 0.05 mm³, monoclinic, space group P2₁/n, Z = 4, a = 9.1013(5), b = 30.685(2), c = 9.4384(6) Å, β = 94.1290(10)°, V = 2635.9(3) Å³, ρcalc = 1.385 g·cm⁻³, μ = 0.998 mm⁻¹, ω- and φ-scans, 19882 measured intensities (2.7° ≤ 2θ ≤ 64.1°), Mo-Kα radiation, λ = 0.71073 Å, semi-empirical absorption correction (0.8813 ≤ T ≤ 0.9518), 6208 independent (Rint = 0.0243) and 4472 observed intensities (I ≥ 2σ(I)), refinement of 291 parameters against |F²| of all measured intensities with hydrogen atoms on calculated positions. R = 0.0389, wR = 0.0997, Rall = 0.0558, wRall = 0.1032. The asymmetric unit contains one formula unit.

[3]PF₆: Yellow-orange crystals of [3]PF₆ were obtained by slow diffusion of diethyl ether into a saturated dichloromethane solution of [3]PF₆. C₂₀H₃₈N₂ClF₆P₃Ni, M = 607.59, yellow-orange crystal, 0.10 × 0.08 × 0.04 mm³, monoclinic, space group P2₁/n, Z = 4, a = 11.6060(4), b = 16.3414(6), c = 15.5441(5) Å, β = 104.3890(10)°, V = 2855.6(2) Å³, ρcalc = 1.413 g·cm⁻³, μ = 0.992 mm⁻¹, ω- and φ-scans, 34098 measured intensities (3.7° ≤ 2θ ≤ 61.0°), Mo-Kα radiation, λ =
0.71073 Å, semi-empirical absorption correction ($0.9073 \leq T \leq 0.9614$), 8704 independent ($R_{int} = 0.0227$) and 7215 observed intensities ($I \geq 2\sigma(I)$), refinement of 305 parameters against $|F^2|$ of all measured intensities with hydrogen atoms on calculated positions. $R = 0.0433$, $wR = 0.1190$, $R_{all} = 0.0539$, $wR_{all} = 0.1274$. The asymmetric unit contains one formula unit.

References


NMR Spectra of 1: $^1$H NMR (400 MHz) and $^{13}$C($^1$H) NMR (100 MHz) measured in CDCl$_3$. 
NMR Spectra of [2]BF₄. ¹H NMR (400 MHz), ¹³C{¹H} NMR (100 MHz) and ³¹P{¹H} NMR (162 MHz) measured in CD₂Cl₂.
NMR Spectra of [3]BF₄⁻. ¹H NMR (400 MHz), ¹³C{¹H} NMR (100 MHz) and ³¹P{¹H} NMR (162 MHz) measured in CD₂Cl₂.
NMR Spectra Data of [3]PF₆. ¹H NMR (400 MHz), ¹³C{¹H} NMR (100 MHz) and ³¹P{¹H} NMR (162 MHz) measured in CD₂Cl₂.