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Catalytic Carbon-Carbon Bond Formation via Selective Carbon-Fluorine Bond Activation

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Contents:

General considerations

Materials and methods

Reactions were carried out with standard Schlenk technique under an atmosphere of dry nitrogen. Nickel(II) diacetylacetonate was bought from Merck AG, Germany. Other chemicals were purchased from Fluka and Aldrich and used as received. Bis(1,5-cyclooctadiene)nickel(O) was prepared as described in the literature.[1]

Except for work-up of reaction mixtures, catalysis was carried out under an atmosphere of dry nitrogen. THF was dried and deoxygenated over Na / benzophenone; pentane and hexane were dried according to a literature procedure.[2] All other reagents have not been dried or deoxygenated prior to use. The preparation of the imidazolium salts does not require inert atmosphere or dry solvents.

Physical and analytical methods

NMR spectra (^{1}H, ^{13}C) were recorded on a Jeol JMX-GX 400 or a Bruker DPX 400 instrument and are referenced to residual protons in the solvent (^{1}H) or the solvent carbon-13 signal (^{13}C). NMR multiplicities are abbreviated as s = singlet, d = doublet, t = triplet, sept = septet, br = broad signal. Coupling constants *J* are given in Hz. GC-MS spectra were measured on a Hewlett Packard gas chromatograph GC 5890 A equipped with a mass selective detector MS 5970 B. Elemental analyses were carried out by the Microanalytical Laboratory at the TU München. Catalysis yields were generally determined by gas chromatography and the products were identified by comparison to authentic samples and by their mass spectra:[3] 4-trifluoromethylbiphenyl,[4] 4-methylbiphenyl,[5] 4-methoxybiphenyl,[6] 2-methylbiphenyl,[7] 2,4,6-trimethylbiphenyl,[8,9] 4-methoxy-2',4',6'-trimethylbiphenyl,[8,10] 4-trifluoromethyl-2',4',6'-trimethylbiphenyl,[10] 2,4,4',6-tetramethylbiphenyl,[11] 2,2',4,4',6,6'-hexamethylbiphenyl,[12-14] 4-*tert.*-butylbiphenyl,[15,16] 4,4'-bis-*tert.*-butylbiphenyl,[17,18] 4-*tert.*-butyl-2'-methylbiphenyl.[17,18]

Synthesis of *N,N*-bis(2',6'-di-*iso*-propylphenyl)glyoxalimine [19,20]

20.0 mL 2,6-di-*iso*-propylaniline (18.8 g, 109 mmol) and 6.1 mL glyoxal (40 wt. % in water, 55 mmol) are dissolved in 100 mL ethanol. After addition of some drops of formic acid (approximately 0.08 mL) as the catalyst the reaction mixture is stirred at room temperature. The solution turns yellow and after several hours the product starts to precipitate. The mixture is stirred of a period of 24 h, the product is isolated by filtration over a Büchner funnel and washed 3 times with 10 mL of cold methanol. Yield: 20.5 g (50 %).

^{1}H (400 MHz, $CDCl_3$, 22 °C, TMS): *d* [ppm] = 8.11 (s (br), 2 H, NCHCHN), 7.13–7.21 (m, 6 H, aryl), 2.94 (sept, ^{3}J (H,H) = 6.8 Hz, 4 H, $CH_{i\text{-Pr}}$), 1.21 (d, ^{3}J (H,H) = 6.8 Hz, 24 H, $H_3C_{i\text{-Pr}}$).

$^{13}C\{^{1}H\}$ (100 MHz, $CDCl_3$, 22 °C, TMS): *d* [ppm] = 163.1 (NCHCHN), 148.0 (aryl), 136.7 (aryl), 125.1 (aryl), 123.2 (aryl), 28.0 ($CH_{i\text{-Pr}}$), 23.4 ($H_3C_{i\text{-Pr}}$).

$C_{26}H_{36}N_2$ (376.58): calcd C 82.93, H 9.64, N 7.44; found C 83.12, H 9.49, N 7.20.

Synthesis of 1,3-di(2',6'-di-*iso*-propylphenyl)imidazolium tetrafluoroborate (3) [21]

3.7 g of *N*,*N*-bis(2',6'-di-*iso*-propylphenyl)glyoxalimine (10 mmol) and 0.3 g of paraformaldehyde (10 mmol) are dissolved in 20 mL of toluene. The mixture is stirred and heated until the solution does not clearify any further. After cooling to room temperature, 1.4 mL of a $H[BF_4]$ solution (54 wt. % in diethyl ether, 10 mmol) are added dropwise over a period of 1 h. The resulting mixture is stirred for an additional 8 h at room temperature while it darkens. During this period a white precipitate forms which is filtered and washed 3 times with 2 mL of cold THF. Yield: 1.8 g (38 %).

^{1}H (400 MHz, [D$_6$]-DMSO, 22 °C, TMS): ***d*** [ppm] = 10.15 (s, 1 H, NCHN), 8.55 (s (br), 2 H, NCHCHN), 7.68 (t, ^3J (H,H) = 7.7 Hz, 2 H, 4-H$_{\text{aryl}}$), 7.52 (d, ^3J (H,H) = 7.7 Hz, 4 H, 3,5-H$_{\text{aryl}}$), 2.34 (sept, ^3J (H,H) = 7.0 Hz, 2 H, CH$_{i\text{-Pr}}$), 2.34 (sept, ^3J (H,H) = 6.6 Hz, 2 H, CH$_{i\text{-Pr}}$), 1.25 (d, ^3J (H,H) = 6.6 Hz, 12 H, H$_3$C$_{i\text{-Pr}}$), 1.15 (d, ^3J (H,H) = 7.0 Hz, 12 H, H$_3$C$_{i\text{-Pr}}$).

^{13}C{^{1}H} (100 MHz, [D$_6$]-DMSO, 22 °C, TMS): ***d*** [ppm] = 144.8 (NCHN), 139.3 (aryl), 131.9 (aryl), 130.0 (aryl), 126.2 (aryl), 124.6 (NCHCHN), 28.6 (CH$_{i\text{-Pr}}$), 24.1 (H$_3$C$_{i\text{-Pr}}$), 23.1 (H$_3$C$_{i\text{-Pr}}$).

$C_{27}H_{37}N_2BF_4$ (476.41): calcd C 68.07, H 7.83, N 5.88; found C 68.33, H 8.09, N 6.00.

The synthesis of the corresponding chloride salt, which can also be used in the synthesis of **2** and **3** as well as in catalysis, has been described in the literature.[19–23]

Synthesis of 1,3-di(2',6'-di-*iso*-propylphenyl)imidazolin-2-ylidene (2) [24]

In a previously described apparatus by our group,[24] 2.5 g of 1,3-di(2',6'-di-*iso*-propylphenyl)-imidazolium tetrafluoroborate **3** (5.25 mmol) are slurried in 20 mL of THF. After cooling to –78 °C with an acetone / dry ice bath, 15 mL of NH_3 are condensed in, dissolving most of the salt and resulting in an almost clear solution. 130 mg NaH (5.40 mmol) are added against a constant stream of nitrogen. A larger excess of NaH may be used to eliminate traces of water in NH_3. The cold bath is removed and the reaction mixture is stirred for 2.5 h under steady reflux of NH_3 resulting in a light yellow slurry. The volatiles are removed under vacuum and the product is extracted from the remaining solids 3 times with 15 mL of pentane. Upon storing at –30 °C the white product crystallizes. Yield: 1.74 g (85 %).

^{1}H (400 MHz, C$_6$D$_6$, 22 °C, TMS): *d* [ppm] = 7.29 (t, ^{3}J (H,H) = 7.5 Hz, 2 H, 4-H$_{\text{aryl}}$), 7.18 (d, ^{3}J (H,H) = 7.5 Hz, 4 H, 3,5-H$_{\text{aryl}}$), 6.62 (s, 2 H, NCHCHN), 2.96 (sept, ^{3}J (H,H) = 6.9 Hz, 4 H, CH$_{i\text{-Pr}}$), 1.28 (d, ^{3}J (H,H) = 6.9 Hz, 12 H, H$_3$C$_{i\text{-Pr}}$), 1.18 (d, ^{3}J (H,H) = 6.9 Hz, 12 H, H$_3$C$_{i\text{-Pr}}$).

^{13}C{^{1}H} (100 MHz, C$_6$D$_6$, 22 °C, TMS): *d* [ppm] = 220.5 (NCN), 146.2 (aryl), 138.9 (aryl), 129.0 (aryl), 123.6 (aryl), 121.5 (NCHCHN), 28.7 (CH$_{i\text{-Pr}}$), 24.8 (H$_3$C$_{i\text{-Pr}}$), 23.6 (H$_3$C$_{i\text{-Pr}}$).

Alternative procedures in the literature use K(O*t*-Bu) in THF to deprotonate the imidazolium salt **3**.[22,23]

Synthesis of bis(1,3-di(2',6'-di-*iso*-propylphenyl)imidazolin-2-ylidene)nickel(O) (1) [25]

107 mg of bis(1,5-cyclooctadiene)nickel(O) (0.389 mmol) are dissolved in 30 mL of THF. A solution of 300 mg of 1,3-di(2',6'-di-*iso*-propylphenyl)imidazolin-2-ylidene **2** (0.778 mol) in 20 mL of THF was slowly added at room temperature. A very dark colored solution is thus obtained. After stirring the mixture for 20 min, the volatiles are removed under vacuum. The remaining solid is dissolved in 5 mL of hexane and cooled at –30 °C to give the product as black crystals. Yield: 259 mg (80 %).

^{1}H (400 MHz, C$_6$D$_6$, 22 °C, TMS): *d* [ppm] = 7.27 (t, ^{3}J (H,H) = 7.7 Hz, 2 H, 4-H$_{\text{aryl}}$), 7.07 (d, ^{3}J (H,H) = 7.7 Hz, 4 H, 3,5-H$_{\text{aryl}}$), 6.09 (s, 2 H, NCHCHN), 3.05 (sept, ^{3}J (H,H) = 7.0 Hz, 4 H, CH$_{i\text{-Pr}}$), 1.23 (d, ^{3}J (H,H) = 7.0 Hz, 12 H, H$_3$C$_{i\text{-Pr}}$), 1.09 (d, ^{3}J (H,H) = 7.0 Hz, 12 H, H$_3$C$_{i\text{-Pr}}$).

^{13}C{^{1}H} (100 MHz, C$_6$D$_6$, 22 °C, TMS): *d* [ppm] = 195.1 (NCHN), 146.6 (aryl), 145.7 (aryl), 139.6 (aryl), 138.1 (aryl), 123.6 (NCHCHN), 30.8 (H$_3$C$_{i\text{-Pr}}$), 28.6 (CH$_{i\text{-Pr}}$).

CI-MS: m/z (%) = 834 (0.14) [M^{+}], 387 (52.41) [NHC^{+}], 281 (94.48), 225 (100).

C$_{54}$H$_{72}$N$_4$Ni (835.87): calcd C 77.59, H 8.68, N 6.70; found C 77.87, H 8.96, N 6.55.

The Kumada-Corriu reaction

A typical procedure is as follows: 16.8 mg of complex **1** (0.02 mmol) or 5.1 mg of Ni(acac)$_2$ and 9.6 mg of **3** (0.02 mmol each) are suspended in 1 mL of dry and degassed THF under an atmosphere of dry nitrogen. After addition of 37.5 µL of fluorobenzene (38.4 mg, 0.4 mmol) and 25 mg of the internal standard diethyleneglycol-di-*n*-butylether the mixture is stirred for 5 min at room temperature until catalysis is commenced by dropwise addition of 600 µL of the Grignard reagent 4-*tert.*-butylphenylmagnesium bromide (0.6 mmol, 1 M in THF).[26] After the desired run time, the reaction is quenched by addition of 1 mL of methanol and examined by GC / MS.

The Hammett correlation

The reaction is performed exactly as described above with **1**, Ni(acac)$_2$ / **3** and NiCl$_2$ as the catalysts but with two important exceptions: (i) Instead of using 0.6 mmol of a single aryl fluoride, fluorobenzene and another aryl fluoride are used in excess as 3.0 mmol each. (ii) The Grignard reagent 4-*tert.*-butylphenylmagnesium bromide is used as the minor reagent in 400 µL only (0.4 mmol, 1 M in THF).

After 18 h the reaction is quenched by the addition of 1 mL of methanol and examined by GC / MS. The product ratios were determined by multiple integrations and taken as indicative for relative reaction rates of the aryl fluorides compared to fluorobenzene.

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