

Aluminium-Mediated Carbon-Carbon Coupling of an Isonitrile

Supporting Information

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1. Synthesis

All manipulations were carried out under an atmosphere of argon using standard Schlenk or glovebox techniques. Solvents were dried under argon over sodium dispersion and benzophenone and distilled before use. C₆D₆ was dried over potassium metal and distilled. CD₂Cl₂ was dried over CaH₂ and distilled. NMR spectra were recorded on a Bruker PRO 500 MHz or an AVA 600 MHz spectrometer. ¹H and ¹³C spectra were referenced to residual solvent signals, and ²⁷Al spectra were referenced externally to Al(NO₃)₃ in D₂O (1.1 M). (Cp*Al)₄^[1] was synthesised using the literature procedure. Diphenylacetylene and 2,6-dimethylphenylisocyanide were purchased from commercial suppliers and used without further purification.

Synthesis of (Cp*Al)₂(PhCCPh)₂ (**1**)

(Cp*Al)₄ (1.07 g, 1.65 mmol) and diphenylacetylene (1.16 g, 6.53 mmol, 4.0 eq) were suspended in toluene (40 mL) and heated to 100 °C (all material dissolves to form a yellow solution at this stage) for 2 days. After cooling, volatiles were removed from the now dark-orange solution. The residue was washed once with hexane (5 mL) to provide compound **1** as beige powder, (1.85 g, 2.72 mmol, 83 %). X-ray quality crystals were grown from a saturated hexane solution stored at room temperature for one month. ¹H NMR (500.2 MHz, 298 K, C₆D₆): δ = 7.40 – 6.97 (m, 16H, -Ph), 6.84 – 6.75 (m, 4H, -*p*CH), 1.71 (s, 30H, -CCH₃) ppm. ¹³C NMR (125.8 MHz, 298 K, C₆D₆): δ = 148.36 (-AlC=CAI), 128.06 (-Ph), 127.95 (-*i*Ph), 127.05 (-Ph), 123.67 (-*p*Ph), 115.88 (-CCH₃), 10.63 (-CCH₃) ppm. ²⁷Al NMR no signal. m.p: 258-260 °C. High Resolution Mass Spec (EI): m/z = 680.35369 [C₄₈H₅₀Al₂]⁺ (theoretical = 680.35547). Anal: Expected: C, 84.67; H, 7.40; Found: C, 80.91; H, 8.18. Compound **1** is not amenable to combustion analysis. Despite repeated attempts, expected figures were not obtained.

Ether adducts of **1**

Compound **1** (ca. 20 μmol) was dissolved in C₆D₆ and two equivalents (ca. 40 μmol) of the appropriate ethereal solvent was added. The NMR of the resulting solutions is shown in figure S1, showing shifted signals indicating adduct formation.

Diethylether adduct ¹H NMR (500.2 MHz, 298 K, C₆D₆): δ = 7.02 – 6.97 (m, 16H, ArH), 6.85 – 6.75 (m, 4H, *p*ArH), 3.24 (q, J = 6.9 Hz, 8H, OCH₂CH₃), 1.74 (s, 30H, Cp*), 1.05 (t, J = 6.9 Hz, 12H, OCH₂CH₃).

Dimethoxyethane adduct ¹H NMR (500.2 MHz, 298 K, C₆D₆): δ = 7.03 – 6.98 (m, 8H, ArH), 6.98 – 6.93 (m, 8H, ArH), 6.83 (tt, J = 7.2, 1.4 Hz, 4H, *p*ArH), 3.14 (s, 12H, CH₂OCH₃), 2.97 (s, 18H, CH₂OCH₃), 1.90 (s, 30H, Cp*).

Tetrahydrofuran adduct ^1H NMR (500.2 MHz, 298 K, C_6D_6): $\delta = 7.04 - 6.98$ (m, 16H, ArH), $6.87 - 6.80$ (m, 4H, $p\text{ArH}$), 3.55 (s, 16H, OCH_2CH_2), 1.99 (s, 30H, Cp^*), 1.12 (s, 16H, OCH_2CH_2).

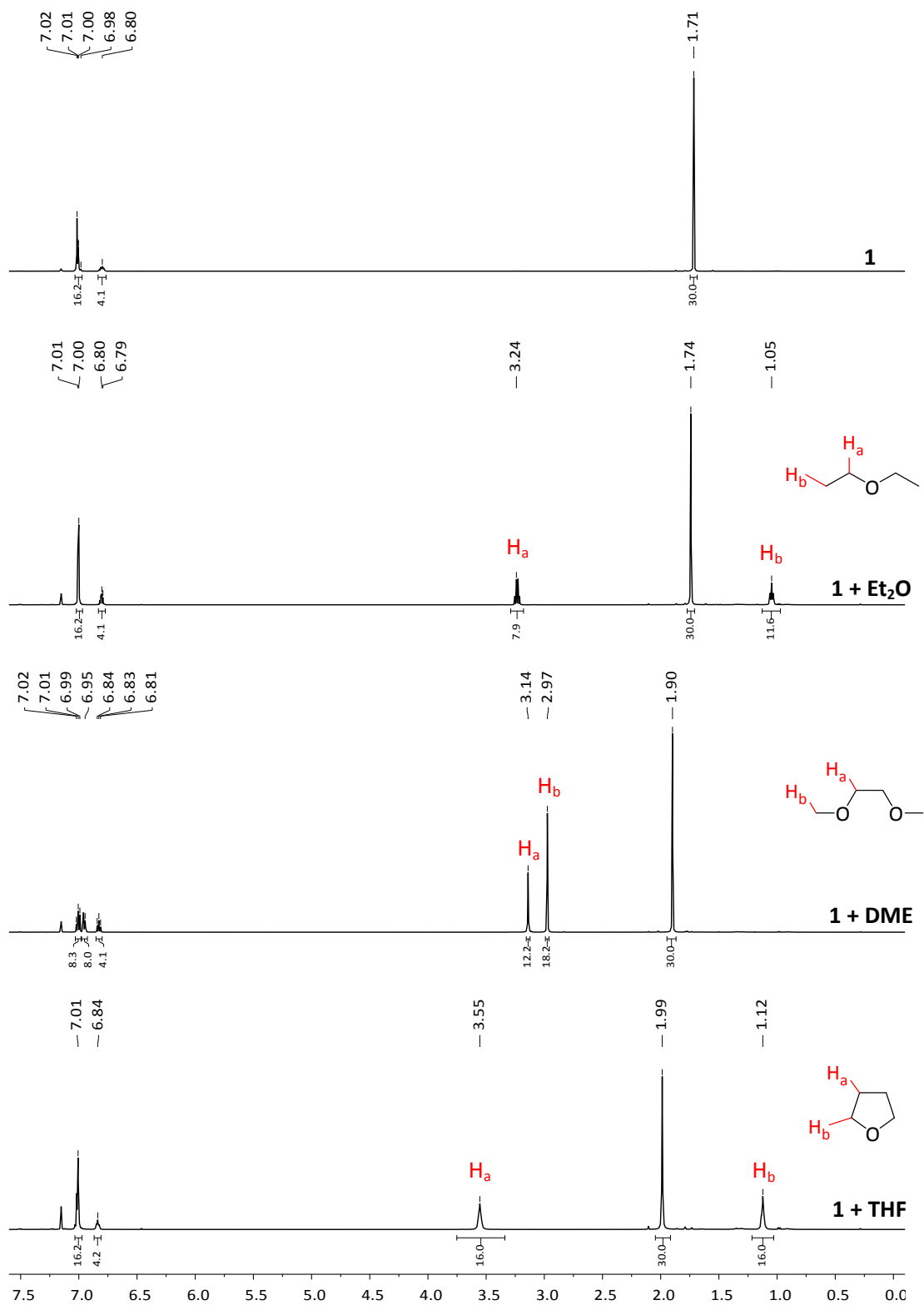


Figure S1 ^1H NMR spectra of ether adducts of **1** (all in C_6D_6)

Synthesis of **2**

Compound **1** (216.7 mg, 0.32 mmol) was dissolved in C_6H_6 (0.5 mL) and a solution of 2,6-dimethyl isocyanide (167.6 mg, 1.27 mmol, 4 eq) in C_6H_6 (1.5 mL) was added dropwise. The dark red solution was left to stand without stirring for 48 hours. The precipitated dark red solid was isolated by filtration as the benzene solvate, and dried under vacuum (130.6 mg, 0.10 mmol, 32.0 %). ^1H NMR (601 MHz, 298 K, CD_2Cl_2): δ = 7.40 (s, C_6H_6), 7.19 (d, J = 7.3 Hz, 4H, Xylyl ArH), 7.03 (t, J = 7.3 Hz, 4H, Xylyl ArH), 6.95 – 6.91 (m, 4H, Xylyl ArH), 6.75 (d, J = 8.2 Hz, 4H, PhH), 6.68 (d, J = 8.2 Hz, 4H, PhH), 6.55 – 6.50 (m, 4H, PhH), 6.46 (d, J = 7.3 Hz, 4H, PhH), 5.73 (d, J = 7.3 Hz, 4H, PhH), 2.71 (s, 12H, Xylyl-Me), 1.50 (s, 12H, Xylyl-Me), 1.41 (s, 12H, $\text{C}=\text{CCH}_3$), 0.58 (s, 12H, C^+CCH_3), 0.26 (s, 6H, C^+CH_3) ppm. ^{13}C NMR (125.8 MHz, 298 K, CD_2Cl_2): δ = 151.23 (d, J = 11.1 Hz, C^+), 146.63 (Al-C=C-Al), 136.55 (quaternary C), 133.97 (quaternary C), 133.57 (N-C=C-N), 133.13 (xylyl- CCH_3), 129.57 (xylyl- $m\text{PhH}$), 129.10 (xylyl- $m\text{PhH}$), 128.28 (xylyl- $m\text{PhH}$), 127.93 (phenyl- $m\text{PhH}$), 127.69 (phenyl- $m\text{PhH}$), 126.09 (phenyl- $o\text{PhH}$), 125.79 (phenyl- $o\text{PhH}$), 122.85 (xylyl- $p\text{PhH}$), 121.66 (phenyl- $p\text{PhH}$), 121.34 (phenyl- $p\text{PhH}$), 96.23 (C^+CCH_3), 61.83 ($\text{H}_3\text{CC}=\text{CCH}_3$), 23.28 (xylyl- CH_3), 20.55 (xylyl- CH_3), 11.12 ($\text{H}_3\text{CC}=\text{CCH}_3$), 8.90 (C^+CCH_3), 1.27 (C^+CH_3). ^{27}Al NMR no signal. Melting Point: 160 °C (decomposes). High Resolution Mass Spec (EI): m/z = 1204.64778 [$\text{C}_{84}\text{H}_{86}\text{N}_4\text{Al}_2$] $^+$ (theoretical = 1204.64586). Anal: Calcd. for $\text{C}_{48}\text{H}_{50}\text{Al}_2$ Expected: C, 84.21; H, 7.22; N 4.36; Found: C, 77.44; H, 7.00, N, 5.60. Compound **2** is not amenable to combustion analysis. Despite repeated attempts, expected figures were not obtained.

2. Spectra of New Compounds

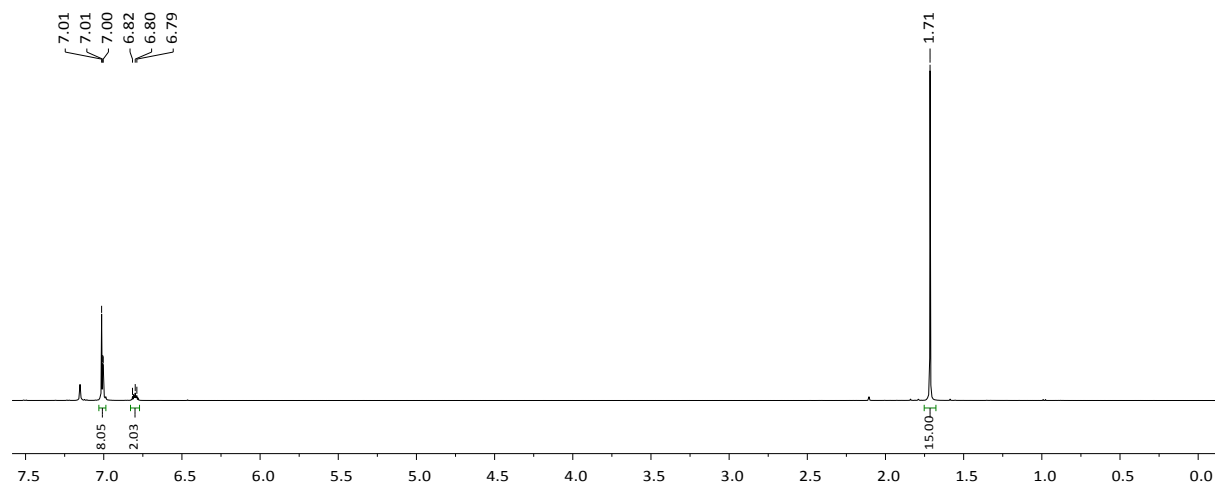


Figure S2 ^1H NMR of **1** (298 K, C_6D_6)

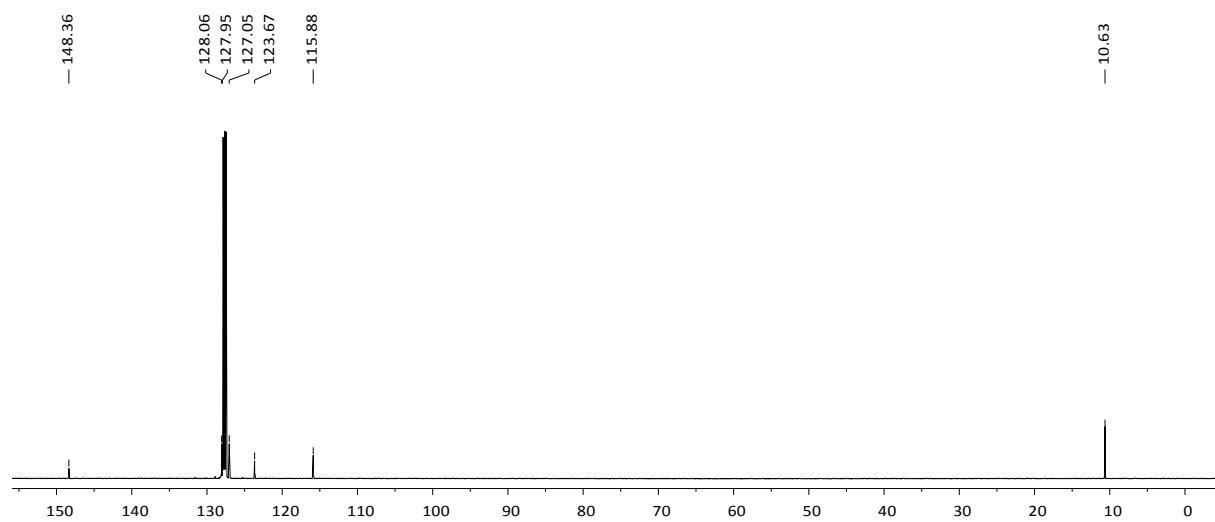


Figure S3 ^{13}C $\{^1\text{H}\}$ NMR of **1** (298 K, C_6D_6)

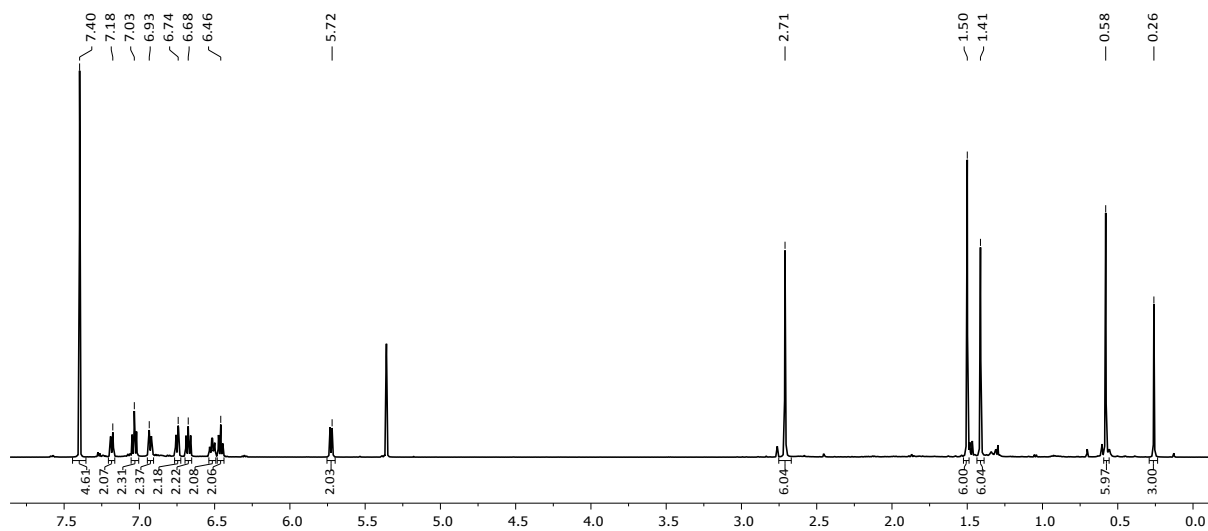


Figure S4 ^1H NMR of $2.\text{C}_6\text{H}_6$ (298 K, CD_2Cl_2)

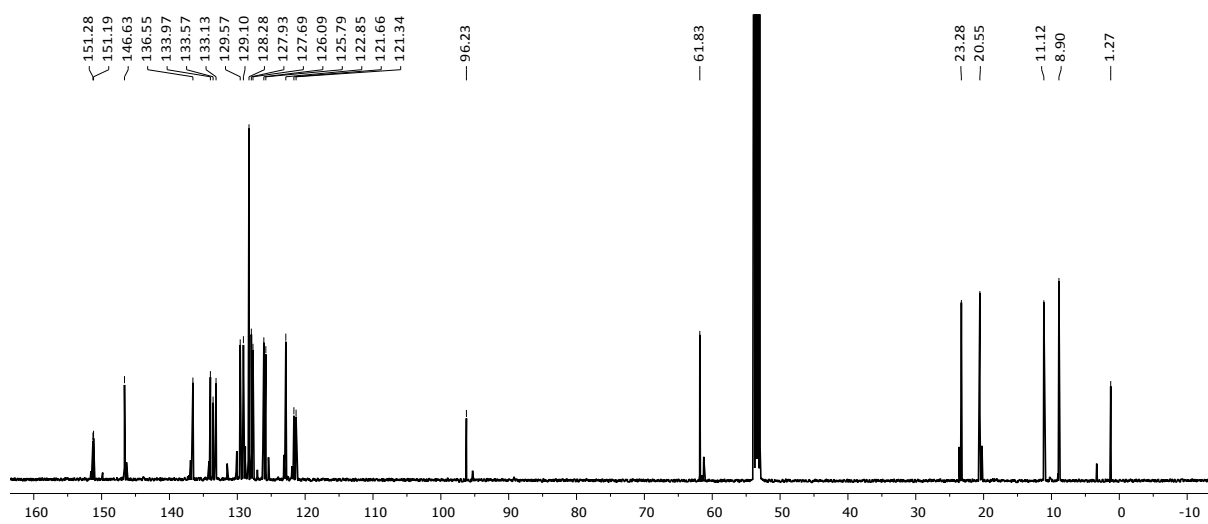


Figure S5 ^{13}C $\{^1\text{H}\}$ NMR of $2.\text{C}_6\text{H}_6$ (298 K, CD_2Cl_2)

3. X-Ray Crystallographic Data

	1	2
Formula	C ₄₈ H ₅₀ Al ₂	C ₉₀ D ₆ Al ₂ H ₈₆ N ₄
$D_{calc.}/g\text{ cm}^{-3}$	1.172	1.210
μ/mm^{-1}	0.911	0.751
Formula Weight	680.84	1289.67
Colour	colourless	dark red
Shape	block	prism
Size/mm ³	0.12×0.11×0.09	0.13×0.08×0.08
T/K	120.0	120.0
Crystal System	triclinic	monoclinic
Space Group	P-1	la
$a/\text{Å}$	11.0642(4)	15.4666(6)
$b/\text{Å}$	11.5289(4)	15.1699(5)
$c/\text{Å}$	16.8850(4)	30.7695(10)
$\alpha/^\circ$	99.424(2)	90
$\beta/^\circ$	98.234(2)	101.336(4)
$\gamma/^\circ$	111.443(3)	90
$V/\text{Å}^3$	1928.70(11)	7078.5(4)
Z	2	4
Z'	1	1
Wavelength/Å	1.54184	1.54184
Radiation type	CuK α	CuK α
$\theta_{min}/^\circ$	4.238	4.122
$\theta_{max}/^\circ$	76.188	76.497
Measured Refl.	29640	34446
Independent Refl.	7908	13900
Reflections Used	6635	8661
R_{int}	0.0797	0.1336
Parameters	461	884
Restraints	0	2
Largest Peak	0.387	0.396
Deepest Hole	-0.378	-0.480
GooF	1.031	0.916
wR_2 (all data)	0.1442	0.1875
wR_2	0.1342	0.1719
R_1 (all data)	0.0616	0.1037
R_1	0.0516	0.0728

4. References

- 1 C. Ganesamoorthy, S. Loerke, C. Gemel, P. Jerabek, M. Winter, G. Frenking and R. Fischer, *Chem. Commun.*, 2013, **49**, 2858–2860.