Supporting Information

Pentadienyl migration and abstraction in yttrium aluminabenzene complexes including a single-component catalyst for isoprene polymerization

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Experimental Section

General Considerations. All manipulations were performed under rigorous exclusion of air and moisture using standard Schlenk, high-vacuum, and glovebox techniques (MBraun UNIlab^{pro} ECO); <0.5 ppm O₂, <0.5 ppm H₂O, argon atmosphere). *n*-Hexane, toluene and THF were purified using Grubbs Columns (MBraun SPS, solvent purification system). Benzene was dried over Na/K alloy and distilled onto molecular sieves (3 Å). C₆D₆ (99.6%, Sigma-Aldrich) and toluene-d₈ (99.6%, Sigma-Aldrich) were dried by letting the solvents stand over Na/K-alloy for at least 24 h and subsequent filtration. All solvents were stored inside a glovebox. Me₂AlCl and Et₂AlCl were purchased from Sigma-Aldrich and used as received. [CPh₃][B(C₆F₅)₄], $[PhNMe_2H][B(C_6F_5)_4]$, and $B(C_6F_5)_3$ were obtained from Boulder Scientific and used without further purification. Isoprene was purchased from Sigma-Aldrich, dried over $Al(n-oct)_3$ for 24 h and distilled prior to use. Complex 1 and lithium bis(dimethylsilylamide) were synthesized according to literature procedures.^{1, 2} NMR spectra of air and moisture sensitive compounds were recorded by using J. Young valve NMR tubes at ambient temperature on either a Bruker AVII+400 (¹H, ¹³C, ¹⁹F), a Bruker DRX-250 (¹¹B, ²⁹Si) or a Bruker AVII+500 (⁸⁹Y). NMR chemical shifts are referenced to internal solvent resonances and reported in parts per million relative to tetramethylsilane (TMS), CFCl₃, BF₃, and Y(NO₃)₃. Coupling constants are given in Hertz. Elemental analyses were performed on an Elementar Vario Micro Cube. IR spectra were recorded on a Nicolet 6700 FTIR spectrometer with a DRIFT cell (KBr window), and the samples were prepared in a glovebox and mixed with KBr powder. Size-exclusion chromatography (SEC) was performed on a Viscotek GPCmax consisting of a GPCmax apparatus and a model TDA 302 triple detector array. Sample solutions (1.0 mg polymer per mL THF) were filtered through a 0.45 µm syringe filter prior to injection. The flow rate was 1 mL/min. dn/dc and dA/dc data were determined by means of the integrated OmniSec software. The microstructure of the polyisoprenes was determined on a Bruker AVBII+400 spectrometer in CDCl₃ at ambient temperatures. Glass transition temperatures of the polyisoprenes (T_g) were recorded on a Perkin-Elmer DSC 8000, calibrated with cyclohexane and indium standards, and by scanning from -100 °C up to + 100 °C with heating rates of 20 K/min and cooling rates of 60 K/min in N₂ atmosphere.

[(1-{N(SiMe₃)₂}-1-Me-3,5-*t*Bu₂-C₅H₃Al)Y(2,4-dtbp)] (2). To a stirred solution of 1 (100 mg, 0.2 mmol) in 5 mL of toluene, a solution of lithium bis(dimethylsilyl) amide (27.8 mg, 0.2 mmol) in 5 mL of toluene was added and the reaction mixture was stirred for 2 h at ambient temperature. After removal of the solvent in vacuo, the remaining yellow solids were re-

dissolved in a *n*-hexane/TMS mixture. After standing for 24 h at -40 °C, complex 2 could be isolated as orange crystals. As the crystals of 2 are initially contaminated with co-crystallizing side product 2a, the batch was recrystallized three times to yield complex 2 in a sufficiently pure form (18 mg, 0.03 mmol, 15%). ¹H NMR (400 MHz, C₆D₆, 26 °C): δ 5.66 (t, 1H, ⁴J_{H,H} = 2.41 Hz, -CH=), 5.14 (dd, 2H, ${}^{4}J_{H,H} = 2.35$ Hz, ${}^{4}J_{H,H} = 0.69$ Hz, -Al-CH=), 4.99 (t, 1H, ${}^{4}J_{H,H}$ = 2.11 Hz, -CH=), 4.20 (dd, 2H, ${}^{2}J_{H,H}$ = 3.35 Hz, ${}^{4}J_{H,H}$ = 2.56 Hz, = CH_{exo}), 3.73 (m, 2H, Si-*H*), 3.39 (d, 2H, ${}^{2}J_{H,H} = 2.87$ Hz), 1.32 (s, 18H, $-CMe_{3}$), 1.20 (s, 18H, $-CMe_{3}$), 0.42 (d, 12H, ${}^{3}J_{H,H} = 2.95 \text{ Hz}, Me_{2}\text{SiH}, -0.23 \text{ (s, 3H, Al-}Me) \text{ ppm. } {}^{13}\text{C} \{{}^{1}\text{H}\} \text{ NMR (101 MHz, C_{6}\text{D}_{6}, 26 °C):}$ δ 172.7 (s, -CCMe₃), 163.7 (s, -CCMe₃), 106.5 (s, -Al-CH=), 83.3 (s, -CH=), 78.5 (s, -CH=), 78.4 (s, =CH₂), 39.6 (s, -CCMe₃), 39.5 (s, -CCMe₃), 31.5 (s, -CCMe₃), 31.4 (s, -CCMe₃), 1.8 (s, Me₂SiH), -2.3 (s, Al-Me) ppm. The signals at 106.5 and -2.3 ppm could be resolved via an ¹H-¹³C HSQC experiment. ²⁹Si{¹H} NMR (80 MHz, C₆D₆, 26 °C) d -12.9 (s, Me₂SiH) ppm. DRIFT (KBr, cm⁻¹): 3103 (w), 2962 (vs), 2904 (s), 2868 (s), 2116 (m, Si-H), 1935 (m, Si-H), 1478 (s), 1462 (s), 1439 (S), 1390 (m), 1356 (s), 1292 (w), 1251 (s), 1216 (m), 1183 (w), 1162 (w), 1115 (w), 1023 (m), 1006 (m), 942 (s), 900 (vs), 866 (m), 841 (s), 788 (s), 766 (m), 718 (w), 693 (m), 646 (m), 633 (m), 569 (w), 426 (w). Anal. Calc. for C₃₁H₆₁AlNSi₂Y: C, 60.07; H, 9.92; N, 2.26%. Found: C, 58.73; H, 9.33; N, 3.07%. The deviation of the elemental analysis data from the theoretical values results from a small amount of side product which could not be removed via recrystallization.

[(1-(2,4-dtbp)-1-Me-3,5-*t*Bu₂-C₅H₃Al)Y{N(SiMe₃)₂}(thf)₂] (3). To a solution of 2 (50 mg, 0.08 mmol) in *n*-hexane, excess THF (~ 10 equiv.) was added and the reaction mixture was left standing at -40 °C overnight. After this time, a small quantity of orange crystals of 3 suitable for X-ray crystallography could be collected. Compound 3 is not stable in aliphatic and aromatic solvents or when exposed to a vacuum and rearranges back to complex 2 with loss of THF.

[(1-Me-3,5-*t*Bu₂-C₅H₃Al)(μ -Me)Y(benzene)][B(C₆F₅)₄] (4). To a stirred solution of 1 (153 mg, 0.30 mmol) in 2.5 mL of toluene, a solution of [CPh₃][B(C₆F₅)₄] (281 mg, 0.30 mmol) in 2.5 mL of toluene was added. The reaction mixture was stirred for 30 min. at ambient temperature and concentrated in vacuo. After addition of *n*-hexane (toluene/*n*-hex. = 5:1), an orange solid precipitated. The precipitate was re-dissolved in benzene and after standing at ambient temperature overnight, orange crystals of 4 (108 mg, 0.10 mmol, 33%) could be obtained. ¹H NMR (400 MHz, [D₈]toluene, 26 °C): δ = 7.12 (6 H, s, C₆H₆), 5.20 (1 H, t, ⁴J_{H,H} = 2.45 Hz, =CH–), 5.06 (2 H, dd, ⁴J_{H,H} = 2.55 Hz, ⁴J_{H,H} = 1.13 Hz, –AlCH=),

0.90 (18 H, s, $-C(CH_3)_3$), -0.47 (3 H, s, $-AlCH_3$), -0.97 (3 H, d, ${}^2J_{H,Y} = 4.55$ Hz, $Al-CH_3-Y$) ppm. ${}^{13}C$ NMR (101 MHz, [D₈]toluene, 26 °C): $\delta = 173.3$ ($-CC(CH_3)_3$), 149.0 (Ar–F), 138.8 (Ar–F), 137.1 (Ar–F), 128.6 (C_6H_6), 115.6 (-AlCH=), 105.3 (Ar–B), 87.1 (=CH-), 39.7 ($-CC(CH_3)_3$), 30.4 ($-CC(CH_3)_3$), -5.7 (Al– CH_3-Y), -6.4 ($-AlCH_3$) ppm. ${}^{19}F$ NMR (376 MHz, [D₈]toluene, 26 °C): $\delta = -136.5$ (8 F, s, *ortho*-F), -165.3 (4 F, t, ${}^{3}J_{F,F} = 21.5$ Hz, *para*-F), -170.4 (8 F, br s, *meta*-F) ppm. ${}^{11}B$ NMR (128 MHz, [D₈]toluene, 26 °C): $\delta = -16.1$ ppm. ${}^{89}Y$ NMR (20 MHz, [D₈]toluene, 26 °C): $\delta = 175.5$ ppm. The ${}^{89}Y$ signal could be resolved with a ${}^{1}H-{}^{89}Y$ HSQC NMR experiment. *Anal*. Calc. for C₄₅H₃₃F₂₀BAIY: C, 50.03; H, 3.08%. Found: C, 49.48; H, 2.97%. The discrepancy between the elemental analysis formula and that given in the crystallography data (Table S1) derives from one half molecule of benzene per unit cell which is removed when the complex is dried under vacuum.

[(2,4-dtbp)₂**AlMe] (5).** To a stirred solution of **1-Y** (10 mg, 0.02 mmol) in 0.5 mL of C₆D₆, a solution of Me₂AlCl (3.6 mg, 0.02 mmol) in 0.5 mL of C₆D₆ was added. The reaction mixture was stirred at ambient temperature for 30 minutes. A subsequently recorded ¹H NMR spectrum showed >99% conversion of **1-Y** to [(2,4-dtbp)₂AlMe] and an yttrium chloride containing species. Crystals of **5** suitable for X-ray structure analysis could be grown from a saturated *n*-hexane solution. ¹H NMR (400 MHz, C₆D₆, 26 °C): δ 5.98 (s, 2H, –CH=), 3.04 (s, 8H, –CH₂), 1.05 (s, 36H, –CC*Me*₃), 0.02 (s, 3H, Al–*Me*) ppm. ¹³C {¹H} NMR (101 MHz, C₆D₆, 26 °C): δ 175.2 (s, –CCMe₃), 98.4 (s, –CH=), 59.7 (s, –CH₂), 39.0 (s, –CCMe₃), 29.1 (s, –CC*Me*₃), –4.7 (s, Al–*Me*) ppm. Elemental analysis of **5** could not be performed due to co-crystallization of an unknown side product.

Polymerization of Isoprene. A detailed polymerization procedure is described as a typical example (Table 1, entry 1). A solution of $[CPh_3][B(C_6F_5)_4]$ (**A**) (1 equiv., 18.4 mg, 0.02 mmol) in toluene (3.5 mL) was added to a solution of **1** (10.0 mg, 0.02 mmol) in toluene (8 mL) and the mixture was stirred at ambient temperature for 30 min. After addition of isoprene (2.00 mL, 20 mmol), the polymerization was carried out at ambient temperature for 2 h. The polymerization mixture was quenched in a large quantity (50 mL) of methanol containing 0.1% (w/w) 2,6-di-*tert*-butyl-4-methylphenol as a stabilizer. After washing with methanol, the polymer was dried in vacuo at ambient temperature to constant weight. The monomer conversion was determined gravimetrically. The microstructure of the polymer was examined by ¹H and ¹³C NMR spectroscopy in CDCl₃.

The following polymerization runs did not produce any polymer (conditions as described in Table 1):

- 2 without cocatalyst/toluene/2 h/25 $^{\circ}\mathrm{C}$
- 2 without cocatalyst/toluene/thf/2 h/25 $^{\circ}\mathrm{C}$
- 2 with 1 equiv A/toluene/thf/2 h/25 $^{\circ}$ C

- 1-Y with 1 equiv $[Et_3NH][BPh_4]/toluene/2 h/25 °C$; the ¹H NMR spectrum of this reaction indicates that the reaction is incomplete and that H(2,4-dtbp), Et₃N and another unidentified product had formed (Figure S6); the isolation of any yttrium complex was not successful.

NMR Spectra



Figure S1. ¹H NMR spectrum (400 MHz) of **2** in C₆D₆ at 26 °C. The solvent residual signal is marked with an asterisk.



Figure S2. ¹³C{¹H} NMR spectrum (101 MHz) of **2** in C₆D₆ at 26 °C. The solvent residual signal is marked with an asterisk.



Figure S3. ¹H-¹³C HSQC NMR spectrum of **2** in C₆D₆ at 26 °C. The solvent residual signal is marked with an asterisk.



Figure S4. ²⁹Si{¹H} INEPT NMR spectrum of 2 in C_6D_6 at 26 °C.



Figure S5. ¹H NMR spectrum (400 MHz) of **3** in C₆D₆ at 26 °C. The solvent residual signal is marked with an asterisk. # for rearranged complex **2**. + for THF.



Figure S6. ¹H NMR spectrum (400 MHz) of the reaction of **1-Y** with [Et₃NH][BPh₄] in toluene-d₈ at 26 °C. The solvent residual signals are marked with asterisks. + for H(2,4-dtbp), # for unreacted **1-Y**, & for Et₃N.



Figure S7. ¹H NMR spectrum (400 MHz) of **4** in toluene-d₈ at 26 °C. The solvent residual signals are marked with asterisks.



Figure S8. ¹³C{¹H} NMR spectrum (101 MHz) of **4** in toluene-d₈ at 26 °C. The solvent residual signals are marked with asterisks.



Figure S9. ${}^{19}F{}^{1}H$ NMR spectrum (377 MHz) of 4 in toluene-d₈ at 26 °C.



Figure S10. ¹¹B NMR spectrum (96 MHz) of 4 in toluene-d₈ at 26 °C.



Figure S11. ¹H-⁸⁹Y HSQC NMR spectrum of 4 in toluene-d₈ at 26 °C.



Figure S12. ¹H NMR spectrum (400 MHz) of catalyst system 1/A in toluene-d₈ at 26 °C. The solvent residual signals are marked with asterisks.



Figure S13. ${}^{19}F{}^{1}H$ NMR spectrum (377 MHz) of catalyst system 1/A in toluene-d₈ at 26 °C.



Figure S14. ¹H NMR spectrum (400 MHz) of catalyst system 1/2A in toluene-d₈ at 26 °C. The solvent residual signals are marked with asterisks.



Figure S15. ¹⁹F $\{^{1}H\}$ NMR spectrum (377 MHz) of catalyst system 1/2A in toluene-d₈ at 26 °C.



Figure S16. ¹H NMR spectrum (400 MHz) of catalyst system 1/B in toluene-d₈ at 26 °C. The solvent residual signals are marked with asterisks.



Figure S17. ¹⁹F{¹H} NMR spectrum (377 MHz) of catalyst system 1/B in toluene-d₈ at 26 °C.



Figure S18. ¹H NMR spectrum (400 MHz) of catalyst system 1/2B in toluene-d₈ at 26 °C. The solvent residual signals are marked with asterisks.



Figure S19. ¹⁹F $\{^{1}H\}$ NMR spectrum (377 MHz) of catalyst system 1/2B in toluene-d₈ at 26 °C.



Figure S20. ¹H NMR spectrum (400 MHz) of the reaction of **1-Y** with Me₂AlCl in C₆D₆ at 26 °C. The solvent residual signal is marked with an asterisk. # for unknown side product.



Figure S21. ¹³C NMR spectrum (101 MHz) of the reaction of **1-Y** with Me₂AlCl in C₆D₆ at 26 °C. The solvent residual signal is marked with an asterisk. # for unknown side product.



Figure S22. [!]H NMR spectrum (500 MHz) of the reaction of **1-Y** with Me₂AlCl in toluene-d₈ at -80 °C. The solvent residual signals are marked with asterisks.



Figure S23. ¹H NMR spectrum (400 MHz) of the reaction of **4** (#) with 1 equivalent of isoprene (+) in toluene-d₈ at 26 °C. The solvent residual signals are marked with asterisks. **&** for polyisoprene.

X-Ray Crystallography

Suitable crystals for X-ray structure analyses were selected in a glovebox and coated with Parabar 10312 (previously known as Paratone N, Hampton Research) and fixed on a nylon/loop glass fiber. X-ray data for compounds **2** to **5** were collected on a Bruker APEX II DUO instrument equipped with an ImS microfocus sealed tube and QUAZAR optics for MoK α (l= 0.71073) and CuK α (l=1.54184) radiation. The data collection strategy was determined using COSMO³ employing ω -scans. Raw data were processed using APEX⁴ and SAINT.⁵ Corrections for absorption effects were applied using SADABS.⁶ The structures were solved by direct methods and refined against all data by fullmatrix least-squares methods on F2 using SHELXTL⁷ and SHELXLE.⁸ All graphics were produced employing CCDC Mercury 3.10.1.⁹



Figure S24. Molecular structure of **2** (ellipsoids set at 50%). All hydrogen atoms except for H2 have been omitted for clarity. Selected interatomic distances (Å) and angles (°): Y–C1 2.5798(2), Y–C2 2.6930(2), Y–C3 2.5490(2), Y–C4 2.7050(2), Y–C5 2.5671(2), Y–C15 2.6310(2), Y–C16 2.7396(2), Y–C17 2.6210(2), Y–C18 2.7388(2), Y–C19 2.6779(2), Y–N 2.5246(1), Y–H2 2.3461(9), Y^{...}Al 2.8437(5), Y–Si1 3.995(4), Y–Si2 3.104(3), Al–C1 1.9794(2), Al–C5 2.0014(2), Al–C14 1.9591(2), Al–N 1.9827(1), N–Si1 1.7466(1), N–Si2 1.7316(1), Si1–H1A 1.412(2), Si2–H2 1.462(2), C1–C2 1.382(2), C2–C3 1.438(2), C3–C4 1.442(2), C4–C5 1.383(2), C15–C16 1.370(3), C16–C17 1.432(2), C17–C18 1.432(2), C18–C19 1.376(2), Al(benzene)–Y–(2,4-dtbp) 144.85, Y–N–Si1 134.86(7), Y–N–Si2 91.73(6), Y–H2–Si2 46.3(7), C1–Al–C5 94.00(7), C14–Al–N 112.34(7), Al–N–Y 77.20(5), Si1–N–Si2 117.27(8), C1–C2–C3 122.64(2), C2–C3–C4 125.80(2), C3–C4–C5 122.35(2), C4–C5–Al 124.57(1), Al–C1–C2 125.44(1)



Figure S25. Molecular structure of 2a (ellipsoids set at 50%). All hydrogen atoms except for H01-H04 have been omitted for clarity. Selected interatomic distances (Å) and angles (°): Y1-C14 2.500(5), Y1-C15 2.641(5), Y1-C16 2.558(5), Y1-C17 2.700(5), Y1-C18 2.522(5), Y1-C35 2.719(6), Y1-C5 2.543(5), Y1-N1 2.265(5), Y1-Si1 3.610(8), Y1-Si2 3.028(0), Y1...H02 2.680(3) Y1...Al 3.101(9), Y1...Li 3.922(0), Y1...Y2 3.263(0), Y2-C1 2.790(5), Y2-C2 2.733(5), Y2-C3 2.615(5), Y2-C4 2.703(6), Y2-C5 2.663(5), Y2-C14 2.426(5), Y2-C18 2.475(5), Y2-N2 2.339(4), Y2-Si3 3.065(4), Y2-Si4 3.584(3), Y2-H03 2.556(0), Y2-Li 2.983(1), Y2...Al 3.461(3), Al-C1 1.976(6), Al-C5 2.014(6), Al-C35 2.027(6), Al-C36 1.998(5), N1-Si1 1.765(1), N1-Si2 1.680(6), N2-Si3 1.697(5), N2-Si4 1.709(5), Si1-H01 1.49(2), Si2-H02 1.48(9), Si3-H03 1.46(6), Si4-H04 1.39(6), Li-C14 2.368(1), Li-C15 2.365(1), Li-C16 2.449(1), Li-C17 2.403(1), Li-C18 2.528(1), Li-N2 2.207(1), C1-C2 1.370(7), C2–C3 1.456(8), C3–C4 1.409(9), C4–C5 1.412(8), C14–C15 1.390(7), C15–C16 1.445(7), C16-C17 1.471(7), C17-C18 1.372(7), Li-Yttracycle-Y1 176.83, Y1-N1-Si1 126.9(4), Y1-N1-Si2 99.2(2), Y2-N2-Si3 97.5(2), Y2-N2-Si4 123.9(2), Y1-C35-Al 80.1(9), Y1-C5-Al 84.9(2), C1-Al-C5 95.2(2), Al-C1-C2 91.5(2), C1-C2-C3 121.2(5), C2-C3-C4 128.8(5), C3-C4-C5 124.4(5), C4-C5-Al 111.3(4), C14-Y2-C18 72.36(2), Y2-C14-C15 138.7(4), C14-C15-C16 120.4(5), C15-C16-C17 126.6(5), C16-C17-C18 122.4(5), C17–C18–Y2 134.1(4), N2–Y2–Al(benzene) 155.2(1)



Figure S26. Molecular structure of **3** (ellipsoids set at 50%). All hydrogen atoms except for H1A and H30 have been omitted for clarity. Selected interatomic distances (Å) and angles (°): Y–C1 2.5183(2), Y–C2 2.7150(1), Y–C3 2.5934(1), Y–C4 2.6673(1), Y–C5 2.4808(2), Y–O1 2.3776(1), Y–O2 2.4162(1), Y–N 2.2757(2), Y–H1A 2.4461(7), Y–Si1 3.059(5), Y–Si2 3.645(0), Y1^{...}Al 3.1656(2), N–Si1 1.6944(1), N–Si2 1.7004(1), Si1–H1A 1.4331(7), Si2–H30 1.4611(7), Al–C1 2.0320(2), Al–C5 2.0288(2), Al–C14 2.0255(2), Al–C27 2.0032(2), C1–C2 1.3908(2), C2–C3 1.4554(2), C3–C4 1.4386(2), C4–C5 1.4031(2), C14–C15 1.497(2), C15–C16 1.350(2), C16–C17 1.486(3), C17–C18 1.332(2), Al(benzene)–Y–N 129.70, Y–N–Si1 99.8(0), Y–N–Si2 132.4(1), C1–Al–C5 93.9(1), Al–C1–C2 113.8(1), C1–C2–C3 122.0(3), C2–C3–C4 128.0(9), C3–C4–C5 122.4(5), C4–C5–Al 113.9(3), C14–Al–C27 111.4(8), Al–C14–C15 118.0(1), C14–C15–C16 123.3(7), C15–C16–C17 126.3(2), C16–C17–C18 121.6(1)

	2	2a	3	4	5
CCDC	1909565	1909561	1909562	1909563	1909564
formula	$C_{31}H_{61}AlNSi_2Y \\$	C ₃₆ H ₇₆ AlLiN ₂ Si ₄ Y ₂	C ₃₉ H ₇₇ AlNO ₂ Si ₂ Y	C48H36AlBF20Y	C27H49Al
$M_r \left[g \; mol^{-1}\right]$	619.87	861.08	764.08	1119.47	400.64
color	yellow/plate	colorless/block	yellow/block	yellow/plate	light yellow/block
crystal dimensions [mm]	0.315 x 0.156 x 0.074	0.352 x 0.188 x 0.158	0.399 x 0.261 x 0.222	0.304 x 0.182 x 0.078	0.441 x 0.146 x 0.135
cryst syst	monoclinic	monoclinic	triclinic	triclinic	monoclinic
space group	$P2_1/n$	$P2_1/c$	ΡĪ	ΡĪ	$P2_1/c$
a [Å]	20.8047(5)	12.0838(4)	9.622(3)	10.5894(8)	12.3276(9)
b [Å]	18.2082(4)	20.2609(6)	14.892(9)	11.8158(9)	11.8951(8)
c [Å]	21.5805(5)	20.2692(6)	16.656(5)	20.8872(15)	19.0841(14)
α [°]	90	90	97.74(2)	83.602(2)	90
β [°]	117.8930(10)	107.130(2)	98.209(16)	80.112(2)	107.151(2)
γ [°]	90	90	107.16(2)	65.546(2)	90
V[Å ³]	7225.3(3)	4742.3(3)	2217.1(17)	2341.3(3)	2674.0(3)
Z	8	4	2	2	4
<i>T</i> [K]	100(2)	100(2)	100(2)	100(2)	100(2)
$\rho_{calcd} \left[g \ cm^{-3}\right]$	1.140	1.206	1.145	1.588	0.995
$\mu \; [\mathrm{mm}^{-1}]$	1.723	2.579	1.419	1.379	0.085
F (000)	2672	1824	828	1122	896
θ range [°]	1.546/29.130	1.454/27.103	1.257/28.281	1.8945/28.281	1.729/27.102
unique reflns	19398	10444	10987	11627	5889
observed reflns (I $> 2\sigma$)	137168	86860	85846	90834	92611
$R1/wR2~(I > 2\sigma)^{[a]}$	0.0319/0.0661	0.0624/0.1575	0.0265/0.0669	0.0302/0.0740	0.0364/0.0921
R1/wR2 (all data) ^[a]	0.0559/0.0747	0.0794/0.1623	0.0299/0.0683	0.0368/0.0767	0.0453/0.0987
GOF ^[a]	0.929	1.066	1.035	1.033	1.015

Table S1. Crystallographic data for compounds 2, 2a, 3, 4, and 5

 $\boxed{[\mathbf{a}] R1 = \Sigma(||F_0| - |F_c||)/\Sigma|F_0|, F_0 > 4\sigma(F_0). wR2 = \{\Sigma[w(F_0^2 - F_c^2)^2/\Sigma[w(F_0^2)^2]\}^{1/2}.}$

References

- 1. D. Barisic, D. Schneider, C. Maichle-Mossmer and R. Anwander, *Angew. Chem. Int. Ed.*, 2019, **58**, 1515-1518.
- 2. R. Anwander, O. Runte, J. Eppinger, G. Gerstberger, E. Herdtweck and M. Spiegler, *J. Chem. Soc., Dalton Trans.*, 1998, 847-858.
- 3. COSMO, v. 1.61; BRUKER AXS Inc., Madison, WI, 2012.
- 4. APEX 3, v. 2016.5-0, BRUKER AXS Inc., Madison, WI, 2012.
- 5. SAINT, v. 8.34A, BRUKER AXS Inc., Madison, WI, 2010.
- 6. L. Krause, R. Herbst-Irmer, G. M. Sheldrick and D. Stalke, *J. Appl. Crystallogr.*, 2015, **48**, 3-10.
- 7. G. M. Sheldrick, *Acta Crystallogr. A*, 2015, **71**, 3-8.
- 8. C. B. Hubschle, G. M. Sheldrick and B. Dittrich, *J. Appl. Crystallogr.*, 2011, **44**, 1281-1284.
- 9. C. F. Macrae, I. J. Bruno, J. A. Chisholm, P. R. Edgington, P. McCabe, E. Pidcock, L. Rodriguez-Monge, R. Taylor, J. van de Streek and P. A. Wood, *J. Appl. Crystallogr.*, 2008, **41**, 466-470.