

Electronic supplementary information (ESI)

A pyrazolate-stabilized sodium hydride complex

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Contents:	Page
1. Experimental section	S2
1.1 General considerations	S2
1.2 [Na(pz)]	S2
1.3 Synthesis of [(pz) ₆ Na ₇ H] 1	S3
1.4 [K(pz)]	S4
2. X-ray crystallography	S4
2.1 General remarks	S4
2.2 Crystal structure of [(pz) ₆ Na ₇ H]·0.5 C ₆ H ₆ , 1 ·0.5 C ₆ H ₆	S5
2.3 Crystal structure of [Na(pz)]·0.167 C ₇ H ₈	S6
2.4 Crystallographic details	S7
3. References	S8

1. Experimental section

1.1 General considerations

All manipulations were carried out using standard Schlenk and glove box techniques under an atmosphere of high purity dinitrogen. Benzene, toluene, tetrahydrofuran and hexane were dried and distilled over molten potassium. ^1H and $^{13}\text{C}\{^1\text{H}\}$ NMR spectra were recorded on a Bruker DPX 300 or Bruker Avance 400 spectrometer in deuterated benzene and were referenced to the residual ^1H or $^{13}\text{C}\{^1\text{H}\}$ resonances of the solvent used. The IR spectrum was recorded using an Agilent Cary 630 ATR FTIR spectrometer. The melting point was determined in a sealed glass capillary under dinitrogen and is uncorrected. The elemental analysis was performed by the Elemental Analysis Service at London Metropolitan University. 3,5-Di-tert-butyl-1H-pyrazole (pzH)^{S1} was prepared according to a literature procedure. Solid $[\text{Na}^n\text{Bu}]$ and $[\text{K}^n\text{Bu}]$ were prepared from the reaction of $^n\text{BuLi}$ with $[\text{MO}^t\text{Bu}]$ ($\text{M} = \text{Na}, \text{K}$) as described elsewhere,^{S2} and stored in a glove box freezer at -30°C . Ph_2SiH_2 (Sigma-Aldrich) was used as received. NMR experiments were carried out in 5 mm NMR tubes with J.Young stopcock in dried deuterated benzene (*ca.* 0.55 mL).

1.2 $[\text{Na}(\text{pz})]$. The compound was reported previously and was prepared from the reaction of pzH with Na metal at elevated temperatures.^{S3,S4}

Preparation of $[\text{Na}(\text{pz})]$ from $[\text{Na}\{\text{N}(\text{SiMe}_3)_2\}]$ and pzH: Toluene (15 cm³) was added to a solid mixture of $[\text{Na}\{\text{N}(\text{SiMe}_3)_2\}]$ (0.60 g, 3.27 mmol, 1.05 eq) and pzH (0.56 g, 3.11 mmol, 1.0 eq) and stirred at room temperature for two hours giving a clear solution. All volatiles were removed and the residue was dried under vacuum at elevated temperature (*ca.* 50-60°C). *n*-Hexane (15 mL) was added and the mixture was vigorously stirred for one hour and then left to settle. The precipitate of $[\text{Na}(\text{pz})]$ was filtered off and dried under vacuum. The *n*-hexane solution was concentrated under reduced pressure to approximately one third in volume and further crystalline material was obtained. Further concentration and cooling to 4°C afforded a small third crop. All crops were dried under vacuum. Yield: (0.39 g, 1.93 mmol, 62%).

Reaction of pzH with NaH: $[\text{Na}(\text{pz})]$ was cleanly obtained by heating a sample of pzH with an excess of solid NaH in a sealed NMR tube in deuterated benzene to 60°C. Essentially complete conversion for a small sample was achieved after one day. Further heating for three additional days did not yield a different compound such as $[(\text{pz})_6\text{Na}_7\text{H}]$ **1** and no NaH resonance (*e.g.* 5.17 ppm) was found. H_2 was detected as the expected by-product.

Reaction of pzH with [NaⁿBu]: Alternatively, [Na(pz)] can also be obtained from pzH and solid [NaⁿBu] in toluene or benzene, for example, when further conversion of excess [NaⁿBu] to **1** is carried out as the next step.

NMR data from the pzH and NaH experiments:

[Na(pz)] in deuterated benzene: δ_{H} (300.13 MHz; C₆D₆; 298K; Me₄Si): 1.16 (s, 18H, C(CH₃)₃), 6.10 (s, 1H, CH).

For comparison: pzH in deuterated benzene δ_{H} (300.13 MHz; C₆D₆; 298K; Me₄Si): 1.32 (s, 18H, C(CH₃)₃), 6.00 (s, 1H, CH), 11.70 (s, 1H, NH)

X-ray structural study: during the study a different solvate from toluene, [Na(pz)]·0.167 C₇H₈, was characterised, see the X-ray crystallography section.

1.3 Synthesis of [(pz)₆Na₇H] **1.** Toluene (12 cm³) was added to a solid mixture of [Na(pz)] (0.18 g, 0.890 mmol, 1.4 eq) and [NaⁿBu] (50 mg, 0.624 mmol, 1.0 eq) and stirred at room temperature. Ph₂SiH₂ (0.14 mL, 0.139 g, 0.754 mmol, 1.2 eq) was added, the mixture almost fully dissolved and was stirred for two hours at 90°C to yield a colourless solution. After cooling to room temperature, all volatiles were removed (via a gel-like solid) and the residue was dried under vacuum. *n*-Hexane (12 mL) was added and the mixture was vigorously stirred at 50°C for one hour and cooled to room temperature. The precipitate was filtered off and dried under vacuum to yield [(pz)₆Na₇H] **1** (0.12 g). Note: concentration and cooling of the silane-rich *n*-hexane solution afforded a very small crop of [(pz)₆Na₇H] **1** after drying under vacuum. The compound can be recrystallised from benzene and the crystal structure of [(pz)₆Na₇H]·0.5 C₆H₆, **1**·0.5 C₆H₆, was determined, see the X-ray crystallography section. Yield: 0.12 g (0.0970 mmol, 65%) of solvent-free [(pz)₆Na₇H] **1**. M.p.: slowly changes towards off-white above 300°C, no visible full decomposition or melting up to 350°C. Elemental analysis (on [(pz)₆Na₇H] **1**): found: C, 64.2; H, 9.5; N, 13.4. Calc. for C₆₆H₁₁₅N₁₂Na₇ (1237.63 g/mol): C, 64.05; H, 9.4; N, 13.6%. ¹H and ¹³C {¹H} solution NMR data for [(pz)₆Na₇H] in deuterated benzene: δ_{H} (300.13 MHz; C₆D₆; 298K; Me₄Si): 1.14 (s, 108H, C(CH₃)₃), 5.17 (s, br, 1H, NaH), 6.09 (s, 6H, CH). δ_{C} (75.5 MHz; C₆D₆; 298K; Me₄Si): 31.7 (C(CH₃)₃), 32.1 (C(CH₃)₃), 97.1 (pz-CH), 165.7 (pz-NC). IR (ATR, solid): ν_{max} /cm⁻¹ 3025w, 2960s, 2930m, 2905m, 2861m, 1567m, 1489s, 1459s, 1359m, 1284m, 1247s, 1205m, 1196m, 1128w, 1015m, 1003s, 991s, 957m, 901w, 864s, 801s, 777m, 728s, 705m, 700m, 682m, 674m, 666m, 657m.

Note: Room temperature preparations using [Na(pz)], [NaⁿBu] and Ph₂SiH₂ in hydrocarbon solvents did afford some crystals of [(pz)₆Na₇H] **1**, but the reaction mixtures were very difficult to work-up and purify, and filtrations were near impossible, with some gel-like precipitate present. Changing the reactions conditions to hot toluene afforded a more straightforward synthesis. *In-situ* NMR experiments in deuterated benzene did produce resonances for some symmetric compound plus

silane by-products, though a potential NaH resonance is hidden by very strong SiH peaks and thus these experiments were not suitable for studying the formation of [(pz)₆Na₇H] **1** in solution.

1.4 [K(pz)]. The compound was reported previously and was prepared from the reaction of pzH with K metal at elevated temperatures.^{S3} It can similarly to [Na(pz)] be prepared from pzH and [K{N(SiMe₃)₂}] in toluene to form a precipitate of [K(pz)] that can be washed with *n*-hexane and dried under vacuum, or by reacting pzH with a slight excess of KH in toluene. The latter reaction proceeds already at room temperature (*c.f.* the NaH reaction) due to the higher reactivity of KH vs. NaH, though is faster at elevated temperatures. The product [K(pz)] is virtually insoluble in toluene and can be extracted with THF and crystallises as a solvent-free polymer. In experiments using [K(pz)], [KⁿBu] and Ph₂SiH₂, similar to the synthesis of **1**, we only obtained crystallised polymeric [K(pz)] from neat THF so far.

2. X-ray crystallography

2.1 General remarks

Suitable crystals were mounted in silicone oil and were measured at the MX1 beamline at the Australian Synchrotron using synchrotron radiation with a wavelength close to Mo_{Kα} radiation. Data collection was performed using the Blu-Ice^{S5} software package, and data reduction was performed using XDS.^{S6} All structures were solved and refined by direct methods using SHELX.^{S7} Semi-empirical (multi-scan) absorption corrections were performed on all datasets. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms on organic groups were included in calculated positions using the riding model. The central hydride in [(pz)₆Na₇H]·0.5 C₆H₆, **1**·0.5 C₆H₆, was located from difference maps and its position was freely refined. Refinement details are summarized in 2.4, Table S1. CCDC 1043423 (**1**·0.5 C₆H₆) and 1043424 ([Na(pz)]·0.167 C₇H₈) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

2.2 Crystal structure of [(pz)₆Na₇H]·0.5 C₆H₆, 1·0.5 C₆H₆

Crystals of the benzene solvate of [(pz)₆Na₇H] **1** were obtained from a concentrated benzene solution at room temperature. The complex crystallises with a full molecule in the tetragonal crystal system (Fig. S1). Four tert-butyl groups are disordered and were modelled using two positions for the methyl groups and were refined using geometry restraints. This resulted in two positions each for C16-C18 (75 and 25% parts), C27-C29 (55 and 45% parts), C38-C40 (71 and 29% parts) and C64-C66 (77 and 23% parts), and their respective attached hydrogen atoms.

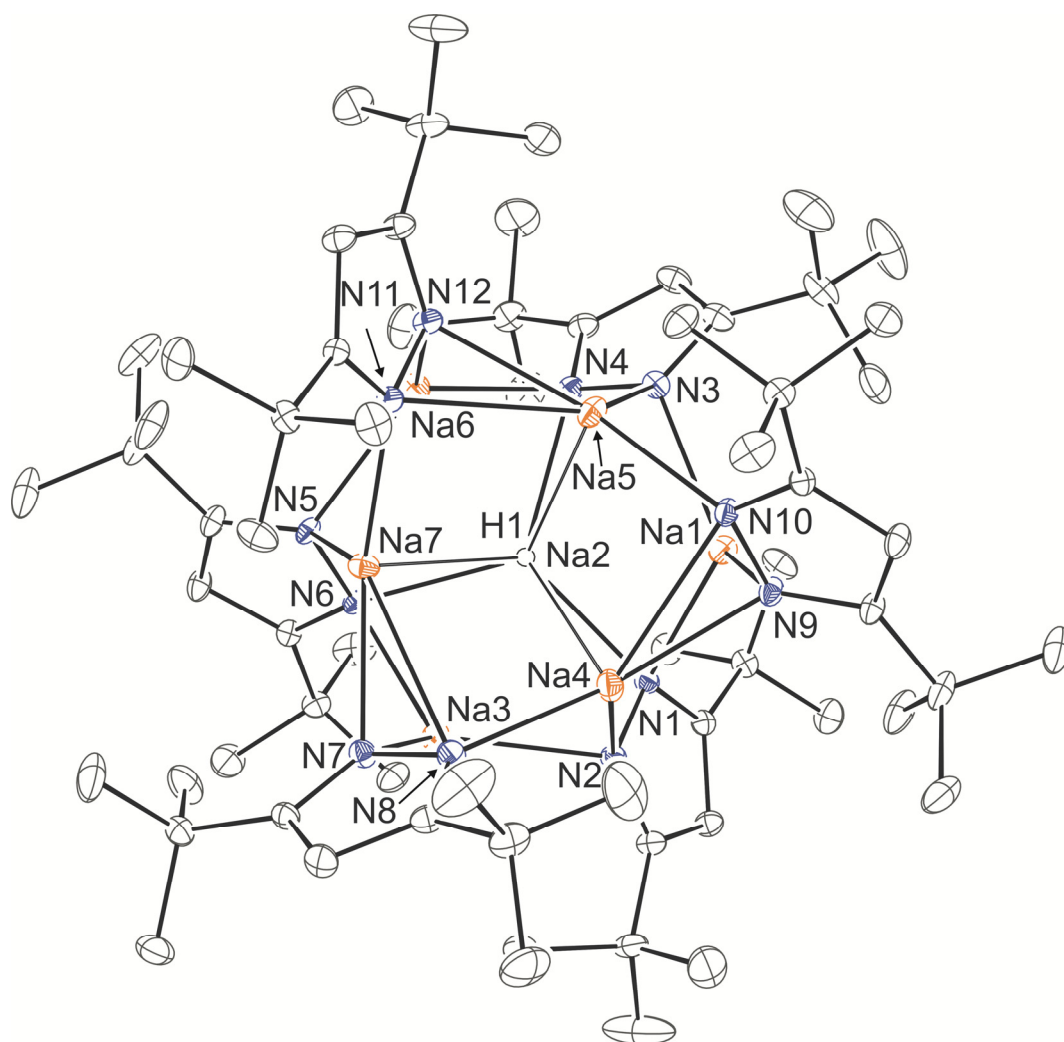


Fig. S1 Molecular structure of [(pz)₆Na₇H] **1**·0.5 C₆H₆ (ORTEP drawing, 30% thermal ellipsoids): view along the H1···Na2 contact. Solvent molecule, minor disordered parts and hydrogen atoms except H1 are omitted for clarity.

2.3 Crystal structure of $[\text{Na}(\text{pz})]\cdot 0.167 \text{C}_7\text{H}_8$

This compound could be crystallized as a toluene solvate in one-dimensional chains in a similar manner to previously characterised solvates or polymorphs.^{S3,S4} The asymmetric unit (see Fig. S2) contains six independent (pz)Na-fragments and one full toluene molecule. One tert-butyl group is disordered and was modelled using two positions for the methyl groups and was refined using geometry restraints. This resulted in two positions each for C16-C18 (72 and 28% parts) and their respective attached hydrogen atoms.

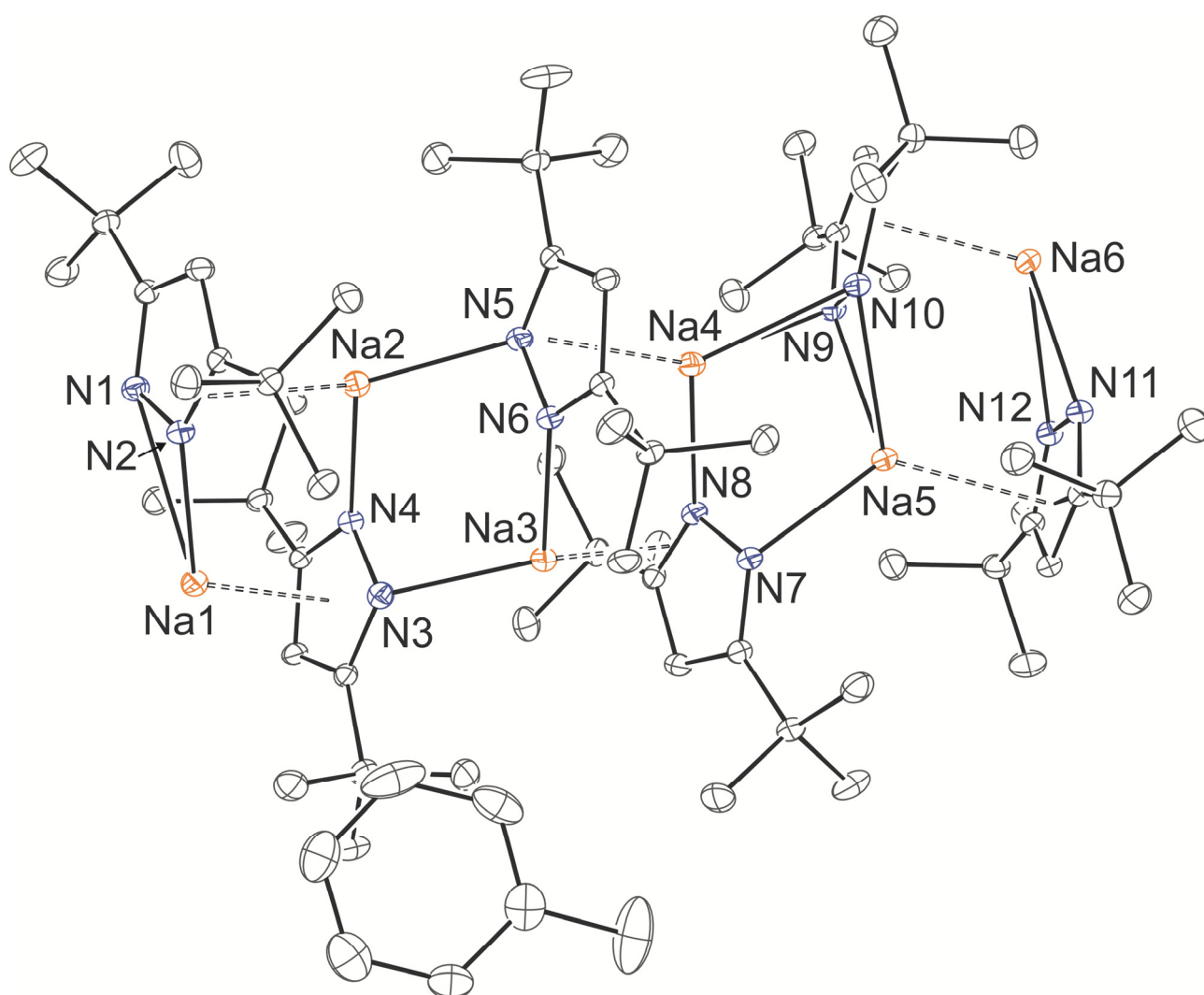


Fig. S2 Asymmetric unit of the molecular structure of $[\text{Na}(\text{pz})]\cdot 0.167 \text{C}_7\text{H}_8$ (30% thermal ellipsoids) containing six (pz)Na fragments (that grow into a one-dimensional polymer) and one toluene molecule. A minor disordered part and hydrogen atoms are omitted for clarity.

2.4 Crystallographic details

Table S1 Crystallographic data.

Compound reference	[(pz) ₆ Na ₇ H]·0.5 C ₆ H ₆ , 1·0.5 C ₆ H ₆	[Na(pz)]·0.167 C ₇ H ₈
Chemical formula	C ₆₉ H ₁₁₈ N ₁₂ Na ₇	C _{12.17} H _{20.33} N ₂ Na
Formula Mass	1276.68	217.63
Crystal system	Tetragonal	Monoclinic
<i>a</i> /Å	32.759(5)	15.184(3)
<i>b</i> /Å	32.759(5)	19.831(4)
<i>c</i> /Å	29.376(6)	26.107(5)
<i>α</i> /°	90	90.00
<i>β</i> /°	90	100.11(3)
<i>γ</i> /°	90	90.00
Unit cell volume/Å ³	31525(11)	7739(3)
Temperature/K	100(2)	100(2)
Space group	<i>I</i> -42 <i>d</i>	<i>P</i> 2 ₁ / <i>c</i>
<i>Z</i>	16	24
Radiation type, λ/Å	Synchrotron, 0.71080	Synchrotron, 0.71080
Crystal size/mm	0.12 × 0.10 × 0.07	0.10 × 0.04 × 0.03
Absorption coefficient, μ/mm ⁻¹	0.097	0.095
Theta range/°	0.931-27.998	1.297-31.206
Data completeness	99.7% (at theta max)	99.6% (at 25.00° theta)
No. of reflections measured	178030	75996
No. of independent reflections	18969	22016
<i>R</i> _{int}	0.1649	0.1059
Final <i>R</i> ₁ values (<i>I</i> > 2σ(<i>I</i>))	0.0539	0.0675
Final <i>wR</i> (<i>F</i> ²) values (<i>I</i> > 2σ(<i>I</i>))	0.1389	0.1635
Final <i>R</i> ₁ values (all data)	0.0547	0.1179
Final <i>wR</i> (<i>F</i> ²) values (all data)	0.1398	0.1923
Goodness of fit on <i>F</i> ²	1.065	1.019
Largest diff. peak and hole/e·Å ⁻³	0.414 and -0.505	0.719 and -0.405
CCDC number	1043423	1043424

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