Supporting information

A Versatile Hard-Soft N/S-Ligand for Metal Coordination and Cluster Formation

Callum G. M. Benson, Alex Plajer, Raul Garcia-Rodriguez, Andrew D. Bond, Sanjay Singh, Lutz H. Gade and Dominic S. Wright

Synthetic Section

All manipulations were done under dry, O_2-free N_2 using standard inert-atmosphere procedures and the use of a high-integrity glove box. The synthesis of the precursor **1**H_2 was undertaken according to a published literature procedure **1** (ref. 17 of the paper). BnNa was synthesised according to literature procedure.[1]

*Synthesis of [Mg(**1**)·2thf] (**2**)*; A solution of Bu_2Mg (0.185 ml, 0.5M in heptane, 0.092 mmol) was added to a solution of **1** (50 mg, 0.18 mmol) in thf (5 ml) at -78°C. The solution was warmed to room temperature with stirring and then the solvent removed under vacuum. The resulting foamy powder was washed with *n*-pentane with vigorous stirring (2x10ml) and the solid residue was suspended in toluene (10 ml) with the slow addition of thf (*ca* 2 ml) and gentle heating until the powder was dissolved. The product **2** crystallises as colourless clear crystals after storage at -12°C (16h) (56 mg 70%). Elemental Analysis: Calc; C, 44.0; H, 7.8; N, 6.4. Measured; C,43.8; H, 8.1; N, 5.3.[2] ^{1}H NMR (500.2 MHz, d_8-thf, +25°C): δ/ppm = 3.61 (7.5H, bs, CH_2-thf), 1.75 (9.3H, br.s, CH_2-thf), 1.32 (18H, s, ^{t}Bu) ^{31}P NMR (161.7 MHz, d_8-thf, rel. 85% H_3PO_4/D_2O. +25°C): δ/ppm = 186.5 (br.s).

*Synthesis of [Na$_{16}$(**1**)$_8$·NaSH·8thf] (**3**)*; A solution of NaBn (84.43 mg, 0.74 mmol) in thf (10 ml) was added dropwise to a stirred solution of **1** (100 mg, 0.37 mmol) in thf (10 ml). A deep blue colour was generated initially but as addition continued this gave way to a colourless solution. After stirring at room temperature for 1 h, storage at -12°C (16 h) gave colourless crystals of **3**. If the solvent is removed before crystallisation and the resulting powder washed with *n*-hexane (2 x 10ml), **3** is obtained as a white powder (quantitative yield). Elemental Analysis: Calc; C, 36.6; H, 6.7; N, 7.1;[1] Found C, 36.2; H, 6.6; N 5.1.[2] FTIR (Nujol, NaCl windows): 2579 cm^{-1} (S-H str). ^{1}H NMR (500.2 MHz, d_8-thf, +25°C): δ/ppm = 3.40 (1.4 H, s, Na-SH) 1.29 (144H, s, ^{t}Bu). ^{31}P NMR (161.7 MHz, d_8-thf, rel. 85% H_3PO_4/D_2O. +25°C): δ/ppm = 190.01 (s).

*Synthesis of [Ph$_2$Sn(**1**)] (**4**)*; A solution of **1** was prepared *in situ* by the deprotonation of **1**H_2 (100 mg, 0.32 mmol) in thf (20 ml) with Bu_2Mg (1 equivalent) or BnNa (2 equivalents). This solution was then added dropwise to a solution of Ph_2SnCl_2 (109.4 mg, 0.32 mmol) in thf (20 ml) at -78°C. The solution was warmed to room temperature and stirred (1 h) and the solvent removed under vacuum. The product was extracted into *n*-hexane (20 ml) and filtered. Removal of the solvent gave a white powder of **4** (151 mg, 88%). Crystals suitable for X-ray diffraction were grown from a concentrated *n*-hexane solution (RT, 16 h). ^{1}H NMR (500.2 MHz, C_6D_6, +25°C): δ/ppm = 7.73 (4H, m, *o*-Ph), 7.13-7.09 (4H, m, *m*-Ph), 7.09-7.06(2H, m, *p*-Ph), 1.27 (s, ^{t}Bu). ^{31}P NMR (161.7 MHz, d_8-thf, rel. 85% H_3PO_4/D_2O. +25°C): δ/ppm = 206.7 (app t, $^2J_{P\text{-}Sn}$= 195 Hz). No satisfactory elemental analysis on **4** could be obtained.

1. M. O. Study, D. Hoffmann, W. Bauer, F. Hampe, N. J. R. V. E. Hommes, P. Von Rag, P. Otto, U. Pieper, D. Stalke, D. S. Wright and R. Snaith, *J. Am. Chem. Soc.*, 1994, **116**, 528–536.
2. NB the consistently low values of N content in the elemental analyses of **2** and **3** is typical of phosph(III)azanes, and is probably the result of incomplete combustion during and the formation of metal nitrides (see, for example, A. Bashall, E. L. Doyle, C. Tubb, S. J. Kidd, M. McPartlin, A. D. Woods, D. S. Wright, *J. Chem. Soc.*, *Chem. Commun.*, **2001**, 2542-2543).

Spectroscopic Data

Compound 1:

Prepared as in literature and used as a white crystalline solid from crystallisation in toluene.

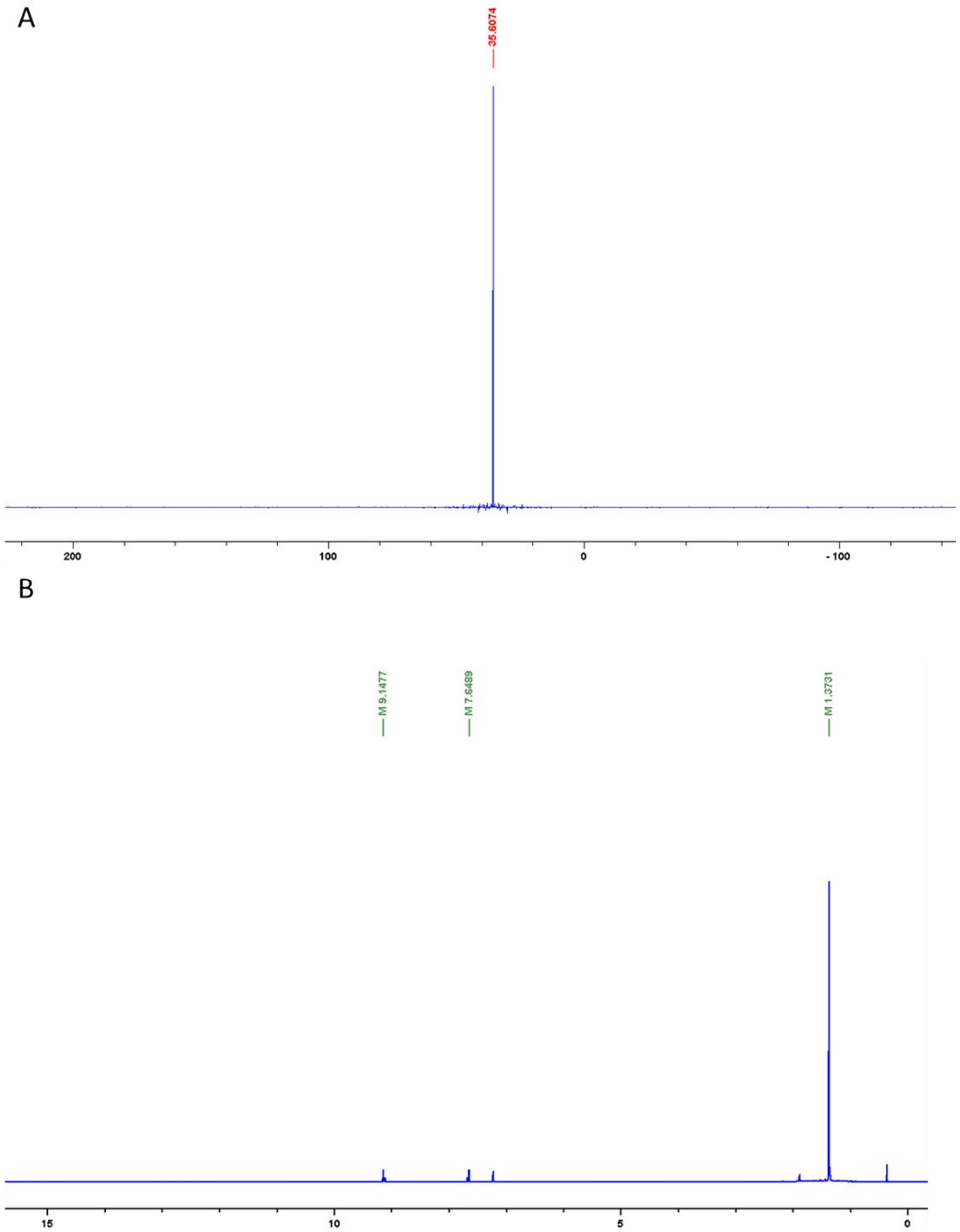


Fig SI 1: A: $^{31}P\{^{1}H\}$ NMR (161.7 MHz, 25 ^{o}C) and B: ^{1}H NMR (400 MHz, 25 ^{o}C) of **1** in d_6-benzene.

Compound 2:

Di-*n*-butyl magnesium (2 M in heptanes) acquired from Sigma-Aldrich.

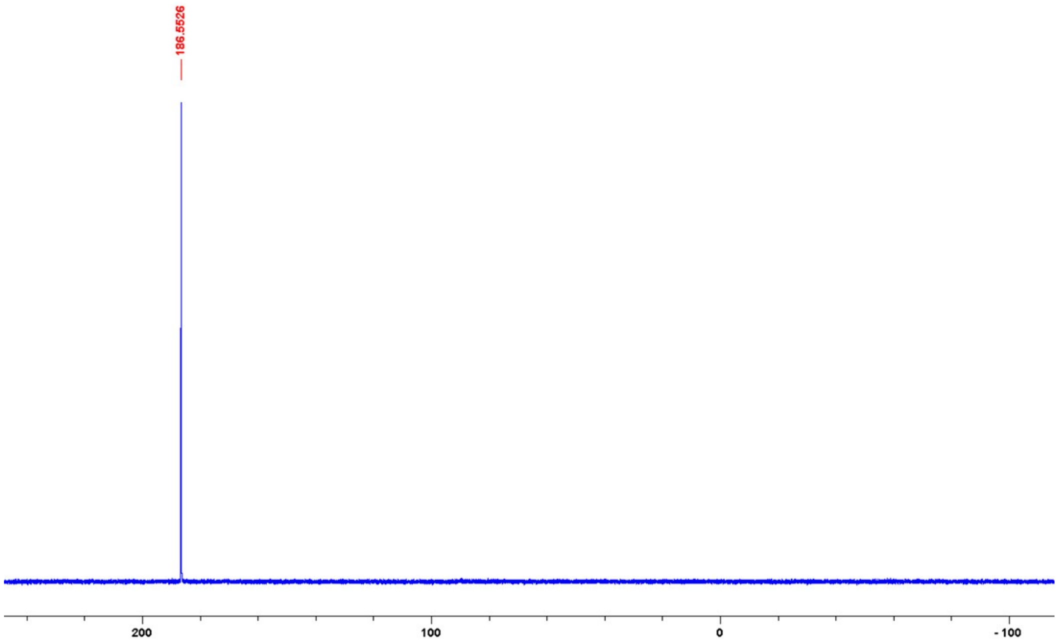


Fig SI 2: $^{31}P\{^{1}H\}$ (161.7 MHz, 25^{o}C) NMR of **2** in d_{8}-THF.

2

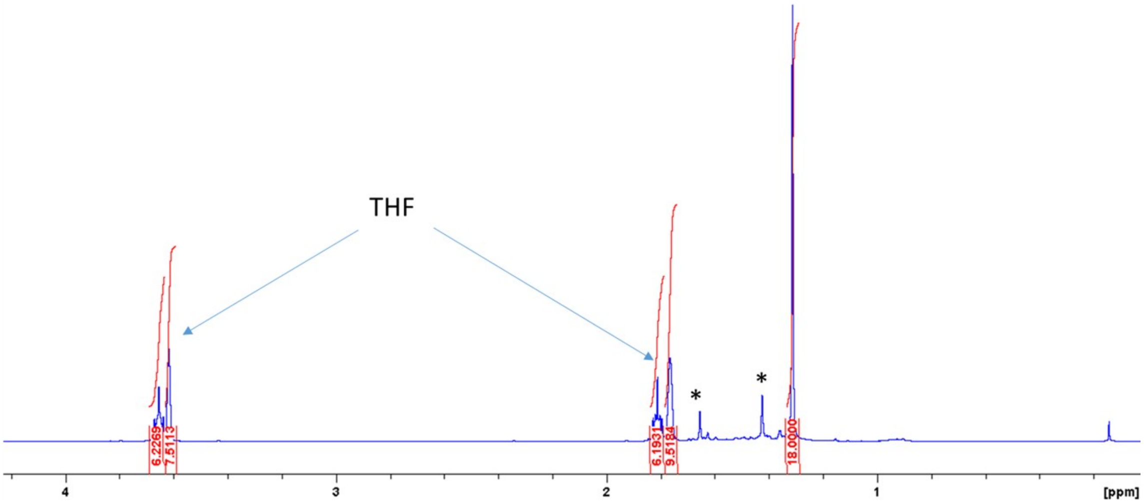


Fig SI 3: ^{1}H (400 MHz, 25^{o}C) NMR of **2** in d_{8}-THF.

Compound 3:

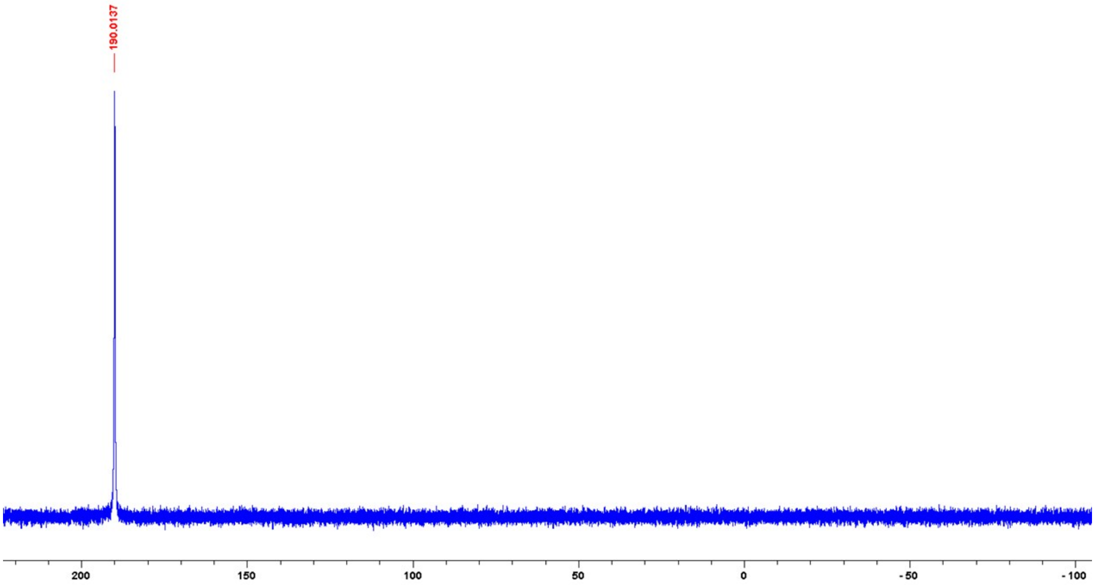


Fig SI 4: $^{31}P\{^{1}H\}$ (161.7 MHz, 25^{o}C) *in situ* NMR of **3** in thf (d_6-acetone capillary).

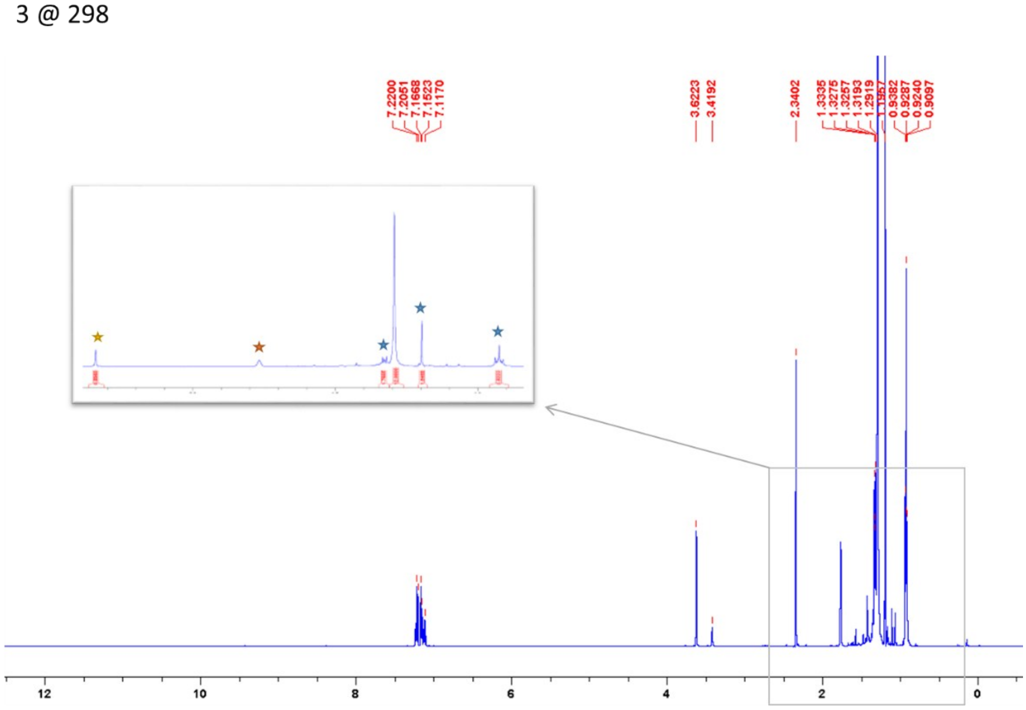


Fig SI 5: ^{1}H *in situ* NMR (500.2 MHz, 25 ^{o}C) of **3** in THF. Hexane (from BnNa purification, blue), thf (orange) and toluene (yellow) solvent marked with stars.

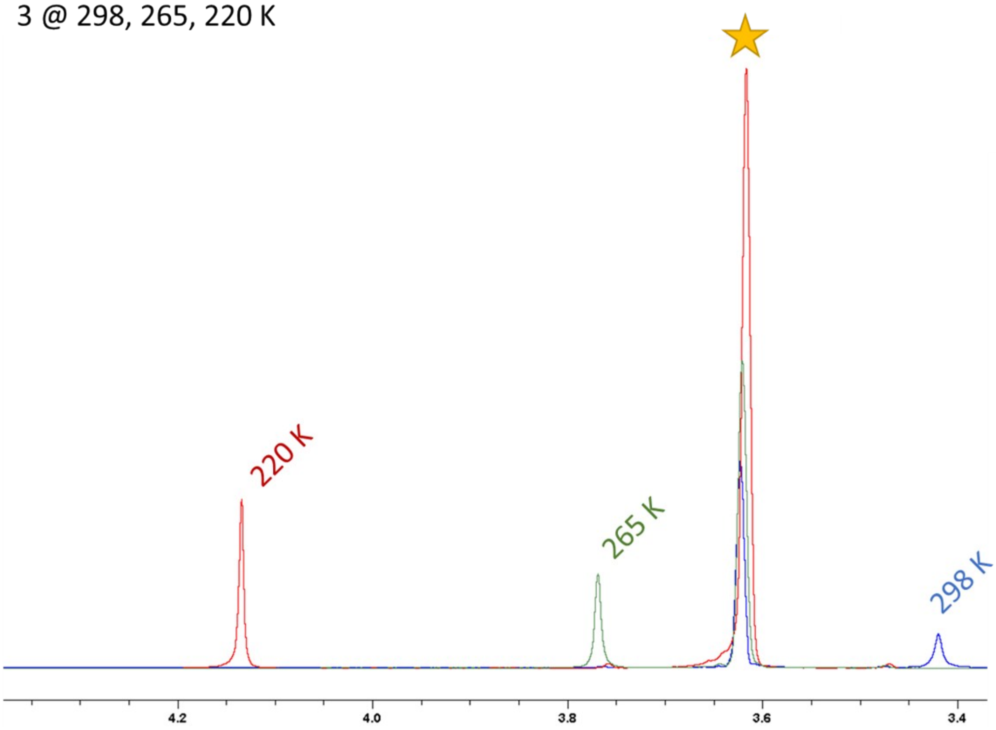


Fig SI 6: Variable temperature ^{1}H NMR of **3** in d$_8$-thf (500.2 MHz) showing movement of Na-SH peak at 3.47 ppm with descending temperatures. THF solvent marked with yellow star.

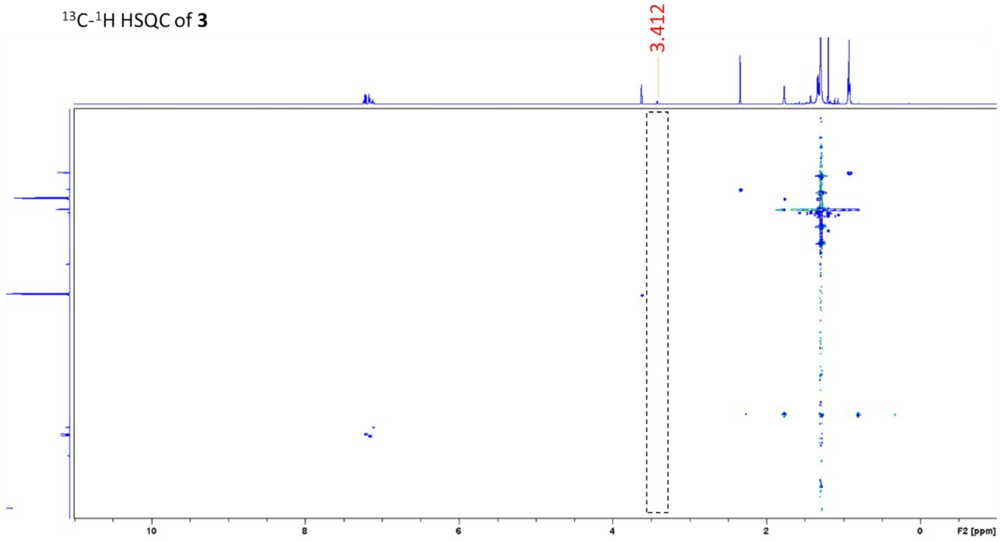


Fig SI 7: ^{13}C-^{1}H HSQC of **3** in d$_8$-thf (500 MHz, 125.7 MHz, 25 ^{o}C) showing no carbon correlation for NaSH ^{1}H signal at 3.41 ppm.

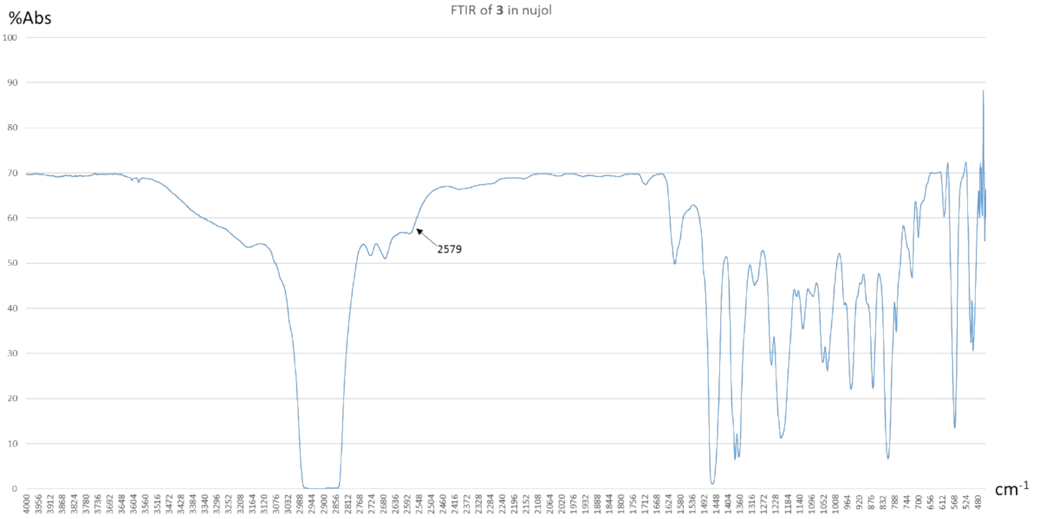


Fig SI 8: FTIR of **3** in Nujol, NaCl windows.

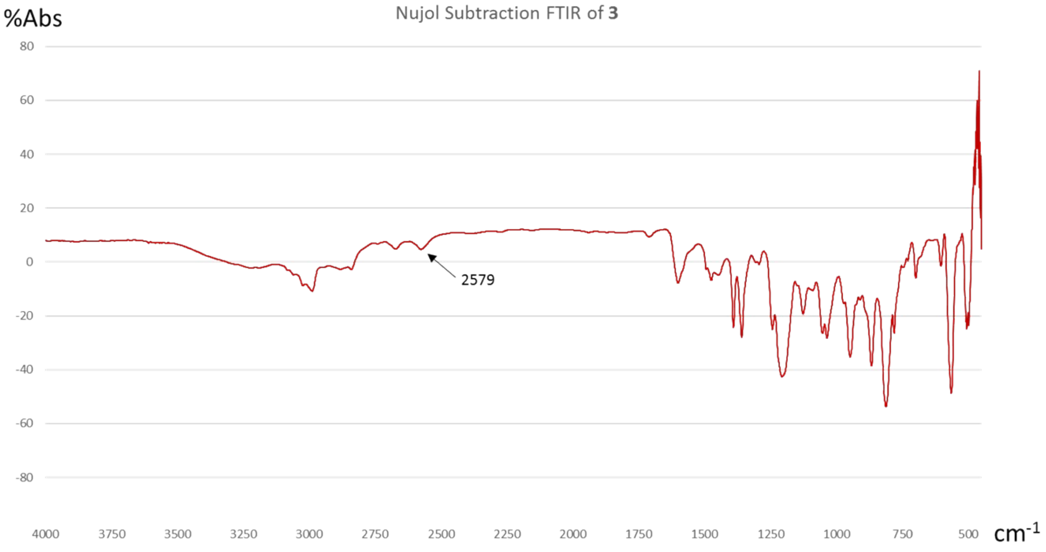


Fig SI 9: FTIR of **3** with Nujol spectrum subtracted (NaCl windows) showing S-H stretch at 2579cm^{-1} (N.B. deformed baseline between 2750 and 3250 are due to strong Nujol C-H absorptions).

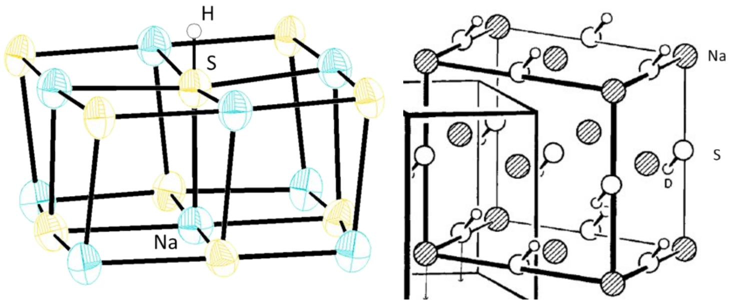


Fig SI 10: Na-S core of the solid state structure of **3** (left) showing close relation to the Na-SH high temp phase as characterised by Jacobs *et al* (right).[1]

Compound 4:

4

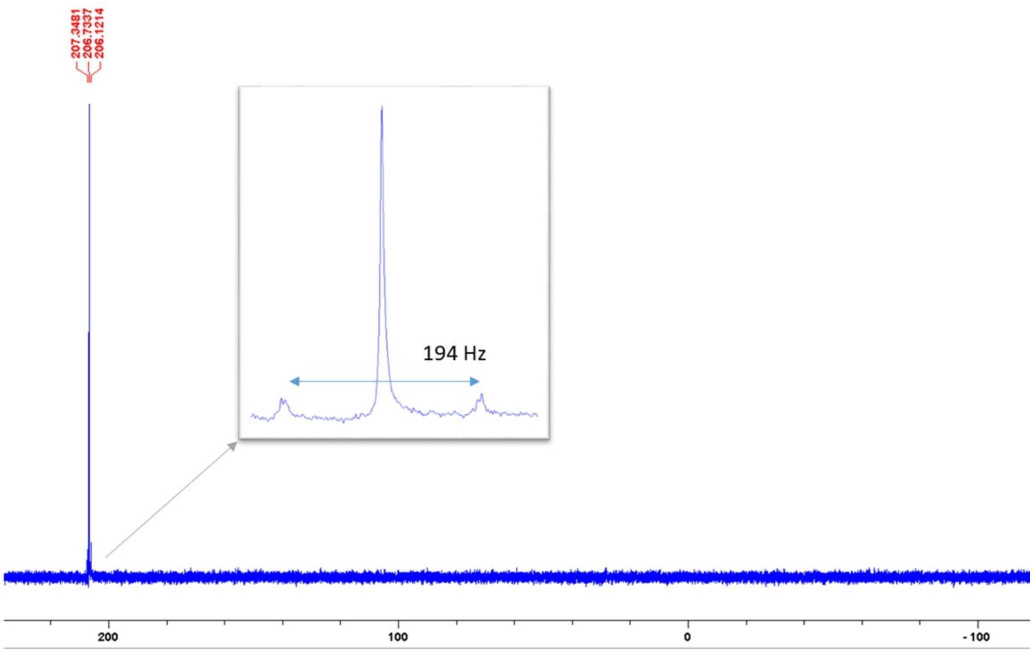


Fig SI 11: $^{31}P\{^{1}H\}$ (161.7 MHz, 25 ^{o}C) NMR of **4** in d_6-benzene showing $^{2}J_{P\text{-}Sn}$ coupling.

4

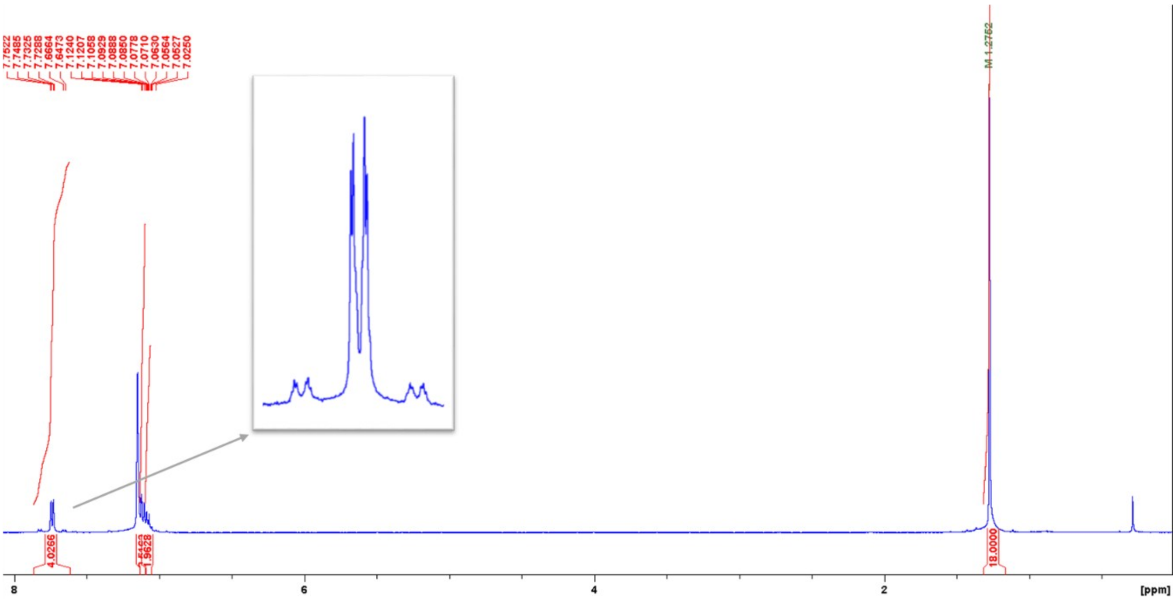


Fig SI 12: ^{1}H (400 MHz, 25 ^{o}C) NMR of **4** in d_6-benzene showing $^{2}J_{H\text{-}Sn}$ coupling.

Decomposition of 4 to 5

Characterisation of {[O=PH(μ-N^{t}Bu)]$_2$}$_2$(μ-O) from literature:[2] ^{31}P (^{1}H-coupled) NMR (161.98 MHz, d$_8$-toluene, 25^{o}C, rel. 85% H_3PO_4/D_2O), δ = 98.7 (d, $^2J_{PP}$ = 14.7 Hz, P–O–P), 3.2 (dd, $^1J_{PH}$ = 590.0, $^2J_{PP}$ = 14.7 Hz, P(H)=O]

Characterisation of {[S=PH(μ-N^{t}Bu)]$_2$}$_2$(μ-S): ^{31}P (^{1}H-coupled) NMR (161.98 MHz, d$_6$ Acetone, 25^{o}C, rel. 85% H_3PO_4/D_2O) δ = 133.23 (d, $^2J_{PP}$ = 15 Hz, P-S-P), 44.37 (dd, $^1J_{PH}$ = 547.6 Hz, $^2J_{PP}$ = 15.31 Hz, P(H)=S]

1 H. Jacobs, U. Metzner, R. Kirchgässner, H. D. Lutz and K. Beckenkamp, *Z. Anorg. Allg. Chem.*, 1991, **598**, 175–192.

2 E. L. Doyle, F. García, S. M. Humphrey, R. A. Kowenicki, L. Riera, A. D. Woods and D. S. Wright, *Dalton Trans.*, 2004, 807–812.

X-Ray Crystallography

*X-ray Crystallography on **2**, **3** and **4***; **2**: $C_{16}H_{34}MgN_2O_2P_2S_2$, *M* = 436.82, monoclinic, space group *P*2$_1$/*n*, Z = 4, *a* = 13.2446(2), *b* = 10.2823(2), *c* = 17.0713(3) Å, β = 97.7952(7)^o, *V* = 2303.37(7) Å^3, μ(Mo-Kα) = 0.410 mm^{-1}, ρ_{calc} = 1.260 g cm^{-3}, *T* = 180(2) K. Total reflections 21092, unique 5117 (R_{int} = 0.037). *R*1 = 0.033 [*I*>2σ(I)] and *wR*2 = 0.079, (all data). **3**: $C_{96}H_{209}N_{16}Na_{17}O_8P_{16}S_{17}$, *M* = 3147.15, tetragonal, space group *P4cc*, Z = 4, *a* = *b* = 23.7198(2), *c* = 37.5449(6) Å, *V* = 21252.3(5) Å^3, μ(Mo-Kα) = 0.365 mm^{-1}, ρ_{calc} = 0.984 g cm^{-3}, *T* = 180(2) K. Total reflections 39076, unique 12141 (R_{int} = 0.088). *R*1 = 0.073 [*I*>2σ(I)] and *wR*2 = 0.216, (all data). The SQUEEZE procedure has been applied to handle diffuse solvent regions (see ESI). **4**: $C_{20}H_{28}N_2P_2S_2Sn$, *M* = 541.19, triclinic, space group *P*-1, Z = 4, *a* = 8.5948(4), *b* = 9.7615(4), *c* = 14.7996(6) Å, α = 85.955(2), β = 87.786(2), γ = 73.175(2)^o, *V* = 1185.33(9) Å^3, μ(Cu-Kα) = 11.552 mm^{-1}, ρ_{calc} = 1.516 g cm^{-3}, *T* = 180(2) K. Total reflections 34420, unique 4338 (R_{int} = 0.045). *R*1 = 0.020 [*I*>2σ(I)] and *wR*2 = 0.049 (all data). CCDC 1475941, 1475943 and 1475942 contain the supplementary crystallographic data for **2**, **3**, and **4,** respectively.

	2	**3**[a]	**4**
CCDC number	1475941	1475943	1475942
Chemical formula	$C_{16}H_{34}MgN_2O_2P_2S_2$	$C_{96}H_{209}N_{16}Na_{17}O_8P_{16}S_{17}$	$C_{20}H_{28}N_2P_2S_2Sn$
Formula mass	436.82	3147.15	541.19
Crystal system	monoclinic	tetragonal	triclinic
a/Å	13.2446(2)	23.7918(2)	8.5948(4)
b/Å	10.2823(2)	23.7918(2)	9.7615(4)
c/Å	17.0713(3)	37.5449(6)	14.7996(6)
α/°	90	90	85.955(2)
β/°	97.7952(7)	90	87.786(2)
γ/°	90	90	73.175(2)
Unit cell volume/Å^3	2303.37(7)	21252.3(5)	1185.33(9)
Temperature/K	180(2)	180(2)	180(2)
Space group	*P*2$_1$/*n*	*P4cc*	*P*–1
Z	4	4	2
Calculated density/g cm^{-3}	1.260	0.984[a]	1.516
Radiation type	MoKα	MoKα	CuKα

Absorption coefficient, μ/mm^{-1}	0.410	0.365	11.552
No. of reflections measured	21092	39076	34420
No. of independent reflections	5117	12141	4338
No. observed reflections ($I > 2\sigma(I)$)	4329	8445	4188
R_{int}	0.037	0.088	0.045
$R1$ ($I > 2\sigma(I)$)	0.033	0.073	0.020
$wR2$ (all data)	0.079	0.216	0.049
Goodness of fit on F^2	1.03	1.03	1.05
Flack parameter (Parsons)		–0.01(7)	

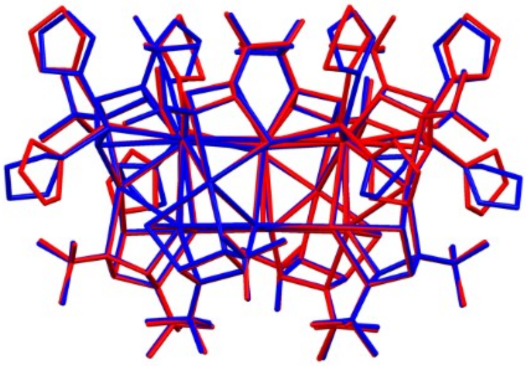
[a] The SQUEEZE algorithm (Spek, 2015) has been applied to handle diffuse solvent regions.

Data for **2** and **3** on were collected on a Nonius KappaCCD diffractometer, using graphite-monochromated MoKα radiation (λ = 0.7107 Å). Data for **4** were collected on a Bruker D8-QUEST diffractometer using an Incoatec IμS Cu microsource (λ = 1.5418 Å). Structures were solved using SHELXT (Sheldrick, 2015) and refined using SHELXL (Sheldrick, 2015). Refinements were routine for **2** and **4**. For **3**, the crystals diffracted weakly, and the data set used for refinement is limited to 0.95 Å resolution. Numerous crystals were examined, also using the Cu microsource of the D8-QUEST instrument. The same unit cell was always obtained, but the MoKα data set produced the best refinement result. Numerous restraints are applied to the ^{t}Bu groups and coordinated THF molecules:

- N–C(CH$_3$)$_3$ bond distances 1.50(1) Å
- C–C bond distances in ^{t}Bu 1.54(1) Å
- C…C distances in ^{t}Bu 2.51(1) Å
- C–C and C–O bond distances in THF 1.48(1) Å
- ISOR restraint (esd 0.01) on C atoms of THF

The SH group is assigned on the basis of the additional characterisation information, as described in the main manuscript. For charge balance, the atom/group at the site must have a 1– charge. The refinement could be made equally well with Cl assigned, but this is ruled out by the elemental analysis. With the SH group independently identified, the H atom was placed on the 4-fold rotation axis (for both independent complexes) with S–H = 1.20 Å; only the *z* coordinate needs to be specified. The coordinates of these H atoms were not refined in the final cycles, so small shifts in the S coordinates mean that the final S–H distances deviate slightly from the specified 1.20 Å.

There are two independent complexes in the structure, lying on crystallographic 4-fold axes, with basically identical geometry (aside from minor variations in the coordinated THF positions). An overlay of the two molecules (coloured red and blue) is shown:



The structure contains substantial void space (SQUEEZE estimate, 1.2 Å probe radius = 6652 Å^3 = *ca* 30% of the unit-cell volume), within which it was not possible to resolve any solvent (THF) molecules. The SQUEEZE procedure (Spek, 2015) has therefore been applied. The procedure corrects for 3205 electrons per unit cell in voids, which corresponds to 80 THF molecules (C_4H_8O = 40 electrons). This is approximately consistent with the available void space, giving 6652 / (80*5) = 16.6 Å^3 per non-H atom.

The absolute structure, assessed using the quotient method of Parsons, is satisfactorily determined.

References

SHELXT: G. M. Sheldrick, Acta Cryst. (2015), A71, 3–8

SHELXL: G. M. Sheldrick, Acta Cryst. (2015), C71, 3–8

SQUEEZE: A. L. Spek, Acta Cryst. (2015), C71, 9–18

Absolute structure: S. Parsons, H. D. Flack & T. Wagner, Acta Cryst. (2013), B69, 249–259