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Supplementary Information

Reactivity of Bulky Ln(II) Amidinates towards P_4, As_4, and As_4S_4

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Experimental Section

General Considerations

All manipulations of air-sensitive materials were performed with the rigorous exclusion of oxygen and moisture in flame-dried Schlenk-type glassware either on a dual manifold Schlenk line, interfaced to a high vacuum (10^{-3} torr) line, or in an argon-filled MBraun glove box. Elemental analyses were carried out with an Elementar vario Micro Cube. Hydrocarbon solvents were predried by using an MBraun solvent purification system (SPS-800) and degassed, dried and stored in vacuo over $LiAlH_4$. Tetrahydrofuran was distilled under nitrogen from potassium benzophenone ketyl before storage over $LiAlH_4$. IR spectra were obtained on a Bruker Tensor 37 FTIR spectrometer equipped with a room temperature DLaTGS detector and a diamond ATR (attenuated total reflection) unit; for the mid infrared region a KBr beamsplitter was used. NMR spectra were recorded on a Bruker Avance II 300 MHz or Avance 400 MHz. ^{1}H chemical shifts were referenced to the residual ^{1}H of the deuterated solvents and are reported relative to tetra-methylsilane. [(DippForm$_2$Sm)*2(thf)][1] [(DippForm$_2$Yb)*2(thf)][1b] and [As_4S_4][2] were prepared according to literature procedures.

Synthesis

NOTE: All analytical data and yields are based on single crystalline material.

Synthesis of **1** [(DippForm$_2$Sm)$_2$$P_4$]

In a Young flask [(DippForm)$_2$Sm*2(thf)] (300 mg, 0.294 mmol) and P_4 (18 mg, 0.145 mmol) were dissolved in ca. 10 mL of toluene. The reaction mixture was stirred at rt for 16 h, filtered to a double section ampule, degassed and flame sealed. Crystals were grown of the toluene solution by slow evaporation: yield 268 mg (94 %); ^{1}H-NMR (300.13 MHz, 298 K, C_6D_6): due to

paramagnetism no further evaluation was made. ^{31}P-NMR (121.49 MHz, 298 K, C_6D_6): 453 ppm. IR (cm^{-1}): ν = 2959 (s), 2926 (w), 2866 (w), 2665 (vs), 1640 (s), 1587 (w), 1511 (m), 1458 (s), 1438 (s), 1383 (w), 1361 (w), 1317 (m), 1285 (m), 1254 (s), 1235 (m), 1185 (m), 1161 (w), 1098 (w), 1055 (w), 1042 (w), 1002 (w), 934 (w), 822 (w), 799 (s), 765 (m), 753 (vs), 730 (w), 695 (w), 672 (w), 604 (w), 535 (w), 508 (w), 465 (w), 433 (w), 413 (w). Raman (cm^{-1}): ν = 3062 (m), 2931 (s), 2869 (s), 2712 (vw), 1634 (m), 1590 (vs), 1506 (m), 1444 (s), 1369 (s), 1308 (m), 1233 (m), 1178 (m), 1101 (m), 1044 (s), 954 (w), 911 (w), 883 (m), 805 (vw), 755 (w), 721 (m), 630 (w), 604 (m), 539 (w), 497 (m), 448 (m), 341 (vw), 294 (m), 196 (w), 141 (m), 110 (w). Anal. calcd. (%) for [$C_{100}H_{140}N_8P_4Sm_2$*toluene] (1971.03): C 65.20; H 7.57; N 5.69; found C 65.14; H 7.69; N 5.89.

Synthesis of **2** [$(DippForm_2Sm)_2As_4$]

In a Young flask [$(DippForm)_2Sm$*2(thf)] (200 mg, 0.196 mmol) were dissolved in ca. 5 mL of toluene. A freshly prepared statured solution of As_4 in toluene was added via cannula. The reaction mixture was stirred at rt for 16 h, filtered to a double section ampule, degassed and flame sealed. Crystals were grown of the toluene solution by slow evaporation. Due to impurities further characterization could not be obtained.

Synthesis of **3** and **4:**

On a mixture of 1eq [$(DippForm)_2Ln$*2(thf)] (Sm: 100 mg, 0.10 mmol; Yb: 100 mg, 0.10 mmol) and 1eq As_4S_4 (Sm: 42 mg, 0.10 mmol; Yb: mg, mmol) were ca. 10 mL of toluene condensed. The reaction mixture was stirred at rt for 16h in case of Yb and in the case of Sm 2h. The solvent was evaporated in vacuum. The residue was extracted with *n*-heptane and filtered

into a double section ampule and flame sealed. Crystals were obtained by slow evaporation of the solvent.

3: Yield 40 mg (37 %); IR (cm^{-1}): ν = 3061 (w), 2960 (vs), 2926 (m), 2867 (m), 1665 (m), 1640 (m), 1587 (w), 1518 (s), 1458 (m), 1437 (m), 1382 (w), 1361 (w), 1314 (m), 1280 (m), 1185 (m), 1104 (w), 1051 (w), 936 (w), 800 (w), 755 (m). Anal. calcd. (%) for [$C_{54}H_{78}AsN_4OS_2Sm$] (1088.65): C 59.58; H 7.22; N 5.15; S 5.89 found C 60.23; H 6.85; N 5.45; S 6.47.

4: Yield 54 mg (50 %); IR (cm^{-1}): ν = 3059 (w), 2960 (vs), 2885 (m), 1669 (w), 1591 (w), 1545 (s), 1514 (vs), 1458 (s), 1438 (s), 1382 (w), 1360 (w), 1334 (m), 1311 (m), 1267 (s), 1185 (m), 1104 (w), 1012 (w), 935 (w), 856 (m), 802 (m), 755 (m). Anal. calcd. (%) for [$C_{54}H_{78}AsN_4OS_2Yb$] (1111.34): C 58.36; H 7.07; N 5.04; S 5.77; found C 57.52; H 6.89; N 4.39; S 6.14.

NMR-Spectra

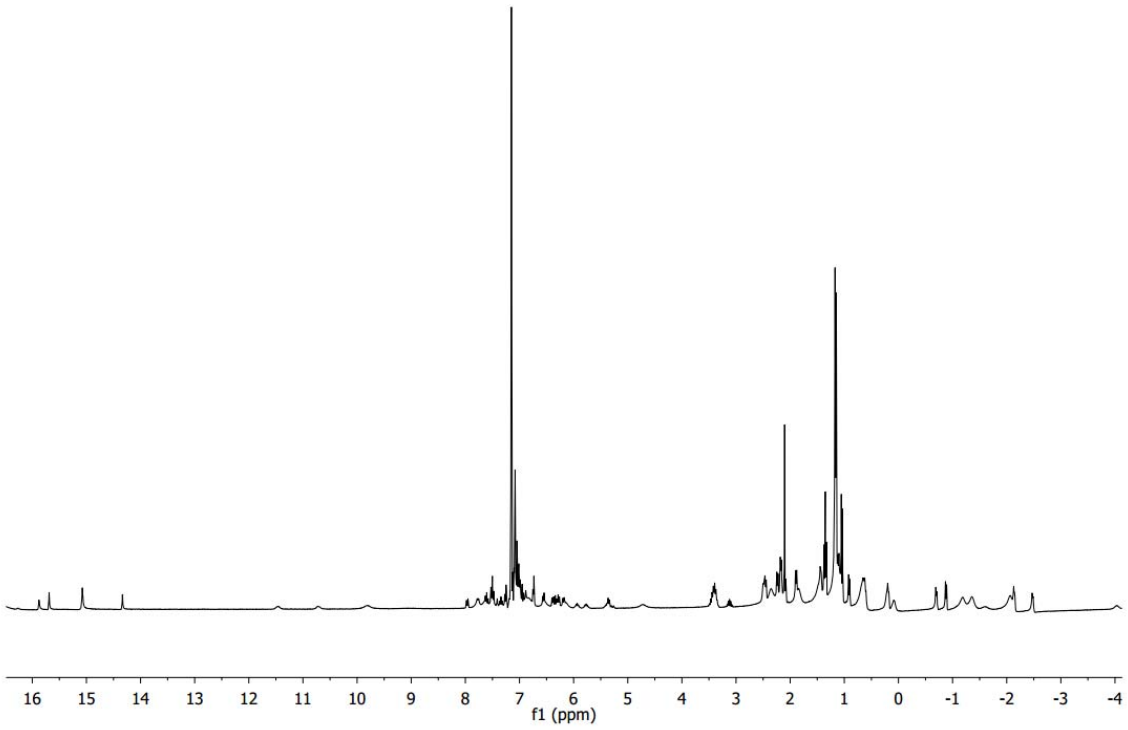

Figure S1 ^{1}H-NMR-Spectra of **1** (300.13 MHz, 298 K, C_6D_6).

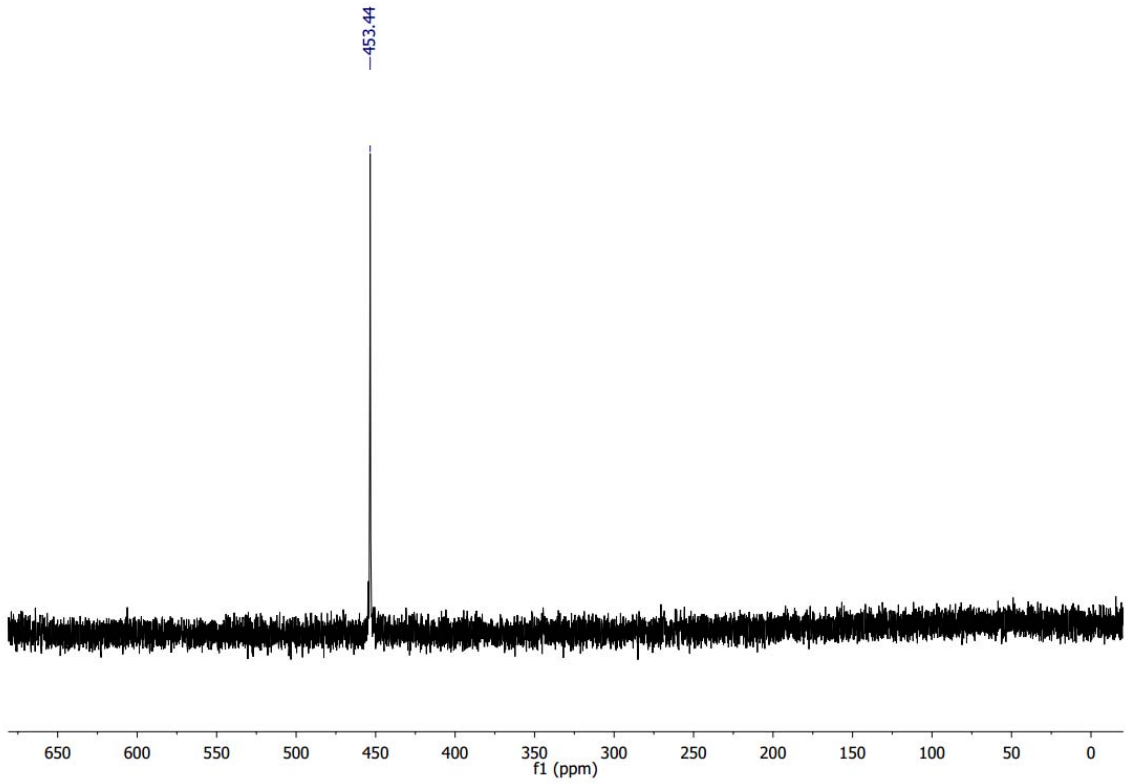

Figure S2 ^{31}P-NMR-Spectra of **1** (121.49 MHz, 298 K, C_6D_6).

IR and Raman Spectra:

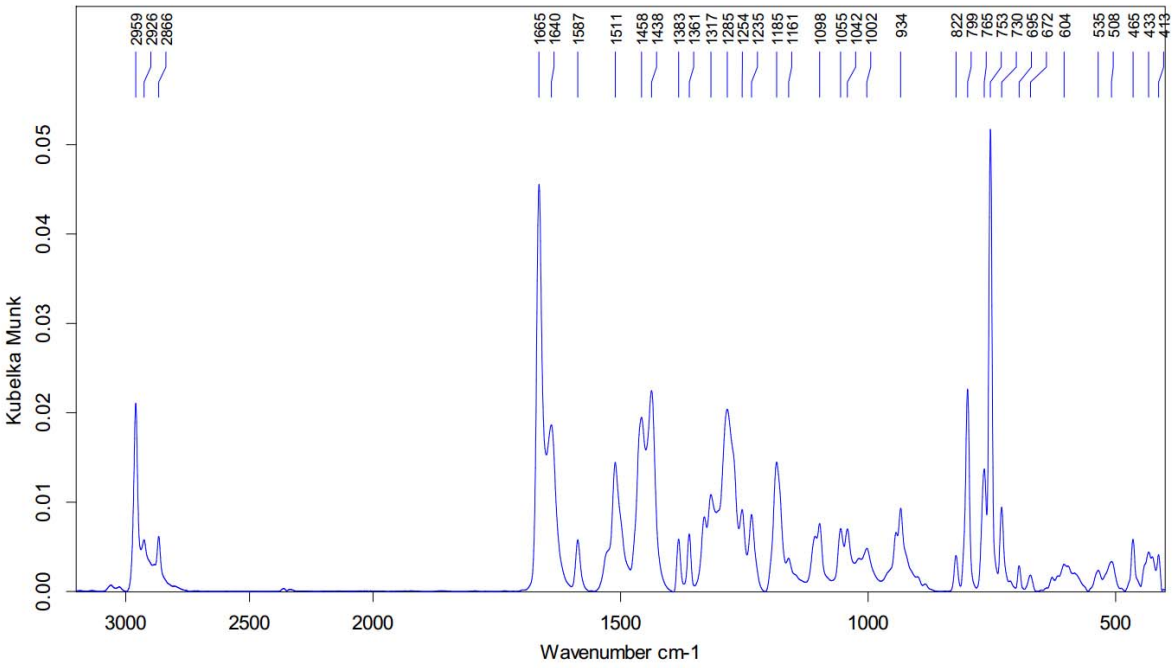

Figure S3 IR Spectra of **1**

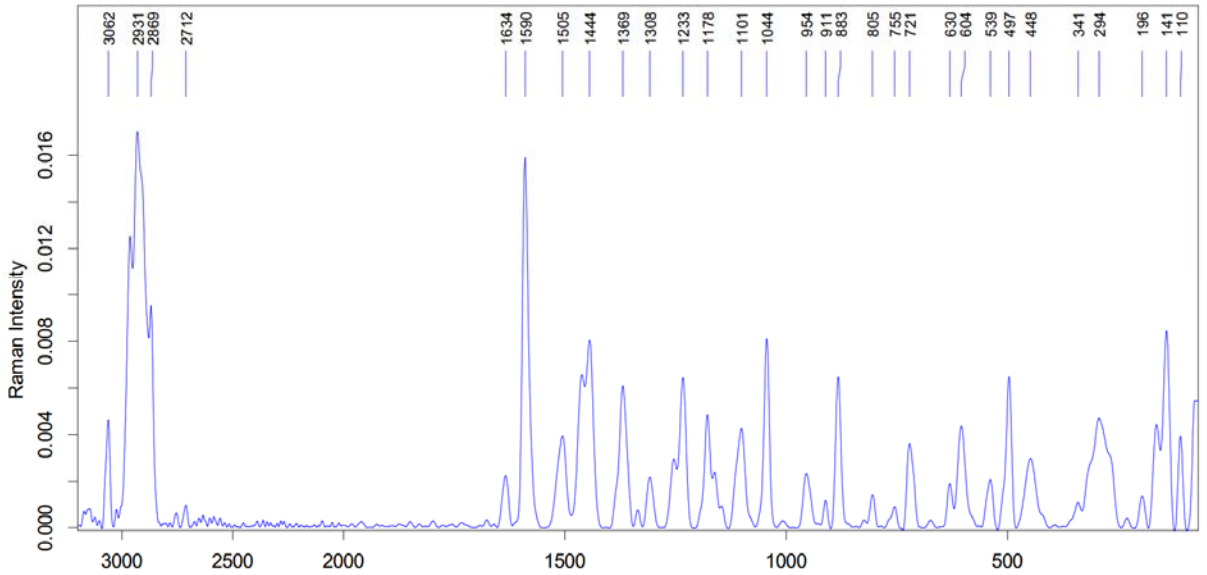

Figure S4 Raman Spectra of **1**

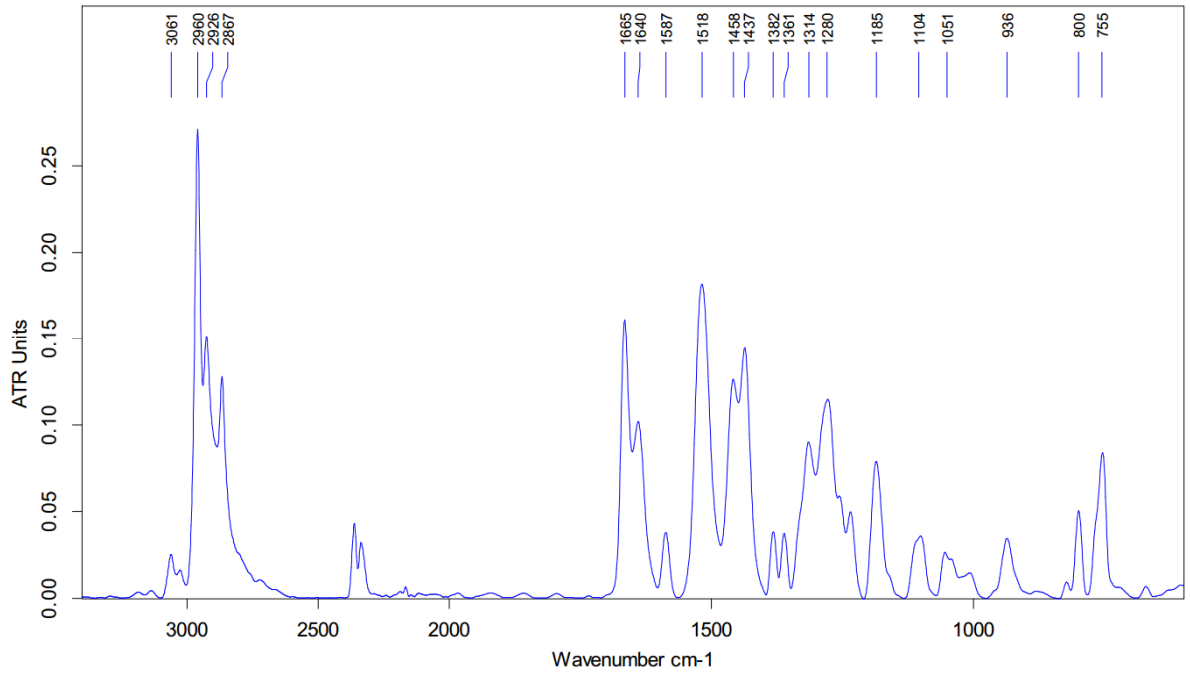

Figure S5 IR Spectra of **3**

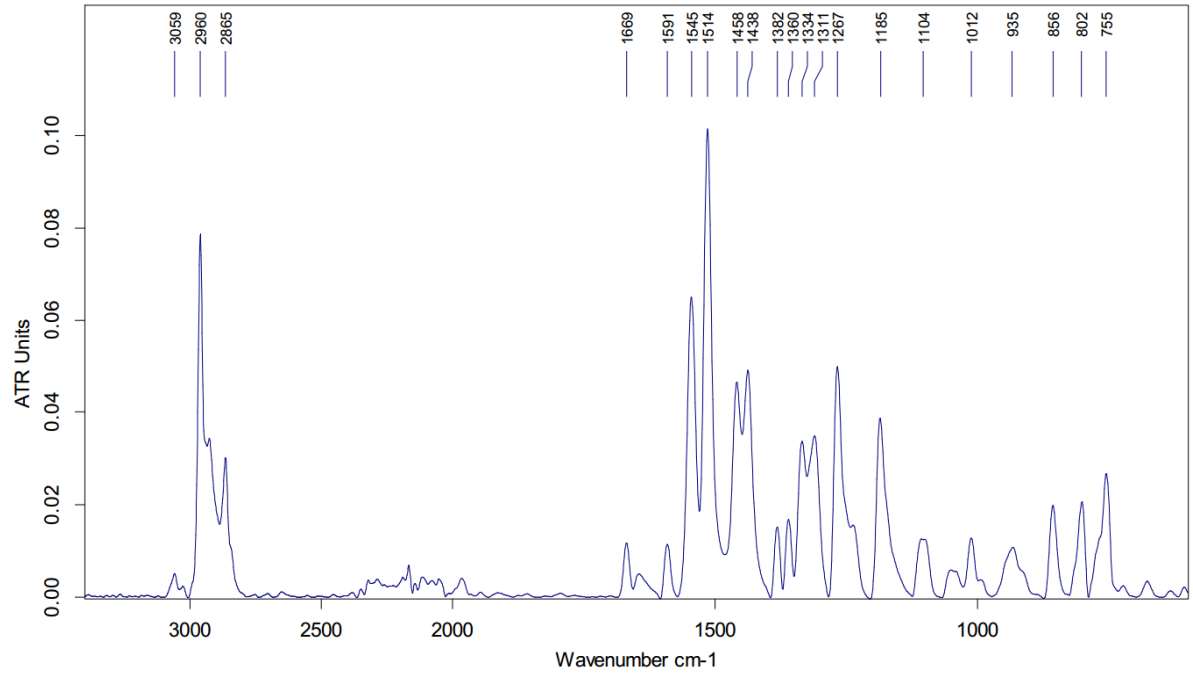

Figure S6 IR Spectra of **4**

X-ray Crystallographic Studies of 1-4. A suitable crystal was covered in mineral oil (Aldrich) and mounted on a glass fiber. The crystal was transferred directly to the cold stream of a STOE IPDS 2 or STOE StadiVari diffractometer.

All structures were solved by using the program SHELXS/T[3] using Olex2.[4] The remaining non-hydrogen atoms were located from successive difference Fourier map calculations. The refinements were carried out by using full-matrix least-squares techniques on F^2 by using the program SHELXL.[3] In each case, the locations of the largest peaks in the final difference Fourier map calculations, as well as the magnitude of the residual electron densities, were of no chemical significance. Positional parameters, hydrogen atom parameters, thermal parameters, bond distances and angles have been deposited as supporting information.

Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as a supplementary publication no. 1818425-1818428. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB21EZ, UK (fax: (+(44)1223-336-033; email: deposit@ccdc.cam.ac.uk).

Table S1: Crystal data and structure refinement

Compound	1 * 0.5 toluene	2	3	4
Formula	$C_{103.5}H_{144}N_8P_4Sm_2$	$C_{100}H_{140}As_4N_8Sm_2$	$C_{54}H_{78}AsN_4OS_2Sm$	$C_{54}H_{78}AsN_4OS_2Yb$
$D_{calc.}$/ g cm^{-3}	1.282	1.407	1.334	1.379
m/mm^{-1}	1.279	2.601	1.805	2.479
Formula Weight	1924.84	2054.57	1088.59	1111.28
Colour	clear orange	clear orange	clear yellow	clear yellow
Shape	prism	plate	needle	plate
Size/mm^3	0.35×0.28×0.22	0.14×0.09×0.03	0.17×0.11×0.04	0.18×0.14×0.10
T/K	110	110	150	150
Crystal System	triclinic	triclinic	monoclinic	monoclinic
Space Group	P-1	P-1	$P2_1/c$	$P2_1/c$
a/Å	14.1425(2)	13.6808(7)	14.6528(8)	14.5485(16)
b/Å	14.9026(2)	16.1681(8)	17.1717(7)	17.0540(7)
c/Å	26.1273(4)	22.4917(11)	21.7016(11)	21.7258(15)
a/°	98.3430(10)	99.664(4)	90	90
b/°	96.4380(10)	94.939(4)	96.826(4)	96.905(7)
g/°	111.5060(10)	95.996(4)	90	90
V/Å^3	4986.58(13)	4850.2(4)	5421.7(5)	5351.3(7)
Z	2	2	4	4
Z'	1	1	1	1
Wavelength/Å	0.71073	0.71073	0.71073	0.71073
Radiation type	Mo K_a	Mo K_a	Mo K_a	Mo K_a
Q_{min}/°	1.551	1.287	1.516	1.848
Q_{max}/°	26.082	26.097	25.378	26.068
Measured Refl.	43509	44165	21499	23186
Independent Refl.	19417	19049	9801	10442
Reflections Used	15993	12156	5508	7380
R_{int}	0.0238	0.0616	0.0561	0.0311
Parameters	1108	1059	584	584
Restraints	123	0	0	0
Largest Peak	1.429	5.192	0.475	0.506
Deepest Hole	-0.592	-1.334	-0.939	-0.394
GooF	1.005	1.019	0.904	0.934
wR_2 **(all data)**	0.0737	0.1755	0.0557	0.0327
wR_2	0.0695	0.1527	0.0495	0.0310
R_1 **(all data)**	0.0383	0.1106	0.0896	0.0466
R_1	0.0284	0.0642	0.0374	0.0237

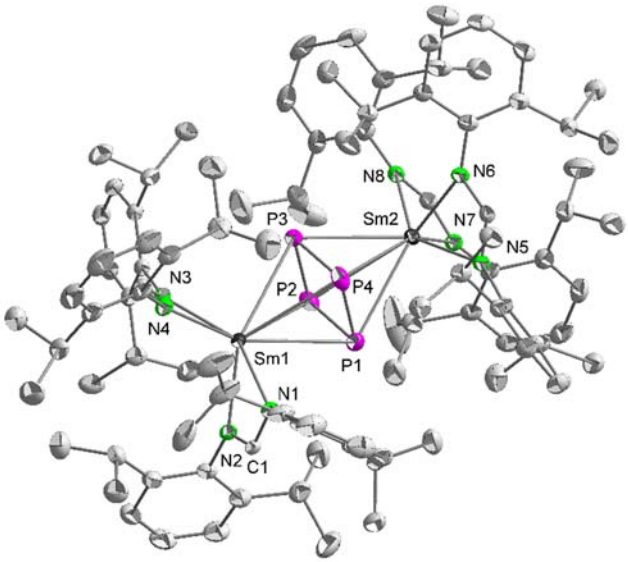

Figure S7 Molecular structure of **1** in the solid state. Hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and angles [°]:Sm1 P4 3.0413(7), Sm1-P2 3.1568(7), Sm1-P3 3.1009(7), Sm1-P1 3.0980(7), Sm2-P4 3.1012(7), Sm2-P2 3.1156(7), Sm2-P3 3.0954(7), Sm2-P1 3.1336(7),Sm1-N1 2.437(2), Sm1-N2 2.387(2), Sm1-N3 2.424(2), Sm1-N4 2.441(2), Sm2-N5 2.424(2), Sm2-N6 2.400(2), Sm2-N7 2.394(2), Sm2-N8 2.446(2), P4-P3 2.1618(10), P4-P1 2.1583(11), P2-P3 2.1511(10), P2-P1 2.1443(11), N1-C2 1.435(3), N1-C1 1.322(3), P1-P4-P3 89.89(4), P1-P2-P3 90.55(4), P2-P3-P4 89.65(4), P2-P1-P4 89.92(4), N1-C1-N2 118.5(2).

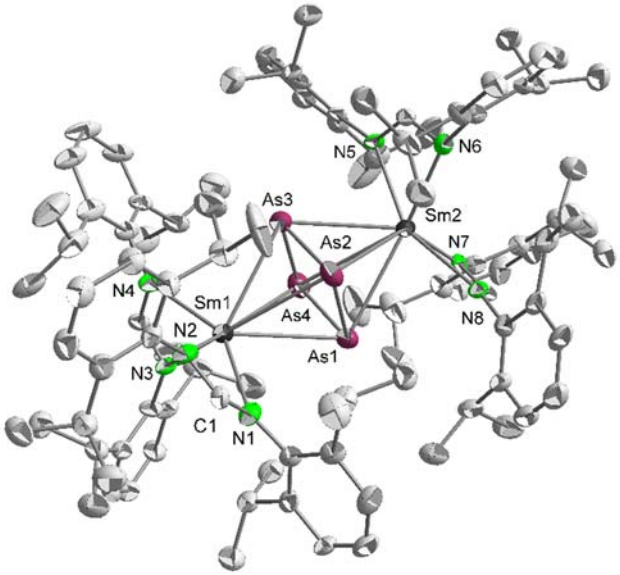

Figure S8 Molecular structure of **2** in the solid state. Hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and angles [°]: Sm1-As1 3.2040(10), Sm1-As2 3.1673(9), Sm1-As3 3.1947(9), Sm1-As4 3.2445(10), Sm2-As1 3.1964(9), Sm2-As2 3.1430(10), Sm2-As3 3.2349(10), Sm2-As4 3.2481(10), Sm1-N2 2.446(6), Sm1-N1 2.425(6), Sm1-N3 2.392(6), Sm1-N4 2.427(6), Sm2-N5 2.416(6), Sm2-N6 2.466(6), Sm2-N7 2.419(7), Sm2-N8 2.436(6), As1-As2 2.3796(14), As1-As4 2.3814(13), As2-As3 2.3887(13), As3-As4 2.3652(14), N1-C1 1.326(10), N2-C1 1.324(10), As2-As1-As4 89.50(4), As1-As2-As3 90.14(5), As4-As3-As2 89.67(4), As3-As4-As1 90.67(4), N2-C1-N1 119.9(7).

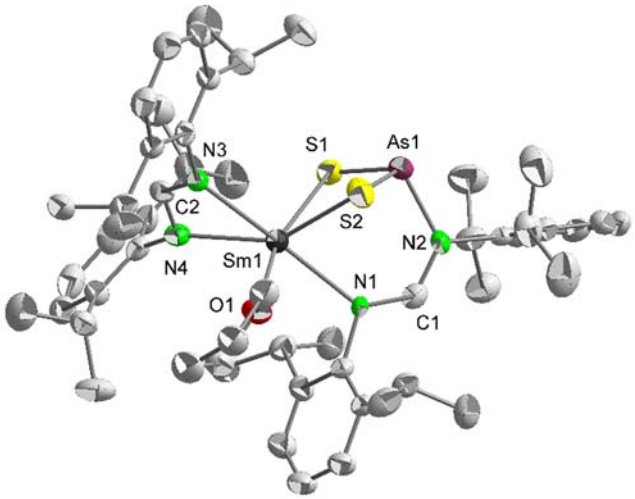

Figure S9 Molecular structure of **3** in the solid state. Hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and angles [°]: Sm1-S2 2.6859(14), Sm1-S1 2.6922(13), Sm1-N1 2.471(3), Sm1-N3 2.466(4), Sm1-N4 2.433(4), As1-S1 2.2031(14), As1-S2 2.2120(15), As1-N2 1.950(4), N1-C1 1.283(6), N2-C1 1.355(6), N3-C2 1.325(5), N4-C2 1.329(5), S2-Sm1-S1 81.88(4), S1-As1-S2 105.91(5), N2-As1-S2 99.74(12), N2-As1-S1 98.65(11), As1-S1-Sm1 83.34(4), As1-S2-Sm1 83.32(4), N1-C1-N2 125.6(4), N3-C2-N4 117.5(4).

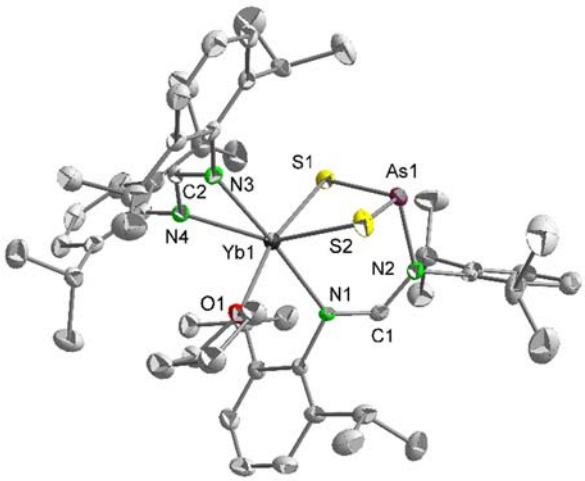

Figure S10 Molecular structure of **4** in the solid state. Hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and angles [°]: Yb1 S1 2.6062(7), Yb1 S2 2.5982(8), Yb1 N1 2.384(2), Yb1-N3 2.352(2), Yb1 N4 2.380(2), As1 S1 2.1983(8), As1 S2 2.2107(8), As1 N2 1.957(2), N1 C1 1.305(3), N2 C1 1.336(4), N3 C2 1.316(3), N4 C2 1.328(3), S2 Yb1 S1 84.21(2), S1 As1 S2 104.65(3), N2 As1 S2 99.33(6), N2 As1 S1 97.72(7), As1 S1 Yb1 82.75(2), As1 S2 Yb1 82.71(3), N1 C1 N2 126.7(2), N3 C2 N4 117.9(2).

Quantum chemical calculations on 1a and 2a:

The quantum chemical RI-DFT calculations were performed by means of the program system TURBOMOLE[5] using the RI-BP86 functional.[6] The basis sets for C, H, and N were of def2-SV(P) quality.[7] For Sm, a relativistic corrected effective core potential has been used to simulate the 51 inner electrons (ECP51).[8] The inclusion of the 5 f electrons into the ECP is allowed due to the expected ionic nature of the complex containing Sm in the formal oxidation state +III.[16] The geometry optimization by means of analytically derived gradients using redundant internal coordinates[17] lead to molecules of D_{2d} symmetry. The theoretical vibrational spectra were obtained by calculation of the second derivatives using the module AOFORCE.[18] Population analyses based on occupation numbers were performed (Roby-Davidson-Ahlrichs-Heinzmann population analysis).[9] Partial charges (Q) to interpret the ionicity of the bonds were obtained. Shared electron numbers (SEN) served as a measure for the covalent bond strength. All data of interest are summarized in Table S2. The strong polar character of the Sm-P bond was not only confirmed by SEN values but also after localization of MOs (LMOs) using the method of Pipek–Mezey.[20] Appropriate LMOs for **1a** are given in Figure S11. Even these LMOs are completely localized on phosphorus. Energy differences of reactions given in the text are calculated using the E_{tot} values of the calculated molecules.

Table S2: Results of the DFT calculations on E_2, E_4, Na_2E_4, Na_4E_8 and [{(PhForm)$_2$Sm}$_2$(μ^2-η^4:η^4-E_4)] (**1a, 2a**;E = P, As). Distances are given in Å, vibrational energies of the Pn-Pn valence motions ν in cm^{-1}. Shared electron numbers (SEN) and partial charges Q are determined by a population analysis based on occupation numbers (Ahrlichs-Heinzmann). For Sm, C, P, As, and H 9, 5, 9, 18 und 1 modified atomic orbital (MAO) were chosen.

Pn = P, As M = Na, Sm	symmetry	r(Pn-Pn)	r(Pn-Pn)	r(Pn-M)	ν(Pn-Pn)	SEN (Pn-Pn)	SEN (Pn-Pn)	SEN (Pn-Na)	Q(Pn)
P_2	$D_{\infty h}$	1.916			778.6	2.46			0
P_4	T_d	2.233				1.08			0
Na_2P_4	D_{2d}	2.227		2.879	449.6 (a1) 469.6 (b2) 399.3 (e)	1.28		0.33	-0.21
Na_4P_8	D_{2d}	2.250	2.439	2.719		1.15	0.85	0.38	-0.33/-0.02
1a	D_{2d}	2.224		3.124	457.5 (a1) 476.5 (b2) 414.2 (e)	1.28		0.l46	-0.12
As_2	$D_{\infty h}$	2.123			436.5	2.28			0
As_4	T_d	2.469				1.00			0
Na_2As_4	D_{2d}	2.456		2.973	266.5 (a1) 268.3 (b2) 236.6 (e)	1.18		0.33	-0.20
Na_4As_8	D_{2d}	2.478	2.641	2.803		1.04	0.79	0.38	-0.38/0.00
2a	D_{2d}	2.450		3.228	267.1 (a1) 273.6 (b2) 245.9 (e)	1.17		0.60	-0.01

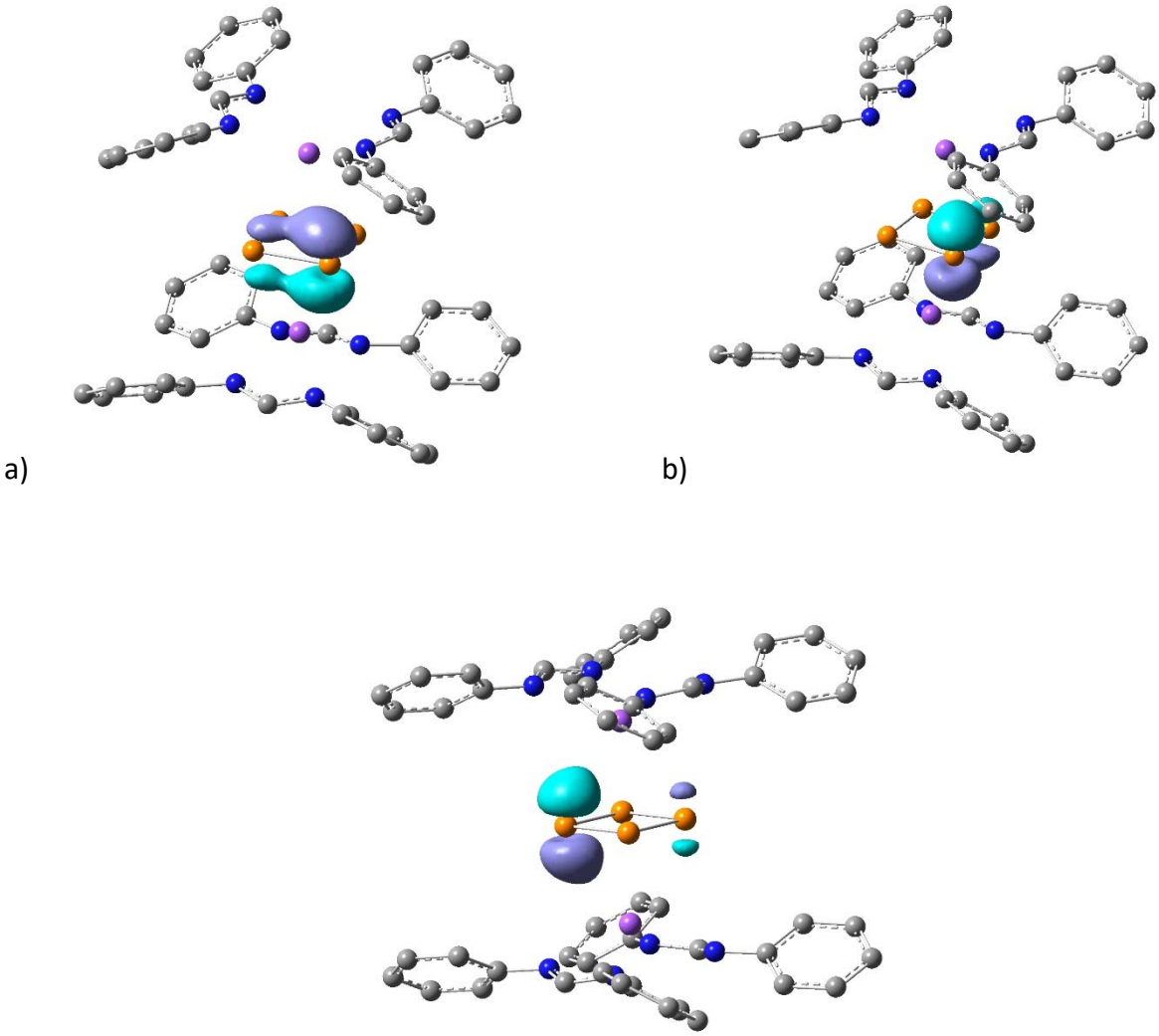

Figure S11 Localized MOs a) 195, b) 228, c) 242 representing only minimal partial charges on both Sm and P. The sketches confirm the description of P_4^{2-} as an isolated dianion in **1**.

References

1. (a) C. Schoo, S. Bestgen, M. Schmidt, S. N. Konchenko, M. Scheer and P. W. Roesky, *Chem. Commun.*, 2016, **52**, 13217; (b) G. B. Deacon, P. C. Junk, J. Wang and D. Werner, *Inorg. Chem.*, 2014, **53**, 12553.
2. W. Bues, M. Somer and W. Brockner, *Z. Anorg. Allg. Chem.*, 1983, **499**, 7.
3. (a) G. Sheldrick, *Acta Crystallogr. Sect. A*, 2008, **64**, 112; (b) G. Sheldrick, *Acta Crystallogr. Sect. C*, 2015, **71**, 3.
4. O. V. Dolomanov, L. J. Bourhis, R. J. Gildea, J. A. K. Howard and H. Puschmann, *J. Appl. Crystallogr.*, 2009, **42**, 339.
5. (a) R. Ahlrichs, M. Bär, M. Häser, H. Horn and C. Kölmel, *Chem. Phys. Lett.*, 1989, **162**, 165; (b) O. Treutler and R. Ahlrichs, *J. Chem. Phys.*, 1995, **102**, 346.
6. (a) A. D. Becke, *Phys. Rev. A*, 1988, **38**, 3098; (b) J. P. Perdew, *Phys. Rev. B*, 1986, **34**, 7406; (c) J. P. Perdew, *Phys. Rev. B*, 1986, **33**, 8822.
7. (a) F. Weigend, *PCCP*, 2006, **8**, 1057; (b) F. Weigend and R. Ahlrichs, *PCCP*, 2005, **7**, 3297.
8. S. Dehnen, M. R. Bürgstein and P. W. Roesky, *J. Chem. Soc., Dalton Trans.*, 1998, 2425.
9. R. Heinzmann and R. Ahlrichs, *Theor. Chim. Acta*, 1976, **42**, 33.