Journal of Molecular Structure 1036 (2013) 188–195

Contents lists available at SciVerse ScienceDirect

Journal of Molecular Structure

journal homepage: www.elsevier.com/locate/molstruc

Synthesis and structural studies of dimeric sodium compounds having pentametallacyclooctane and hexametallacyclo undecane structure using different phosphinamine derivatives

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HIGHLIGHTS

- Various bulky phosphinamines and derivatives have been synthesized.
- Very straight forward synthesis, i.e. easily accessible of the compounds.
- Novel structural motifs in sodium complexes using heteroatoms are observed.
- Three hetero atoms (N, P, S or O) are making the poly metallacycles.

ARTICLE INFO

Article history:
Received 6 August 2012
Received in revised form 27 September 2012
Accepted 27 September 2012
Available online 9 October 2012

Keywords:
Phosphinamines
Polymetallacycles
Sodium
Sulfur
Phosphorus

ABSTRACT

The treatment of two bulky phosphinamines [$Ph_2PNH(CHPh_2)$] (**1**) and [$Ph_2PNH(CPh_3)$] (**2**) with 30% hydrogen peroxide afforded phosphinicamides [$Ph_2P(O)NH(CHPh_2)$] (**3**) and [$Ph_2P(O)NHCPh_3$] (**4**) in good yield. When the same phosphinamines are reacted with elemental sulfur, corresponding sulfur compounds [$Ph_2P(S)NH(CHPh_2)$] (**5**) and [$Ph_2P(S)NHCPh_3$] (**6**) are obtained. Further reactions of **4**–**6** with sodium bis(trimethylsilyl)amide in THF solution afforded corresponding sodium salts of molecular formula [$\{(THF)_2Na(Ph_2P(O)NCPh_3)\}_2$] (**8**), [$\{(THF)_2Na(Ph_2P(S)NCHPh_2)\}_2$] (**7**) and [$\{(THF)_2Na(Ph_2P(S)NCPh_3)\}\{(THF)Na(Ph_2P(S)NCPh_3)\}$] (**9**) and all the sodium complexes **7**–**9** are dimeric and form highly strained polymetallacyclic motif in solid state structures. Molecular structure of all the complexes are established by single crystal X-ray diffraction analysis.

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1. Introduction

Use of various P—N ligands is one of the alternatives of cyclopentadienyl ligands and using this approach, amide ligands are successfully used today for the design of new transition-metal compounds having well defined reaction centres [1,2]. Recently, there has been a significant research effort in employing inorganic amines and imines. The P—N systems like monophosphanylamides (R_2PNR') [3–6] diphosphanylamides ($(Ph_2P)_2N$) [4,7,8], phospho-raneiminato (R_3PN) [9], phosphiniminomethanides [$((RNPR'_2)_2CH)$] [10–14], phosphiniminomethandiides ($((RNPR'_2)_2C$) [15–18], and diiminophosphinates ($R_2P(NR')$ [19] are well known today as ligands and proved their potency into the transition and f-block metals. Roesky and co-workers introduced one chiral phosphinamine $HN(CHMePh)(PPh_2)$ into the early transition-metal chemistry as well as in lanthanide chemistry [20]. It was shown that some of the early transition metal complexes having P—N ligands in the coordination sphere, may not only exhibit unusual co-ordination modes but also can be used for a number of catalytic transformations such as polymerization reactions [21]. Very recently, Fryzuk and co-workers have reported a series of three member lanthanide phosphinamido complexes by using alkane elimination route [22]. Other approach to introduce the ligand system into the metal chemistry is salt metathesis reaction. In our on-going project, we have synthesized various transition metal complexes of N-(diphenylphosphino)-2,6-dimethylaniline [$Ph_2PNH(2,6\text{-}Me_2C_6H_3)$] and their chalcogenides [$Ph_2P(O)NH(2,6\text{-}Me_2C_6H_3)$] and [$Ph_2P(S)NH(2,6\text{-}Me_2C_6H_3)$] [23]. To get more insight about the influence of various phosphinamine ligands toward the transition and lanthanide chemistry we decided to use the salt metathesis reaction involving metal halides and alkali metal salts of the ligand. Therefore, we planned a series of alkali metal salts of various phosphinamines and their derivatives.

Herein we report the syntheses and structural studies of two bulky phosphinamines [$Ph_2PNH(CHPh_2)$] (**1**) and [$Ph_2PNH(CPh_3)$] (**2**) and their chalcogen derivatives [$Ph_2P(O)NH(CHPh_2)$] (**3**) and

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http://dx.doi.org/10.1016/j.molstruc.2012.09.077

$[Ph_2P(O)\text{-}NH(CPh_3)]$ (**4**), $[Ph_2P(S)NH(CHPh_2)]$ (**5**) and $[Ph_2P(S)NH(CPh_3)]$ (**6**) along with various polycyclic structural motifs formed by the sodium complexes $[\{(THF)_2Na(Ph_2P(O)NCPh_3)\}_2]$ (**8**), $[\{(THF)_2Na(Ph_2P(S)NCHPh_2)\}_2]$ (**7**) and $[\{(THF)_2Na(Ph_2P(S)NCPh_3)\}\{(THF)Na(Ph_2P(S)NCPh_3)\}]$ (**9**) with these compounds.

2. Experimental

2.1. General

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^{-4} torr) line, or in an argon-filled M. Braun glove box. THF was pre-dried over Na wire and distilled under nitrogen from sodium and benzophenone ketyl prior to use. Hydrocarbon solvents (toluene and *n*-pentane) were distilled under nitrogen from $LiAlH_4$ and stored in the glove box. ^1H NMR (400 MHz), $^{13}C\{^1H\}$ and $^{31}P\{^1H\}$ NMR (161.9 MHz) spectra were recorded on a BRUKER AVANCE III-400 spectrometer. BRUKER ALPHA FT-IR was used for FT-IR measurement. Elemental analyses were performed on a BRUKER EURO EA at the Indian Institute of Technology Hyderabad. The starting materials chlorodiphenylphosphine, benzdihydrylamine, triphenylmethyl amine, sodium bis(trimethyl)silylamide were purchased from Sigma Aldrich and used without further purification. The NMR solvent C_6D_6 and $CDCL_3$ were purchased from sigma Aldrich.

2.2. Synthesis of $Ph_2PNHCHPh_2$ (1)

In a flame dried Schlenk flask 1.32 g (6.0 mmol) of chlorodiphenylphosphine was dissolved in 5 ml of dry toluene. To this solution, 2.19 g (12.0 mmol) of benzhdrylamine in 5 ml of dry toluene was added dropwise under stirring at 0 °C, immediate white turbidity was observed. The solution mixture was stirred for another 3 h at room temperature, and then white precipitate was filtered by using G4 frit and filtrate is collected. Solvent was removed in *vacuo*; pale yellow colored powder is obtained. Yield was 2.0 g (90%). ^1H NMR (400 MHz, $CDCl_3$): δ 7.00–7.34 (m, 20H, ArH), 5.26–5.37 (dd, ^1H, J = 6.67 Hz, 2.37 Hz, CH), 2.52 (br t, ^1H, J = 6.5 Hz, NH) ppm. $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 144.8 (ArC), 144.7(ArC), 141.9 (P-ArC), 141.8 (P-ArC), 131.4 (P attached *o*-ArC), 131.2 (P attached *o*-ArC), 128.5 (*m*-ArC), 128.4 (*o*-ArC), 128.2 (P attached *p*-ArC), 128.1 (P attached *p*-ArC) 127.4 (P attached *m*-ArC), 126.9 (*p*-ArC), 65.2, 65.0 (CH) ppm. $^{31}P\{^1H\}$NMR (161.9 MHz, $CDCl_3$): δ 35.2 ppm. FT-IR (selected frequencies): ν = 3262 (N—H), 1432 (P—C), 876 (P—N) cm^{-1}. Elemental Analysis ($C_{25}H_{22}NP$): Calcd. C 81.72, H 6.04, N 3.81; Found C 80.96, H 5.82, N 3.43.

2.3. Synthesis of $Ph_2PNHCPh_3$ (2): same as above for 1

Yield is 2.0 g (90%). ^1H NMR (400 MHz, $CDCl_3$): δ 7.29–7.31 (m, 6H, ArH), 7.06–7.16 (m, 19H, ArH), 3.06 (d, ^1H, J = 9.8 Hz, NH) ppm. $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 147.4 (ArC),147.3 (ArC), 135.3 (P-ArC), 135.2 (P-ArC), 131.3 (P attached *o*-ArC), 131.2 (P attached *o*-ArC), 128.9 (*o*-ArC), 128.2 (P attached *p*-ArC), 128.1 (P attached *m*-ArC), 128.0 (P attached *m*-ArC), 127.8 (*m*-ArC), 126.5 (*p*-ArC), 71.32 (triphenylmethyl C) ppm. $^{31}P\{^1H\}$NMR (161.9 MHz, $CDCl_3$): δ 26.3 ppm. FT-IR (selected frequencies): ν = ~3300 (very week broad N—H), 1434 (P—C), 896 (P—N) cm^{-1}. Elemental Analysis ($C_{31}H_{26}NP$): Calcd. C 83.95, H 5.91, N 3.16; Found C 83.26, H 5.72, N 2.91.

2.4. Synthesis of $Ph_2P(O)NHCHPh_2$ (3)

A 30% solution of H_2O_2 (0.15 ml) was added to a THF solution (10 ml) of N-benzhydryl-1,1-diphenylphosphinamine (500 mg, 1.46 mmol) with stirring and cooling. When the exothermal process finished the mixture was evaporated in *vacuo*. A white powder was formed, which was washed with *n*-pentane and then dried in *vacuo*. Yield was 0.525 g (100%). ^1H NMR (400 MHz, $CDCl_3$): δ 7.73–7.78 (m, 4H, ArH), 7.36–7.39 (m, 2H, ArH), 7.26–7.31 (m, 4H, ArH), 7.14–7.24 (m, 10H, ArH), 5.34–5.40 (t, ^1H, J = 10.84 Hz, CH), 3.16–3.19 (t, ^1H, J = 9.09 Hz, NH) ppm. $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 143.4 (ArC),143.3 (ArC), 132.9 (P-ArC), 132.3 (P attached *o*-ArC), 132.2 (P attached *o*-ArC), 131.9 (P attached *p*-ArC), 131.6 (P-ArC), 128.5 (*m*-ArC), 128.4 (P attached *m*-ArC), 128.3 (P attached *m*-ArC), 127.6 (*o*-ArC), 127.2 (*p*-ArC), 58.6 (CH) ppm. $^{31}P\{^1H\}$NMR (161.9 MHz, $CDCl_3$): δ 23.4 ppm. FT-IR (selected frequencies): ν = 3196 (N—H), 1435 (P—C), 997 (P—N), 1181 (P=O) cm^{-1}. Elemental Analysis ($C_{25}H_{22}NPO$): Calcd. C 78.31, H 5.78, N 3.65; Found C 77.79, H 5.61, N 3.42.

2.5. Synthesis of $Ph_2P(O)NHCPh_3$ (4): same as above for compound 3

Yield was 0.525 g (100%). ^1H NMR (400 MHz, $CDCl_3$): δ 7.61–7.66 (m, 4H, ArH), 7.15–7.28 (m, 13H, ArH), 7.08–7.09 (m, 8H, ArH), 4.20–4.19 (d, ^1H, J = 5.12 Hz, NH) ppm. $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 144.0 (ArC),143.9 (ArC), 134.3 (P-ArC), 133.0 (P-ArC), 130.6 (P attached *o*-ArC), 130.5 (P attached *o*-ArC), 130.0 (P attached *p*-ArC), 128.5 (*m*-ArC), 127.2 (P attached *m*-ArC), 127.1 (P attached *m*-ArC), 126.6 (*o*-ArC), 126.2 (*p*-ArC), 70.2 (triphenylmethyl C) ppm. $^{31}P\{^1H\}$NMR (161.9 MHz, $CDCl_3$): δ 18.4 ppm. FT-IR (selected frequencies): ν = ~3300 (very week broad N—H), 1439 (P—C), 866 (P—N), 1184 (P=O) cm^{-1}. Elemental Analysis ($C_{31}H_{26}NPO$): Calcd. C 81.03, H 5.70, N 3.05; Found C 80.75, H 5.31, N 2.87.

2.6. Synthesis of $Ph_2P(S)NHCHPh_2$ (5)

N-benzhydryl-1,1-diphenylphosphinamine (300 mg, 0.82 mmol) and elemental sulfur S_8 (26.3 mg, 0.82 mmol) were heated to 60 °C in toluene (5 ml) for 6 h. After removal of solvent *in vacuo* white solid was obtained. (Yield: 300 mg, (92%). The title compound $Ph_2P(S)NHCHPh_2$ recrystallized from hot toluene. ^1H NMR (400 MHz, $CDCl_3$): δ 7.74–7.79 (m, 4H, ArH), 7.32–7.36 (m, 2H, ArH), 7.12–7.28 (m, 12H, ArH), 5.58–5.64 (dd, ^1H, J = 8.71 Hz, 5.72 Hz, CH), 3.16–3.19 (dd, ^1H, J = 5.21 Hz, J = 2.58 Hz, NH) ppm. $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 143.2 (ArC),143.1 (ArC), 134.7 (P-ArC), 133.7 (P-ArC), 131.8 (P attached *o*-ArC), 131.7 (P attached *o*-ArC), 131.6 (P attached *p*-ArC), 131.5 (P attached *p*-ArC), 128.4 (*m*-ArC), 128.3 (P attached *m*-ArC), 128.2 (P attached *m*-ArC), 127.8 (*o*-ArC), 127.2 (*p*-ArC), 58.9 (CH) ppm. $^{31}P\{^1H\}$NMR (161.9 MHz, $CDCl_3$): δ 60.3 ppm. FT-IR (selected frequencies): ν = 3261 (N—H), 1432 (P—C), 902 (P—N), 625 (P=S) cm^{-1}. Elemental Analysis ($C_{25}H_{22}NPS$): Calcd. C 75.16, H 5.55, N 3.51; Found C 74.87, H 5.44, N 3.37.

2.7. Synthesis of $Ph_2P(S)NHCPh_3$ (6): same as above for compound 5

Yield: 500 mg, (92%). The title compound $[Ph_2P(S)NHCPh_3]$ recrystallized from hot toluene. ^1H NMR (400 MHz, $CDCl_3$): δ 7.20–7.31 (m, 13H, ArH), 7.08–7.17 (m, 12H, ArH), 3.92 (d, ^1H, J = 4.2 Hz, NH) ppm. $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 143.8 (ArC),143.7 (ArC), 135.8 (P-ArC), 134.8 (P-ArC), 130.4 (P attached *o*-ArC), 130.3 (P attached *o*-ArC), 129.9 (P attached *p*-ArC), 129.8 (P attached *p*-ArC), 128.8 (*m*-ArC), 127.2 (P attached *m*-ArC), 127.1 (P attached *m*-ArC), 126.5 (*o*-ArC), 126.2 (*p*-ArC), 70.9 (triphenylmethyl C) ppm. $^{31}P\{^1H\}$NMR (161.9 MHz, $CDCl_3$): δ

53.3 ppm. FT-IR (selected frequencies): ν = 3359 (N—H), 1437 (P—C), 860 (P—N), 640 (P═S) cm^{-1}. Elemental Analysis ($C_{31}H_{26}NPS$): Calcd. C 78.29, H 5.51, N 2.95; Found C 77.86, H 5.32, N 2.71.

2.8. Synthesis of [{Na(THF)$_2$Ph$_2$P(S)NH(CHPh$_2$)}$_2$] (**7**)

In a 10 ml sample viol 1 equivalent (50 mg, 0.125 mmol) of ligand **5** and 1 equivalent of sodium bis(trimethyl)silylamide (23 mg, 0.125 mmol) were mixed together with small amount of toluene, after 6 h small amount of THF and *n*-pentane were added to it and kept in −40 °C freezer, after 24 h sodium-PNS complex crystals were obtained. ^{1}H NMR (400 MHz, C_6D_6): δ 7.82–7.87 (m, 4H, ArH), 7.07 (m, 4H, ArH), 6.82–7.06 (m, 12H, ArH), 5.78–5.84 (dd, ^{1}H, J = 8.88 Hz, 5.88 Hz CH) ppm, 3.45–3.48 (m, THF), 1.29–1.33 (m, THF) ppm. ^{13}C{^{1}H} NMR (100 MHz, C_6D_6): δ 143.8 (ArC),143.7 (ArC), 135.9 (P-ArC), 134.9 (P-ArC), 132.2 (P attached *o*-ArC), 132.1 (P attached *o*-ArC), 131.2 (P attached *p*-ArC), 131.1 (P attached *p*-ArC), 128.4 (P attached *m*-ArC), 128.2 (*m*-ArC), 127.9 (*o*-ArC), 127.1 (*p*-ArC), 58.9 (CH) ppm. ^{31}P{^{1}H} NMR (161.9 MHz, C_6D_6): δ 73.3 ppm. Elemental Analysis ($C_{66}H_{74}N_2Na_2O_4P_2S_2$): Calcd. C 70.07, H 6.59, N 2.48; Found C 69.88, H 6.25, N 2.33.

2.9. Synthesis of [{Na(THF)$_2$Ph$_2$P(O)NH(CPh$_3$)}$_2$] (**8**)

In a 10 ml sample vial 1equivalent (50 mg, 0.105 mmol) of ligand **6** and 1 equivalent of sodium bis(trimethyl)silylamide (23 mg, 0.125 mmol) were mixed together with small amount of toluene, after 6 h small amount of THF and *n*-pentane were added to it and kept in −40 °C freezer, after 24 h complex **9** crystals were obtained. ^{1}H NMR (400 MHz, C_6D_6): δ 7.73–7.68 (m, 3H, ArH), 7.39–7.38 (m, 4H, ArH), 7.06–6.82 (m, 18H, ArH) ppm. ^{13}C{^{1}H} NMR (100 MHz, C_6D_6): δ 143.8 (ArC), 143.7 (ArC), 135.8 (P-ArC), 134.8 (P-ArC), 130.4 (P attached *o*-ArC), 130.3 (P attached *o*-ArC), 129.9 (P attached *p*-ArC), 129.8 (P attached *p*-ArC), 128.8 (*m*-ArC), 127.2 (P attached *m*-ArC), 127.1 (P attached *m*-ArC), 126.5 (*o*-ArC), 126.2 (*p*-ArC), 70.9 (triphenylmethyl C) ppm. [{(THF)$_2$Na(Ph$_2$P(S)NCHPh$_2$)}$_2$] (7) NMR (161.9 MHz, C_6D_6): δ 73.1 ppm. Elemental Analysis ($C_{74}H_{74}N_2Na_2O_3P_2S_2$): Calcd. C 73.37, H 6.16, N 2.31; Found C 73.05, H 5.96, N 1.99.

2.10. Synthesis of [{Na(THF)$_2$Ph$_2$P(S)N(CPh$_3$)} {Na(THF)Ph$_2$P(S)-N(CPh$_3$)}] (**9**)

In a 10 ml sample vial 1equivalent (50 mg, 0.105 mmol) of ligand **6** and 1 equivalent of sodium bis(trimethyl)silylamide (23 mg, 0.125 mmol) were mixed together with small amount of toluene, after 6 h small amount of THF and *n*-pentane were added to it and kept in −40 °C freezer, after 24 h complex **9** crystals were obtained. ^{1}H NMR (400 MHz, C_6D_6): δ 7.73–7.68 (m, 3H, ArH), 7.39–7.38 (m, 4H, ArH), 7.06–6.82 (m, 18H, ArH) ppm. ^{13}C{^{1}H} NMR (100 MHz, C_6D_6): δ 143.8 (ArC), 143.7 (ArC), 135.8 (P-ArC), 134.8 (P-ArC), 130.4 (P attached *o*-ArC), 130.3 (P attached *o*-ArC), 129.9 (P attached *p*-ArC), 129.8 (P attached *p*-ArC), 128.8 (*m*-ArC), 127.2 (P attached *m*-ArC), 127.1 (P attached *m*-ArC), 126.5 (*o*-ArC), 126.2 (*p*-ArC), 70.9 (triphenylmethyl C) ppm. [{(THF)$_2$Na(Ph$_2$P(S)NCHPh$_2$)}$_2$] (7) NMR (161.9 MHz, C_6D_6): δ 73.1 ppm. Elemental Analysis ($C_{74}H_{74}N_2Na_2O_3P_2S_2$): Calcd. C 73.37, H 6.16, N 2.31; Found C 73.05, H 5.96, N 1.99.

2.11. X-ray crystallographic studies

Single crystals of compounds **1, 2** were grown from a solution of CH_2Cl_2 at a temperature of −4 °C, compound **6** from hot toluene under argon atmosphere whereas crystals of compounds **7–9** were grown from toluene, THF and pentane mixture. In each case a crystal of suitable dimensions was mounted on a CryoLoop (Hampton Research Corp.) with a layer of light mineral oil and placed in a nitrogen stream at 150(2) K. All measurements were made on an Oxford Supernova X-calibur Eos CCD detector with graphite-monochromatic Cu Kα (1.54184 Å) radiation. Crystal data and structure refinement parameters are summarized in Table 1. The structures were solved by direct methods (SIR92) [29] and refined on F^2 by full-matrix least-squares methods; using SHELXL-97 [30]. Non-hydrogen atoms were anisotropically refined. H-atoms were included in the refinement on calculated positions riding on their carrier atoms. The function minimized was $[\Sigma w(Fo^2 - Fc^2)^2]$ ($w = 1/[\sigma^2(Fo^2) + (aP)^2 + bP]$), where $P = (\mathrm{Max}(Fo^2, 0) + 2Fc^2)/3$ with $\sigma^2(Fo^2)$ from counting statistics. The function R_1 and wR_2 were $(\Sigma||Fo| - |Fc||)/\Sigma|Fo|$ and $[\Sigma w(Fo^2 - Fc^2)^2/\Sigma(wFo^4)]^{1/2}$, respectively. The ORTEP-3 program was used to draw the molecule. 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. CCDC 889246-889251. 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).

3. Results and discussion

The phosphinamines [Ph$_2$PNH(CHPh$_2$)] (**1**) and [Ph$_2$PNH(CPh$_3$)] (**2**) were prepared in good yield by the aminolysis reaction by the respective amines, and diphenylphosphine chloride in 2:1 molar ration at room temperature by using toluene solvent (Scheme 1) [24]. In ^{31}P {^{1}H} NMR spectra compound **1** shows a signal at 35.2 ppm which is slightly downfield shifted to that of compound **2** (26.3 ppm). Compound **1** crytallizes in monoclinic space group Cc whereas compound **2** crystallizes in monoclinic space group $P2_1/c$. The structural parameters and selected bond distances, bond angles are given Tables 1 and 2 respectively. In the solid state structure of the compound **1** and **2** show similar P—N distances which are within the range of reported values (Table 2) [25]. The respective phosphinic amides [Ph$_2$P(O)NH(CHPh$_2$)] (**3**) and [Ph$_2$P(O)NH(CPh$_3$)] (**4**) were prepared in high yield by the straightforward reactions involving compounds **1** or **2** with aqueous hydrogen peroxide in 1:1 molar ratio at room temperature in THF (Scheme 1) [24]. In FT-IR spectra of **3** and **4**, a strong absorption (1181 and 1184 cm^{-1}) is observed and can be assigned as P═O bond stretching frequency along with the absorbance for P—N (997 and 866 cm^{-1}), and N—H (3196 and 3300 cm^{-1}) bond stretching which are well in the expected ranges [26]. In the ^{31}P{^{1}H} NMR spectra one signal is observed at 23.4 and 18.4 ppm for compound **3** and **4** respectively, representing slightly high field shift compare to their respective phosphinamines.

The compounds **5** and **6** were prepared over 90% yield by the reaction involving compound **1** or **2** and elemental sulfur in 1:1 molar ratio at room temperature in toluene (Scheme 2) [24]. In FT-IR spectra of compounds **5** and **6**, the strong absorptions at 625 and 640 cm^{-1} respectively are observed which can be assigned as P═S bond stretching frequency. In the ^{31}P{^{1}H} NMR spectra, one signal (60.3 for **5**, and 53.3 ppm for **6**) is observed representing significantly low field shift compare to their respective phosphinamine compounds. In the solid state, compound **6** crystallizes in the monoclinic space group $P2_1/c$ having four molecules in the unit cell (Table 1). The phosphorus atom is tetra-coordinated by two phenyl carbons, one nitrogen atom and one sulfur atom (Fig. 1). The P—S distance 1.9472(8) Å (Table 2) are well agreement to consider the P—S bond as double bond and compatible with literature values (1.4921(7) Å) [25,26].

3.1. Sodium salts

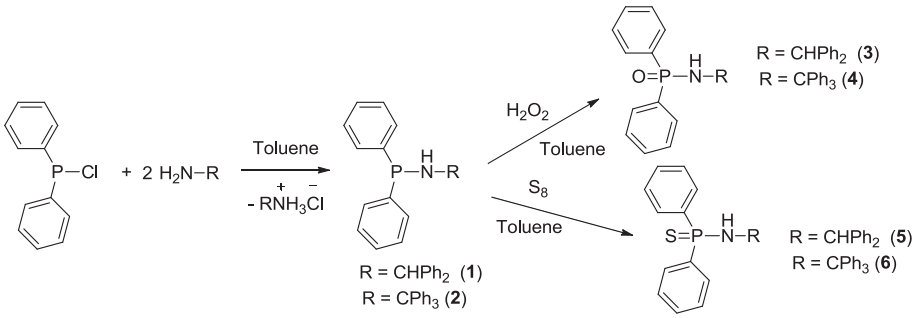
The dimeric sodium complex of molecular formula [{(THF)$_2$Na(Ph$_2$P(S)NCHPh$_2$)}$_2$] (**7**) was prepared by the reaction of compound

Table 1
Crystal data and structure refinement for **1**, **2** and **6–9.**

CCDC No.	889249	889247	889251
Empirical formula	$C_{25}H_{22}N_1P_1$	$C_{31}H_{26}N_1P_1$	$C_{31}H_{26}N_1P_1S_1$
Formula weight	367.41	443.5	475.56
T (K)	150(2)	150(2)	150(2)
λ (Å)	1.54184	1.54184	1.54184
Crystal system	Monoclinic,	Monoclinic	Monoclinic
Space group	Cc	$P2_1/c$	$P2_1/c$
a (Å)	22.237(4)	8.9955(8)	14.5362(5)
b (Å)	10.648(2)	18.6976(16)	10.9798(4)
c (Å)	9.551(2)	15.5059(19)	15.6321(4)
α (°)	90	90	90
β (°)	112.38(3)	108.089(9)	90.970(3)
α (°)	90	90	90
V (Å^3)	2091.1(7)	2479.1(4)	2494.60(14)
Z	4	4	4
D_{calc} g cm^{-3}	1.167	1.188	1.266
μ (mm^{-1})	1.208	1.106	1.896
F (000)	776	936	1000
Theta range for data collection	4.30–71.25°.	3.82–70.76°	3.04–70.81°
Limiting indices	$-27 \leqslant h \leqslant 18$, $-11 \leqslant k \leqslant 12$, $-10 \leqslant l \leqslant 11$	$-10 \leqslant h \leqslant 9$, $-16 \leqslant k \leqslant 22$, $-15 \leqslant l \leqslant 18$	$-16 \leqslant h \leqslant 17$, $-13 \leqslant k \leqslant 11$, $-19 \leqslant l \leqslant 18$
Reflections collected/unique	3859/2385 [R(int) = 0.0432]	10,162/4624 [R(int) = 0.0776]	10,314/4704 [R(int) = 0.0287]
Completeness to theta = 71.25	97.10%	97.00%	97.80%
Absorption correction	Empirical	Empirical	Empirical
Max. and min. transmission	0.880 and 0.790	0.876 and 0.81	0.738 and 0.616
Refinement method	Full-matrix Least-squares on F^2	Full-matrix Least-squares on F^2	Full-matrix Least-squares on F^2
Data/restraints/parameters	2385/2/245	4624/0/299	4704/0/307
Goodness-of-fit on F^2	0.962	0.96	1.028
Final R indices [$I > 2$ sigma(I)]	R_1 = 0.0774, wR_2 = 0.1949	R_1 = 0.0807, wR_2 = 0.1766	R_1 = 0.0446, wR_2 = 0.1143
R indices (all data)	R_1 = 0.0889, wR_2 = 0.2104	R_1 = 0.1970, wR_2 = 0.2671	R_1 = 0.0541, wR_2 = 0.1232
Absolute structure parameter	0.12(7)	0.0029(4)	
Largest diff. peak and hole	0.303 and −0.262 e A^{-3}	0.326 and −0.365 e A^{-3}	0.580 and −0.345 e A^{-3}

	7	**8**	**9**
CCDC No.	889246	889248	889250
Empirical formula	$C_{66}H_{74}N_2Na_2O_4P_2S_2$	C78 H82 N2 Na2 O6 P2	C74 H74 N2 Na2 O3 P2 S2
Formula weight	1131.33	1251.38	1211.42
T (K)	150(2)	150(2)	150(2)
λ (Å)	1.54184	1.54184	1.54184
Crystal system	Triclinic	Triclinic	Triclinic
Space group	$P-1$	$P-1$	$P-1$
a (Å)	10.5054(11)	11.0777(13)	10.7308(6)
b (Å)	12.9521(12)	13.3008(18)	11.6146(8)
c (Å)	13.3762(13)	14.0442(19)	26.1362(17)
α (°)	108.731(9)	100.720(11)	79.662(6)
β (°)	108.054(9)	112.259(12)	85.030(5)
α (°)	104.940(9)	111.066(12)	78.126(5)
V (Å^3)	1504.2(3)	1658.1(4)	3131.8(3)
Z	1	1	2
D_{calc} g cm^{-3}	1.249	1.253	1.285
μ (mm^{-1})	1.83	1.163	1.784
F (000)	600	664	1280
Theta range for data collection	3.86–70.69°	3.67–71.07°	3.44–71.04°
Limiting indices –	$-12 \leqslant h \leqslant 12$, $-15 \leqslant k \leqslant 15$, $-16 \leqslant l \leqslant 16$	$-12 \leqslant h \leqslant 13$, $-15 \leqslant k \leqslant 16$, $-17 \leqslant l \leqslant 11$	$-12 \leqslant h \leqslant 11$, $-14 \leqslant k \leqslant 14$, $-31 \leqslant l \leqslant 22$
Reflections collected/unique	10,292/5570 [R(int) = 0.0514]	11,652/6230 [R(int) = 0.0643]	20,573/11,831 [R(int) = 0.0346]
Completeness to theta = 71.25	96.20%	97.10%	97.60%
Absorption correction	Empirical	Empirical	Empirical
Max. and min. transmission	0.71 and 0.60	0.890 and 0.810	0.740 and 0.630
Refinement method	Full-matrix Least-squares on F^2	Full-matrix Least-squares on F^2	Full-matrix Least-squares on F^2
Data/restraints/parameters	5570/0/352	6230/0/406	11,831/1/782
Goodness-of-fit on F^2	1.036	1.054	1.027
Final R indices [$I > 2$ sigma(I)]	R_1[a] = 0.0582, wR_2[b] = 0.1528	R_1[a] = 0.0679, wR_2[b] = 0.1603	R_1[a] = 0.0600, wR_2[b] = 0.1639
R indices (all data)	R_1[a] = 0.0862, wR_2[b]=0.1721	R_1[a] = 0.1215, wR_2[b]=0.1965	R_1[a] = 0.0857, wR_2[b]=0.1883
Absolute structure parameter			
Largest diff. peak and hole	0.551 and −0.376 e A^{-3}	0.274 and −0.434 e A^{-3}	0.681 and −0.500 e A^{-3}

[a] $R_1(F) = \Sigma||Fo| - |Fc||/\Sigma|Fo|$.
[b] $wR_2(F^2) = [\Sigma w(Fo^2 - Fc^2)^2/\Sigma(wFo^4)]^{1/2}$.

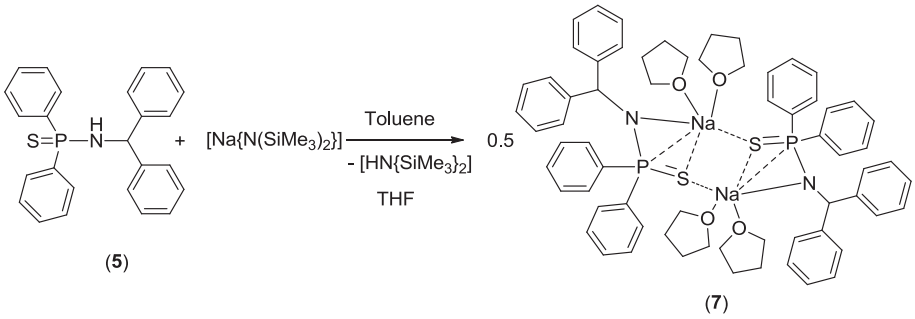


Scheme 1. Syntheses of compounds **1–6.**

Table 2
Selected bond lengths (Å) and angles (°) of **1, 2, 6, 7, 8 and 9**.

	1	2	6	7	8	9
Bond Length (Å)						
P(1)—N(1)	1.673(6)	1.6907(17)	1.6768(17)	1.593(3)	1.564(3)	1.583(2)
P(1)—X[a] (1)			1.9472(7)	1.9934(12)	1.520(2)	2.0133(10)
N(1)—C(1)	1.453(8)	1.494(2)	1.485(2)	1.471(4)	1.448(4)	1.473(3)
P(1)—C(14)	1.842(6)					
P(1)—C(20)	1.841(6)	1.828(2)	1.816(2)			
P(1)—C(26)		1.862(2)	1.822(2)			
Na(1)—N(1)				2.381(3)	2.792(3)	2.430(2)
Na(1)—X[a] (1)				2.9521(15)	2.369(3)	2.758(15)
Na(1)—X[a] (2)				2.8570(16)	2.218(3)	2.8498(15)
Na(1)—P(1)				3.1733(14)	3.0348(17)	3.1367(13)
Na(2)—X[a] (1)				2.8570(16)		3.1553(16)
Na(1)—C(19)					3.086(4)	
Na(1)—C(10)						3.017(3)
Bond angle (°)						
P(1)—N(1)—C(1)	118.2(4)	125.2(3)	129.55(13)	113.26(14)	136.8(3)	134.87(18)
N(1)—P(1)—X[a] (1)			116.70(6)	111.62(10)	114.94(15)	108.69(9)
X[a] (1)—P(1)—C(20)			112.56(7)	111.54(11)	105.14(15)	104.17(10)
X[a] (1)—P(1)—C(26)			114.19(7)		106.51(16)	108.05(10)
C(20)—P(1)—C(26)	98.1(3)	99.5(2)			105.20(17)	103.36(13)
C(14)—C(1)—N(1)	113.4(5)	108.9(4)				
C(20)—P(1)—N(1)	103.0(3)	101.3(2)			107.70(17)	115.74(13)
C(26)—P(1)—N(1)	104.2(3)	101.5(2)			116.37(16)	115.97(13)
N(1)—Na(1)—P(1)				29.11(6)	30.79(6)	29.73(5)
N(1)—Na(1)—X[a] (1)				66.87(7)	59.85(9)	68.52(6)
N(1)—Na(1)—X[a] (2)				118.37(8)	112.08(10)	134.94(8)
P(1)—Na(1)—X[a] (1)				37.77(3)	29.52(6)	39.29(2)
P(1)—Na(1)—X[a] (2)				115.24(5)	141.92(9)	118.67(5)
X[a] (1)—Na(1)—X[a] (2)				99.43(4)	82.70(10)	96.02(4)
Na(1)—P(1)—X[a] (1)				77.15(4)	50.16(10)	60.15(4)
Na(1)—X[a] (1)—Na(2)				80.57(4)	97.30(10)	84.96(4)

[a] Here X = S for **6**,**7** and **9** and X = O for **8**.



Scheme 2. Synthesis of compounds **7.**

5 sodium bis(trimethyl)silylamide in toluene through the elimination of volatile bis(trimethyl)silylamine (Scheme 2) [24]. The complex **7** crystallizes in triclinic space group *P*-1 having one molecule in the unit cell (Table 1). Selected bond lengths and angles are given in Table 2. In the centrosymmetric molecule **7**, two phosphinthioic amide ligands are coordinating to two sodium atoms by one sulfur, one phosphorus and one amido nitrogen atom exhibiting a diamond shaped Na_2S_2 core with mean S1—Na—S1[i] of

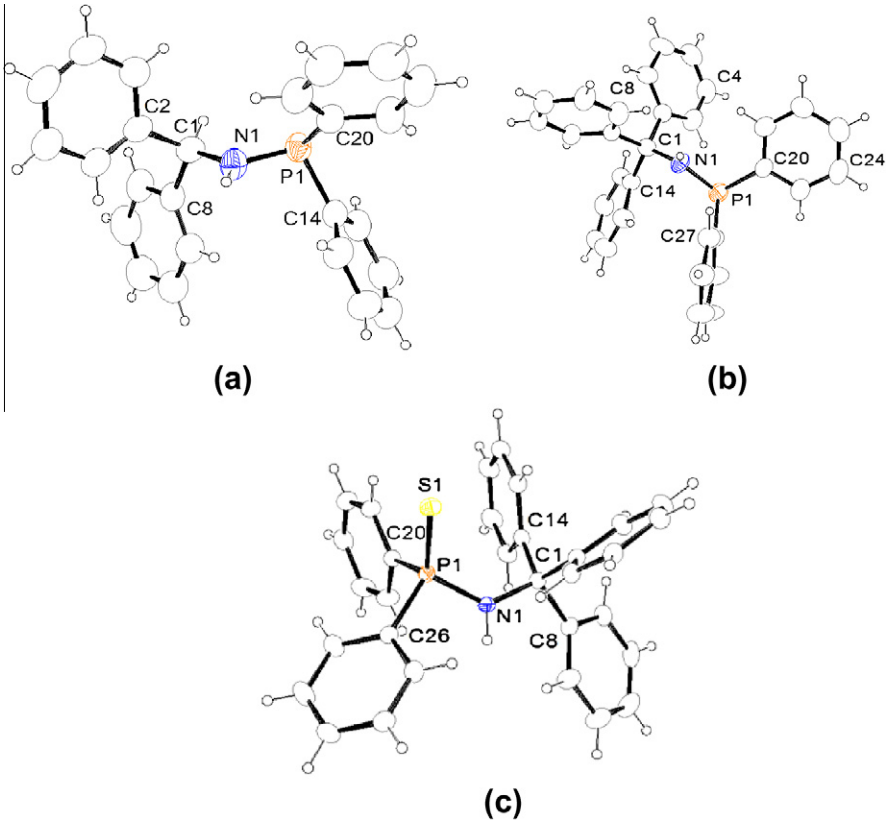
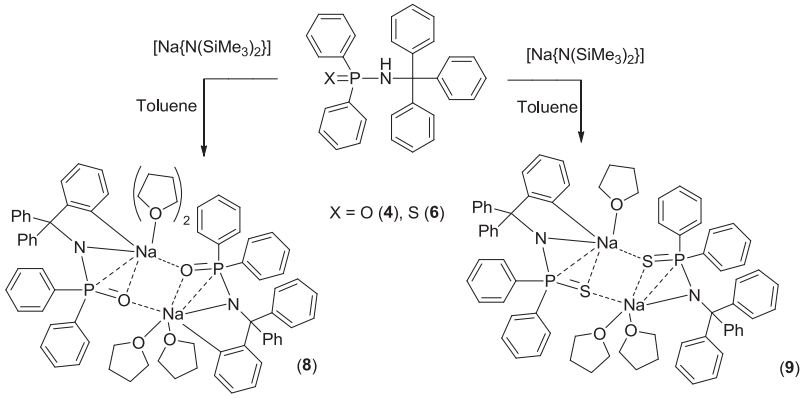


Fig. 1. Solid state structure of compound **1** (a) **2** (b) and **6** (c). Selected bond lengths [Å] and bond angles [°]: 1: P1—N1 1.673(6), N1—C1 1.453(8), P1—C20 1.841(6), P1—C14 1.842(6), C1—N1—P1 118.2(4), N1—P1 C20 103.0(3), N1—P1—C14 104.2(3), C20—P1—C14 98.1(3); **2**; P1—N1 1.692(4), N1—C1 1.487(6), P1—C20 1.844(6), P1—C28 1.831(5), C1—N1—P1 125.2(3), N1—P1—C20 101.3(2), N1—P1—C26 101.5(2), C26—P1—C20 99.5(2). **6:** P1—N1 1.6768(17), P1—S1 1.9472(7), P1—C20 1.816(2), P—C26 1.822(2), N1—C11.485(2), P1—N1—C1 129.55(13), N1—P1—S1 116.70(6), S1—P1—C20 112.56(7), S1—P1—C26 114.19(7).



Scheme 3. Syntheses of compounds **8** and **9**.

99.43(4)° and Na1—S1—Na1^{i} of 80.57(4)° angels (Table 2). The Na1—S1 and Na1—S1^{i} bond distances are also almost similar 2.9521(15), and 2.8570(16) Å. Each of the sulfur atoms is μ-coordinated in between the two sodium atoms. Additionally, each phosphorus atom is coordinated to each sodium atom to form highly strained three membered metallacycles having P1—Na1 3.1733(14) Å. In complex **7**, two additional THF molecules are also coordinated to each sodium atom and the geometry of each sodium atom can be best described as distorted octahedral. The bond distances Na1—N1 2.381(3), Na1—O1 2.378 (3), and Na1—O2 2.418(3) Å are in the range of the previously reported values. The whole structure consists four three member rings fused together forming a penta-metallacyclo[4.2.0.0^{1,7}.0^{2,5}.0^{2,4}]octane structure. To the best of our knowledge, this is the first example of such kind of structural motif in sodium complexes [28].

The other two dimeric sodium salts [{(THF)$_2$Na(Ph$_2$P(O)NCPh$_3$)}$_2$] (**8**) and [{(THF)$_2$Na(Ph$_2$P(S)NCPh$_3$)}{(THF)Na(Ph$_2$P(S)NCPh$_3$)}] (**9**) were prepared in a similar fashion involving the reaction of bulky phosphinic amide **4** and phosphinthioic amide **6** with sodium bis(trimethyl)silyl amide respectively in toluene at room temperature via the elimination of volatile hexamethyldisilazane (Scheme 3) [24]. In the solid state, both the complexes **8** and **9** crystallize in triclinic space group *P*-1 having one molecule (for **8**) and two independent molecules in the unit cell (for **9**) (Table 1).

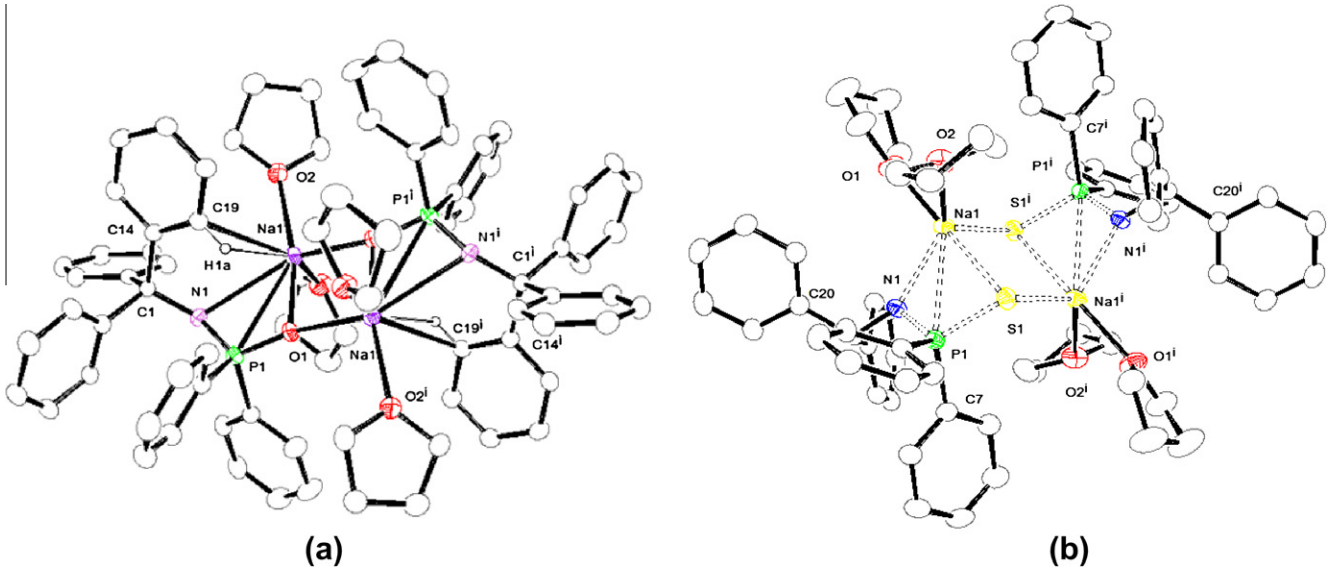


Fig. 2. Solid state structure of compound **7** (a) and **8** (b) omitting hydrogen atoms for clarity. Selected bond lengths [Å] and bond angles[°]: **7**; Na1—N1 2.381(3), Na1—P1 3.1733(14), Na1—S1 2.9521(15), Na1—S1^{i} 2.8570(16), Na1—O1 2.378(3), N1—O2 2.418(3), N1—P1 1.593(3), P1—S1 1.9934(12), N1—Na1—P1 29.11(6), N1—Na1—S1 66.87(7), N1—Na1—S1^{i} 118.37(8), P1—Na1—S1 37.77(3), P1—Na1—S1^{i} 115.24(5), S1—Na1—S1^{i} 99.43(4), N1—Na1—O1 112.89(11), N1—Na1—O2 109.53(10), Na1—P1—S1 77.15(4), Na1—S1—Na1^{i} 80.57(4), P1—Na1—O1 141.01(9), P1—Na1—O2 98.46(7), S1—Na1—O1 171.28(8), S1—Na1—O2 84.45(7), Na1—S1^{i}—P1^{i} 115.85(5), O1—Na1—O2 87.59(10), O1—Na1—S1^{i} 88.36(7), O2—Na1—S1^{i} 129.39(8), N1—P1—C1 113.26(14). **8**; Na1—N1 2.792(3), Na1—P1 3.0348(17), Na1—O1 2.369(3), Na1—C19 3.086(4), Na1—O1^{i} 2.218(3), Na1—O2 2.363(3), Na1—O3 2.338(3), Na1—N1—P1 83.20(12), P1—O1 1.520(2), P1—N1 1.564(3), Na1—P1—O1 50.16(10), Na1—O1—P1 100.31(13), N1—Na1—P1 30.79(6), P1—Na1—O1 29.52(6), Na1—N1—C1 118.3(2), C19—Na1—O1 78.12(10), C19—Na1—O2 82.93(11), C19—Na1—O3 149.33(11), C19—Na1—P1 68.72(8), C19—Na1—N1 57.91(9), N1—Na1—O1 59.85(9), O1—Na1—O1^{i} 82.70(10), O3—Na1—O1 110.59(11), O2—Na1—O1 160.76(12), O1^{i}—Na1—P1 112.19(9), O1^{i}— Na1—C19 107.54(11), O1—P1—N1 114.94(15), Na1—O1—Na1^{i} 97.30(10).

Selected bond lengths and angles are given in Table 2. The sodium complex **8** is centrosymmetric and dimeric (Fig. 2) in nature where each sodium atoms are coordinated by two *P,P*-diphenyl-N-trityl-phosphinic amido groups via one oxygen, one phosphorus and one amido nitrogen atom exhibiting a diamond shaped Na_2O_2 core with mean O1—Na—O1^{i} of 82.70(10) Å and Na1—O1—Na1^{i} of 97.30(10)° angels. Both the oxygen atoms are bridging coordinated with two sodium atoms. Besides, each phosphorus atom is coordinated to each sodium atom to form highly strained three membered metallacycles having P1—Na1 3.0348(17) Å. In complex **8**, two parallel planes containing Na1,O1, P1,N1 and Na1^{i},O1^{i}, P1^{i},N1^{i} atoms are placed at a distance of 0.429 Å and two planes containing Na1, O1, P1, N1 and Na1, O1, Na1^{i}, O1^{i} make a dihedral angle of 10.25°. A short contact Na···H between sodium and one of the phenyl proton (Na1···C19 (3.086(4) Å and Na1···H1a 2.598 Å) is observed which can be attributed as remote or secondary M—C—H interaction [27]. However, in solution all phenyl protons are appeared equivalent as observed in ^{1}H NMR study presumably due to dynamic behavior of the complex. Thus in the solid state, two additional five member metallacycles Na1—N1—C1—C14—C19 and Na1^{i}—N1^{i}—C1^{i}—C14^{i}—C19^{i} are formed. An unusual structural motif is formed by fusion of four three member and two five member metallacycle rings.

Unlike compound **8**, the sodium complex **9** is noncentrosymmetric and dimeric and two phosphinthioic amide ligands are coordinating to two sodium atoms by sulfur, phosphorus and one amido nitrogen atom exhibiting a diamond shaped Na_2S_2 core with mean S1—Na—S1^{i} of S1—Na1—S2 96.02 (4)° and S1—Na2—S2 88.10 (4)° and Na1—S1—Na2 84.96(4)° and Na1—S2—Na2 89.65(4)° angels. Each of the sulfur atoms is μ-coordinated in between the two sodium atoms. In addition, each phosphorus atom is coordinated to each sodium atom to form highly strained three membered metallacycles having P1—Na1 distance of 3.1367(13) Å. In complex **9**, sodium atom Na2 is attached to two THF molecules and adopts distorted octahedral geometry whereas the second sodium atom Na1 is coordinated only with one THF

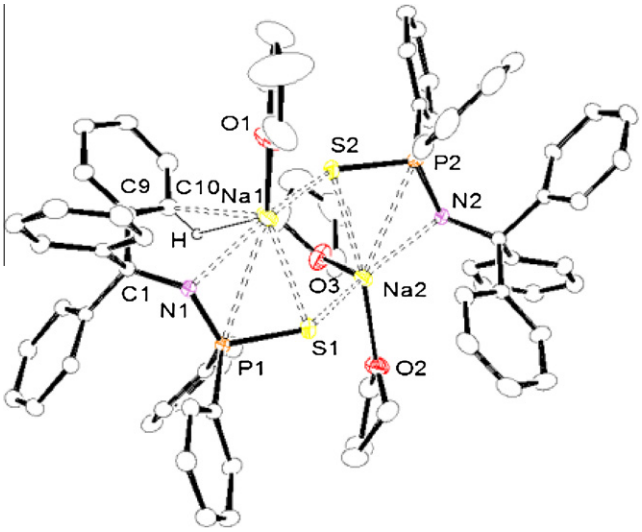


Fig. 3. Solid state structure of compound **9** omitting hydrogen atoms for clarity. Selected bond lengths [Å] and bond angles[°]: Na1—O1 2.271(3), Na1—N1 2.430(2), Na1—S1 2.7580(15), Na1—S2 2.8498(15), Na1—P1 3.1367(13), Na2—O2 2.299(3), Na2—N2 2.419(2), Na2—O3 2.535(3), Na2—S2 2.8307(14), Na2—S1 3.1553(16), Na2—P2 3.1616(13), Na1—C10 3.017(3), O1—Na1—N1 120.41(10), O1—Na1—S1 141.00(10), N1—Na1—S1 68.52(6), O1—Na1—S2 98.54(8), N1—Na1—S2 134.94(8), S1—Na1—S2 96.02(4), O1—Na1—C10 111.15(11), N1—Na1—C10 60.86(8), S1—Na1—C10 105.86(7), S2—Na1—C10 85.67(7), O1—Na1—P1, 142.72(8), N1—Na1—P1 29.73(5), S1—Na1—P1 39.29(2), S2—Na1—P1 118.67(5), C10—Na1—P1 76.08(6), O1—Na1—Na(2) 136.71(8), N1—Na1—Na2 102.78(7), O2—Na2—N2 118.77(10), O2—Na2—O3 90.38(10), N2—Na2—O3 106.30(10), O2—Na2—S2 172.92(8), N2—Na2—S2 68.14(6), O3—Na2—S2 88.87(8), O2—Na2—S1 87.01(8), N2—Na2—S1 118.34(8), O3—Na2—S1 130.16(8), S2—Na2—S1 88.10(4), O2—Na2—P2 147.99(8), N2—Na2—P2 29.25(5), O3—Na2—P2 100.55(8), S2—Na2—P2 38.89(2), S1—Na2—P2 107.49(4), P1—S1—Na1 80.56(4), P1—S1—Na2 119.37(5), Na1—S1—Na2 84.96(4), P2—S2—Na2 79.45(4), P2—S2—Na1 128.52(5), Na2—S2—Na1 89.65(4), N1—P1—S1 108.69(9), S1—P1—Na1 60.15(4), N2—P2—S2 110.01(9), N2—P2—Na2 48.35(8), S2—P2—Na2 61.66(4).

molecule and one phenyl carbon (C10) making a distance of 3.017 Å (Na1···H 2.649 Å) can be attributed as short M—C—H interactions [27]. However, in solution all phenyl protons are equivalent as observed in ^{1}H NMR spectra. Thus, a five member metallacycle Na1—N1—C1—C9—C10 is formed and the geometry of Na1 is best described as distorted tetrahedral. In complex **9**, whole structure consists four three membered rings along with one five member ring fused together forming a hexametallacyclo-[5.4.0.0^{1,5}.0^{1,6}.0^{8,10}.0^{8,11}] undecane structure (Fig 3). To the best of our knowledge, this kind of structural motif is not previously described in the literature for sodium compounds [28]. The three member metallacycles are highly strained as we can observe from the angles Na1—N1—P1 29.73(5)°, N1—P1—S1 60.15(4)°, P1—S1—N1 80.56(4)° and S1—Na1—N1 68.52(6)°. Even though the complex **9** is noncentrosymmetric in the solid state, only one set of signals were recorded in the ^{1}H, ^{31}P{^{1}H} and ^{13}C{^{1}H} NMR spectra in each case.

4. Conclusions

In conclusion, we have reported two bulky phosphinamines and their respective chalcogenides. Using the phsophinamine chalcogenides three different sodium complexes are prepared where two different structural motifs of pentametallacyclo-[4.2.0.01,7.02,5.02,4]octane and hexametalla-cyclo-[5.4.0.01,5.01,6.08,10.08,11]undecane are observed. The sodium complexes having various structural motifs can serve as the structural synthon for d- block and f-block metallacycles via salt metathesis reaction. Further reactions with these ligands are under progress in our laboratory.

Acknowledgments

This work was supported by the Department of Science and Technology India (DST) under the SERC Fast Track Scheme (SR/FT/CS-74/2010) and start-up grant from IIT Hyderabad. R.K. and K. N. thanks UGC, India for their PhD fellowship. Generous support from K. Mashima, Osaka University, Japan is gratefully acknowledged.

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