Journal of Inorganic and General Chemistry
ZAAC
Zeitschrift für anorganische und allgemeine Chemie
DOI: 10.1002/zaac.201800508

SHORT COMMUNICATION

Synthesis of Binam-P Derived C_2-Symmetric bis-Iminophosphonamide Ligands. Molecular Structure of [(*R*)-Binam($Ph_2PN(H)tBu)_2$]

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Abstract. The Staudinger reaction of organic azides $tBuN_3$, 1-Ad-N_3, and $DippN_3$ (Dipp = 2,6-diisopropylphenyl) with (*R*)-*N*,*N*′-*bis*(diphenylphosphanyl)-2,2′-diamino-1,1′-binaphthyl [(*R*)-Binam-P], obtained by an optimized procedure from (*R*)-(+)-Binam, Ph_2PCl, and Et_3N in DCM, leads to preparation of a series of new C_2-symmetric bis-iminophosphonamide ligands [(*R*)-Binam($Ph_2PN(H)R)_2$] [R = *t*Bu (**1**), Ad (**2**), and Dipp (**3**)]. The molecular structure of **1**·2DMSO was confirmed by X-ray structure analysis.

Iminophosphonamide anions $[R_2P(NR')_2]^-$ (NPN) are isolobal analogues of phosphinate anions, in which oxygen atoms are replaced by imido-groups. Synthesis of this NPN-ligand family is known from the literature and it is based on two main protocols – the Staudinger reaction[1,2] of phosphorus(III) compounds with organic azides and the Kirsanov condensation[3] of bromophosphonium bromides with primary amines in the presence of the auxiliary base and subsequent deprotonation (Chart 1).

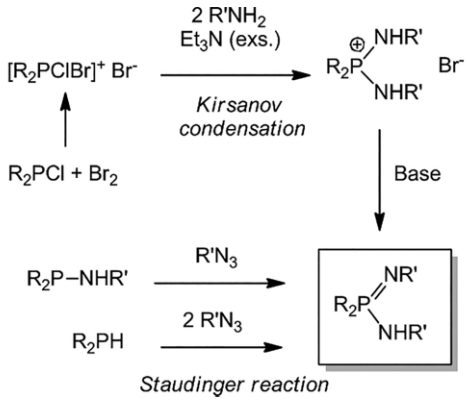

Chart 1. Synthetic protocols to iminophosphonamide species.

Iminophosphonamides belong to the class of P_1-phosphazenes, those chiral species are receiving increasing attention as superbase organocatalysts, performing a broad scope of stereodifferentiating reactions.[4] Among them there are two types that dominate to date as chiral catalysts – *P*-spirocyclic mono-NPN scaffolds of the type **A**[5] and bifunctional iminophosphoranes bearing a chiral pendant hydrogen bonding unit of the type **B** (Chart 2).[6]

The class of bis-iminophosphonamides has been presented by two series of C_2-symmetric molecules known so far. Earlier *Hill* and co-workers introduced *rac*-DACH-bridged ligands (DACH = *trans*-1,2-diaminocyclohexane) (Chart 2, **C**).[7] Chelating bis-NPN aluminum and rare-earth metal complexes with these NPN-ligands showed high activity as a single-component catalysts for the stereoselective polymerization of α-methylmethacrylate.

Next, one of us communicated two novel chiral superbases with dimethylamino and pyrrolidino substituents each of two P_2-phosphazenyl groups linked via a C_2-symmetric 1,1′-binaphthyl-2,2′-diamine (Binam) backbone (Chart 2, **D**). Their outstanding superbasicity leads to interesting perspectives for application in asymmetric Brønsted base catalysis.[8]

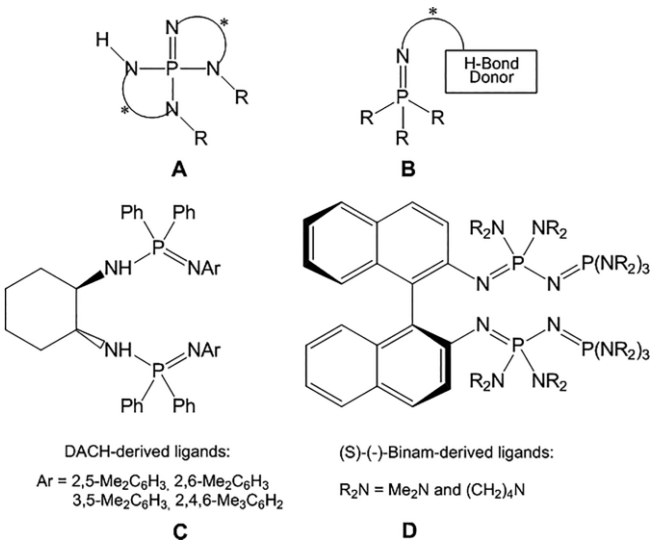

Chart 2. Types of chiral superbases known to date.

In the course of our systematic studies of ambidentate organophosphorus(V) donor ligands of the general type

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$[R_2P(X)Z]^-$ (X, Z = S, NR′, CH_2, CHR′, Cp, Ind, Flu; as for $X = Z$ and $X \neq Z$)[9] our attention has been drawn to the chemistry of this NPN-ligand family.

Recently we reported[10] on the rare-earth metal chemistry of highly basic, easily accessible, sterically demanding and perfectly soluble *N*,*N*′-bis(*tert*-butylimino)-phosphonamide (NPN) ligand $Ph_2P(=N–tBu)N(H)tBu$ and shortly reviewed all NPN complexes known from the literature until 2015. Since then some more chemistry of main-group and transition metals with NPN-ligands has been described.[11–13] This ligand was synthesized by the Staudinger reaction of $Ph_2P–N(H)tBu$ with $tBuN_3$. Synthesis of the precursor phosphonium salt species was earlier described by *Christau*[3a] using the Kirsanov condensation. Yet, we have found that this method is not applicable to the synthesis of iminophosphonamide species from two different amines and in particular to the synthesis of entitled bis-NPN species: tedious work-up, side products formation, and unacceptable low yields of the target compounds were experienced.

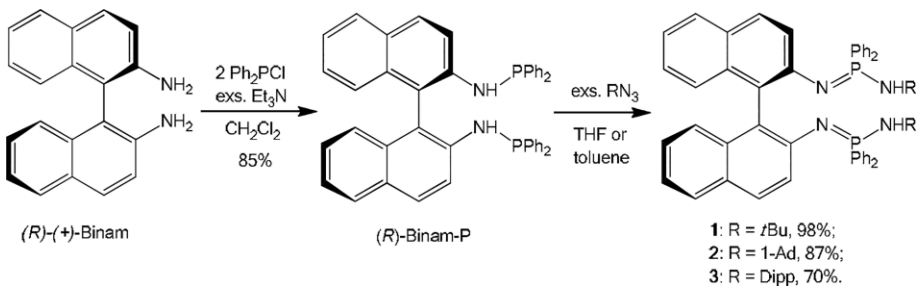
Here, we communicate on preparation of a new series of chiral bis-NPN ligands derived from chiral (*R*)-*N*,*N*′-bis(diphenylphosphanyl)-1,1′-binaphthyl-2,2′-diamine (Binam-P). Notwithstanding to reports of *Miyano* et al.,[14] we faced difficulties trying to reproduce synthesis of the (*R*)-(+)-Binam-P on larger scale; the reported metallation/phosphanylation of (*R*)-(+)-Binam with *n*BuLi and Ph_2PCl failed in our hands. All attempts to enhance the chemoselectivity of the phosphanylation, varying the concentration, temperature and stoichiometry of the reagents were unsuccessful. The tedious multiple crystallization of a bulk amount of the product is another drawback of this method. We found, that a simple one-pot protocol including addition of an excess of Et_3N to a *premixed* solution of Binam and Ph_2PCl is superior to any other synthetic methods towards Binam-P. Our optimized procedure is reproducible, requires no additional purification by chromatography and gives this target material in high yield of 85 % (Scheme 1) (see Experimental Section) Surprisingly, *Miyano* reported on "**…** no detectable amount **…**" in preparation of Binam-P in THF from Binam and Ph_2PCl with Et_3N.[14a] Earlier, preparation of $Binam(PR_2)_2$ (R = 3,5-$Me_2C_6H_3$, *cyclo*-C_6H_{11}) was reported in DCM using catalysis by 10 mol % of DMAP under similar reaction conditions.[15] This protocol using THF as a solvent was successfully applied also for other aromatic diamines (e.g. 1,2-diaminobenzene, 3,4-diaminotoluene, and 1,8-diaminonaphthaline).[16]

Thus obtained (*R*)-(+)-Binam-P was transformed by the Staudinger reaction with three different organic azides – $tBuN_3$, AdN_3, and $DippN_3$ (Ad = adamantyl-1, Dipp = 2,6-diisopropylphenyl) into a series of sterically hindered bis-iminophosphonamides (NPN ligands): [(*R*)-$Binam(Ph_2PN(H)R)_2$] [R = *t*Bu (**1**), Ad (**2**), and Dipp (**3**)] (Scheme 1). In all three cases, the reaction conditions are rather hard compared with aminophosphines without Binam-backbone.

Generally, the chiral compounds **1**–**3** possess rather low solubility in most organic solvents (e.g. **2** was found soluble only in C_6D_5Br for NMR studies). When the synthesis of **3** was performed in THF, formation of an air-stable powdery solid, which is almost insoluble in all common organic solvents, was observed. The composition of **3**·THF was established by elemental analysis and $^1H/^{31}P$ NMR spectrum of very poor quality. Unexpectedly, performing the same reaction in toluene (at 100 °C) instead of THF results in formation of a clear solution. In this case, the proceeding of the reaction was continuously monitored by ^{31}P NMR spectroscopy. The isolated product found to be solvent-free and possesses high solubility even in aromatic hydrocarbons! Irreversible formation of insoluble **3**·THF was observed upon addition of THF to a toluene solution of **3**. The isolation of **3**·THF and the crystal structure determination of **1**·2DMSO (vide infra) showed a high tendency of these bis-NPN species to capture polar solvent molecules via N–H···O hydrogen bridges. Interestingly, due to the bifunctional character and rigidity of the Binam backbone such formed solvates reveal an extremely low solubility, e.g. **3**·THF was not soluble enough to obtain highly resolved ^{31}P NMR spectra or crystals of sufficient quality for performing XRD studies.

Compounds **1**–**3** were characterized by ^1H, ^{31}P NMR spectroscopy, EI-MS, and elemental analysis. The ^{13}C NMR spectra were recorded for **1** and **3** showing sufficient solubility in C_6D_6. ^{31}P NMR resonances of **1**–**3** are shifted to δ_P –12.7 (**1**), –13.8 (**2**), –17.0 (**3**) ppm that is rather close to those of mono-NPN bis-alkyl species $Ph_2P(=N–tBu)N(H)tBu$ with δ_P –21.9 ppm[10] and particularly to mono-NPN bis-aryl species $Ph_2P(=N–Ar)N(H)Mes$ (Ar = Mes, Dipp; Mes = 2,4,6-$Me_3C_6H_2$) with δ_P –13.04 and –15.34 ppm, respectively.[11a]

In ^1H NMR spectra, the N*H* proton resonances for **1** and **2** having aliphatic substituents at the terminal N atom are close to each other and shifted to 2.86 and 2.56 ppm, respectively. The N*H* proton of **3** resonates at δ = 5.70 ppm. This value is even more down-field shifted compared with those found in



Scheme 1. Synthesis of (*R*)-Binam-P and therefrom derived bis-NPN ligands **1**–**3**.

analogous *N*,*N*′-bis-aryl-substituted mono-NPN species $Ph_2P(=NAr)N(H)Mes$ (Ar = Mes, Dipp), 4.10 and 4.13 ppm, respectively.[11a] The broadened N*H* resonance found for **2** is rather typical for mono-iminophosphonamides (cf. with those in $Ph_2P(=N$*t*$Bu)N(H)$*t*Bu) suggesting an equilibrium of tautomers in this case. Two-bond scalar couplings ($^2J_{HP}$) of 6.8 Hz and 10.0 Hz were observed for N*H* protons of **1** and **3**, respectively, pointing out that tautomeric equilibrium in these cases is hindered. Finally, the high-field chemical shifts in **1** and **2** strongly suggest the location of the proton at N-Alk group, whereas its location in case of **3** remains uncertain.

Yellow crystals of **1**, suitable for X-ray structure determination, were grown by very slow cooling of slightly oversaturated solution of **1** in DMSO from 60 °C down to room temperature (see Experimental Section). **1** crystallizes with two molecules of DMSO (**1**·2DMSO) in the monoclinic space group *C*2/*c*. Each of terminal H–N bonds is coordinated to one disordered DMSO molecule. The molecular structure of **1**·2DMSO is shown in Figure 1.

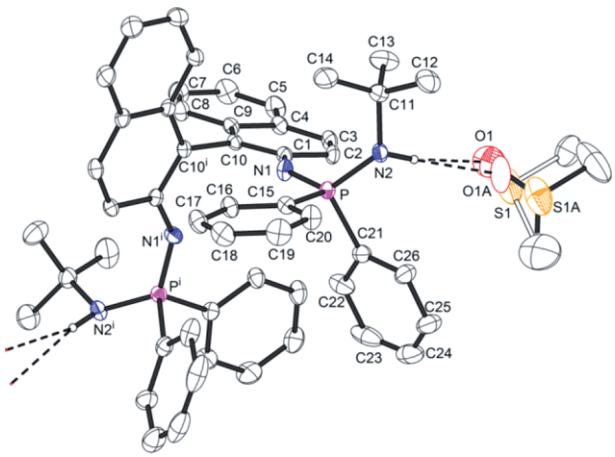


Figure 1. Molecular structure of **1**·2DMSO. Hydrogen atoms connected to carbon atoms are omitted for clarity. Selected bond lengths / Å and angles /°: C1–N1 1.388(3), P–N1 1.548(2), P–N2 1.656(2); N1–P–N2 122.95(14), C1–C10–C10'–C1' –94.1(5).

In conclusion, we have succeeded to develop simple reproducible procedure to the Binam-P and the chiral (*R*)-Binam-P was prepared in high yield. Using the Staudinger reaction with three representative organic azides – *t*BuN_3, Ad-N_3 and $DippN_3$ – corresponding chiral bis-iminophosphonamide (bis-NPN) ligands **1**–**3** with an axial chiral 1,1′-binaphthyl-backbone were synthesized and characterized. The molecular structure of (*R*)-Binam$(Ph_2PN(H)$*t*$Bu)_2$ (**1**) as a solvate with two DMSO molecules was determined by XRD. On example of **3**, formation of very stable, almost insoluble 1:1 solvate with THF, **3**·THF, was shown. Contrastingly to the known chiral non-protic NPN superbases,[8] these bis-NPN species have both basic N and acidic NH groups, proven by solvate formation, making them promising for asymmetric (organo)catalysis and in design of new chiral C_2-symmetric organometallic complexes, e.g. chelating pendants to *ansa*-metallocenes for various catalytic processes.

Experimental Section

Synthesis of (*R*)-*N*,*N*′-bis(diphenylphosphanyl)-1,1′-binaphthyl-2,2′-diamine (Binam-P): To a stirred slurry of (*R*)-Binam (3.00 g, 10.6 mmol) in dry dichloromethane (90 mL) pure Ph_2PCl (5.00 g, 22.7 mmol, 2.14 equiv.) was added, whereupon a yellow solution turns green-brownish. To thus obtained clear solution an excess of Et_3N (10 mL) was added via dropping funnel (**CAUTION! Exothermic reaction!**). Due to formation of triethylammonium chloride, the reaction mixture turns very thick. After stirring for 1 h all volatiles were removed in vacuo and dry toluene (60 mL) was added. The solid salt was filtered off, washed on filter with toluene (2 × 20 mL) and to thus obtained solution dry methanol (100 mL) was added. The mixture was allowed to stay for crystallization in a fridge at +10 °C. The reaction product precipitates as a microcrystalline solid that was collected by filtration, washed with cold methanol (3 × 5 mL) and dried in vacuo. Yield: 85 % (5.88 g). **^{1}H NMR** ($CDCl_3$, 300.1 MHz, 300 K): δ = 4.88 (d, $^2J_{HP}$ = 8.1 Hz, 1 H, N*H*), 6.82 (m, 2 H, *p-Ph*), 6.87 (m, 1 H, 6-/7-*Naph*), 6.93–6.96 (m, 4 H, *m-Ph*), 7.04 (m, 2 H, *o-Ph*), 7.07 (m, 1 H, 7-/6-*Naph*), 7.22 (m, 1 H, *Naph*), 7.21 – 7.24 (m, 2 H, *o-Ph'*), 7.58 (d, $^2J_{HH}$ = 8.0 Hz, 1 H, 5-*Naph*), 7.64 (d, $^3J_{HP}$ = 9.0 Hz, 1 H, 4-*Naph*), 8.11 (dd, $^3J_{HH}$ = 9.0, $^3J_{HP}$ = 4.0 Hz, 1 H, 3-*Naph*) ppm. **^{13}C{^{1}H} NMR** ($CDCl_3$, 75.5 MHz, 300 K): δ = 115.6 (d, $^3J_{CP}$ = 2 Hz, 1-*Naph*), (24 Hz, 3-*Naph*) 123.3, 124.8, 127.4, 128.5 – 129.0 (4–5 resonances), 129.4 (d, $^4J_{CP}$ = 1.5 Hz, 9-*Naph*), 130.3 (*J* = 1.6 Hz), 130.7, 131.0 (2 × d, $^2J_{CP}$ = 26 Hz, 2 × *o-Ph'*/*Ph*), 134.2 (10-*Naph*), 140.8, 141 (2 × d, $^1J_{CP}$ = 24 Hz, 2 × *ipso-Ph*), 144.0 (d, $^2J_{CP}$ = 18 Hz, 2-*Naph*) ppm. **^{31}P{^{1}H} NMR** ($CDCl_3$, 81.0 MHz, 300 K): δ = +27.6 ppm. **EI-MS** (*m*/*z*): 468 (9) $[MH - PPh_2]^+$, 284 (34) $[MH_2 - 2\ PPh_2]^+$, 267 (18) $[MH - NPPh_2]^+$, 201 (7) $[Ph_2PNH_2]^+$, 200 (8) $[Ph_2PNH]^+$, 186 (46) $[Ph_2PH]^+$.

Synthesis of Binam$(Ph_2PN(H)$*t*$Bu)_2$ (1): To a stirred solution of Binam-P (2.00 g, 3.06 mmol) in 20 mL THF, *t*BuN_3 (1.10 g, 11.1 mmol, 3.64 equiv.) was added and the reaction mixture was refluxed for 15 h (slow gas evolution), whereupon a colorless, microcrystalline solid forms. Upon cooling to room temperature the precipitate was filtered off and dried in vacuo. Yield: 98 % (2.40 g). **^{1}H NMR** (C_6D_6, 300.1 MHz, 300 K): δ = 1.04 (s, 9 H, Me_3C), 2.86 (d, $^2J_{HP}$ = 6.8 Hz, 1 H, *H*NCMe_3), 6.60 (m, 2 H, Ar), 7.0 – 7.2 (m, 7 H, Ar), 7.4 – 7.8 (m, 7 H, Ar) ppm. **^{13}C{^{1}H} NMR** (C_6D_6, 75.5 MHz, 300 K): δ = 32.0 (d, $^3J_{CP}$ = 4 Hz, CMe_3), 52.5 (d, $^2J_{CP}$ = 2 Hz, *C*Me$_3$), 120.7 (C_{Ar}), 124.3 (C_{Ar}), 125.5 (d, J_{CP} = 12 Hz, 2-C_{Ar}), 127.9 (d, $^3J_{CP}$ = 5.8 Hz, *m-Ph*), 127.9, 129.7 (9-,10-C_{Ar}), 130.0, 130.3 (2×s, *p-Ph*), 132.0, 132.5 (2×d, $^2J_{CP}$ = 9.4 Hz, *o-Ph*), 134.1, 136.0 (2×d, $^1J_{CP}$ = 82 Hz, *ipso-Ph*), 135.3 (d, J_{CP} = 35 Hz, 2-C_{Ar}), 146.6 (1-C_{Ar}) ppm. **^{31}P{^{1}H} NMR** (C_6D_6, 81.0 MHz, 300 K):δ = –12.7 ppm. **ESI-MS** inMeOH(*m*/*z*): 795 (100) $[MH]^+$, 740 (2) $[MH_2 - CMe_3]^+$, 398 (20) $[MH_2]^{2+}$. $C_{52}H_{52}N_4P_2$ (794.96): calcd. C 78.57, H 6.59, N 7.05 %; found: C 79.01, H 6.57, N 6.98 %.

Synthesis of Binam$(PPh_2N(H)Ad)_2$ (2): To a stirred solution of Binam-P (1.13 g, 1.73 mmol) in toluene (20 mL), AdN_3 (0.65 g, 3.7 mmol, 2.14 equiv.) was added at ones. By heating to 80–90 °C slow reaction with gas evolution takes place, accompanied with color change of the reaction mixture to deep yellow. After ca. 30 min a formation of precipitate started. The mixture was stirred at this temperature overnight. It was filtered off, washed twice with the same solvent and dried in vacuo. The product is poorly soluble in acetone, DCM, $CHCl_3$, and toluene. The compound is soluble in hot PhBr only. Yield: 87 % (1.43 mmol). **^{1}H NMR** (C_6D_5Br, 300.1 MHz, 300 K): δ = 1.00 (m, 6 H, Ad), 1.35 (m, 3 H, *H*C$(CH_2)_3$), 1.45 (m, 6 H, Ad), 2.56 (br. s, 1 H, N(*H*)Ad), 6.03 – 7.70 (m, 16 H, *Ar, Ph*) ppm. **^{13}C{^{1}H} NMR**(C_6D_5Br): no data available due to low solubility. **^{31}P{^{1}H} NMR**

(C_6D_5Br, 81.0 MHz, 300 K): δ = –13.8 ppm. **EI-MS** (*m/z*): 950 (56) $[M]^+$, 815 (7) $[M - Ad]^+$. $C_{64}H_{64}N_4P_2$ (951.19): calcd. C 80.81, H 6.78, N 5.89 %; found: C 80.56, H 6.81, N 5.94 %.

Synthesis of Binam(PPh$_2$N(H)Dipp)$_2$ (3): To a stirred solution of Binam-P (5.76 g, 8.83 mmol) in 50 mL toluene, $DippN_3$ (3.80 g, 18.7 mmol, 2.12 equiv.) was added and heated at 100 °C for 15 h (slow gas evolution). The reaction proceeding was monitored by ^{31}P NMR spectroscopy. The yellow reaction mixture was concentrated to one-fourth of the original volume, heated until dissolution of small amount of precipitate and hexane (60 mL) was added in six portions whilst stirring. The solid formed was filtered off and dried in vacuo. Yield: 70 % (6.20 g). Performing the same reaction in THF resulted in formation of **3**·THF solvate, which was identified only by ^{1}H and ^{31}P NMR spectroscopy and elemental analysis, due to very low solubility in all common organic solvent. **^{1}H NMR** (C_6D_6, 300.1 MHz, 300 K): δ = 0.92, 1.07 (2×d, $^3J_{HH}$ = 7.1 Hz, 2 × 6 H,*Me*$_2$CH), 3.50 (sept, $^3J_{HH}$ = 7.1 Hz, 2 H, Me$_2$C*H*), 5.70 (d, $^2J_{HP}$ = 10 Hz, 1 H, N(*H*)), 6.70–7.10 (m, 9 H, *Ar*), 7.35– 7.50 (m, 4 H, Ar), 7.86 (m, 2 H, *o-Ph*), 7.98 (d, *J* = 8.9 Hz, 1 H, *o-Ph*) ppm. **^{13}C{^{1}H} NMR** (C_6D_6, 75.5 MHz, 300 K): δ = 23.7, 23.8 (2 × s, *Me*$_2$CH), 28.9 (Me$_2$*C*H), 116.1 (d, J_{CP} = 8.7 Hz, 2-C_{Ar}), 119.0 (*p-Dipp*), 120.5(C_{Ar}), 123.1 (*m-Dipp*), 124.3 (C_{Ar}), 124.9 (C_{Ar}), 129.9 (d, J_{CP} = 6.3 Hz, *p-Ph*), 131.1 (d, J_{CP} = 9.8 Hz, *o-Ph*), 131.2, 131.7,132.7 (d, J_{CP} = 9.8 Hz, *o-Ph'*), 133.3, 134.2, 139.8 (C_{Dipp}-CHMe$_2$), 142.0 (d, J_{CP} = 7.5 Hz, *ipso-Dipp*), 143.4 ppm. **^{31}P{^{1}H} NMR** (C_6D_6, 81.0 MHz, 300 K): δ = –17.0 ppm. $C_{68}H_{68}N_4P_2$ (1003.27): calcd. C 81.41, H 6.83, N 5.58 %; found: C 81.18, H 7.00, N 5.78 %.

X-ray Diffraction: Data were collected with a STOE IPDS1 diffractometer using graphite monochromated Mo-K_α radiation (λ = 0.71073 Å) at 180(2) K. The structures were solved by direct methods using and SHELXS-97[17a] and refined by full-matrix least-squares on F^2 Fourier syntheses using SHELXL-2014/7[17b] software. The hydrogen atoms were introduced at calculated positions using a riding model. The program Diamond 3.1c was used for structure representations.[18]

Crystal Data for 1·2DMSO: $C_{56}H_{64}N_4O_2S_2P_2$, M_r = 951.17, monoclinic, space group *C*2/*c*, *a* = 19.129(2) Å, *b* = 9.7850(10) Å, *c* = 27.595(5) Å, β = 91.98(2)°, *V* = 5162.1(12) Å^3, *Z* = 4, d_{calcd} = 1.224 g·cm^{-3}, μ = 0.210 mm^{-1}, *F*(000) = 2024, R_1 = 0.0514 [from 2443 unique reflections with $I > 2\sigma(I)$], wR_2 = 0.1105 [for all 4091 unique reflections], GooF = 0.891.

Crystallographic data (excluding structure factors) for the structure in this paper have been deposited with the Cambridge Crystallographic Data Centre, CCDC, 12 Union Road, Cambridge CB21EZ, UK. Copies of the data can be obtained free of charge on quoting the depository number CCDC-1414731 for **1**·2DMSO (Fax: +44-1223-336-033; E-Mail: deposit@ccdc.cam.ac.uk, http://www.ccdc.cam.ac.uk)

Acknowledgements

K. A. R. thanks the Deutscher Akademischer Austausch Dienst (DAAD) for funding of a research fellowship at Philipps-Universität Marburg within the Ostpartnerschaftsprogramm.

Keywords: Staudinger reaction; Iminophosphonamide

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Received: December 12, 2018
Published Online: ■

Journal of Inorganic and General Chemistry
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