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N-(2,6-Dimethylphenyl)diphenylphosphinamine chalcogenides (S, Se) and a zirconium complex possessing phosphanylamide in the coordination sphere[†]

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We report the syntheses of *N*-(2,6-dimethylphenyl)-*P*,*P*-diphenylphosphinothioic amide Ph₂P(S)NH-(2,6-Me₂C₆H₃)] (**2**) and *N*-(2,6-dimethylphenyl)-*P*,*P*-diphenylphosphinoselenoic amide Ph₂P(Se)NH-(2,6-Me₂C₆H₃)] (**3**) by the reaction of *N*-(2,6-dimethylphenyl)-*P*,*P*-diphenylphosphinamine [Ph₂PNH-(2,6-Me₂C₆H₃)] (**1**) with elemental sulphur and selenium respectively. When the phosphinamine compound **1** was treated with *n*-BuLi and subsequently with zirconocenedichloride in an equimolar ratio, the corresponding zirconium complex [$\{\eta^5-Cp_2ZrCl(\eta^2-N(2,6-Me_2C_6H_3)PPh_2\}$] (**5**) was obtained in good yield. The solid state structures of all the compounds were established by single crystal X-ray diffraction analysis. In zirconium complex **5**, a highly strained three membered metallacycle was observed. In addition, the solid state structure, compound **4** shows extensive intermolecular hydrogen bonding through oxygen atoms, whereas a lesser extent of intermolecular hydrogen bonding was noted in compound **2**, due to the presence of the less electronegative sulphur atom.

Introduction

Use of various P-N ligands is one of the alternatives to using cyclopentadienyl ligands, and in 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 significant research effort in employing inorganic amines and imines. P-N ligand systems, such as monophosphanylamides (R_2PNR') , ³⁻⁶ diphosphanylamides [(Ph₂P)₂N],^{4,7,8} phosphoraneiminato (R₃PN),⁹ phosphinimino-methanides [(RNPR'2)2CH],10-14 phosphiniminomethandiides $[(RNPR'_2)_2C]$,^{15–18} and diiminophosphinates $[R_2P(NR')]^{19}$ are well known today as ligands and have proved their potency in transition and rare earth metal chemistry. Roesky and co-workers introduced one chiral phosphinamine [HN(CHMePh)(PPh2)] into the early transitionmetal 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 metallacycle of lanthanide phosphinoamido complexes [$\{3,5-Me_2C_6H_3NP(CHMe_2)_2\}_3$ -M(THF)] (M = Sc, Y) by using alkane elimination route.²²

Herein we describe the syntheses of *N*-(2,6-dimethylphenyl)-*P*,*P*-diphenylphosphinothioic amide [Ph₂P(S)NH-(2,6-Me₂-C₆H₃)] (**2**), *N*-(2,6-dimethylphenyl)-*P*,*P*-diphenylphosphinoselenoic amide Ph₂P(Se)NH-(2,6-Me₂C₆H₃)] (**3**) and the zirconium complex [{ η^{5} -Cp₂ZrCl(η^{2} -PPh₂N(2,6-Me₂C₆H₃)}] (**5**). Full characterization and structural studies of all the compounds have been made. In addition, the solid structure of [Ph₂P(O)NH(2,6-Me₂C₆H₃)] (**3**) is also reported.

Compound **2** was prepared in good yield by the reaction involving N-(2,6-dimethylphenyl)-diphenylphosphinamine [Ph₂P-NH(2,6-Me₂C₆H₃)] (1) with elemental sulphur in a 1 : 1 molar ratio at ambient temperature in toluene (Scheme 1). The title compound has been characterized by standard analytical/ spectroscopic techniques and the solid-state structure was established by single crystal X-ray diffraction.

In the FT-IR spectrum of the compound **2**, a strong absorption at 643 cm⁻¹ is observed, which can be assigned as characteristic P=S bond stretching. The absorbances for P-N (923 cm⁻¹), P-Ph (1434 cm⁻¹) and N-H (3267 cm⁻¹) bond stretchings are positioned well in the expected ranges. For compound **2**, the ¹H NMR spectrum shows a sharp singlet

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[†] Crystallographic details for compounds **2–5** are available. CCDC reference numbers 878241–878242 and 893244–893245. For crystallographic data in CIF or other electronic format see DOI: 10.1039/ c2nj40646b



Scheme 1 Syntheses of chalcogenides of [Ph₂PNH(2,6-Me₂C₆H₃)].

for six methyl groups at the 2,6-position of the phenyl groups of the aniline moiety at 2.00 ppm. The amine N–H proton shows a broad signal at $\delta = 4.24$ ppm which is slightly high frequency shifted compared to that of diphenylphosphinamine $1 (\delta = 3.70 \text{ ppm}).^{23}$ The signals of the phenyl protons are in the expected range in the ¹H NMR spectrum. In the ³¹P{¹H} NMR spectra one signal is observed at 56.3 ppm, representing that one phosphorus atom is present in the molecule. The significantly high frequency shift of the phosphorus signal compared to compound $1 (\delta 35.8 \text{ ppm})$ can be explained due to the presence of moderately electronegative sulphur atoms over the phosphorus atom (Fig. 1).

Compound 2 crystallizes in the tetragonal space group P41, having four molecules in the unit cell. Structural parameters for compound 2 are given Table 1. The bond distances of P1–N1 [1.662(2) Å] and P1–C9 [1.811(2) Å], P1–C15 [1.821(2) Å] are in the range of that in phosphorus compounds known in the literature.²³ The P-S distance 1.952(8) Å is elongated compared to the P-S bond as a double bond, and is comparable with the literature [1.4921(7) Å].²³ The C1-N1 bond distance of 1.437(3) Å and P1-N1-C1 angle of 124.76(18)° are unperturbed by sulfur on the phosphorus, and nicely matches with the sp³ hybrid geometry of the middle amine nitrogen atom which bears a amine proton in it. The phosphorus atoms is also sp³ hybridized and adopts a tetrahedral geometry around it, and the bond angles of S1-P1-N1 111.84(8)°, S1-P1-C15 115.03(10)°, N1-P1-C9 105.80(11)° and C15-P1-C9 102.35(10)° are comparable to the ideal angle (109°) for tetrahedral arrangements. In the solid state structure



Fig. 1 Molecular structure of **2** (left) and **3** (right) with thermal ellipsoids drawn at the 30% level. Selected bond lengths (Å) and bond angles (°) — compound **2**: P1–S1 1.9516(8), P1–N1 1.662(2), C1–N1 1.437(3), P1–C15 1.821(2), P1–C9 1.811(2), P1–N1–C1 124.76(18), N1–P1–S1 111.84(8), N1–P1–C15 108.02(12), N1–P1–C9 105.80(11), C15–P1–C9 102.35(10), C9–P1–S1 114.03(9), C15–P1–S1 115.03(10); compound **3**: P1–Se1 2.1019(8), P1–N1 1.656(3), C1–N1 1.441(4), P1–C15 1.822(3), P1–C9 1.811(3), P1–N1–C1 125.2(2), N1–P1–Se1 111.27(10), N1–P1–C15 108.29(15), N1–P1–C9 105.78(15), C15–P1–C9 102.28(13).C9–P1–Se1 114.02(11), C15–P1–Se1 114.47(12).

of compound **2** (Fig. 1, left), a relatively weak interaction between the N–H proton of one molecule and the sulfur atom in the adjacent molecule is observed (N1 \cdots S1 3.461 and H21a \cdots S1 2.660 Å).²⁵

The selenium compound 3 was prepared in good yield in a similar fashion to compound 2, involving reaction with 1 and elemental selenium in a 1:1.5 molar ratio at ambient temperature in toluene (Scheme 1). The characterization of 3 was made by standard analytical/spectroscopic techniques and the solidstate structure was established by single crystal X-ray diffraction (Fig. 1, right). For compound 3, a strong absorption at 909 cm^{-1} is observed, and can be attributed to characteristic P=Se bond stretching.²³ In the ¹H NMR spectrum, a sharp singlet for six methyl groups at the 2,6-position of the phenyl groups of the aniline moiety at 1.99 ppm, and for the amine N-H proton, a broad signal at $\delta = 4.20$ ppm is observed, which is comparable to that of compound 1 (2.04 and 3.70 ppm) and 2 (2.00 and 4.24 ppm) respectively.²³ In the ${}^{31}P{}^{1}H$ NMR spectra, one signal is observed at 53.6 ppm, which is slightly lower frequency shifted compared to that of compound 2 (56.3 ppm). Compound 3 crystallizes in the tetragonal space group P43, having four molecules in the unit cell. Structural parameters for compound 3 are given Table 1. The P-Se distance of 2.1019(8) Å is in agreement with the reported value and can be considered as a P-Se double bond.²⁶ P1-N1 1.656(3) Å, C1-N1 1.441(4) Å are also similar to that of compound 2. Like compound 2, the phosphorus geometry is tetrahedral and the bond angles around the phosphorus atom are also similar. However, no hydrogen bonding was observed in the selenium compound.

Compound 4, $[Ph_2P(O)NH(2,6-Me_2C_6H_3)]$ was synthesized in a straight forward reaction compared to the literature procedure, and the spectroscopic data was in accordance with the reported values (Scheme 1).²⁷ The solid-state structure of compound 4 was established by single crystal X-ray diffraction analysis (Fig. 2).

Compound 4 crystallizes in the orthorhombic space group $P2_12_12_1$, having two molecules in the asymmetric unit and eight molecules present in the unit cell. Structural parameters for compound 4 are given Table 1. The bond distances of P1-N1 (P2-N2) [1.6455(19) and 1.6478(19) Å] are slightly shorter than those of compound 2 and 3 [1.662(2) and 1.656(3) Å], and P1-C9 (P2-C29) [1.809(3) and 1.809(3) Å], P1-C15 (P2-C35)[1.796(2) and 1.804(2) Å] are also slightly shorter, but in the range of those in phosphorus compounds known in the literature.²⁸ The P-O distances, 1.4901(16) and 1.4914(16) Å, are in good agreement for considering the P-O bond as double bond and is comparable with the literature [1.4736(19) Å in 2,6-*i*Pr₂C₆H₃NHP(O)Ph₂].²⁸ The C1–N1 (C21-N2) bond distances [1.446(3) and 1.441(3) Å] and P1-N1-C1 (P2-N2-C21) angles [124.30(14) and 119.04(15)°], are unperturbed by oxidation of phosphorus, and nicely matches with the sp³ hybrid geometry of the middle amine nitrogen atom, which bears an amine proton. The phosphorus atom is also sp³ hybridized and adopts a tetrahedral geometry, and the bond angles of O1-P1-N1 (O2-P2-N2) [113.46(10) and 111.98(9)°], O1–P1–C15 (O2–P2–C35) [112.47(10) and 113.26(10)°], N1-P1-C9 (N2-P2-C29) [109.17(10) and 109.93(10)°], and C15-P1-C9 (C35-P2-C29) [105.65(11) and 104.62(11)°] are

Table 1 Crystal data and structure refinement for 2-5

	2	3	4	5
CCDC No. Empirical	878241 C ₂₀ H ₂₀ NPS	893245 C ₂₀ H ₂₀ NPSe	878242 C ₂₀ H ₂₀ NOP	$\begin{array}{c} 893244 \\ C_{176}H_{180}Cl_4N_4P_4Zr_4 \end{array}$
Formula weight	337.40	384.30	321.34	2981.80
Temperature Wavelength Crystal sys- tem, space	150(2) K 1.54184 Å Tetragonal, <i>P</i> 41	150(2) K 1.54184 Å Tetragonal, <i>P</i> 43	150(2) K 0.71069 Å Orthorhombic, <i>P</i> 2 ₁ 2 ₁ 2 ₁	150(2) K 1.54184 Å Orthorhombic, <i>Pnma</i>
Unit cell dimensions Volume Z, Calculated	$a = 11.8572(2) \text{ Å}, b = 11.8572(2) \text{ Å}, c = 12.3816(3) \text{ Å}, \alpha = 90^{\circ}, \beta = 90^{\circ}, \gamma = 90^{\circ} 1740.77(6) \text{ Å}^{3} 4, 1.287 \text{ Mg m}^{-3}$	$a = 11.8869(2) \text{ Å}, b = 11.8869(2) \text{ Å}, c = 12.6006(3) \text{ Å}, \alpha = 90^{\circ}, \beta = 90^{\circ}, \gamma = 90^{\circ} 1780.44(6) \text{ Å}^{3} 4, 1.424 \text{ Mg m}^{-3}$	$a = 9.068(5) \text{ Å}, b = 19.055(5) \text{ Å}, c = 20.228(5) \text{ Å}, \alpha = 90^{\circ}, \beta = 90^{\circ}, \gamma = 90^{\circ} \text{ 3495(2) Å}^{3} \text{ 8, 1.221 Mg m}^{-3}$	$a = 14.2392(12) \text{ Å}, b = 14.6310(18) \text{ Å}, c = 180321(17) \text{ Å}, \alpha = 90^{\circ}, \beta = 90^{\circ}, \gamma = 90^{\circ} 3756.7(7) \text{ Å}^{3} \text{ I}, 1.318 \text{ Mg m}^{-3}$
Absorption	2.489 mm^{-1}	3.676 mm^{-1}	0.161 mm^{-1}	3.682 mm^{-1}
F(000) Theta range for data	712 3.73 to 70.80°	784 3.72 to 70.80°	1360 1.47 to 25.81	1552 3.89 to 70.85
Limiting indices- Reflections collected/	$\begin{array}{l} -14 \leq h \leq 14, -14 \leq k \leq 4, \\ -13 \leq l \leq 15 \\ 3803/2402 \; [R(\mathrm{int}) = 0.0290] \end{array}$	$-14 \le h \le 11, -14 \le k \le 7, -11 \le l \le 15 3497/2336 [R(int) = 0.0169]$	$\begin{array}{l} -6 \leq h \leq 10, -23 \leq k \leq 17, \\ -24 \leq l \leq 23 \\ 8782/5909 \ [R(\text{int}) = 0.0249] \end{array}$	$-17 \le h \le 16, -17 \le k \le 9,$ $-21 \le l \le 18$ 10002/3695 [R(int) = 0.0491]
Completeness to $\theta = 71.25$	98.3%	96.7%	97.9%	98.1%
Absorption	Empirical	Empirical	Empirical	Empirical
Max. and min.	0.74 and 0.58	0.599 and 0.470	0.988 and 0.95	0.60 and 0.42
transmission Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
Data/ restraints/	2402/1/210	2336/1/210	5909/0/419	3695/260/320
parameters Goodness-of- ft on E^2	1.070	1.059	1.036	1.047
Final R indices	$R_1 = 0.0321, wR_2$	$R_1 = 0.0292, wR_2 = 0.0783$	$R_1 = 0.0385, wR_2 = 0.0123$	$R_1 = 0.0509, wR_2 = 0.1186$
$[I > 2\sigma(I)]$ <i>R</i> indices (all data)	$R_1 = 0.0336, wR_2 = 0.0827$	$R_1 = 0.0296, wR_2 = 0.0786$	$R_1 = 0.0402, wR_2 = 0.1043$	$R_1 = 0.0674, wR_2 = 0.1304$
Absolute structure	0.01(2)	-0.04(2)	-1.73(8)	
parameter Largest diff. peak and hole	$0.155 \text{ and } -0.376 \text{ eA}^{-3}$	0.579 and -0.316 eA^{-3}	$0.274 \text{ and } -0.293 \text{ eA}^{-3}$	$0.505 \text{ and } -1.291 \text{ eA}^{-3}$

comparable to the ideal angle (109°) for tetrahedral arrangements. The solid state structure of compound **4** reveals that the N–H proton of one molecule of compound **4** is intermolecularly hydrogen bonded (O···H–N) to the more electronegative oxygen atom present in the adjacent molecule of **4** (N2···O1 2.814 and H2···O1 2.059 Å). The interaction between the methyl protons (H8C···O1 2.566 Å) and adjacent phenyl protons (H36···O1 2.823 Å) with the oxygen atom of the second molecule are also noticed, and they are within the range of hydrogen bonding distances.²⁹ However, in the ¹H NMR spectra, all the methyls protons give only one singlet, indicating the dynamic behaviour of the molecule, where the short interactions might be due to close packing in the solid state.

The zirconium complex $[{\eta^5-Cp_2ZrCl(\eta^2-PPh_2N(2,6-Me_2C_6H_3)}]$ (5) was obtained as the major product by a two step reaction of phosphinamine (1), *n*-BuLi and subsequently with zirconocene dichloride in THF, followed by crystallization from toluene/ *n*-pentane (Scheme 2). The new complex has been characterized by standard analytical/spectroscopic technique and the solid state structure of the complex **5** was determined by single crystal X-ray diffraction analysis (Fig. 3).

Compound **5** crystallizes in the orthorhombic space group *Pnma*, having one molecule of **5** in the unit cell along with one disordered toluene. Structural parameters for compound **5** are given Table 1. The [Ph₂PN(2,6-Me₂C₆H₃)]⁻ ligand is co-ordinated to the center metal zirconium atom in a chelating (η^2) fashion. The structure reveals a pseudo-five-fold co-ordination



Fig. 2 Molecular structure of 4 with thermal ellipsoid drawn at the 30% level. Selected bond lengths (Å) and bond angles (°) — molecule 1 (bottom): P1–O1 1.4901(16), P1–N1 1.6455(19), C1–N1 1.446(3), P1–C15 1.796(2), P1–C9 1.809(3), P1–N1–C1 124.30(14), N1–P1–O1 113.46(10), N1–P1–C15 105.85(10), N1–P1–C9 109.17(10), C15–P1–C9 105.65(11), O1–P1–C15 112.47(10), O1–P1–C9 109.87(10); molecule 2 (top): P2–O2 1.4914(16), P2–N2 1.6478(19), C21–N2 1.441(3), P2–C29 1.809(3), P2–C35 1.804(2), P2–N2–C21 119.04(15), N2–P2–O2 111.98(9), N2–P2–C29 109.93(10), N2–P2–C35 105.89(10), O2–P2–C35 113.26(10), O2–P2–C29 110.80(11).

02



Scheme 2 Synthesis of zirconium complex $[{\eta^5-Cp_2ZrCl(h^2-PPh_2N-(2,6-Me_2C_6H_3))}](5).$



Fig. 3 Molecular structure of 5 with thermal ellipsoid drawn at the 30% level omitting hydrogen atoms for clarity. Selected bond lengths (Å) and bond angles (°): Zr1–N1 2.201(4), Zr1–P1 2.634(2), Zr1–C1 2.5273(14), Zr1–C5 2.522(4), Zr1–C2 2.528(4), Zr1–C6 2.529(4), Zr1–C1 2.544(4), Zr1–C3 2.568(4), P1–N1 1.640(4), P1–C4 1.823(4), N1–C10 1.442(6), Zr–Ct 2.240, N1–Zr–C12 81.64(11), N1–Zr1–P1 38.33, N1–P1–Zr1 85.26(18), N1–Zr1–Ct1 115.6, P1–Zr1–Ct1 104.3 (Ct = centroid).

sphere of the ligands around the zirconium atom if the ring centroids of the cyclopentadienyl rings are considered as co-ordination positions. A three membered metallacycle N1–Zr1–P1 is formed. The P and N atoms are co-ordinated to the $(\eta^{5}-C_{5}H_{5})_{2}ZrC1$ fragment, and the N, P, Zr and Cl

atoms are perfectly coplanar. The cyclopentadienyl rings are asymmetrically attached to the metal ion having Zr–C distances of 2.522(4) to 2.568(4) Å. The Zr–Ct distance is 2.240 Å, where Ct represents the centroid of the cyclopentadienyl ring. A three membered metallacycle N1–P1–Zr1 is formed by nitrogen, phosphorus, and zirconium atoms, having the bond distances of Zr1–N1 2.201(4) and Zr1–P1 2.634(2) Å. In the literature, a similar geometry is observed for compounds $[\eta^5-Cp_2Zr(Cl)[\{\eta^2-N(SiMe_3)P(H)N(SiMe_3)_2\}]$, which can be prepared by reaction of Me₃SiN=P–N(SiMe₃)₂ with $[\eta^5-Cp_2Zr(Cl)H]^{30}$ and in $[\eta^5-Cp_2Zr(Cl)\{\eta^2-N(PPh_2)_2]$.³¹

The ¹H NMR spectra shows a sharp doublet for the protons of the Cp unit, which is shifted to a lower frequency (δ 6.06) when compared with the starting material [η^5 -Cp₂ZrCl₂] (δ 6.50).³² The doublet is a result of coupling to the phosphorus atom, with a coupling constant of 1.6 Hz, which is much smaller than the reported value (17.5 Hz) in [η^5 -C₅H₅)₂Zr(Cl)N-(CHMePh)(PPh₂)].²⁰ The [Ph₂PN(2,6-Me₂C₆H₃)]⁻ ligand shows a characteristic signal of a singlet for the methyl groups at the 2,6-position, and the expected signals for phenyl photons. Also, characteristic is the ³¹P NMR spectrum. At room temperature, compound **5** shows one signal in the ³¹P{¹H} NMR spectrum (δ 49.2 ppm), which is slightly shifted relative to **1** (δ 35.8).

Conclusions

In conclusion we have synthesized two chalcogenides N-(2,6-dimethylphenyl)-P,P-diphenylphosphinothioic amide and N-(2,6-dimethylphenyl)-P,P-diphenylphosphinoselenoic amide and observed that the analogous oxygen compound [Ph₂P(O)NH(2,6-Me₂C₆H₃)] shows extensive intermolecular hydrogen bonding in the solid state compared to the sulphur analogue. We have also introduced the N-(2,6-dimethylphenyl)-P,P-diphenylphosphinamine ligand into zirconium chemistry by synthesizing [{ η^{5} -Cp₂ZrCl(η^{2} -PPh₂N(2,6-Me₂C₆H₃)}]. Further reactions of these phosphinamine derivatives as ligands in transition and rare earth metal chemistry are currently in progress in our laboratory.

Experimental section

General

All manipulations of air-sensitive materials were performed with the rigorous exclusion of oxygen and moisture in flamedried 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 LiAlH₄ and stored in the glove box. ¹H NMR (400 MHz) and ³¹P{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. HRMS was measured by an Agilent Technology Q-TOF instrument. Elemental analyses were performed on a BRUKER EURO EA at the Indian Institute of Technology Hyderabad. N-(2,6-Dimethylphenyl)-diphenylphosphinamine $[Ph_2P-NH(2,6-Me_2C_6H_3)]$ (1) was prepared according to the literature procedure.²⁴

Syntheses

 $[Ph_2P(S)NH-(2,6-Me_2C_6H_3)]$ (2). Compound 1 (0.50 g, 1.63 mmol) and elemental sulfur (0.05 g, 1.63 mmol) were placed in a 50 mL Schlenk tube and 20 mL toluene was added to it. The reaction mixture was heated to 60 °C for 6 h. After removal of the solvent *in vacuo*, a white solid of compound 2 was formed. Yield: 480 mg, (87%). The compound was recrystallized from toluene at room temperature.

¹H NMR (400.1 MHz, CDCl₃): δ = 7.91 (d, 2H, J_{H-H} = 7.5 Hz, Ph), 7.88 (d, 2H, J_{H-H} = 7.5 Hz, Ph), 7.45–7.30 (m, 6H, Ph), 6.90–6.88 (m, 3H, Ph), 4. 24 (br, 1H, NH), 2.00 (s, 3H, CH₃) ppm. ³¹P-{¹H} NMR (161.9 MHz, CDCl₃): δ = 56.31 ppm. IR, (selected peaks): v = 923 (P–N), 1434 (P–Ph), 3267 (N–H), 643 (P=S) cm⁻¹. Elemental analysis: C₂₀H₂₀NPS (337.11) Calcd C 71.19 H 5.95 N 4.15; Found C 70.89 H 5.79 N 4.02.

[Ph₂P(Se)NH-(2,6-Me₂C₆H₃)] (3). Similar to the synthesis of compound 2. Yield: 0.54 g (91%). ¹H NMR (400.1 MHz, CDCl₃): δ = 7.92–7.87 (m, 4H, Ph), 7.43–7.37 (m, 6H, Ph), 6.90–6.88 (br. s, 3H, Ph), 4.20 (br, 1H, –NH), 1.99 (s, 3H, –CH₃), ppm. ³¹P-{¹H} NMR (161.9 MHz, CDCl₃): δ = 53.6 ppm. IR, (selected peaks): v = 909 (P–N), 1358 (P–Ph), 3224 (N–H), 568 (P=S) cm⁻¹. C₂₀H₂₀NPSe (384.31), Calcd C 62.50 H 5.25 N 3.64; Found C 61.99 H 4.95 N 3.43.

[Ph₂P(O)NH(2,6-Me₂C₆H₃)] (4). Compound 4 was synthesized in a modified method compared to the literature procedure.²⁷ Aqueous hydrogen peroxide (30% w/w, 0.15 mL, 1.46 mmol) was added drop wise to a suspension of compound 1 (0.45 g, 1.46 mmol) in THF (20 mL) and the mixture was kept under stirring conditions for 30 min at room temperature. The volume was concentrated *in vacuo* to *ca.* 1–2 mL and addition of *n*-hexane (20 mL) gave a white solid which was collected by filtration [Yield: 0.56 g, (86%). m.p. 145 °C]. Compound **4** was crystallized from THF solution.

¹H NMR (400.1 MHz, C₆D₆): $\delta = 8.0$ –7.80 (m, 4H, Ph), 7.10–6.70 (m, 6H, Ph), 7.90 (br. s, 3H), 3.77 (br, 1H, Ph₂P-NH), 2.05 (s, 3H, –CH₃), ppm. ³¹P-{¹H} NMR (161.9 MHz, CDCl₃): $\delta = 67.83$ ppm. IR, (selected peaks): v = 929 (P–N), 1446 (P–Ph), 3162 (N–H), 1195 (P=O) cm⁻¹. C₂₀H₂₀NOP (321.35), Calcd C 74.75 H 6.27 N 4.36; Found C 74.05 H 5.87 N 4.09.

 $[\{\eta^5-Cp_2ZrCl(\eta^2-PPh_2N(2,6-Me_2C_6H_3)\}](5)$. To a stirring solution of zirconocenedichloride (94 mg, 0.32 mmol) in THF (10 mL), lithium salt (*N*-diphenylphosphino)-2,6-dimethyl aniline in THF [prepared from *n*-BuLi (0.32 mL of 1.6 M solution) and 1 (102 mg, 0.32 mmol)] was added dropwise at room temperature and stirred for 24 h. The reaction mixture evaporated to dryness and was extracted using toluene. The filtrate was evaporated *in vacuo* to produce a white residue which was crystallized in toluene/pentane. Yield: 155 mg (65%).

¹H NMR (400 MHz, C₆D₆): δ = 7.64–7.59 (m, 4H, Ph), 7.48–7.44 (m, 2H, Ph), 7.07–7.06 (m, 4H, Ph), 6.94–6.90 (m, 3H, Ar), 6.06 (d, 10H, Cp, ³*J*(H,P) 1.6 Hz), 2.05 (s, 6H, –CH₃) ppm. ³¹P-{¹H} NMR (161.9 MHz, C₆D₆): δ = 49.2 ppm. C₁₇₆H₁₈₀Cl₄N₄P₄Zr₄(2981.82), Calcd C 70.89 H 6.08 N 1.88; Found C 70.12 H 5.74 N 1.58.

X-ray crystallographic studies of 2, 3, 4 and 5

Single crystals of compounds 2-4 were grown from a solution of toluene or THF (for 4) and compound 5 was grown from toluene/pentane under an inert atmosphere at a temperature of -35 °C. In each case, a crystal of suitable dimensions was mounted on a CrvoLoop (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 a Oxford Supernova X-calibur Eos CCD detector with graphite-monochromatic CuK α (1.54184 Å) (for 2, 3, and 5) and MoK α (0.71069 Å) (for 4) radiation. Crystal data and structure refinement parameters are summarized in the Table 1. The structures were solved by direct methods $(SIR92)^{33}$ and refined on F^2 by fullmatrix least-squares methods; using SHELXL-97.34 Nonhydrogen atoms were anisotropically refined. H-atoms were included in the refinement on calculated positions riding on their carrier atoms. The function minimized was $\left[\sum w(F_{o}^{2}-F_{c}^{2})^{2}\right](w = 1/[\sigma^{2}(F_{o}^{2}) + (aP)^{2} + bP]), \text{ where } P =$ $(Max(F_o^2, 0) + 2F_c^2)/3$ with $\sigma^2(F_o^2)$ from counting statistics. The function R_1 and wR_2 were $(\sum ||F_o| - |F_c||)/\sum |F_o|$ and $[\sum w(F_o^2 - F_c^2)^2/\sum (wF_o^4)]^{1/2}$, respectively. The solvent toluene molecules were disordered about special positions. In order to model these it was necessary to apply rigid hexagon constraints to the rings and additional restraints were used to ensure appropriate bond lengths and angles for the methyl groups. The thermal parameters did not refine to appropriate values and so thermal similarity and vibration restraints were also applied. The ORTEP-3 program was used to draw the molecule. Crystallographic data (excluding structure factors) for the structures reported in this paper [CCDC 878241 (2), 878242 (4), 893245 (3), and 893244 (5)] is available.⁺

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