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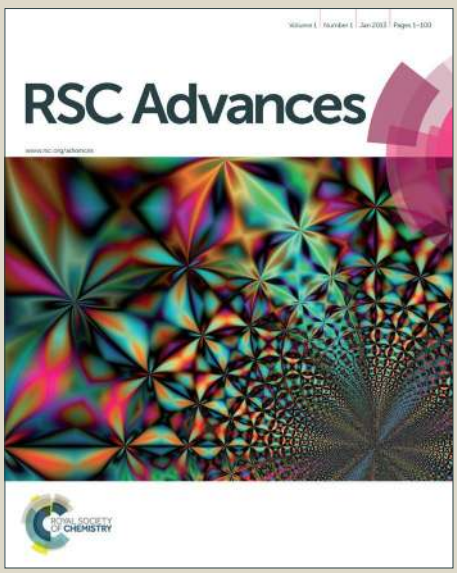

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ARTICLE TYPE

Calcium Complexes with Imino-phosphinanilido Chalcogenide Ligands for Heterofunctionalisation Catalysis

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The syntheses, characterisation and utilisation of the calcium complexes [{L^x}CaN(SiMe$_3$)$_2$·(THF)] supported by monoanionic, tridentate imino-phosphinanilido chalcogenide ligands {Ph$_2$P(E)-N-C$_6$H$_4$-CH=N(Dipp)}$^-$ (E = S, {L^2}$^-$; E = Se, {L^3}$^-$; Dipp = 2,6-diisopropylphenyl) as molecular precatalysts for the heterofunctionalisation of styrene are reported. The protio-ligand {L^1}H (for E = O) was obtained upon reaction of the aniline-iminophosphane {Ph$_2$PHN-C$_6$H$_4$-CH=N(Dipp)} ({L^0}H) and hydrogen peroxide at room temperature. The related sulphide and selenide compounds {L^2}H and {L^3}H were prepared by treatment of {L^0}H with elemental sulphur and selenium. Beside, reaction of {L^0}H with Me$_2$S.BH$_3$ yielded the corresponding imino-phosphinanilido borane protio-ligand {Ph$_2$P(BH$_3$)N-C$_6$H$_4$-CH=N(Dipp)}H ({L^4}H). The heteroleptic calcium complexes [{L^x}CaN(SiMe$_3$)$_2$·(THF)] (E = S, **2**; E = Se, **3**) were synthesised by one-pot reaction of {L^2}H and {L^3}H with 2 equiv of [KN(SiMe$_3$)$_2$] and CaI$_2$ at room temperature. The reaction of {L^2}H with [KN(SiMe$_3$)$_2$] and CaI$_2$ in 2:2:1 proportions yielded the homoleptic complex [Ca{L^2}$_2$] (**5**). The molecular structures of the protio-ligand {L^3}H and complexes **3** and **5** were established by single crystal X-ray analysis. The heteroleptic complexes **2** and **3** constitute moderately efficient precatalysts for the intermolecular hydrophosphination and hydroamination of styrene with diphenylphosphine or pyrrolidine, respectively, to mediate the formation of C–P and C–N σ-bonds.

Introduction

Catalysed heterofunctionalisations of unsaturated substrates (alkenes, carbonyls) continue to receive significant attention, primarily because of their 100% atom efficiency.[1] Alkene hydroamination (C–N σ-bond formation) and hydrophosphination (C–P σ-bond formation) have attracted a great deal of attention in recent years, not least because the resulting amines and phosphines constitute valuable products for a plethora of applications. Substantial advances were achieved for intramolecular hydroamination in the 90's with alkali or transition metal complexes.[2-3] Most prominently for oxophilic metals, Mark's lanthanide(III) catalysts are remarkable for their efficiency in the cyclisation of aminoalkenes, aminoalkynes[4] and in the cyclohydrophosphination of phosphinoalkenes.[5] More recently, the cyclohydroamination of aminoalkenes was catalysed by d^0 complexes of the alkalino-earth metals (Ae) as shown by Hill,[6] Roesky,[7] Sarazin/Carpentier[8] and Ward.[9] These groups have developed various original heteroleptic Ae complexes of the type [{L}Ae(X)(solvent)$_n$], where Ae is Ca, Sr or Ba, {L}$^-$ is a monoanionic ancillary ligand such as a β-diketiminate, bis-phosphinomethanide, bis(imino)pyrrolide, aminotroponiminate, tris(pyrazolyl)borate, iminoanilide or aminoetherphenolate, and X$^-$ is a reactive group such as an amide (e.g. N(SiMe$_3$)$^-$ or N(SiMe$_2$H)$^-$) or, sometimes, an alkyl (CH(SiMe$_3$)$_2^-$). The bulky ancillary ligand is essential to control the kinetic lability of these complexes and tame their propensity to engage in deleterious ligand redistribution (Schlenk-like) equilibria.[6-10]

The catalytic activity of these precatalysts built around large, electropositive Ae ions compares well with that of isoelectronic trivalent lanthanide systems. The calcium complex [{BDI}CaN(SiMe$_3$)$_2$·(THF)] ({BDI} = HC{C(Me)N–2,6–(^{i}Pr)$_2$C$_6$H$_3$}$_2$) proved a very versatile and effective precatalyst not only for intramolecular hydroaminations, but also for the more challenging intermolecular hydrophosphination of alkynes and activated alkenes.[6,11] Several other heteroleptic calcium, strontium and barium complexes supported by a related iminoanilido or aminoetherphenolato ligands have also been reported for the intermolecular hydroamination and hydrophosphination of activated alkenes.[8]

In the course of our ongoing research into the chemistry of heavy alkaline earths, we have recently introduced a series of amidophosphine-chalcogenides/boranes [R$_2$NHPh$_2$P(E)]$_n$ (R = bulky alkyl; E = O, S, Se, BH$_3$; n = 1 or 2) and sterically demanding nitrogen ancillary ligands [2-(Ph$_3$CN=CH)C$_4$H$_3$NH] into alkali and alkalino-earth metal coordination chemistry.[12] In all cases, the ligand with multiple donor atoms stabilised the oxophilic ions, and the molecular structures of the resulting complexes were authenticated. The Ae compounds showed excellent catalytic activity towards the ring-opening polymerisation of ε-caprolactone. However, the major disadvantage of these ligands was their relatively limited ability to prevent ligand redistribution in solution. Thus, we were led to conclude that greater steric bulkiness might be necessary to

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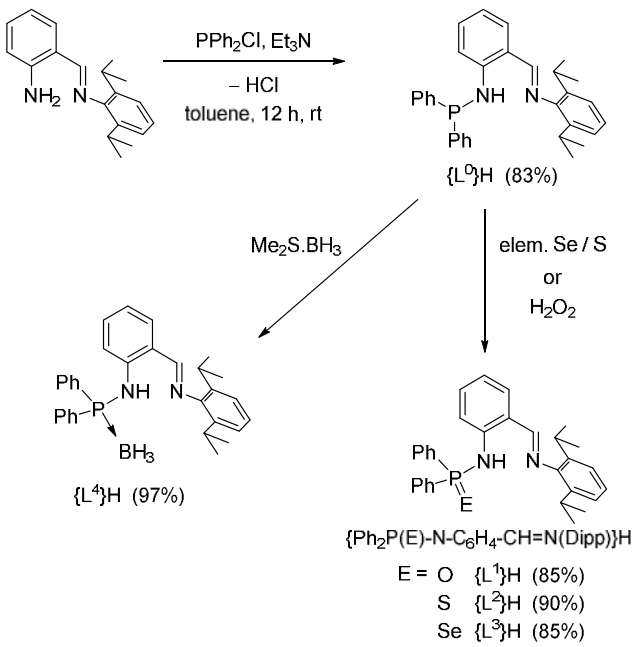
prevent these deleterious equilibria from taking place. To circumvent this problem, sterically more demanding multidentate monoanionic ligands were devised for the kinetic stabilisation of heteroleptic Ae complexes. We report here the syntheses of imino-phosphinanilido chalcogenides {$Ph_2P(E)$-N-C_6H_4-CH=N(Dipp)}H (E = O, {L^1}H; S, {L^2}H; Se, {L^3}H; Dipp = 2,6-diisopropylphenyl) and imino-phosphinanilidoborane {$Ph_2P(BH_3)$N-C_6H_4-CH=N(Dipp)}H ({L^4}H)) along with the syntheses and structural aspects of the calcium complexes [{L^x}$CaN(SiMe_3)_2$·(THF)] (E = S, x = 2, **2**; E = Se, x = 3, **3**) and [Ca{L^2}$_2$] (**5**). The ability of **2** and **3** to catalyse the intermolecular hydrophosphination and hydroamination of styrene is also presented.

Results and discussion

Synthesis and characterisation: The phosphinanilido-imine precursor {Ph_2PHN-C_6H_4-CH=N(Dipp)} ({L^0}H) was readily obtained in good yield and high purity by equimolar aminolysis of chlorodiphenylphosphine with {$H_2NC_6H_4CH$=N(Dipp)} in toluene at room temperature, using a slight excess of triethylamine to trap the released HCl (Scheme 1).



Scheme 1. Synthesis of imino-phosphinanilido chalcogenides and borane protio-ligands {L^x}H, x = 1–4.

The precursor {L^0}H was characterised by conventional techniques. In the ^{1}H NMR spectrum, the signal for the amine N*H* hydrogen atom appears at δ_{1H} = 10.28 ppm as a doublet due to coupling with the phosphorus atom ($^2J_{HP}$ of 9.1 Hz). The resonance for the imine proton appears as a singlet at δ_{1H} = 8.27 ppm. In the ^{31}P NMR spectrum, the compound exhibits a sharp singlet at δ_{31P} = 23.3 ppm.

The oxide ligand {L^1}H was prepared in 85% yield by treatment of {L^0}H with hydrogen peroxide, whereas the action of elemental sulphur and selenium onto {L^0}H afforded the corresponding sulphide {L^2}H and selenide {L^3}H congeners in yields above 85% (Scheme 1). The borane adduct {L^4}H was isolated in quantitative yield as yellow precipitate by the reaction of {L^0}H and $Me_2S.BH_3$ in toluene (Scheme 1). These protio-ligands were characterised by multinuclear NMR and combustion analysis. In the ^{1}H NMR spectra, the amine N*H* hydrogen atom can be seen at δ_{1H} = 11.41-11.44 ppm as a doublet with $^2J_{HP}$ coupling constants of 13.7 for {L^1}H, 10.2 for {L^2}H, and 9.0 Hz for {L^3}H. In {L^4}H, its resonance is seen at δ_{1H} = 11.19 ppm, with $^2J_{HP}$ = 4.0 Hz. In all cases, there is hence a significant downfield shift as compared with {L^0}H. In their ^{31}P{^{1}H} NMR spectra, {L^2}H and {L^3}H exhibit similar resonances at δ_{31P} = 49.8 and 45.0 ppm, respectively. This is shifted downfield compared to the data for {L^1}H (δ_{31P} = 19.0 ppm), presumably due to the adjacent hard oxygen atom. However, the borane derivative {L^4}H displays an even more downfield broad resonance signal at δ_{31P} = 65.8 ppm. Additionally, in the ^{11}B{^{1}H} NMR spectrum, a broad resonance signal at δ_{11B} = –36.0 ppm was detected for the P–*B*H_3 moiety. These observations indicate that the BH_3 group formed the phosphine-borane adduct rather than the amine-borane one. The selenium-containing {L^3}H was characterised by ^{77}Se{^{1}H} NMR spectroscopy; it features a doublet at δ_{77Se} = –251 ppm, with $^1J_{SeP}$ coupling constant of 776 Hz (Figure 1) which matches that measured in this compound's ^{31}P{^{1}H} NMR spectrum (Fig. 1).

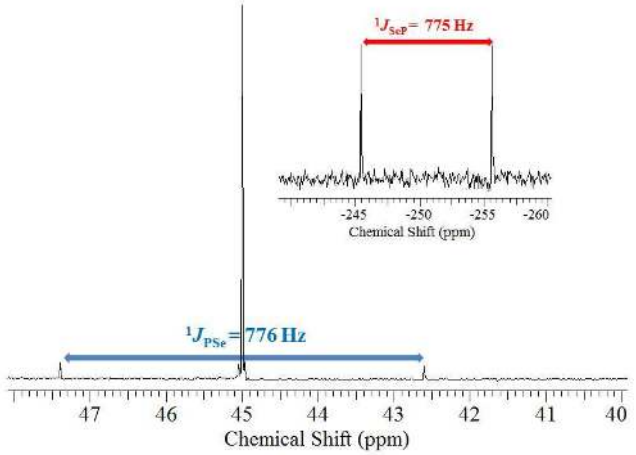


Figure 1. ^{77}Se{^{1}H} NMR ($CDCl_3$, 76.31 MHz, 25 ºC) (top right) and ^{31}P{^{1}H} NMR ($CDCl_3$, 161.9 MHz, 25 ºC) spectra for {Ph_2P(Se)-N-C_6H_4-CH=N(Dipp)}H ({L^3}H).

The solid state structure of {L^3}H was established by single crystal X-ray diffraction. Its molecular structure is depicted in Fig. 2. The P–Se bond distance of 2.0930(7) Å is very similar to that previously reported for [Ph_2P(Se)-NH(2,6-$Me_2C_6H_3$)][13] (2.1019(8) Å) and is hence diagnostic of P=Se double bonds. The P–N bond distance of 1.662(2) Å is consistent with those measured in other phosphinamines.[12,13]

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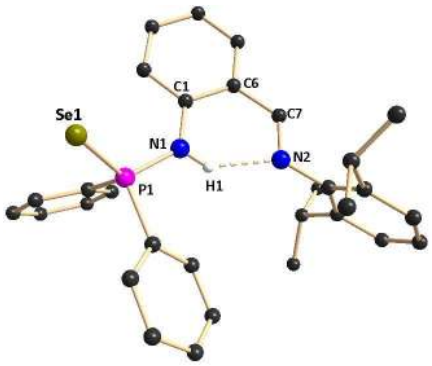
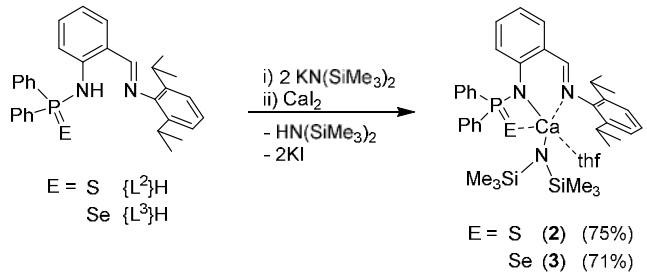


Figure 2. Molecular solid-state structure of {$Ph_2P(Se)$-N-C_6H_4-CH=N(Dipp)}H ({L^3}H). Hydrogen atoms except that on N1 are omitted for clarity. Selected bond lengths (Å) and angles (°): Se1–P1 2.0933(7), P1–N1 1.662(2), N2–C7 1.264(3), N1–C1 1.384(3), N1–P1–Se1 117.11(9), C1–N1–P1 129.59(2), N1–C1–C6 119.1(2), C7–N2–C8 119.8(2).

Using a known strategy,[8] the one-pot reaction of {L^2}H with [$KN(SiMe_3)_2$] in THF followed by the addition of CaI_2 (in 1:2:1 molar ratio) cleanly yielded the desired heteroleptic complex [{L^2}$CaN(SiMe_3)_2$·(THF)] (**2**) in 75% yield. The analogous reaction with the selenide {L^3}H afforded analytically pure [{L^3}$CaN(SiMe_3)_2$·(THF)] (**3**) in 71% yield (Scheme 2). However, all attempts to prepare the congeneric complex [{L^1}$CaN(SiMe_3)_2$·(THF)] (**1**) using the oxygen-containing {L^1}H proved unsuccessful and gave intractable mixtures of unidentified species, presumably because of issues stemming from the combined presence of the phosphine oxide with oxophilic element such as calcium. Note also that, similarly, the use of the borane ligand {L^4}H afforded a complex with the putative formulation [{L^4}$CaN(SiMe_3)_2$·(THF)] (**4**), but NMR data were inconclusive and the composition could not be confirmed by elemental analysis either. Nonetheless, analysis of a small crop of single crystals by XRD techniques confirmed the proposed formulation, and showed coordination of two of the three hydrogen atoms in the borane moiety onto the calcium center; a representation of the molecular structure and the XRD data for **4** is available in the electronic supporting information.



Scheme 2. Synthesis of the heteroleptic calcium complexes [{L^2}$CaN(SiMe_3)_2$·(THF)] (**2**) and [{L^3}$CaN(SiMe_3)_2$·(THF)] (**3**).

Complexes **2** and **3** were characterised by multinuclear NMR spectroscopy and elemental analysis, and the solid-state structure of **3** was confirmed by X-ray diffraction analysis. In the ^{1}H NMR spectra recorded in C_6D_6, the resonance for the imine proton appears at δ_{1H} = 7.91 and 7.92 ppm for complexes **2** and **3** respectively, i.e. slightly shifted towards high fields with respect to the protio-ligands (δ_{1H} = 8.26 and 8.27 ppm); the presence of one molecule of coordinated THF per metal is unambiguous. In the $^{31}P\{^1H\}$ NMR spectra, sharp resonances were detected at δ_{31P} = 40.6 (for **2**) and 31.1 ppm (for **3**, Fig. 3), i.e. at higher field than in the respective protio-ligands. In the $^{77}Se\{^1H\}$ NMR spectra of **3** (Fig. 3), a doublet was observed at δ_{77Se} = –61 ppm, with a coupling constant $^1J_{SeP}$ of 589 Hz. The substantial low-field shift and the lower coupling constant compared to the pertaining data for {L^3}H are indicative of coordination of the selenium atom onto the calcium ion in **3**.

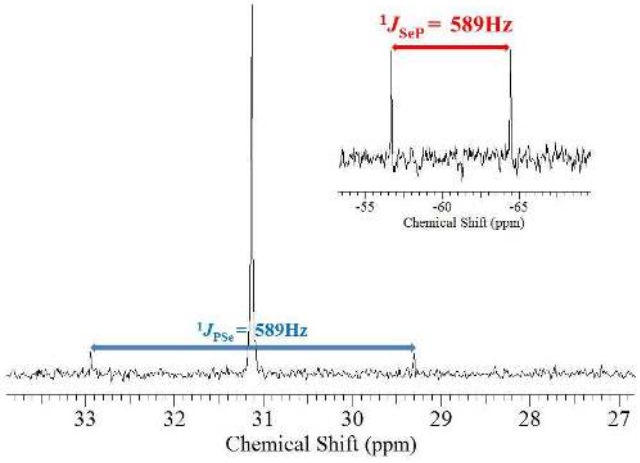


Figure 3. $^{77}Se\{^1H\}$ NMR (C_6D_6, 76.31 MHz, 25 ºC (top right) and $^{31}P\{^1H\}$ NMR (C_6D_6, 161.9 MHz, 25 ºC) spectra for [{L^3}$CaN(SiMe_3)_2$·(THF)] (**3**).

X-ray quality crystals of complex **3** were grown at –30 ºC from a concentrated pentane solution, and its structure was determined (Fig. 4). The κ^3-coordination mode of the ligand is plain in the structure of **3**, and the corresponding metric parameters are diagnostic. The additional presence of coordinated THF takes the formal coordination number around Ca to five.

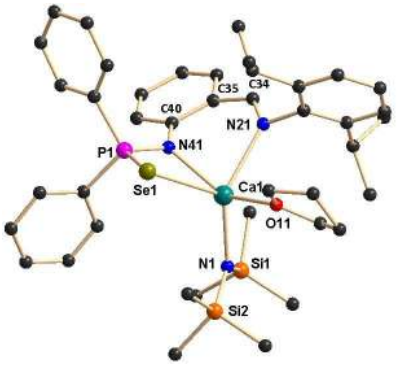


Figure 4. Solid-state structure of [{L^3}$CaN(SiMe_3)_2$·(THF)] (**3**). All hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (°): Ca1–N1 2.395(5), Ca1–N41 2.369(4), Ca1–N21 2.502(5), Ca1–Se1 3.016(2), Ca1–O11 2.387(4), Ca1–P1 3.240(2), Se1–P1 2.152(1), N41–P1 1.616(4), N21–C34

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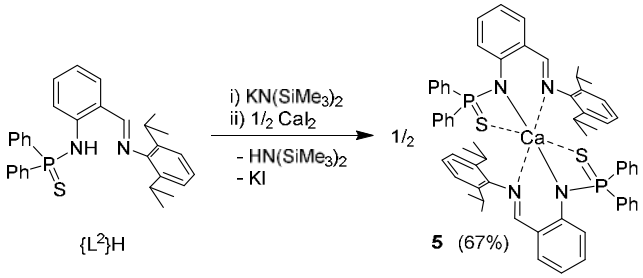
1.276(7), N1–Ca1–O11 100.26(2), N1–Ca1–N41 112.92(2), O11–Ca1–N41 146.61(1), N1–Ca1–N21 129.02(2), O11–Ca1–N21 89.09(1), N41–Ca1–N21 73.23(1), N41–Ca1–Se1 120.66(1), O11–Ca1–Se1 93.43(1), N41–Ca1–Se1 67.01(1), N21–Ca1–Se1 108.44(1), N1–Ca1–P1 113.94(1), O11–Ca1–P1 131.62(1), N41–Ca1–P1 28.64(1), N21–Ca1–P1 94.33(1), Se1–Ca1–P1 40.04(3).

The arrangement around the calcium ion is intermediate between a square base pyramidal and trigonal bipyramidal. However, with a geometric parameter of τ_5 = 0.63,[14] the geometry around the metal ion can be best described as a highly distorted trigonal bipyramidal with N1, N21 and Se1 sitting in equatorial positions and O1 and N41 in axial ones. The dihedral angle of 53.2 ° between the two planes defined by N21, Ca1, N41, C34 and Ca1, Se1, P1, N1 indicates that the two metallacycles are not coplanar. The distance from Ca1 to the imine N2 atom (2.502(5) Å) is greater than that to the amido N1 (2.329(5) Å) and N3 (2.396(4) Å) atoms; the discrepancy between the Ca1–N1 and Ca1–N3 bond lengths reflects the formation of the Ca1–N1–P1–Se1 metallacycle, and the bulkiness of the hexamethyldisilazide group. The Ca1–Se1 distance of 3.0164(16) Å compares with those in $[Ca\{Ph_2P(Se)N(CHPh_2)\}_2\cdot(THF)_2]$ (2.989(8) Å)[12a] and $[Ca\{(PyCH)(Se)PPh_2\}_2(THF)_2]$ (2.945(1) Å),[15] but it is much shorter than in $[Ca\{Ph_2P(Se)\text{-}NCH_2CH_2NPPh_2(Se)\}\cdot(THF)_3]$ (3.252(2) Å) where the calcium centre is 7-coordinate.[12d]
The homoleptic complex $[Ca\{L^2\}_2]$ (**5**) was prepared in 67% yield by the one-pot treatment of $\{L^2\}H$, $[KN(SiMe_3)_2]$ and CaI_2 in 2:2:1 molar ratio in THF (Scheme 3). The analytical data (NMR, combustion analysis) testify to its purity and show that no THF is found in the complex.



Scheme 3. Synthesis of the homoleptic complex $[Ca\{L^2\}_2]$ (**5**).

Its molecular structure was determined by single crystal X-ray diffraction, and showed a six-coordinate calcium centre sitting in a distorted octahedral environment (N2-Ca1-N2^i 173.00 °) where both ligands feature κ^3-coordination (Fig. 5). The details of structural parameters are available in Table TS1 in the supporting information. In the complex **5**, the metal coordination polyhedron is formed by κ^3-coordination of the two monoanionic $\{Ph_2P(S)NH\text{-}C_6H_4CH{=}N(Dipp)\}^-$ moieties. The Ca1–S distances of 2.8372(5) Å are expectedly shorter than the Ca–Se distance (3.0164(16) Å) observed in **3**, but it resembles that in [Ca(S-2,4,6-tBu$_3$-C$_6$H$_2$)$_2$(THF)$_4$] (2.8177(8) Å).[16] The solid-state structure of complex **5** is consistent with its NMR spectra in solution, as only one set of resonances was detected in the spectra recorded in C_6D_6. A singlet resonance at δ_{1H} = 7.88 ppm was observed for the two imine (N=CH) protons. The 2,6-diisopropyl groups in the ligand gave rise to a septet at δ_{1H} = 2.89 ppm for C*H*(CH$_3$)$_2$ hydrogen atoms and a broad doublet centred on 1.07 ppm for the methyl moieties. In the ^{31}P NMR spectrum, a singlet at δ_{31P} = 62.6 ppm was observed, i.e. at much lower field than in **2** or in the protio-ligand.

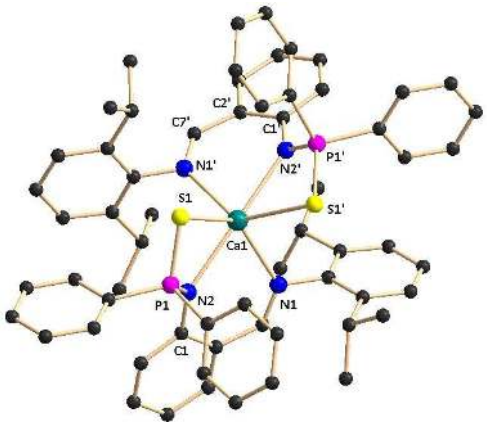
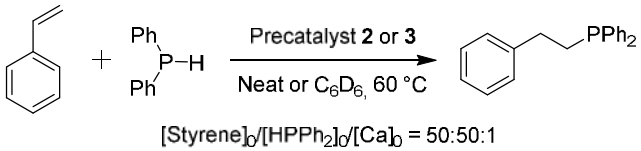


Figure 5. Representation of the molecular solid-state structure of $[Ca\{L^2\}_2]$ (**5**). All hydrogen atoms are omitted for clarity. Selected bond lengths (Å): Ca1–N1 2.451(1), Ca1–N1^i 2.451(1), Ca1–N2^i 2.465(1), Ca1–N2 2.465(1), Ca1–S1 2.837(5), Ca1–S1^i 2.837(5), Ca1–P1^i 3.189(4), Ca1–P1 3.189(4), S1–P1 1.981(6), P1–N2 1.629(1).

Hydroelementation reactions: Preliminary investigations on the performance of the heteroleptic complexes **2** and **3** as precatalysts for the benchmark intermolecular hydrophosphination and hydroamination of styrene were carried out. In a first set of experiments, the addition of Ph_2PH to styrene was examined with a precatalyst loading of 2.0 mol-%, with $[styrene]_0/[HPPh_2]_0/[Ca]_0$ = 50:50:1. Characteristically for calcium,[17] it was found that the reaction was fully regioselective, and afforded exclusively the anti-Markovnikov product (Scheme 4).



Scheme 4. Intermolecular hydrophosphination of styrene with diphenylphosphine catalysed by **2** and **3**.

The reaction proceeds smoothly using complex **3** as precatalyst in neat condition, achieving near-complete conversion of 50 equiv of neat substrates in 12 h (Table 1, entries 1-5). It also converted 53% of 400 equiv of substrates in the same amount of time (entry 9), with a corresponding TOF of 18 mol_{subst} mol_{Ca}^{-1} h^{-1}. Precatalyst **2** was equally competent, compare entries 5 and 6.

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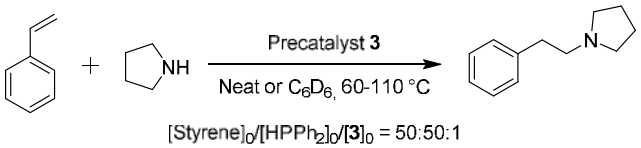
Table 1. Catalytic hydrophosphination of styrene with phosphine catalysed by **2** and **3**.[a]

Entry	Precat.	Time (h)	Conversion (%)	Solvent
1	3	1	16	- (neat)
2	3	2	23	- (neat)
3	3	4	32	- (neat)
4	3	6	47	- (neat)
5	3	12	93	- (neat)
6	2	12	94	- (neat)
7[b]	2	2	8	C_6D_6
8[b]	2	24	22	C_6D_6
9 [c]	3	12	53	- (neat)

[a] All reactions performed at 60 °C, using 2.0 mol-% of precatalyst unless otherwise stated. [b] Reactions in 0.3 mL of C_6D_6 at 0.51 mM in substrates. [c] Precatalyst loading = 0.25 mol-%.

By contrast, the reactions were slower when performed in C_6D_6 (entries 7-8). The poor conversion after 24 h perhaps reflects catalyst decomposition under prolonger reaction time under these experimental conditions. Only two calcium complexes, [{DippN-C_6H_4-CH=N(Dipp)}CaN(SiMe$_3$)$_2$(THF)] and [{BDI}CaN-(SiMe$_3$)$_2$(THF)], displayed overall better catalytic activity in this reaction than complexes **2** and **3**.[6,8] Complex **3** was next employed to catalyse the equimolar hydroamination of styrene with pyrrolidine, using again a standard metal feed ratio of $[styrene]_0/[pyrrolidine]_0/[Ca]_0$ = 50:50:1. The reactions were carried out in the temperature range 60-100 °C, either in neat substrates or in aromatic solvents (Table 2). The catalysed reactions were regiospecific, affording solely the anti-Markovnikov addition product. At 60 °C, the conversion reached 38% after 2 h at 60 °C (entry 1), and only modest progress was observed beyond this time (entries 2-4) ; even after 24 h, only half of the substrates were converted (entry 5), suggesting catalyst deactivation. Only at 110 °C could significantly higher conversions be observed (entries 6-7); in that case also, the conversion reached a maximum of ca. 77-79%, no matter the reaction was performed for 6 or 12 h. This suggests that, at higher temperature, the hydroelementation reaction is favoured over the putative decomposition process, but that the latter process could not be prevented eventually. The reactions were also sluggish in dilute C_6D_6 or toluene-d_8 solutions (entries 8 and 10). Hence the catalytic activity displayed by **3** in intermolecular hydroamination is rather tame, and compares unfavourably with that of other calcium precatalysts.[6-10] Complex **2** showed very much the same performance as **3**.



Scheme 5. Intermolecular hydroamination of styrene with pyrrolidine catalysed by the calcium complex **3**.

Table 2. Hydroamination of styrene with pyrrolidine catalysed by calcium complex **3**.[a]

Entry	Temp (°C)	Time (h)	Conversion (%)	Solvent
1	60	2	38	- (neat)
2	60	3	39	- (neat)
3	60	4	43	- (neat)
4	60	12	49	- (neat)
5	60	24	50	- (neat)
6	110	6	77	- (neat)
7	110	12	79	- (neat)
8[b]	80	12	40	C_6D_6
9	80	12	66	- (neat)
10	110	6	42	Tol-d_8

[a] All reactions performed using 2.0 mol-% of precatalyst **3** unless otherwise stated. [b] Reactions in 0.3 mL of C_6D_6 at 0.51 mM in substrates.

Conclusion

Tridentate monoanionic imino-phosphinanilido chalcogenide ligands have been introduced for the first time in calcium chemistry, and have enabled the preparation of heteroleptic calcium-amide complexes. The molecular solid-state structures of the two calcium complexes **3** and **5** confirm that the ligand adopts a κ^3-coordination mode, with effective coordination of the chalcogen onto the calcium ion. The heteroleptic complexes **2** and **3** showed good performance in the anti-Markovnikov intermolecular hydrophosphination of styrene, but low activity in the intermolecular hydroamination of that same substrate. It was in particular found that the nature of the chalcogen element in the ancillary ligand had little role in the ability of the resulting complex to mediate with two benchmark reactions, highlighting the limited ability of these soft atoms to influence the coordination sphere of the hard, oxophilic calcium ion.

Experimental

General: All manipulations were performed under an inert atmosphere using standard Schlenk techniques or in a dry, solvent-free glove box (Jacomex; O_2 <1 ppm, H_2O <5 ppm) for catalyst loading. CaI_2 (Aldrich, 99.999% anhydrous beads) and $HPPh_2$ were used as received. Styrene was dried and distilled over CaH_2 and stored over 3 Å molecular sieves. Compounds [$O_2NC_6H_4CH$=N(Dipp)],[18] and [$H_2NC_6H_4CH$=N(Dipp)][19] were prepared by following literature protocols. Solvents (THF, Et_2O, pentane, and toluene) were purified and dried (water contents all below 10 ppm) over alumina columns (MBraun SPS). THF was further distilled under argon from sodium mirror/benzophenone ketyl prior to use. All deuterated solvents (Eurisotop, Saclay, France) were stored in sealed ampules over activated 3 Å molecular sieves and were thoroughly degassed by several freeze−thaw−vacuum cycles. NMR spectra were recorded on Bruker AM-400 and AM-500 spectrometers. All ^{1}H, ^{31}P{^{1}H}, and ^{13}C{^{1}H} chemical shifts were determined using residual signals of the deuterated solvents and were calibrated vs $SiMe_4$ and ^{77}Se{^{1}H} NMR spectra were externally calibrated vs. Ph_2Se_2 (δ ^{77}Se = +461 ppm). Assignment of the signals was carried out using 1D (^{1}H, ^{13}C {^{1}H}) and 2D (COSY, HMBC, HMQC) NMR experiments. Coupling constants are given in Hertz. Elemental analyses were performed on a Bruker Euro EA

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and high-resolution mass spectra (HR-MS) were recorded on an Agilent 6538 UHD Q-TOF using multimode source at the Indian Institute of Technology Hyderabad (IITH), or on a Bruker MaXis 4G using electrospray or ASAP sources at the University,of Rennes 1.

$Ph_2PHNC_6H_4CH=N(Dipp)]$ ($\{L^0\}H$). Triethylamine (1.5 mL, 12.8 mmol) and chlorodiphenylphosphine (1.9 mL, 10.7 mmol) were added to a solution of $[H_2NC_6H_4CH=N(Dipp)]$ (3.0 g, 10.7 mmol) in toluene (50 mL). Immediate formation of a white turbidity was observed. The reaction mixture was stirred overnight at room temperature. The insoluble fraction (white solid, ammonium salt) was eliminated by cannula filtration. Toluene was then removed in vacuo, giving a brown sticky solid which was washed with pentane (2 × 20 mL) to yield the title compound as an analytically pure pale yellow solid. Yield 4.1 g, 83%.
^1H NMR ($CDCl_3$, 500.13 MHz, 25 ºC): δ = 10.28 (d, $^3J_{HP}$ = 9.1 Hz, 1H; N*H*), 8.27 (s, 1H; C*H*=N), 7.75 (dd, $^3J_{HH}$ = 8.3 Hz, $^4J_{HH}$ = 5.0 Hz, 1H; NC_6H_3), 7.49 (complex m, 4H; PC_6H_5), 7.36 (m, 2H; PC_6H_5), 7.29 (overlapping m, 6H; PC_6H_5 and C_6H_4), 7.13 (complex m, 3H; NC_6H_3 and C_6H_4), 6.84 (t, $^3J_{HH}$ = 7.4 Hz, 1H; C_6H_4), 2.94 (sept, $^3J_{HH}$ = 8 Hz, 2H; C*H*(CH_3)$_2$), 1.08 (d, $^3J_{HH}$ = 6.9 Hz, 12H; CH(C*H*$_3$)$_2$) ppm; $^{13}C\{^1H\}$ NMR (C_6D_6, 125.76 MHz, 25 ºC): δ = 166.2 (*C*H=N), 150.0 (*i*-NC_6H_3), 148.4 (*i*-NC_6H_4), 139.9 (*i*-PC_6H_5), 138.1 (*o*-NC_6H_3), 134.6 (C_6H_4), 132.1 (*p*-NC_6H_3), 132.1 (*p*-NC_6H_3), 131.2 (*o*-PC_6H_5), 131.1 (*o*-PC_6H_5), 128.8 (*m*-PC_6H_5), 128.3 (*m*-PC_6H_5), 124.8 (*m*-NC_6H_3), 119.0 (C_6H_4), 117.3 (C_6H_4), 115.1 (C_6H_4), 114.9 (C_6H_4) 27.9 (*C*H(CH_3)$_2$), 23.4 (CH(*C*H$_3$)$_2$) ppm; $^{31}P\{^1H\}$ NMR ($CDCl_3$,161.9 MHz, 25 ºC): δ = 23.3 ppm. Elem. anal. Calcd for $C_{31}H_{33}N_2P$ (464.6 g mol^{-1}): C, 80.14; H, 7.16; N, 6.03. Found: C, 79.88; H, 7.01; N, 5.81. ESI-HRMS: $[M + H^+]$ ($C_{31}H_{34}N_2P$) calcd *m/z* 465.2459, found 465.2458.

$[Ph_2P(O)HNC_6H_4CH=N(Dipp)]$ ($\{L^1\}H$). A 30% solution of H_2O_2 (0.15 ml, 5 mmol) in water was added to a toluene solution (30 ml) of $\{L^0\}H$ (2.0 g, 4.3 mmol). The reaction mixture was stirred for 6 h at room temperature. After removal of solvent, a half white solid residue was obtained which was washed with pentane (2 × 10 mL) to yield the title compound as an off-white solid. Yield 1.70 g, 85%.
^1H NMR ($CDCl_3$, 500.13 MHz, 25 ºC): δ = 11.41 (d, $^2J_{HP}$ = 13.7 Hz, 1H; N*H*), 8.30 (s, 1H; C*H*=N), 7.88 (dd, $^3J_{HH}$ = 12.5 Hz, $^4J_{HH}$ = 7.5 Hz, 4H; PC_6H_5), 7.49 (t, $^3J_{HH}$ = 7.6 Hz, 3H; NC_6H_3 and PC_6H_5), 7.41 (m, 5H; PC_6H_5 and C_6H_4), 7.27 (d, $^3J_{HH}$ = 10.1 Hz, 1H; C_6H_4), 7.14 (s, 3H; NC_6H_3 and C_6H_4), 6.99 (t, $^3J_{HH}$ = 7.5 Hz, 1H; C_6H_4), 2.93 (sept, $^3J_{HH}$ = 8 Hz, 2H; C*H*(CH_3)$_2$), 1.09 (d, $^3J_{HH}$ = 6.8 Hz, 12H; CH(C*H*$_3$)$_2$) ppm. $^{13}C\{^1H\}$ NMR (C_6D_6, 125.76 MHz, 25 ºC): δ = 166.3 (*C*H=N), 147.7 (*i*-NC_6H_4), 143.6 (*i*-NC_6H_3) 138.1 (*i*- PC_6H_5) 134.4 (*o*-NC_6H_3), 132.8 (C_6H_4), 132.3 (*o*-PC_6H_5), 132.1 (*o*-PC_6H_5), 131.8 (*p*-PC_6H_5), 131.6 (*p*- PC_6H_5), 131.5 (*p*-NC_6H_3), 128.8 (*m*-PC_6H_5), 128.6 (*m*-PC_6H_5), 124.8 (*m*-NC_6H_3), 120.2 (C_6H_4), 119.9 (C_6H_4), 119.9 (C_6H_4), 118.5 (C_6H_4), 28.1 (*C*H(CH_3)$_2$), 23.3 (CH(*C*H$_3$)$_2$) ppm. $^{31}P\{^1H\}$ NMR ($CDCl_3$, 161.9 MHz, 25 ºC): δ = 19.0 ppm. Elem. anal. calcd for $C_{31}H_{33}N_2PO$ (480.5 g mol^{-1}): C, 77.48; H, 6.92; N, 5.83. Found: C, 77.19; H, 6.73, N, 5.63. ESI-HRMS: $[M + Na^+]$ ($C_{31}H_{34}N_2PO$) calcd *m/z* 503.2228, found 503.2226.

$[Ph_2P(S)HNC_6H_4CH=N(Dipp)]$ ($\{L^2\}H$). $\{L^0\}H$ (2.0 g, 4.3 mmol) and elemental sulphur (138 mg, 4.3 mmol) were heated at 90 °C in toluene (30 mL) for 12 h. After evaporation of solvent, a pale yellow solid residue was obtained which was washed with pentane (2 × 10 mL) to yield the title compound as a pale yellow solid. Yield 1.9 g, 90 %.
^1H NMR ($CDCl_3$, 500.13 MHz, 25 ºC): δ = 11.41 (d, $^2J_{HP}$ =10.2 Hz, 1H; N*H*), 8.26 (s, 1H; C*H*=N), 7.97 (m, 4H; PC_6H_5), 7.47 (t, $^3J_{HH}$ = 8.1 Hz, 2H; NC_6H_3 and C_6H_4), 7.43 (complex m, 2H; PC_6H_5), 7.38 (overlapping m, 5H; PC_6H_5 and C_6H_4), 7.10 (s, 3H; NC_6H_3 and C_6H_4), 6.98 (t, $^3J_{HH}$ = 7.4 Hz, 1H; C_6H_4), 2.85 (sept, $^3J_{HH}$ = 8 Hz, 2H; C*H*(CH_3)$_2$), 1.04 (d, $^3J_{HH}$ = 6.8 Hz, 12H; CH(C*H*$_3$)$_2$) ppm. $^{13}C\{^1H\}$ NMR (C_6D_6, 125.76 MHz, 25 ºC): δ = 166.2 (*C*H=N), 147.5 (*i*-N=CHC_6H_4), 143.3 (*i*-NC_6H_3), 138.0 (*i*- PC_6H_5) 134.5 (*o*-PC_6H_5), 134.4 (*o*-PC_6H_5), 133.5 (*o*-NC_6H_3), 131.9 (*p*-PC_6H_5), 131.8 (*p*-PC_6H_5), 131.3 (C_6H_4), 131.2 (*p*-NC_6H_3), 128.7 (*m*-PC_6H_5), 128.6 (*m*-PC_6H_5), 124.8 (*m*-NC_6H_3), 120.5 (C_6H_4), 120.1 (NC_6H_4), 118.6 (C_6H_4), 28.1 (*C*H(CH_3)$_2$), 23.3 (CH(*C*H$_3$)$_2$) ppm. $^{31}P\{^1H\}$ NMR ($CDCl_3$, 161.9 MHz, 25 ºC): δ = 49.8 ppm. Elem. anal. Calcd for $C_{31}H_{33}N_2PS$ (496.6 g mol^{-1}): C, 74.97; H, 6.70; N, 5.64; S, 6.46. Found: C, 74.69; H, 6.43; N, 5.49; S, 6.35. ESI-HRMS: $[M + Na^+]$ ($C_{31}H_{34}N_2PS$) calcd *m/z* 519.1999, found 519.1998.

$[Ph_2P(Se)HNC_6H_4CH=N(Dipp)]$ ($\{L^3\}H$). $\{L^0\}H$ (2.0 g, 4.3 mmol) and elemental selenium (0.50 g, 6.45 mmol) were heated at 90 °C in toluene (30 mL) for 12 h. Un-reacted excess selenium was filtered off and the filtrate was collected. After evaporation of the solvent, a light yellow solid residue was obtained which was washed with pentane (2 × 10 mL) to yield the title compound as a pale yellow solid. Yield 2.0 g, 85%.
^1H NMR ($CDCl_3$, 500.13 MHz, 25 ºC): δ = 11.44 (d, $^2J_{HP}$ = 9 Hz, 1H; N*H*), 8.27 (s, 1H; C*H*=N), 7.98 (dd, $^3J_{HH}$ = 14.1 Hz, $^4J_{HH}$ = 7.1 Hz, 4H; PC_6H_5), 7.48 (overlapping m, 1H; NC_6H_3), 7.42 (overlapping m, 2H; PC_6H_5), 7.38 (complex m, 5H; PC_6H_5 and C_6H_4), 7.25 (m, mixed with solvent, 1H; C_6H_4), 7.10 (s, 3H; NC_6H_3 and C_6H_4) 7.0 (t, $^3J_{HH}$ = 7.4 Hz, 1H; C_6H_4), 2.85 (sept, $^3J_{HH}$ = 8 Hz, 2H; C*H*(CH_3)$_2$), 1.04 (d, $^3J_{HH}$ = 6.7 Hz, 12H; CH(C*H*$_3$)$_2$) ppm. $^{13}C\{^1H\}$ NMR (C_6D_6, 125.76 MHz, 25 ºC): δ = 166.2 (*C*H=N), 147.4 (*i*-N=CHC_6H_4), 143.3 (*i*-NC_6H_3), 138.0 (*i*-PC_6H_5), 134.5 (*o*-NC_6H_3), 133.9 (*o*-NC_6H_3), 133.0 (*o*-PC_6H_5), 131.9 (*p*-PC_6H_5), 131.7 (*p*-PC_6H_5), 131.6 (C_6H_4), 131.5 (*p*-NC_6H3), 128.7 (*m*-PC_6H_5), 128.5 (*m*-PC_6H_5), 124.8 (*m*-NC_6H_3), 120.7 (C_6H_4), 120.2 (NC_6H_4), 118.6 (C_6H_4), 28.0 (*C*H(CH_3)$_2$), 23.3 (CH(*C*H$_3$)$_2$) ppm. $^{31}P\{^1H\}$ NMR ($CDCl_3$, 161.9 MHz, 25 ºC): δ = 45.0 ($^1J_{PSe}$ = 775 Hz) ppm. $^{77}Se\{^1H\}$ NMR ($CDCl_3$, 76.31 MHz, 25 ºC): δ = – 251 (d, $^1J_{SeP}$ = 776 Hz) ppm. Elem. anal. Calcd for $C_{31}H_{33}N_2PSe$ (543.5 g mol^{-1}): C, 68.50; H, 6.12; N, 5.15. Found: C, 68.55; H, 6.16; N, 5.03. ESI-HRMS: $[M + Na^+]$ ($C_{31}H_{34}N_2PSe$) calcd *m/z* 567.1444, found: 567.1442.

$[Ph_2P(BH_3)NH\text{-}C_6H_4CH=N(Dipp)]$ ($\{L^4\}H$). To a toluene solution (20 mL) of ($\{L^0\}H$) (2 g, 4.3 mmol), was added a borane-dimethyl sulphide (0.4 mL, 4.3 mmol) solution dropwise with stirring at room temperature. The reaction mixture was then stirred for another 12 h. The solvent toluene was evaporated in *vacuo*. The compound ($\{L^4\}H$) was obtained after washing with pentane (2 × 10 mL) as yellow solid. Yield: 2.0 g, 97%.
^1H NMR ($CDCl_3$, 400 MHz, 298 K): δ = 11.19 (d, J_{HP} = 4.0 Hz, 1H; N*H*), 7.98 (s, 1*H*; CH=N), 7.95-7.90 (m, 4H; PC_6H_5), 7.68 (d, J_{HH} = 8, 1H; C_6H_4), 7.08 (t, $^3J_{HH}$ = 7.6 Hz, 3H; NC_6H_3 and C_6H_4), 7.05-7.01 (complex m, 3H; PC_6H_5 and C_6H_4), 6.95-6.93 (m, 4H; PC_6H_5), 6.86 (dt, $^3J_{HH}$ = 7.4 Hz, 1H; C_6H_4), 6.58 (dt, $^3J_{HH}$ = 7.4 Hz, 1H; C_6H_4), 2.98 (sept, $^3J_{HH}$ = 8 Hz, 2H; C*H*(CH_3)$_2$), 2.11 (br, 3H, B*H*$_3$), 1.06 (d, $^3J_{HH}$ = 6.7 Hz, 12H; CH(C*H*$_3$)$_2$) ppm; $^{13}C\{1H\}$ NMR (C_6D_6, 125.8 MHz, 298 K): δ = 166.2 (*C*H=N), 147.4 (*i*-N=CHC_6H_4), 143.3 (*i*-NC_6H_3) 138.0 (*i*-PC_6H_5) 134.5 (o-NC_6H_3), 133.9 (o-NC_6H_3), 133.0 (o-PC_6H_5), 131.9 (*p*-PC_6H_5), 131.7 (*p*-PC_6H_5), 131.6 (C_6H_4), 131.5 (*p*-NC_6H_3), 128.7 (*m*-PC_6H_5), 128.5 (*m*-PC_6H_5),124.8 (*m*-NC_6H_3), 120.7 (C_6H_4), 120.2 (NC_6H_4), 118.6 (C_6H_4), 28.0 (*C*H(CH_3)$_2$), 23.3 (CH(*C*H$_3$)$_2$) ppm; $^{31}P\{^1H\}$ NMR ($CDCl_3$, 161.9 MHz, 298 K): δ = 65.8 ppm; $^{11}B\{^1H\}$ NMR (128.4 MHz, $CDCl_3$, 298 K): δ −36.05 ppm.

$[\{Ph_2P(S)NC_6H_4CH=N\text{-}(Dipp)\}Ca\{N(SiMe_3)_2\}(THF)]$ (2). THF (20 mL) was added to a mixture of $\{L^2\}H$ (0.3 g, 0.60 mmol) and $KN(SiMe_3)_2$ (0.24 g, 1.2 mmol). The reaction mixture was stirred at room temperature for 1 h, and was then added to a suspension of CaI_2 (0.18 g, 0.60 mmol) in THF (20 mL). After stirring at room temperature for 12 h, the solvent was evaporated under vacuum and the residue was extracted with pentane (50 mL). After filtration to eliminate insoluble materials, volatiles were removed in vacuo to afford the title compound as a pale yellow solid. Yield (0.35 g, 75%).

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^{1}H NMR (C_6D_6, 500.13 MHz, 25 ºC): δ = 8.06 (m, 4H; PC_6H_5), 7.91 (s, 1H; C*H*=N), 7.11 (dd, $^3J_{HH}$= 7.6 Hz, $^4J_{HH}$ = 2.8 Hz, 3H; NC_6H_3, PC_6H_5), 7.05 (m, 2H; NC_6H_3), 7.0 (s, 4H; PC_6H_5), 6.95(d, $^3J_{HH}$ = 8.4 Hz, 1H, C_6H_4) 6.89 (d, $^3J_{HH}$ = 7.7 Hz, 1H; C_6H_4), 6.74 (td, $^3J_{HH}$ = 15.6 Hz, $^4J_{HH}$ = 1.6 Hz, 1H; C_6H_4), 6.47 (t, $^3J_{HH}$ = 7.4 Hz, 1H; C_6H_4), 3.41 (br s, 4H; OCH_2CH_2), 3.16 (sept, $^3J_{HH}$ = 8 Hz, 2H; C*H*(CH_3)$_2$), 1.24 (d, $^3J_{HH}$ = 6.8 Hz, 6H; CH(C*H*$_3$)$_2$), 1.08 (br s, 4H; OCH_2CH_2), 0.93 (d, $^3J_{HH}$= 6.7 Hz, 6H; CH(C*H*$_3$)$_2$) 0.38 (s, 18H, Si(C*H*$_3$)$_3$) ppm. ^{13}C{^{1}H} NMR (C_6D_6, 125.76 MHz, 25 ºC): δ = 171.5 (*C*H=N), 152.1 (*i*-N=CH*C*$_6$H$_4$), 152.0 (*i*-NC_6H_3) 149.6 (*i*- P*C*$_6$H$_5$) 139.5 (*o*-N*C*$_6$H$_3$), 136.1 (*o*-N*C*$_6$H$_3$), 132.8 (*o*-P*C*$_6$H$_5$), 131.5 (*p*-P*C*$_6$H$_5$), 130.5 (C_6H_4), 128.1 (*p*- P*C*$_6$H$_5$), 128.0 (*p*-N*C*$_6$H3), 126.3 (*m*-N*C*$_6$H$_3$), 126.2 (*m*-P*C*$_6$H$_5$), 125.7 (*m*-P*C*$_6$H$_5$) 123.4 (*m*-P*C*$_6$H$_5$) 123.3 (C_6H_4), 123.2 (NC_6H_4), 118.2 (C_6H_4), 68.7 (O*C*H$_2$CH$_2$), 28.3 (*C*H(CH$_3$)$_2$), 25.3 (CH(*C*H$_3$)$_2$), 24.5 (OCH$_2$*C*H$_2$), 22.4 (CH(*C*H$_3$)$_2$), 5.9 (Si(*C*H$_3$)$_3$) ppm. ^{31}P{^{1}H} NMR (C_6D_6,161.9 MHz, 25 ºC): δ = 40.6 ppm. Elem. anal. calcd for $C_{41}H_{58}SrN_3OPSeSi_2$ (862.6 g mol^{-1}): C, 57.08; H, 6.78; N, 4.87. Found: C, 56.79; H, 6.63; N, 4.71.

Ph$_2$P(Se)NC$_6$H$_4$CH=N-(Dipp)}Ca{N(SiMe$_3$)$_2$}(THF)] (3). Following the same procedure as that described for **2**, {L^3}H (0.35 g, 0.64 mmol), KN(SiMe$_3$)$_2$ (0.26 g, 1.28 mmol) and CaI$_2$ (0.19 g, 0.64 mmol) were reacted in THF (20+20 mL) to afford the title compound as a pale yellow solid. Yield (0.37 g, 71%). Light yellow crystals of **2** suitable for single-crystal X-ray crystallography were obtained by storage of a concentrated pentane solution at –30 ºC. ^{1}H NMR (C_6D_6, 500.1 MHz, 298 K): δ = 8.06 (dd, $^3J_{HH}$ = 12.8 Hz, $^4J_{HH}$ = 7.7 Hz, 4H; PC_6H_5), 7.92 (s, 1H; C*H*=N), 7.13 (overlapping m, 3H; NC_6H_3, PC_6H_5), 7.02 (complex m, 5H; PC_6H_5 and C_6H_4), 6.94 (d, $^3J_{HH}$ = 7.9 Hz, 2H; NC_6H_3) 6.86 (d, $^3J_{HH}$ = 7.7 Hz, 1H; C_6H_4), 6.73 (t, $^3J_{HH}$ = 7.3 Hz, 1H; C_6H_4), 6.46 (t, $^3J_{HH}$ = 7.3 Hz, 1H; C_6H_4), 3.43 (br s, 4H; O*C*H$_2$CH$_2$), 3.23 (sept, $^3J_{HH}$ = 8 Hz, 2H; C*H*(CH$_3$)$_2$), 1.29 (d, $^3J_{HH}$ = 6.6 Hz, 6H; CH(C*H*$_3$)$_2$), 1.09 (br s, 4H; OCH$_2$C*H*$_2$), 0.95 (d, $^3J_{HH}$ = 6.5 Hz, 6H; CH(C*H*$_3$)$_2$) 0.37 (s, 18H, Si(C*H*$_3$)$_3$) ppm. ^{13}C{^{1}H} NMR (C_6D_6, 125.76 MHz, 298 K): δ = 171.5 (*C*H=N), 152.2 (*i*-N=CH*C*$_6$H$_4$), 152.1 (*i*-N*C*$_6$H$_3$) 149.6 (*i*- P*C*$_6$H$_5$) 139.5 (*o*-N*C*$_6$H$_3$), 135.8 (*o*-N*C*$_6$H$_3$), 132.7 (*o*-P*C*$_6$H$_5$), 131.8 (*p*-P*C*$_6$H$_5$), 130.6 (C_6H_4), 128.0 (*p*-P*C*$_6$H$_5$), 127.9 (*p*-N*C*$_6$H3), 126.7 (*m*-N*C*$_6$H$_3$), 126.5 (*m*-P*C*$_6$H$_5$), 125.7 (*m*-P*C*$_6$H$_5$), 123.9 (*m*-P*C*$_6$H$_5$), 123.7 (C_6H_4), 123.4 (NC_6H_4), 118.5 (C_6H_4), 68.7 (O*C*H$_2$CH$_2$), 28.3 (*C*H(CH$_3$)$_2$), 25.4 (CH(*C*H$_3$)$_2$), 24.5 (O*C*H$_2$CH$_2$), 22.4 (CH(*C*H$_3$)$_2$), 5.9 (Si(*C*H$_3$)$_3$) ppm. ^{31}P{^{1}H} NMR (C_6D_6, 161.9 MHz, 298 K): δ = 31.1 ($^1J_{PSe}$ = 589 Hz) ppm. ^{77}Se{^{1}H} NMR (C_6D_6, 76.31 MHz, 298 K): δ = –61.0 (d, $^1J_{SeP}$ = 589 Hz) ppm. Elem. anal. calcd for $C_{41}H_{58}CaN_3OPSeSi_2$ (815.1 g mol^{-1}): C, 60.41; H, 7.17; N, 5.16. Found: C, 59.99, H, 7.03; N, 4.93.

[Ca{Ph$_2$P(S)NC$_6$H$_4$CH=N-(Dipp)}$_2$] (5). Following the same procedure as that described for **2**, {L^2}H (0.3 g, 0.60 mmol), KN(SiMe$_3$)$_2$ (0.12 g, 0.60 mmol) and CaI$_2$ (88 mg, 0.30 mmol) were reacted in THF (20+20 mL) to afford the title compound as a pale yellow solid. Yield (0.208 g, 67%). Light yellow crystals of **5** suitable for single-crystal X-ray crystallography were obtained by storage of a concentrated ether solution at –30 ºC. ^{1}H NMR (C_6D_6, 400 MHz, 298 K): δ = 8.13 (m, 8H; PC_6H_5), 7.88 (s, 2H; C*H*=N), 7.25 (m, 6H; NC_6H_3, PC_6H_5), 7.06 (m, 10H; PC_6H_5 and C_6H_4), 6.99 (m, 4H, NC_6H_3) 6.89 (d, $^3J_{HH}$ = 7.8 Hz, 2H; C_6H_4), 6.78 (t, $^3J_{HH}$ = 7.4 Hz, 2H; C_6H_4), 6.48 (t, $^3J_{HH}$ = 7.6 Hz, 2H; C_6H_4), 2.89 (sept, $^3J_{HH}$ = 8 Hz, 4H; C*H*(CH$_3$)$_2$), 1.07 (d, $^3J_{HH}$ = 6.8 Hz, 24H; CH(C*H*$_3$)$_2$), ^{13}C{^{1}H} NMR (C_6D_6, 100 MHz, 298 K): δ = 171.2 (*C*H=N), 152.5 (*i*-N=CH*C*$_6$H$_4$), 152.2 (*i*-N*C*$_6$H$_3$) 149.1 (*i*- P*C*$_6$H$_5$) 139.6 (*o*-N*C*$_6$H$_3$), 135.1 (*o*-N*C*$_6$H$_3$), 132.8 (*o*-P*C*$_6$H$_5$), 131.7 (*p*-P*C*$_6$H$_5$), 130.3 (C_6H_4), 128.0 (*p*-P*C*$_6$H$_5$), 127.8 (*p*-N*C*$_6$H3), 126.9 (*m*-N*C*$_6$H$_3$), 126.4 (*m*-P*C*$_6$H$_5$), 125.9 (*m*-P*C*$_6$H$_5$), 123.5 (*m*-P*C*$_6$H$_5$), 123.4 (C_6H_4), 123.1 (NC_6H_4), 118.5 (C_6H_4), 28.2 (*C*H(CH$_3$)$_2$), 25.2 (CH(*C*H$_3$)$_2$), 22.1 (CH(*C*H$_3$)$_2$) ppm. ^{31}P{^{1}H} NMR (C_6D_6,161.9 MHz, 298 K): δ = 62.6 ppm Elem. anal. calcd for for $C_{62}H_{64}CaN_4P_2S_2$ (1030.4 g mol^{-1}): C, 72.20; H, 6.25; N, 5.43 Found: C, 59.99, H, 7.03; N, 4.93.

Typical protocol for intermolecular hydroelementation reactions. In the glovebox, the precatalyst (10 μL) was loaded into an NMR tube. The NMR tube was stored in an appropriate Schlenk tube, which was then removed from the glove-box to allow manipulations on a double manifold Schlenk line. The subsequent manipulations were performed using standard Schlenk techniques. Styrene (58μL 500 μmol) and diphenylphosphine or pyrrolidine (500 μmol) were added to the NMR tube using microsyringes. The NMR tube was sealed and shaken vigorously, then put into an oil bath at desire temperature. The reaction times were measured from this point. After the required amount of time, the reaction was quenched by adding C_6D_6 to the mixture at room temperature. The conversion was determined according to the ^{1}H NMR spectrum of the reaction mixture.

X-ray crystallographic analyses: Single crystals of complex {L^3}H were obtained from a concentrated solution of toluene at room temperature while single crystals of complexes **3** and **5** were obtained from saturated solution of pentane and diethylether respectively under argon atmosphere at a temperature of –35 °C. 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 either on an Agilent Supernova X-calibur Eos CCD detector with either graphite-monochromatic Cu-Kα (1.54184 Å, for **L^{3}H** and **5**) or Bruker-AXS, APEXII CCD detector with Mo-Kα (0.71073 Å for **3**) radiation. Crystal data and structure refinement parameters are summarised in Table TS1 in supporting information. The structures were solved by direct methods (SIR2004)[20] and refined on F^2 using the full-matrix least-squares method, using SHELXL-97.[21] Non-hydrogen atoms were anisotropically refined. H-atoms were included in the refinement on calculated positions riding on their carrier atoms. The function minimised was $[\sum w(Fo^2 - Fc^2)^2]$ (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 $R1$ and $wR2$ were $(\Sigma||Fo| - |Fc||) / \Sigma|Fo|$ and $[\Sigma w(Fo^2 - Fc^2)^2 / \Sigma(wFo^4)]^{1/2}$ respectively. The DIAMOND-3 program was used to draw the molecule. Crystallographic data (excluding structure factors) for the structures reported in this article have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication nos. CCDC 1479903 (**L^{3}H**), 1479904 (**3**) and 1479905 (**5**). 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).

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Notes and references

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† Electronic Supplementary Information (ESI) available: X-ray crystallographic files for {L^3}H, **3** and **5** in CIF format, Table TS1 and the

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spectral data of new compounds, representation of the solid-state structure of **4**. For crystallographic details in CIF see DOI: 10.1039/b000000x/

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Calcium Complexes with Imino-phosphinanilido Chalcogenide Ligands for Heterofunctionalisation Catalysis

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Table of content

The syntheses, characterisation and utilisation of the calcium complexes $[\{L^x\}CaN(SiMe_3)_2\cdot(THF)]$ supported by monoanionic, tridentate imino-phosphinanilido chalcogenide ligands $\{Ph_2P(E)\text{-}N\text{-}C_6H_4\text{-}CH{=}N(Dipp)\}^-$ (E = S, $\{L^2\}^-$; E = Se, $\{L^3\}^-$; Dipp = 2,6-diisopropylphenyl) as molecular precatalysts for the heterofunctionalisation of styrene are reported.