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Full Paper

Calcium-mediated Hydrophosphorylation of Organic Isocyanates with Diphenylphosphane Oxide

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The calcium-mediated addition of diphenylphosphane oxide to organic isocyanates and isothiocyanates yields *N*-alkyl and *N*-aryl substituted diphenylphosphorylformamides (E = O, R = ^{i}Pr, ^{t}Bu, ^{c}Hex, Ph, C_6H_4-4-Br, C_6H_2-2,4,6-Me_3, and Naph) and -thioformamides (E = S, R = ^{i}Pr, ^{c}Hex, Ph, and C_6H_4-4-Me), respectively, of the type $Ph_2P(O)$–C(E)–N(H)R. All derivatives were characterized by IR and NMR spectroscopy as well as X-ray diffraction experiments. The wavenumbers of the N–H stretching modes are smaller for the thio analogues and *N*-aryl substituents. In the solid state all formamides and thioformamides form dimers by N–H···O–P hydrogen bridges. The P–C_{CE} bonds are significantly elongated compared with the P–C_{Ph} distances.

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Introduction

Catalysis is a basic concept to reduce activation barriers of chemical reactions and plays an important role in research and industry. Most industrial products are produced by catalytic processes. However, often these reactions rely on noble, rare, and, hence, expensive metals such as late transition metals and lanthanoids. Therefore, interest in other catalytically active metals is growing in order to circumvent these challenges. One of the most attractive candidates is calcium because this alkaline earth metal is non-toxic regardless of its concentration and is abundant worldwide, easily available, and inexpensive. In addition, it combines the properties of typical s-block metals (highly heteropolar bonds, salt-like compounds) and the early transition metals (availability of 3d orbitals, catalytic activity, Lewis-acidic character), as such, the research on calcium-based catalysis has intensified within the past few years.[1,2]

In all catalytic processes calcium always maintains the oxidation state of +2, thereby excluding redox reactions. Therefore, the catalytic cycle usually only contains addition and substitution reactions as well as calciation steps. Typically, there are two classes of calcium-mediated catalytic processes, namely polymerization procedures (such as the polymerization of lactide[3] or of styrene[4]) and heterofunctionalization reactions (such as hydroamination[5–7] and hydrosilylation[8]). In contrast to intensively investigated hydroamination as well as lactide and styrene polymerization, the calcium-mediated hydrophosphanylation[1,2,9] of carbodiimides,[10,11] alkenes,[12] and alkynes[12,13] plays a minor role. The calcium-mediated phosphanylation of substituted butadiynes with diphenylphosphane yielded regio- and stereoisomers, depending on the substituent at the butadiyne. If the same catalyst $[(thf)_4Ca(PPh_2)_2]$ is used in the addition reaction of diphenylphosphane oxide with substituted butadiynes, different regioisomers were isolated.[14]

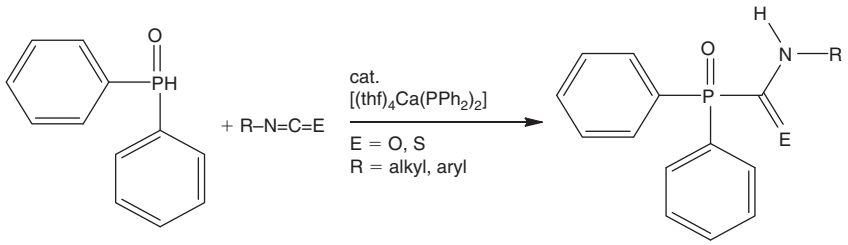
Here we expand our investigations on calcium-mediated hydrophosphanylation of organic isocyanates with diphenylphosphane oxide, which do not react with each other in the absence of a catalyst. This reaction attracted our special interest because a calcium-triggered trimerization of cyclohexyl- and phenylisocyanate was observed earlier.[15] However, addition of $HPPh_2$ to R–N=C=O succeeded with a lanthanum-based catalyst in tetrahydrofuran (THF); the yields of Ph_2P–C(O)–NHR were between 38 (R = adamantyl) and 88 % (R = 4-F_3C-C_6H_4).[16] We reacted $Ph_2P(O)H$ instead of diphenylphosphane because phosphane oxides readily form complexes with calcium ions whereas phosphanes do not represent effective Lewis bases in calcium-based chemistry.[9]

Lithium diphenylphosphanide reacts with equimolar amounts of isocyanates yielding phosphorylformamides after hydrolysis and treatment with dilute hydrogen peroxide.[17] In another protocol, diarylphosphane oxide and diarylphosphane sulfide reacted with isothiocyanates in the presence of catalytic amounts of base (triethylamine) at 70–80°C leading to the formation of phosphorylformamides and phosphorylthioformamides, respectively.[18] In protic solvents (ethanol), tetraaryldiphosphanes reacted with phenylisothiocyanate to form phosphanylthioformamides under P–P bond cleavage.[19]

Results and Discussion

Synthesis

For the calcium-mediated addition of diphenylphosphane oxide to organic isocyanates and isothiocyanates, a 0.1 M THF solution of $[(thf)_4Ca(PPh_2)_2]$ was prepared.[20,21] A few millilitres of this solution (5 mol-%) were added to a THF solution of diphenylphosphane oxide. A slight excess of organylisocyanates and -isothiocyanates was then added to this



Scheme 1. Calcium-mediated synthesis of N-organyl-diphenylphosphorylformamides (E = O) and -thioformamides (E = S).

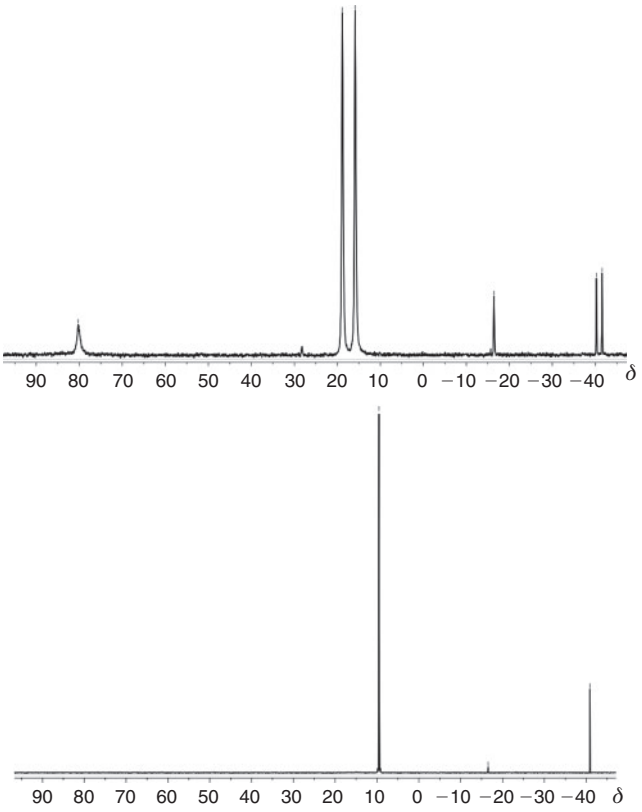


Fig. 1. ^{31}P NMR spectrum of a [D$_8$]THF solution of [(thf)$_4$Ca(PPh$_2$)$_2$] (s, δ −16.4) with four equivalents of HP(O)Ph$_2$ (d, δ 17.4, $^1J_{PH}$ 481.5) leading to an equilibrium with [(thf)$_4$Ca(OPPh$_2$)$_2$] (s, δ 80.3) and HPPh$_2$ (d, δ −40.9, $^1J_{PH}$ 215.4) (25°C, 400 MHz) (top). On the bottom the ^{31}P{^{1}H} NMR spectrum taken after complete conversion of *tert*-butyl isocyanate with HP(O)Ph$_2$ employing the catalyst [(thf)$_4$Ca(PPh$_2$)$_2$] is depicted. Only the resonances of *N*-*tert*-butyl-(diphenylphosphoryl)formamide (**2**) (δ 9.5), [(thf)$_4$Ca(PPh$_2$)$_2$] (δ −16.6), and HPPh$_2$ (δ −40.9) can be seen verifying that [(thf)$_4$Ca(OPPh$_2$)$_2$] is the catalytically active species.

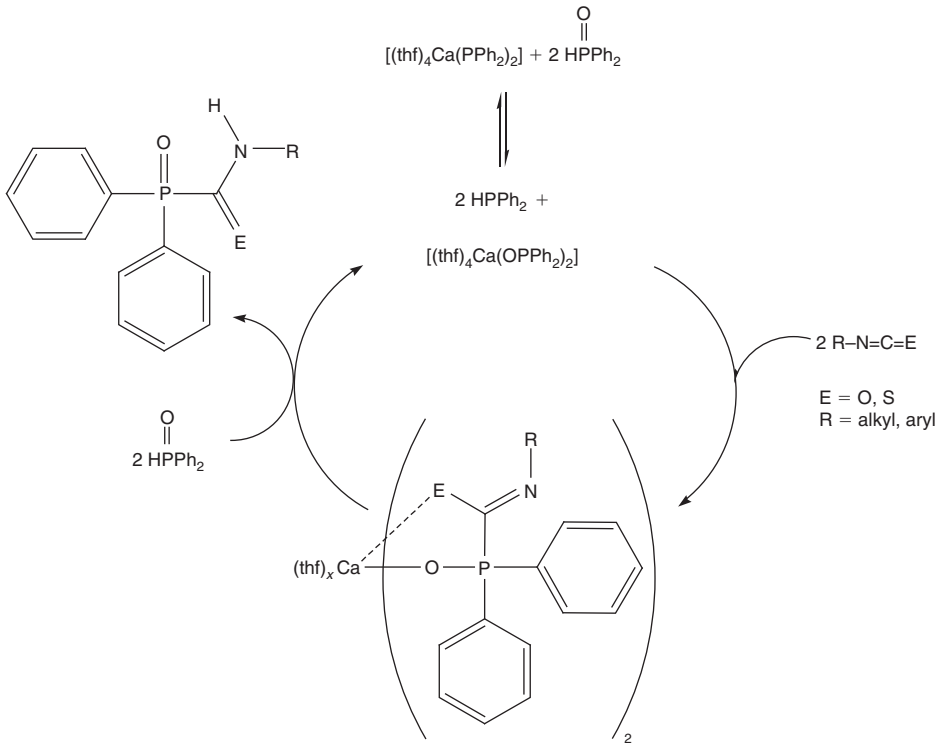
reaction mixture. The rate of conversion was monitored by ^{31}P NMR spectroscopy. After complete conversion of HP(O)Ph$_2$ according to Scheme 1, all volatiles were removed under vacuum and the solid residue was extracted with dichloromethane. Recrystallization from methanol or purification by column chromatography gave analytically pure products.

A ^{31}P NMR study of an equimolar mixture of [(thf)$_4$Ca(PPh$_2$)$_2$] and HP(O)Ph$_2$ in THF showed an equilibrium between these starting materials and the resulting [(thf)$_4$Ca(OPPh$_2$)$_2$] and HPPh$_2$. Fig. 1 shows the NMR spectrum with the resonances of all compounds allowing the determination of the equilibrium constant $K = 0.013$. The large excess of diphenylphosphane oxide shifts the equilibrium towards the already well known calcium bis(diphenylphosphinite).[22] The phosphinite anion adds to the carbon atom of R–N=C=E under formation of a P–C$_{CE}$ bond yielding the intermediate [Ph$_2$P(O)–C(E)–NR]$^-$ anion. Protolysis by diphenylphosphane oxide finally leads to the corresponding formamides and thioformamides under reformation of the catalyst [(thf)$_4$Ca(OPPh$_2$)$_2$]. A catalytic cycle is depicted in Scheme 2 taking into account that the first reaction step is the formation of the catalytic species [(thf)$_4$Ca(OPPh$_2$)$_2$] from the precatalyst [(thf)$_4$Ca(PPh$_2$)$_2$]. After complete conversion the ^{31}P NMR spectrum shows the resonances of the product as well as of HPPh$_2$ and [(thf)$_4$Ca(PPh$_2$)$_2$] (Fig. 1) verifying (i) that calcium bis(diphenylphosphinite) is the catalytically active species and (ii) that a quantitative conversion into the formamides and thioformamides was achieved. The yields given in the experimental part are lower due to the fact that they refer to the isolated crystalline material after recrystallization and are not optimized.

NMR Spectroscopy

Selected NMR and IR spectroscopic data of *N*-substituted diphenylphosphorylformamides (E = O, carbamoylphosphane oxides) and -thioformamides (E = S, thiocarbamoylphosphane oxides) are summarized in Table 1. The thioformamides show low field shifted resonances compared with the formamides. Contrary to the more electronegative nature of oxygen, the phosphorylformamides resonate upfield (~6 ppm in ^{31}P) from the respective phosphorylthioformamides. The heavier chalcogen atom also leads to a strong low field shift of the ^{13}C$_{CE}$ signal (heavy atom effect). The ^1J(P–C$_{CO}$) coupling constants of the formamides are ~30 Hz larger than those of the sulfur pendents. Oxidation of the phosphorus atom results in a lower electronic density and thus in an increased ^1J(P–C) coupling constant. The influence of the *N*-bound substituents on the NMR parameters of the P–C–E fragments is much smaller than the variations related to the chalcogen atom. Aryl groups cause a slight low field shift of the ^{31}P and slight high field shift of the ^{13}C$_{CE}$ resonances. Much more significant is the chemical shift difference of the *N*-bound hydrogen atom; for the aryl-substituted derivatives the $\delta(^1H_N)$ values are shifted by ~2 ppm towards the lower field compared with alkyl-substituted formamides. Furthermore, the deshielding of these H atoms increases for the thioformamides.

The stretching frequencies of the C=O and C=S moieties differ by ~130 cm^{-1} mainly due to the larger reduced mass of the sulfur-containing derivative. The N–H valence bond stretching vibrations depend on the substitution pattern with smaller wavenumbers for the thio-analogues and for *N*-aryl-substituted derivatives. The IR parameters clearly confirm the absence of an amide (A) iminol (B) tautomerism (E = O) or thioamide (A) iminothiol (B) tautomerism (E = S). In the solid state this isomer is stabilized by dimer formation by N–H···O$_{PO}$



Scheme 2. Catalytic cycle for the synthesis of *N*-alkyl and *N*-aryl substituted diphenylphosphorylformamides (E = O, R = ^{i}Pr, ^{t}Bu, ^{c}Hex, Ph, C_6H_4-4-Br, C_6H_2-2,4,6-Me_3, and Naph) and -thioformamides (E = S, R = ^{i}Pr, ^{c}Hex, Ph, and C_6H_4-4-Me) using $[(thf)_4Ca(PPh_2)_2]$ as a precatalyst. Metalation of diphenylphosphane oxide yields catalytically active $[(thf)_4Ca(OPPh_2)_2]$ which adds to R–N=C=E yielding an unobserved intermediate. Reaction with diphenylphosphane oxide gives the products and reforms the calcium-based catalyst.

Table 1. Selected NMR and IR spectroscopic data for *N*-substituted diphenylphosphorylformamides (E = O) and -thioformamides (E = S)

E	R	$\delta(^{31}P\{^{1}H\})$	$\delta(^{13}C{=}E)$	$\delta(^{1}H_N)$	$^{1}J(P–C_{CE})$ [Hz]	ν(N–H) [cm^{-1}]	ν(C=E) [cm^{-1}]
O	^{i}Pr	14.8	168.7	[A]	120.7	3273	1641
	^{t}Bu	14.5	168.9	7.42	119.6	3201	1643
	^{c}Hex	14.9	168.7	7.51	120.7	3190	1643
	Ph	15.6	168.1	9.68	122.8	3178	1643
	C_6H_4-4-Br	15.8	168.3	9.51	122.3	3202	1645
	Mes	16.2	168.5	9.11	121.2	3125	1651
	Naph	16.2	168.5	10.12	122.4	3132	1651
S	^{i}Pr	20.6	195.4	9.44	87.4	3138	1510
	^{c}Hex	20.7	195.2	9.48	88.9	3107	1510
	Ph	21.6	194.1	11.20	89.6	3076	1517
	C_6H_4-4-Me	21.5	193.3	11.15	90.0	3060	1523

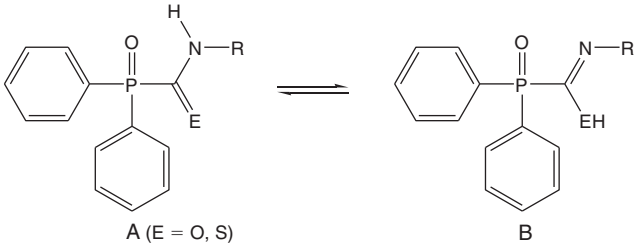
[A]Overlapping with phenyl signals.

hydrogen bridges. In both cases the amide (A) and thioamide derivatives (A, Scheme 3) are present in the solid state which is in agreement with the NMR experiments of dissolved compounds.

Molecular Structures

For comparison reasons the crystal structure of starting diphenylphosphane oxide was determined. The molecular structure and numbering scheme are shown in Fig. 2. Due to the fact that multiple bonds are more demanding than single bonds according to the VSEPR concept, the O–P–C/H angles are larger than the ideal tetrahedral bond angle whereas the other C–P–C/H bond angles are smaller than 109°. For this molecule two mesomeric forms can be drawn with the ionic description being the more appropriate (Scheme 4). The P–O bond shows a small bond length of 148.81(11) pm in accordance with the expectation for a strong P–O bond. This finding can be explained by hyperconjugation from the negatively charged oxygen atom into antibonding σ*(P–C) orbitals, avoiding d-orbital participation at phosphorus (for a detailed discussion see Gilheany[23]), in addition to electrostatic attraction. Similar findings were also published for triphenylphosphane oxide which crystallized as an orthorhombic (*Pbca*, P–O 149.1, av. P–C 180.3 p.m., av. O–P–C 112.4°)[24,25] and a monoclinic polymorph ($P2_1/c$, P–O 149.4, av. P–C 180.0 p.m., av. O–P–C 112.4°).[25,26]

Diphenylphosphane oxide contains a rather negative oxygen atom whereas the P-bound hydrogen atom does not show a distinct acidic behaviour due to very similar electronegativity values (Allred-Rochow electronegativities of P 2.06, H 2.20)



Scheme 3. Representation of the amide iminol (E = O) and thioamide iminothiol (E = S) tautomerism.

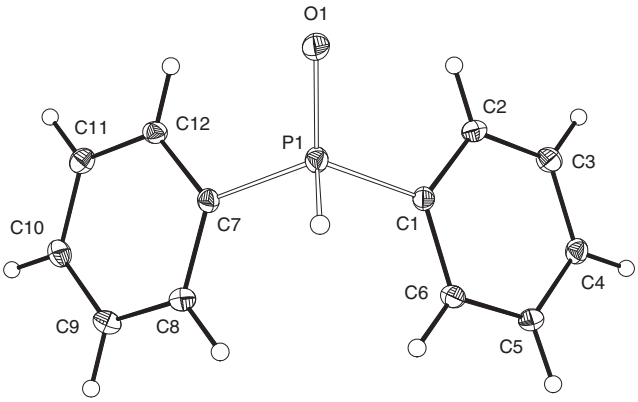
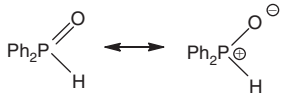


Fig. 2. Molecular structure and numbering scheme of diphenylphosphane oxide. The ellipsoids represent a probability of 40 %, H atoms are drawn with arbitrary radii. Selected bond lengths (pm): P1–O1 148.81(11), P1–C1 180.15(14), P1–C7 179.82(15), P1–H1 132.7(18); angles (deg.): O1–P1–C1 113.31(7), O1–P1–C7 113.20(7), O1–P1–H1 116.2(8), C1–P1–C7 108.40 (7), C1–P1–H1 101.6(7), C7–P1–H1 102.9(8).



Scheme 4. Representation of the mesomeric forms of diphenylphosphane oxide.

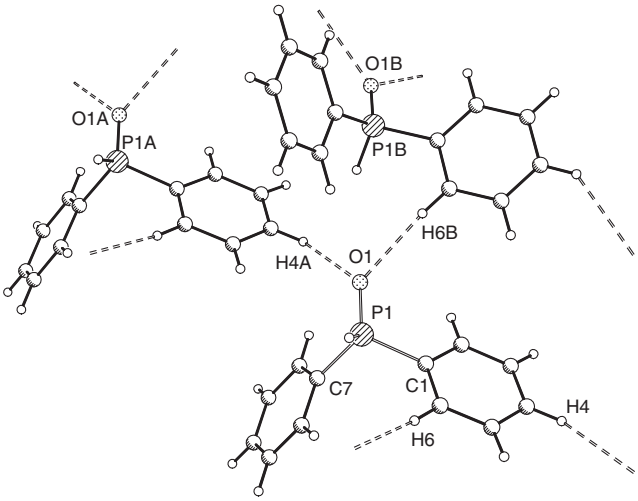


Fig. 3. Part of the framework of diphenylphosphane oxide in the solid state. The aggregation occurs by contacts between the oxygen atoms and hydrogen atoms in *ortho*- and *para*-positions of the phenyl groups. All atoms are shown with arbitrary radii.

characteristic for covalent P–H bonds. Therefore, aggregation in the solid state does not occur by P–H···O–P hydrogen bridges but short contacts are observed between the oxygen atom and phenyl hydrogen atoms in *para*- and *ortho*-positions. These contacts lead to a framework as shown in Fig. 3.

The *N*-substituted diphenylphosphorylformamides (E = O) and -thioformamides (E = S) form dimers in the solid state by two N–H···O–P hydrogen bridges leading to a conformation with the N–H and P–O moieties being directed to the same side of the molecules. Due to the fact that all structures are very similar only selected examples are depicted. The molecular structures and numbering schemes of *N*-4-bromophenyl-diphenylphosphorylformamide and *N*-isopropyl-diphenylphosphorylthioformamide are shown in Figs 4 and 5, respectively. For *N*-mesityl-diphenylphosphorylformamide the aggregation by hydrogen bridges is clarified in Fig. 6. This dimerization occurs regardless of the *N*-bound alkyl or aryl group.

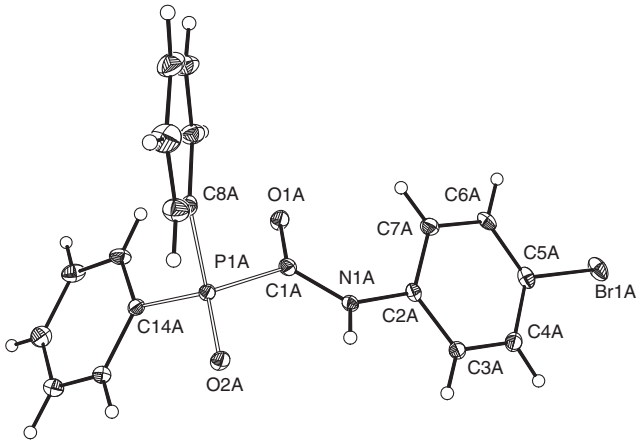


Fig. 4. Molecular structure and numbering scheme of *N*-(4-bromophenyl)-1-(diphenylphosphoryl)formamide (**5**). The asymmetric unit contains two crystallographically independent molecules which are distinguished by the letters 'A' and 'B'; due to very similar structures only molecule A is depicted. The ellipsoids represent a probability of 40 %, H atoms are shown with arbitrary radii.

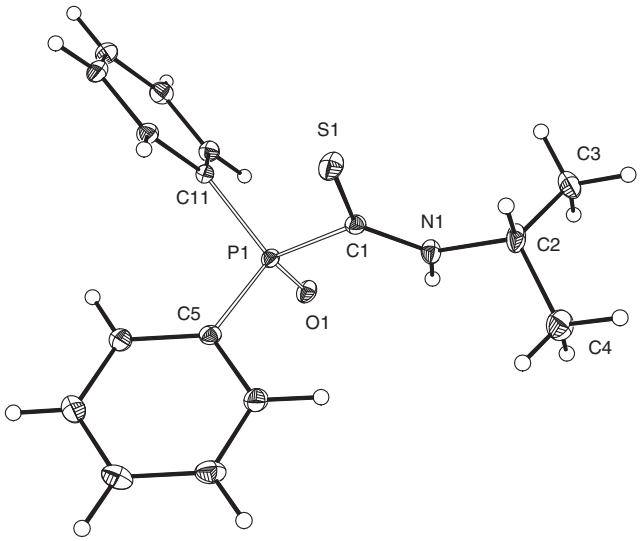


Fig. 5. Molecular structure and numbering scheme of *N*-isopropyl-(diphenylphosphoryl)thioformamide (**8**). The ellipsoids represent a probability of 40 %, hydrogen atoms are drawn with arbitrary radii.

Selected bond lengths and angles of the *N*-substituted diphenylphosphorylformamides (E = O) and -thioformamides (E = S) are listed in Table 2. The diphenylphosphoryl fragment shows structural parameters that are very similar to those of $Ph_2P(O)H$ and Ph_3PO as discussed earlier. Whereas the P–C_{Ph} bond lengths lie in the expected range, the P–C_{CE} bond to the formamide fragment is significantly elongated caused by electrostatic repulsion between positively polarized phosphorus and carbon atoms as depicted in Scheme 5. The oxygen atom (E = O) is more electronegative than sulfur leading to an enhanced positive charge on the carbon atom C_{CE} and therefore, the P–C_{CO} bond lengths of the diphenylphosphorylformamides are ~2 pm longer than the P–C_{CS} values of the diphenylphosphoryl*thio*-formamides. On the one hand, the C–E distances resemble values of slightly elongated double bonds and are significantly smaller than C–E single bonds. On the other hand, the N–C_{CE} distances are only marginally smaller than single bonds.

The central C_{CE} carbon atoms of the formamide unit are in distorted trigonal planar environments. Due to electrostatic reasons, the E–C_{CE}–N bond angles are widened whereas the P–C_{CE}–N angles are narrowed.

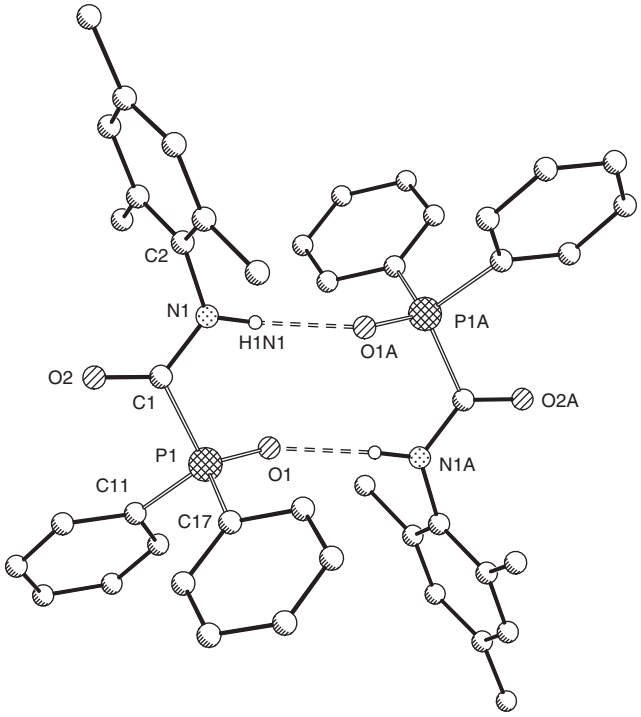
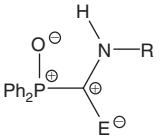


Fig. 6. Representative example of the dimerization by N–H···O–P hydrogen bridges (dashed line) shown for *N*-mesityl-(diphenylphosphoryl)-formamide (**6**). All atoms are shown with arbitrary radii, carbon-bound hydrogen atoms are neglected for clarity reasons.

Conclusion

The calcium complex $[(thf)_4Ca(PPh_2)_2]$ was used as a catalyst system in THF solution. Addition of diphenylphosphane oxide to this solution gave an equilibrium between $[(thf)_4Ca(PPh_2)_2]$ and $HP(O)Ph_2$ on the one side and $[(thf)_4Ca(OPPh_2)_2]$ and $HPPh_2$ on the other with an equilibrium constant $K = 0.013$. Organyl isocyanates and thioisocyanates were added to this solution yielding *N*-organyl-diphenylphosphorylformamides and -thioformamides, respectively. The degree of conversion was monitored by ^{31}P NMR spectroscopy and after complete reaction, the catalyst $[(thf)_4Ca(PPh_2)_2]$ and free phosphane $HPPh_2$ were observed in addition to the product, whereas $HP(O)Ph_2$ was consumed completely.

These *N*-organyl-diphenylphosphorylformamides and -thioformamides crystallize as dimers with N–H···O–P hydrogen bridges. The P–C_{CE} bonds are significantly longer than those to the phenyl groups. This fact is a consequence of electrostatic repulsion between positively polarized phosphorus and carbon atoms. The influence of the *N*-bound alkyl and aryl groups on the bonding parameters is small. The carbon-bound chalcogen atom E influences the P–C_{CE} distance with a significantly elongated bond for E = O because the larger electronegativity of oxygen enhances the positive charge on the carbon atom and hence the repulsion between P and C_{CE}.



Scheme 5. Illustration of the positively polarized P and C_{CE} atoms leading to an elongation of the P–C_{CE} bond.

Table 2. Selected structural data (average values where appropriate, bond lengths [pm] and angle [deg.]) of *N*-substituted diphenylphosphorylformamides (E = O) and -thioformamides (E = S) (comparison: $HP(O)Ph_2$: P=O 148.8(1), av. P–C_{Ph} 180.0, P-H 133(2) pm)

E	R	P=O	av. P–C_{Ph}	P–C_{CE}	C=E	N–C_{CE}	N–C_R	P–C_{CE}–N	P–C_{CE}–E	N–C_{CE}–E
O	^{i}Pr	149.29(9)	179.8	186.4(1)	123.2(2)	132.8(2)	147.1(2)	113.25(9)	120.88(9)	125.9(1)
	^{t}Bu	149.2(1)	180.4	186.8(1)	123.3(2)	133.1(2)	148.9(2)	114.8(1)	118.9(1)	126.2(1)
	^{c}Hex	148.7(1)	179.6	186.5(2)	123.2(2)	133.0(2)	146.3(2)	113.7(1)	120.8(1)	125.5(2)
	Ph	148.8(1)	180.0	186.2(1)	122.9(2)	134.3(2)	142.6(2)	113.66(9)	118.7(1)	127.6(1)
	C_6H_4-4-Br[A]	149.2(2)	180.5	186.1(3)	122.5(4)	134.9(4)	142.6(4)	115.1(2)	118.6(2)	126.2(3)
		149.1(2)	180.1	186.4(3)	122.4(4)	135.1(4)	142.1(4)	113.7(2)	119.2(2)	127.0(3)
	Mes	148.2(1)	180.6	186.7(2)	122.3(2)	134.1(2)	144.3(2)	113.9(1)	120.3(1)	125.8(2)
	Naph[A]	148.7(1)	179.6	186.7(2)	122.5(2)	134.6(2)	143.5(2)	114.5(1)	119.5(1)	125.9(1)
		149.1(1)	179.8	186.6(2)	122.6(2)	134.6(2)	143.0(2)	114.2(1)	119.0(1)	126.8(1)
S	^{i}Pr	149.4(1)	179.8	184.2(2)	166.4(2)	131.8(2)	147.5(2)	112.8(1)	119.43(9)	127.7(1)
	^{c}Hex[A]	149.2(1)	179.5	184.3(2)	166.3(2)	132.3(2)	147.0(2)	112.0(1)	120.2(1)	127.8(1)
		149.1(1)	179.8	184.4(2)	166.4(2)	132.3(2)	147.0(2)	112.7(1)	119.6(1)	127.7(1)
	Ph	148.9(1)	180.6	184.9(2)	165.9(2)	133.3(2)	143.0(2)	112.6(1)	118.72(9)	128.7(1)
	C_6H_4-4-Me	149.3(1)	179.9	184.6(1)	165.6(1)	133.7(2)	143.2(2)	111.61(9)	119.53(8)	128.9(1)

[A]Two crystallographically independent molecules.

Experimental

General Remarks

All manipulations were carried out under an argon or nitrogen gas atmosphere using standard Schlenk techniques. Solvents were dried according to common procedures and distilled under argon or nitrogen. Deuterated solvents were dried with sodium, degassed, distilled, and saturated with inert gas. Chemicals were purchased from Aldrich. All organylisocyanates or -isothiocyanates were distilled before use.

General Procedure

A solution of the catalyst (0.05 equiv.) (0.1 M solution of $[(thf)_4Ca(PPh_2)_2]$ in THF) was slowly added to a solution of diphenylphosphane oxide (1 equiv.) in 30 mL of anhydrous THF (per gram of diphenylphosphane oxide) at room temperature. After stirring for approximately 15 min at room temperature the organylisocyanate or -isothiocyanate (1.1 equiv.), dissolved or suspended in 15 mL of anhydrous THF (per mmol of heterocumulene), was added dropwise. The conversion of the substrates was monitored with ^{31}P NMR experiments at the resonance of diphenylphosphane oxide after 12, 24, and 48 h. After complete consumption of $Ph_2P(O)H$, the solvent was removed and the residual solid was extracted with 50 mL of CH_2Cl_2. After removal of all volatiles under vacuum, the crude product was purified by recrystallization or column chromatography.

Diphenylphosphane Oxide

$HP(O)PPh_2$ was synthesized according to literature procedures.[27,28] Scale: 271 mL (27.1 mmol) of aqueous HCl (1 N) and 0.56 g (2.77 mmol) of chlorodiphenylphosphane; purification: recrystallization from a pentane–THF mixture; yield: 4.3 g (94 %) of colourless crystals of $HP(O)PPh_2$.

N-*Isopropyl-(diphenylphosphoryl)formamide* (***1***)

Scale: 1.4 mL (0.14 mmol) of catalyst solution, 0.56 g (2.77 mmol) of $Ph_2P(O)H$, 0.26 g (3.05 mmol) of isopropylisocyanate; reaction period 24 h; purification: recrystallization from methanol, yield: 0.51 g (61 %) of colourless crystals of **1**. mp 147°C. δ_H (400 MHz, $CDCl_3$) 7.90 (4H,m), 7.51 (7H,m), 4.21 (1H, oct, CH), 1.15 (6H, d, CH_3), 1.41 (9H, s). δ_C (101 MHz, $CDCl_3$) 168.7 (d, $^1J_{C-P}$ 120.7, CO), 132.7 (d, $^4J_{C-P}$ 2.8, *p*-C), 131.7 (d, $^3J_{C-P}$ 9.6, *m*-C), 129.4 (d, $^1J_{C-P}$ 99.8, *i*-C), 128.8 (d, $^2J_{C-P}$ 12.2, *o*-C), 42.3 (d, $^3J_{C-P}$ 5.1, CH), 22.5 (CH_3). δ_P (162 MHz, $CDCl_3$) 14.84. ν_{max} (neat)/cm^{-1} 3273w (NH), 2968w, 1641s (CO), 1524s, 1438m, 1173s (PO), 1147s, 748m, 692s. *m/z* 288 (10 %, $[M+1]^+$), 202 (100, $[HP(O)Ph_2]^+$), 201 (35, $[P(O)Ph_2]^+$), 55 (40), 125 (15, $[HP(O)Ph]^+$), 77 (30, $[C_6H_5]^+$). Anal. Calc. for $C_{16}H_{18}NO_2P$, 287.29: C 66.89, H 6.32, N 4.88. Found: C 66.89, H 6.26, N 4.94 %.

N-tert-*Butyl-(diphenylphosphoryl)formamide* (***2***)

Scale: 0.8 mL (0.08 mmol) of catalyst solution, 0.32 g (1.60 mmol) of $Ph_2P(O)H$, 0.17 g (1.76 mmol) of *tert*-butyl isocyanate; reaction period: 12 h; recrystallization from methanol, yield: 0.34 g (74 %) of colourless crystals of **2**. mp 149°C. δ_H (400 MHz, $CDCl_3$)7.88 (4H, m), 7.56 (2H, m), 7.47 (4H, m), 7.42 (1H, m, NH), 1.41 (9H, s). δ_C (101 MHz, $CDCl_3$) 168.8 (d, $^1J_{C-P}$ 119.6, CO), 132.6 (d, $^4J_{C-P}$ 2.8, *p*-C), 131.7 (d, $^3J_{C-P}$ 9.6, *m*-C), 129.5 (d, $^1J_{C-P}$ 98.7, *i*-C), 128.7 (d, $^2J_{C-P}$ 12.2, *o*-C), 53.4 (d, $^3J_{C-P}$ 6.8, C-^{t}Bu), 28.7 (CH_3). δ_P (162 MHz, $CDCl_3$) 14.53. ν_{max} (neat)/cm^{-1} 3201w (NH), 2974w, 1643s (CO), 1532s, 1437m, 1171s (PO), 1112m, 750s, 691s. *m/z* 302 (15 %, $[M+1]^+$), 202 (100, $[HP(O)Ph_2]^+$), 183 (15), 155 (65), 125 (20, $[HP(O)Ph]^+$), 77 (30, $[C_6H_5]^+$), 57 (15, $[C_4H_9]^+$), 47 (25), 41 (10). Anal. Calc. for $C_{17}H_{20}NO_2P$, 301.32: C 67.76, H 6.69, N 4.65. Found: C 67.63, H 6.79, N 4.68 %.

N-*Cyclohexyl-(diphenylphosphoryl)formamide* (***3***)

Scale: 2.3 mL (0.23 mmol) of catalyst solution, 0.92 g (4.58 mmol) of $Ph_2P(O)H$, 0.63 g (5.04 mmol) of cyclohexyl isocyanate; reaction period: 24 h; recrystallization from methanol, yield: 1.05 g (70 %) of colourless crystals of **3**. mp 169°C. δ_H (600 MHz, $CDCl_3$) 7.90 (4H, m), 7.56 (2H, m), 7.51 (4H, s, NH),7.49 (4H, m), 3.90 (1H, m, CH), 1.93 (2H, m), 1.74 (2H, m), 1.62 (1H, m), 1.35 (2H, m), 1.27 (2H, m), 1.18 (1H, m). δ_C (151 MHz, $CDCl_3$) 168.7 (d, $^1J_{C-P}$ 120.7, CO), 132.6 (d, $^4J_{C-P}$ 2.8, *p*-C), 131.8 (d, $^3J_{C-P}$ 9.7, *m*-C), 129.6 (d, $^1J_{C-P}$ 99.6, *i*-C), 128.8 (d, $^2J_{C-P}$ 12.2, *o*-C), 49.2 (d, $^3J_{C-P}$ 4.9, CH-^{c}Hex), 32.9 (CH_2-^{c}Hex), 25.4 (CH_2-^{c}Hex), 24.9 (CH_2-^{c}Hex). δ_P (162 MHz, $CDCl_3$) 14.87. ν_{max} (neat)/cm^{-1} 3191w (NH), 3024w, 2930m, 2850w, 1643s (CO), 1536s, 1438m, 1169s (PO), 1118s, 748s, 691s. *m/z* 328 (100 %, $[M+1]^+$), 202 (100, $[HP(O)Ph_2]^+$), 183 (20), 155 (80), 125 (40, $[HP(O)Ph]^+$), 83 (20, $[C_6H_{11}]^+$), 77 (70, $[C_6H_5]^+$), 55 (40, $[C_4H_7]^+$), 47 (50), 41 (30), 28 (10). Anal. Calc. for $C_{19}H_{22}NO_2P$, 327.36: C 69.71, H 6.77, N 4.28. Found: C 69.38, H 6.67, N 4.32 %.

N-*Phenyl-(diphenylphosphoryl)formamide* (***4***)

Scale: 0.1 mL (0.5 mmol) of catalyst solution (5 M $(thf)_4Ca(PPh_2)_2$) in THF), 0.78 g (3.9 mmol) of $Ph_2P(O)H$, 0.48 g (4.02 mmol) of phenyl isocyanate; reaction period: 12 h; purification: column chromatography (silica; ethyl acetate/petroleum ether 5 : 1), yield: a few colourless crystals of **4**. mp 157°C. δ_H (600 MHz, $CDCl_3$) 9.68 (1H, s, NH), 7.96 (4H, m), 7.71 (2H, d, $^3J_{H-H}$ 8.6), 7.59 (2H, m), 7.50 (4H, m), 7.33 (2H, t, $^3J_{H-H}$ 8.0), 7.16 (1H, t, $^3J_{H-H}$ 7.3). δ_C (151 MHz, $CDCl_3$) 168.1 (d, $^1J_{C-P}$ 122.8, CO), 136.9 (d, $^3J_{C-P}$ 9.5), 132.9 (d, $^4J_{C-P}$ 2.8, *p*-C), 131.9 (d, $^3J_{C-P}$ 9.8, *m*-C), 129.2, 128.8 (d, $^2J_{C-P}$ 12.4, *o*-C), 128.5, 125.6, 120.0. δ_P (162 MHz, $CDCl_3$) 15.64. ν_{max} (neat)/cm^{-1} 3178 (NH), 3047, 1643 (CO), 1597, 1535, 1497, 1435, 1312, 1242, 1173 (PO), 1111, 795, 748, 725, 694. *m/z* 322 (10 %, $[M+1]^+$), 202 (100, $[HP(O)Ph_2]^+$), 155 (10). Anal. Calc. for $C_{19}H_{16}NO_2P$, 321.31: C 71.02, H 5.02, N 4.36. Found: C 70.72, H 5.26, N 4.36 %.

N-*(4-Bromophenyl)-(diphenylphosphoryl)formamide* (***5***)

Scale: 1.2 mL (0.12 mmol) of catalyst solution, 0.5 g (2.50 mmol) of $Ph_2P(O)H$, 0.54 g (2.75 mmol) of 4-bromophenyl isocyanate; reaction period: 48 h; recrystallization from acetone, yield: 0.44 g (44 %) of colourless crystals of **5**. Mp 201°C (dec.). δ_H (400 MHz, $CDCl_3$) 9.51 (1H, s, NH), 7.94 (4H, m), 7.53 (10H, m). δ_C (151 MHz, $CDCl_3$) 168.3 (d, $^1J_{C-P}$ 122.3, CO), 135.9 (d, $^3J_{C-P}$ 9.6), 132.9 (d, $^4J_{C-P}$ 2.6, *p*-C), 132.1, 131.7 (d, $^3J_{C-P}$ 9.8, *m*-C), 128.8 (d, $^2J_{C-P}$ 12.4, *o*-C), 128.5 (d, $^1J_{C-P}$ 101.0, *i*-C), 121.4, 118.3. δ_P (162 MHz, $CDCl_3$) 15.83. ν_{max} (neat)/cm^{-1} 3202w (NH), 3172w, 1645m (CO), 1592m, 1528m, 1486s, 1437m, 1394m, 1305m, 1237m, 1194s, 1169s (PO), 1113s, 1073m (C–Br), 821s, 796m, 746m, 724s, 691s, 632s (C–Br). *m/z* 399 (10 %, $[M]^+$), 202 (100, $[HP(O)Ph_2]^+$), 155 (20), 125 (10, $[HP(O)Ph]^+$), 77 (30, $[C_6H_5]^+$). Anal. Calc. for $C_{19}H_{15}BrNO_2P$, 400.21: C 57.02, H 3.68, N 3.38, Br 19.97. Found: C 57.21, H 3.68, N 3.38, Br 19.74 %.

N-*Mesityl-(diphenylphosphoryl)formamide* (***6***)

Scale: 0.4 mL (2 mmol) of catalyst solution (5 M $(thf)_4Ca(P(O)Ph_2)_2$) in THF), 0.6 g (3.0 mmol) of $Ph_2P(O)H$, 0.5 g (3.1 mmol) of mesityl isocyanate; reaction period: 12 h; recrystallization from THF, yield: 0.59 g (53 %) of colourless crystals of **7**. mp 161°C. δ_H (600 MHz, $CDCl_3$) 9.11 (1H, s, NH), 7.97 (4H, t, $^3J_{H-H}$ 9.0), 7.5 (2H, t, $^3J_{H-H}$ 7.2), 7.49 (4H, m), 6.70 (2H, s, CH-Mes), 2.25 (3H, s, *p*-CH_3-Mes), 1.74 (6H, s, *o*-CH_3-Mes). δ_C (151 MHz, $CDCl_3$) 168.4 (d, $^1J_{C-P}$ 121.2, CO), 137.6, 134.8, 132.8, 131.8, 131.8, 129.1, 128.8 (d, $^2J_{C-P}$ 11.6, *o*-C), 21.0 (*p*-CH_3-Mes), 18.4 (*o*-CH_3-Mes). δ_P (162 MHz, $CDCl_3$) 16.16. ν_{max} (neat)/cm^{-1} 3125 (NH), 2947, 1651 (CO), 1504, 1435, 1242, 1165 (PO), 1111, 1095, 748, 725, 694. *m*/*z* 364 (2 %, $[M+1]^+$), 202 (100 %, $[HP(O)Ph_2]^+$), 161 (76, $[Mes\text{-}NCO]^+$), 155 (32), 146 (60), 125 (12, $[HP(O)Ph]^+$), 91 (22, $[C_7H_7]^+$), 77 (35, $[C_6H_5]^+$). Anal. Calc. for $C_{22}H_{22}NO_2P$, 363.39: C 72.71, H 6.10, N 3.85. Found: C 71.90, H 6.43, N 3.74 %.

N-*Naphthyl-(diphenylphosphoryl)formamide* (***7***)

Scale: 0.5 mL (2.5 mmol) of catalyst solution (5 M $[(thf)_4Ca(P(O)Ph_2)_2]$ in THF), 0.68 g (3.4 mmol) of $Ph_2P(O)H$, 0.68 g (4.0 mmol) of naphthyl isocyanate; reaction period: 12 h; recrystallization from THF, yield: 0.99 g (79 %) of colourless crystals of **7**. mp 156°C. δ_H (400 MHz, $CDCl_3$) 10.12 (1H, s, NH), 8.20 (1H, d, $^3J_{H-H}$ 7.5), 8.02 (5H, m), 7.86 (1H, d, $^3J_{H-H}$ 9.0,), 7.72 (1H, d, $^3J_{H-H}$ 8.2), 7.60 (2H, m), 7.53 (6H, m), 7.46 (1H, t, *J* 7.9). δ_C (101 MHz, $CDCl_3$) 168.4 (d, $^1J_{C-P}$ 122.4, CO), 134.0, 132.9 (d, $^4J_{C-P}$ 2.7, *p*-C), 131.9 (d, $^3J_{C-P}$ 9.7, *m*-C), 131.0 (d, $^3J_{C-P}$ 9.3, *m*-C), 128.9 (d, $^2J_{C-P}$ 12.4, *o*-C), 128.9 (d, $^1J_{C-P}$ 100.3, *i*-C), 128.8, 126.8, 126.8, 126.5, 126.4, 126.0, 125.6, 120.4, 119.3. δ_P (162 MHz, $CDCl_3$) 16.2. ν_{max} (neat)/cm^{-1} 3132 (NH), 2955, 1651 (CO), 1520, 1497, 1435, 1165 (PO), 1119, 1095, 795, 772, 748, 732, 694. *m*/*z* 372 (10 %, $[M+1]^+$), 371 (10, $[M]^+$), 202 (100, $[HP(O)Ph_2]^+$), 169 (100, $[Naph\text{-}NCO]^+$), 155 (45), 140 (70, $[Naph\text{-}N]^+$), 124 (35, $[P(O)Ph]^+$), 114 (40), 77 (50, $[C_6H_5]^+$). Anal. Calc. for $C_{23}H_{18}NO_2P$, 371.37: C 74.39, H 4.89, N 3.77. Found: C 74.30, H 5.23, N 3.91 %.

N-*Isopropyl-(diphenylphosphoryl)thioformamide* (***8***)

Scale: 1.3 mL (0.13 mmol) of catalyst solution, 0.5 g (2.50 mmol) of $Ph_2P(O)H$, 0.28 g (2.77 mmol) of *N*-isopropyl isothiocyanate; reaction period: 24 h; recrystallization from methanol, yield: 0.38 g (50 %) of yellow crystals of **8**. mp 156°C. δ_H (400 MHz, $CDCl_3$)9.44 (1H, s, NH), 7.96 (4H, m), 7.57 (2H, m, *p*-H), 7.47 (4H, m), 4.73 (1H, m, CH), 1.34 (6H, d, $^3J_{H-H}$ 6.6). δ_C (101 MHz, $CDCl_3$) 195.4 (d, $^1J_{C-P}$ 87.4, CS), 132.8 (d, $^3J_{C-P}$ 9.4, *m*-C), 132.7 (d, $^4J_{C-P}$ 2.8, *p*-C), 129.3 (d, J_{C-P} 107.7, *i*-C), 128.4 (d, $^2J_{C-P}$ 12.6, *o*-C), 47.3 (d, $^3J_{C-P}$ 4.8, CH-^{i}Pr), 21.1 (CH_3-^{i}Pr). δ_P (162 MHz, $CDCl_3$) 20.60. ν_{max} (neat)/cm^{-1} 3138m (NH), 2976w, 1510 (CS), 1455m, 1438s, 1384s, 1189s (PO), 1171s, 1148m, 1132s, 1100s, 1002s, 842m, 829m, 750s, 726s, 712s, 688s, 589s. *m*/*z* 304 (20 %, $[M+1]^+$), 303 (70, $[M]^+$), 202 (100, $[HP(O)Ph_2]^+$), 155 (30), 125 (10, $[HP(O)Ph]^+$), 77 (10, $[C_6H_5]^+$). Anal. Calc. for $C_{16}H_{18}NOPS$, 303.36: C 63.35, H 5.98, N 4.62, S 10.57. Found: C 63.59, H 6.11, N 4.63, S 10.54 %.

N-*Cyclohexyl-(diphenylphosphoryl)thioformamide* (***9***)

Scale: 2.0 mL (0.2 mmol) of catalyst solution, 0.8 g (3.96 mmol) of $Ph_2P(O)H$, 0.61 g (4.35 mmol) of *N*-cyclohexyl isothiocyanate; reaction period: 48 h; recrystallization from methanol, yield: 0.65 g (48 %) of yellow crystals of **9**. mp 200°C. δ_H (400 MHz, $CDCl_3$) 9.48 (1H, s, NH), 7.96 (4H, m), 7.56 (2H, m, *p*-H), 7.47 (4H, m), 4.45 (1H, m, CH), 2.07 (2H, m), 1.77 (2H, m), 1.66 (1H, m), 1.40 (2H, m), 1.26 (2H, m), 1.18 (1H, m). δ_C (101 MHz, $CDCl_3$) 195.1 (d, $^1J_{C-P}$ 88.9, CS), 132.8 (d, $^3J_{C-P}$ 9.4, *p*-C), 132.6 (d, $^4J_{C-P}$ 2.8, *m*-C), 129.4 (d, $^1J_{C-P}$ 107.6, *i*-C), 128.4 (d, $^2J_{C-P}$ 12.6, *o*-C), 54.1 (d, $^3J_{C-P}$ 4.8, CH-^{c}Hex), 31.2 (CH_2-^{c}Hex), 25.4 (CH_2-^{c}Hex), 24.6 (CH_2-^{c}Hex). δ_P (162 MHz, $CDCl_3$) 20.65. ν_{max} (neat)/cm^{-1} 3107w (NH), 2946m, 2855w, 1517s (CS), 1435m, 1384m, 1177s (PO), 1120s, 999s, 730s, 716s, 690s. *m*/*z* 344 (55 %, $[M+1]^+$), 343 (30, $[M]^+$), 202 (100, $[HP(O)Ph_2]^+$), 183 (10), 155 (55), 125 (30, $[HP(O)Ph]^+$), 98 (85, $[HP(O)Ph]^+$), 83 (10, $[C_6H_{11}]^+$), 77 (30, $[C_6H_5]^+$), 55 (20, $[C_4H_7]^+$), 47 (35), 41 (20), 28 (15). Anal. Calc. for $C_{19}H_{22}NOPS$, 343.42: C 66.45, H 6.46, N 4.08, S 9.34. Found: C 66.76, H 6.47, N 4.21, S 9.06 %.

N-*Phenyl-(diphenylphosphoryl)thioformamide* (***10***)

Scale: 1.2 mL (0.12 mmol) of catalyst solution, 0.5 g (2.5 mmol) of $Ph_2P(O)H$, 0.37 g (2.75 mmol) of *N*-phenyl isothiocyanate; reaction period: 48 h; recrystallization from methanol, yield: 0.48 g (57 %) of yellow crystals of **10**. mp 170°C. δ_H (400 MHz, $CDCl_3$)11.22 (1H, s, NH), 8.09 (2H, d, $^3J_{H-H}$ 7.8), 8.01 (4H, m), 7.60 (2H, m), 7.49 (4H, m), 7.43 (2H, t, $^3J_{H-H}$ 7.9), 7.30 (1H, t, $^3J_{H-H}$ 7.4), 1.66 (1H, m), 1.40 (2H, m), 1.26 (2H, m), 1.18 (1H, m). δ_C (101 MHz, $CDCl_3$) 194.1 (d, $^1J_{C-P}$ 89.6, CS), 138.5 (d, J_{C-P} 11.5 Hz), 133.0 (d, $^3J_{C-P}$ 9.4, *p*-C), 132.8 (d, $^4J_{C-P}$ 2.9, *m*-C), 129.2, 129.0 (d, $^1J_{C-P}$ 108.2, *i*-C), 128.5 (d, $^2J_{C-P}$ 12.7, *o*-C), 121.7. δ_P (162 MHz, $CDCl_3$) 21.58. ν_{max} (neat)/cm^{-1} 3076w (NH), 3019w, 2987w, 1594m, 1523m (CS), 1488m, 1479m, 1435s, 1368s, 1180s (PO), 1108s, 1092m, 1010s, 859m, 765m, 749m, 715s, 689s. *m*/*z* 338 (60 %, $[M+1]^+$), 337 (95, $[M]^+$), 202 (90, $[HP(O)Ph_2]^+$), 183 (45), 155 (100), 135 (35, $[Ph\text{-}NCS]^+$), 125 (80, $[HP(O)Ph]^+$), 77 (90, $[C_6H_5]^+$), 47 (70). Anal. Calc. for $C_{19}H_{16}NOPS$, 337.38): C 67.64, H 4.78, N 4.15, S 9.50. Found: C 68.04, H 4.73, N 4.20, S 9.37 %.

N-(p-*Tolyl)-(diphenylphosphoryl)thioformamide* (***11***)

Scale: 2.1 mL (0.21 mmol) of catalyst solution, 0.86 g (4.25 mmol) of $Ph_2P(O)H$, 0.7 g (4.7 mmol) of *N*-*p*-tolyl isothiocyanate; reaction period: 12 h; recrystallization from THF, yield: 0.63 g (42 %) of yellow crystals of **11**. mp 171°C. δ_H (400 MHz, $CDCl_3$) 11.15 (1H, d, *J* 7.8, NH), 8.00 (6H, m), 7.59 (2H, m), 7.49 (4H, m), 7.212 (2H, m), 2.36 (3H, s, CH_3 *p*-Tol). δ_C (101 MHz, $CDCl_3$) 193.2 (d, $^1J_{C-P}$ 90.0, CS), 137.6 (*p*-C *p*-Tol), 136.1 (d, $^3J_{C-P}$ 11.6, *i*-C *p*-Tol), 133.0 (d, $^3J_{C-P}$ 9.4, *p*-C), 132.8 (d, $^4J_{C-P}$ 2.8, *p*-C), 129.6, 129.2 (d, J_{C-P} 104.3, *i*-C), 128.5 (d, $^2J_{C-P}$ 12.6, *o*-C), 121.7, 21.3 (CH_3 *p*Tol). δ_P (162 MHz, $CDCl_3$) 21.52. ν_{max} (neat)/cm^{-1} 3060w (NH), 2941m, 2855w, 1509m (CS), 1433m, 1357m, 1167s (PO), 1117m, 1100m, 1015m, 819m, 750m, 725s, 689s. *m*/*z* 352 (55 %, $[M+1]^+$), 351 (75, $[M]^+$), 202 (100, $[HP(O)Ph_2]^+$), 183 (30), 155 (90), 149 (20, $[p\text{Tol-}NCS]^+$), 125 (50, $[HP(O)Ph]^+$), 91 (25, $[C_7H_7]^+$), 77 (30, $[C_6H_5]^+$), 47 (30). Anal. Calc. for $C_{20}H_{18}NOPS$, 351.40): C 68.36, H 5.16, N 3.99, S 9.12. Found: C 68.78, H 4.73, N 4.20, S 9.37 %.

Structure Determinations

The intensity data for the compounds were collected on a Nonius KappaCCD diffractometer using graphite-monochromated $Mo_{K\alpha}$ radiation. Data were corrected for Lorentz and polarization effects but not for absorption effects.[29,30]

The structures were solved by direct methods (*SHELXS*[31]) and refined by full-matrix least-squares techniques against F_o^2 (*SHELXL-97*[31]). The hydrogen atoms bound to the

Table 3. Crystal data and refinement details for the X-ray structure determinations of the compounds $Ph_2P(O)H$ and 1–5

Parameter	$Ph_2P(O)H$	**1**	**2**	**3**	**4**	**5**
Formula	$C_{12}H_{11}OP$	$C_{16}H_{18}NO_2P$	$C_{17}H_{20}NO_2P$	$C_{19}H_{22}NO_2P$	$C_{19}H_{16}NO_2P$	$C_{19}H_{15}BrNO_2P$
fw [g mol^{-1}]	202.18	287.28	301.31	327.35	321.30	400.20
T [°C]	−140(2)	−140(2)	−140(2)	−90(2)	−140(2)	−140(2)
Crystal system	Monoclinic	Monoclinic	Monoclinic	Monoclinic	Triclinic	Triclinic
Space group	$P2_1/n$	$P2_1/n$	$P2_1/n$	$P2_1/n$	$P\bar{1}$	$P\bar{1}$
a [Å]	8.4539(1)	8.3097(1)	8.5679(2)	11.0400(4)	8.6603(3)	10.1083(2)
b [Å]	13.5102(4)	20.1442(4)	10.6779(2)	11.4605(4)	8.7683(2)	11.2989(3)
c [Å]	9.1050(2)	9.6291(2)	17.1728(4)	14.4545(4)	11.3657(3)	17.5316(3)
α [deg.]	90	90	90	90	109.126(2)	73.282(1)
β [deg.]	103.257(1)	112.209(1)	93.636(1)	107.729(2)	102.485(1)	88.625(1)
γ [deg.]	90	90	90	90	94.979(2)	64.483(1)
V [Å^3]	1012.20(4)	1492.26(5)	1567.93(6)	1741.98(10)	784.43(4)	1719.04(6)
Z	4	4	4	4	2	4
ρ [g cm^{-3}]	1.327	1.279	1.276	1.248	1.360	1.546
μ [cm^{-1}]	2.32	1.85	1.79	1.67	1.84	24.95
Measured data	6142	9619	9389	12 116	4874	10 933
Data with $I > 2\sigma(I)$	2091	3114	3146	2751	3328	6717
Unique data (R_{int})	2313/0.0255	3403/0.0222	3562/0.0259	3974/0.0527	3546/0.0141	7771/0.0240
wR_2 (all data, on F^2)[A]	0.0869	0.0828	0.0917	0.1091	0.0875	0.0956
R_1 ($I > 2\sigma(I)$)[A]	0.0356	0.0330	0.0361	0.0426	0.0362	0.0445
S[B]	1.055	1.055	1.058	1.015	1.029	1.113
Res. dens. [e Å^{-3}]	0.338/−0.354	0.380/−0.340	0.386/−0.292	0.250/−0.337	0.407/−0.338	0.468/−0.552
CCDC No.	936826	936827	936828	936828	936830	936831
Formula	$C_{22}H_{22}NO_2P$	$C_{23}H_{18}NO_2P$	$C_{16}H_{18}NOPS$ 0.5 CH_4O	$C_{19}H_{22}NOPS$	$C_{19}H_{16}NOPS$	$C_{20}H_{18}NOPS$
fw [g mol^{-1}]	363.38	371.35	319.37	343.41	337.36	351.38
T [°C]	−90(2)	−140(2)	−140(2)	−140(2)	−140(2)	−140(2)
Crystal system	Monoclinic	Monoclinic	Monoclinic	Monoclinic	Triclinic	Monoclinic
Space group	$P2_1/n$	$P2_1/c$	$C2/c$	$P2_1/c$	$P\bar{1}$	$P2_1/n$
a [Å]	11.7253(4)	15.6451(3)	13.3165(4)	13.9338(2)	8.5936(3)	12.3787(2)
b [Å]	8.4405(3)	11.2942(1)	15.5250(3)	18.1210(2)	8.7577(2)	10.7739(2)
c [Å]	20.1398(7)	21.9693(3)	16.2116(5)	15.1573(2)	12.0315(4)	13.8783(2)
α [deg.]	90	90	90	90	101.854(2)	90
β [deg.]	105.766(2)	107.800(1)	91.444(1)	109.217(1)	109.716(1)	107.163(1)
γ [deg.]	90	90	90	90	94.235(2)	90
V [Å^3]	1918.20(12)	3696.12(9)	3350.50(16)	3613.88(8)	824.10(4)	1768.48(5)
Z	4	8	8	8	2	4
ρ [g cm^{-3}]	1.258	1.335	1.266	1.262	1.360	1.320
μ [cm^{-1}]	1.59	1.67	2.9	2.71	2.97	2.79
Measured data	13 124	21 719	10 066	22 030	5227	10 662
Data with $I > 2\sigma(I)$	3339	7319	3457	6894	3422	3712
Unique data (R_{int})	4377/0.0441	8458/0.0291	3842/0.0254	8271/0.0390	3712/0.0177	4030/0.0288
wR_2 (all data, on F^2)[A]	0.1080	0.1020	0.0868	0.1007	0.0885	0.0870
R_1 ($I > 2\sigma(I)$)[A]	0.0430	0.0405	0.0369	0.0425	0.0378	0.0326
S[B]	1.005	1.062	1.079	1.076	1.087	1.039
Res. dens. [e Å^{-3}]	0.329/−0.327	0.342/−0.347	0.362/−0.311	0.396/−0.310	0.392/−0.287	0.358/−0.293
CCDC No.	936832	936833	936834	936835	936836	936837

[A]Definition of the R indices: $R_1 = (\Sigma||F_o| - |F_c||)/\Sigma|F_o|$; w$R_2 = \{\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]\}^{1/2}$ with $w^{-1} = \sigma^2(F_o^2) + (aP)^2 + bP$; $P = [2F_c^2 + \mathrm{Max}(F_o^2]/3$.
[B]$S = \{\Sigma[w(F_o^2 - F_c^2)^2]/(N_o - N_p)\}^{1/2}$.

amine-groups N1 of all compounds were located by difference Fourier synthesis and refined isotropically. All other hydrogen atoms were also refined isotropically with the exception of those of compound **3** which were included at calculated positions with fixed thermal parameters. All non-hydrogen atoms were refined anisotropically.[31] Crystallographic data as well as structure solution and refinement details are summarized in Table 3. *XP* (SIEMENS Analytical X-ray Instruments, Inc.) was used for structure representations.

Crystallographic Data

Crystallographic data (excluding structure factors) has been deposited with the Cambridge Crystallographic Data Centre as supplementary publication CCDC-936826 for $Ph_2P(O)H$, CCDC-936827 for **1**, CCDC-936828 for **2**, CCDC-936829 for **3**, CCDC-936830 for **4**, CCDC-936831 for **5**, CCDC-936832 for **6**, CCDC-936833 for **7**, CCDC-936834 for **8**, CCDC-936835 for **9**, CCDC-936836 for **10**, and CCDC-936837 for **11**. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [E- mail: deposit@ccdc.cam.ac.uk].

Supplementary Material

Molecular structures and numbering schemes of compounds **1**–**4**, **6**, **7**, and **9**–**11** are available on the Journal's website.

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