N-Cyano-*P*-hydrogenoiminophosphorane–Trimethylchlorostannane Adducts [$R_2P(H)$=N–C≡N·Me_3SnCl] and Related Species: Building Blocks for Bis(carbodiimides) of Phosphorus

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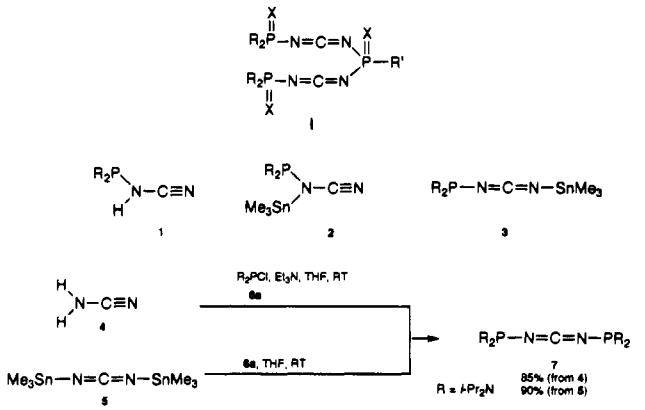
Trimethylstannylcyanamide (**8**) reacts with bis(dialkylamino)chlorophosphanes and (dialkylamino)dichlorophosphanes affording Me_3SnCl adducts of *N*-cyano-*P*-hydrogenoiminophosphoranes **9a,b** (90–95% yield), and bis-Me_3SnCl adducts of *N*-cyano-*P*-hydrogeno-*P*-cyanamidoiminophosphoranes **14a–c** (78 to 92% yield), respectively. Addition of elemental sulfur to **9a** and **14a–c** leads to the Me_3SnCl adducts of [bis(diisopropylamino)-thioxophosphoranyl]cyanamide **10a** (70% yield) and bis(cyanamido)thioxophosphoranes **15a–c** (75–86% yield), respectively. Derivative **10a** reacts with $^1/_2$ equiv of (dichlorophenyl)oxophosphorane giving bis[bis(diisopropylamino)thioxophosphoranylcarbodiimido]phenyloxophosphorane (**13a**) (82% yield), whereas **15c** reacts with 2 equiv of bis(diisopropylamino)chlorophosphane affording bis[bis(diisopropylamino)thioxophosphoranylcarbodiimido]-(diethylamino)thioxophosphorane (**16c**) (90% yield).

Introduction

Carbodiimides are versatile heterocumulene derivatives for organic synthesis,[1] important biological tools,[1,2] well-known ligands in organometallic chemistry,[3] and have found many industrial applications such as stabilizers and crosslinkers for polymers.[1,4] Main group element substituted carbodiimides possess specific properties due to the electronic interaction between the NCN moiety and the heteroatom.[1,5] In fact the structure of heteroatom substituted carbodiimides is intimately related to that of their cyanamide isomers. Depending on the degree of steric hindrance imposed by the substituents, they can be in a tautomeric equilibrium;[1a,6] an extreme example being the bis(trimethylstannyl)carbodiimide which, according to an X-ray crystal diffraction study, has a structure intermediate between that of a carbodiimide, a cyanamide and an ionic derivative.[7] In this paper, we wish to report evidence for a novel prototropic equilibrium between phosphanylcyanamides and *N*-cyano-*P*-hydrogeno iminophosphoranes. These species are key intermediates in the high yield synthesis of bis(carbodiimides) of phosphorus **I**, which are target molecules as cross-linking agents (Scheme 1).

Scheme 1



Results and Discussion

We have recently shown that (silyl)(stannyl)carbodiimides react with dichlorophosphanes to give the corresponding phosphorus-bridged bis(silylcarbodiimides).[8] However, in these compounds, the nitrogen–silicon bonds are inert toward electrophiles, preventing further substitutions. *N*-Hydrogeno and *N*-stannylcyanamides as well as stannylcarbodiimides are known to react with electrophiles giving the corresponding carbodiimides.[1,5b] Therefore, the phosphanylcyanamides **1** or **2** and -carbodiimide **3** were envisaged to be the potential precursors of **I** (Scheme 1).

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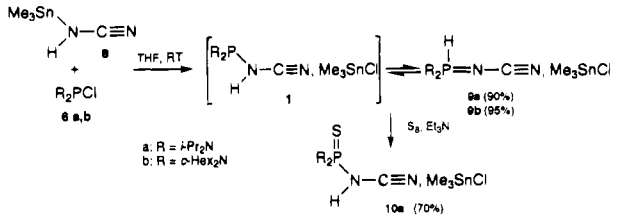
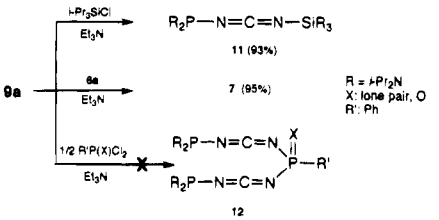
Scheme 2



Scheme 3



All attempts to obtain one of these derivatives by reacting an equivalent of bis(diisopropylamino)chlorophosphane (**6a**) with cyanamide (**4**) or bis(trimethylstannyl)carbodiimide (**5**)[7,8] failed; in both cases, the bis[bis(diisopropylamino)phosphanyl]-carbodiimide (**7**) was isolated in 85 and 90% yield (based on the chlorophosphane), along with unreacted cyanamide (**4**) and carbodiimide **5**, respectively (Scheme 1). The structure of **7** was clearly indicated by the presence in the ^{13}C NMR spectrum of a triplet at 129.02 (J_{PC} = 16.1 Hz) for the NCN carbon atom and by a strong infra-red absorption at 2126 cm^{-1}; furthermore addition of elemental sulfur to **7** quantitatively gave the bis-[bis(diisopropylamino)thioxophosphoranyl]carbodiimide.[9] To the best of our knowledge, **7** is the first stable carbodiimide bearing two λ^3,σ^3-phosphorus substituents;[1a,10] its stability is probably due to the presence of the bulky diisopropylamino groups.

Since it was not possible to prepare unsymmetrical phosphanylcyanamides **1** and **2** or phosphanylcarbodiimide **3** starting from the symmetrical derivatives **4** and **5**, we chose to investigate the reactivity of the trimethylstannylcyanamide (**8**)[11] toward chlorophosphanes. Bis(amino)chlorophosphanes **6a** and **6b** reacted with **8** at −40 °C affording *N*-cyano-*P*-hydrogenoiminophosphoranes **9a** and **9b** in 90 and 95% yield, respectively (Scheme 2). The presence of a PH bond was indicated by a large coupling constant [**9a**: J_{PH} = 560.1; **9b**: 573.2 Hz], while the existence of the P=N−C≡N sequence was supported by the presence of doublets for the NCN [**9a**: 116.81, J_{PC} = 5.6 Hz; **9b**: 116.17, J_{PC} = 6.7 Hz] in the ^{13}C NMR spectra, and strong absorptions in the IR spectra at 2183 cm^{-1} (**9a** and **9b**); these spectroscopic data compare well with those reported for $Ph_3P{=}N{-}C{\equiv}N$ (^{13}C NMR: 118.2; IR: 2172 cm^{-1}).[12] In fact, **9** exist as neutral 1/1 adducts with trimethylchlorostannane as indicated by multinuclear NMR spectroscopy and elemental analysis, and not as an ionic compound of the type $(R_2N)_2HP^+{-}N{=}C{=}N{-}SnMe_3$, Cl^- since **9** were found not to be electrolytes. No phosphorus−tin coupling was observed in the ^{31}P and ^{119}Sn NMR spectra, thus the tin atom is probably bonded to the nitrile nitrogen as already proposed for the $R_2N{-}C{\equiv}N$, Ph_3SnBr adducts.[13]

The formation of **9** deserves some comment. It is quite likely that the phosphanylcyanamide **1** is the precursor of **9**. Indeed, it is well established that the PH-iminophosphorane form is preferred over the NH-aminophosphane form when the phosphorus atom bears electron donating substituents and the nitrogen atom a withdrawing substituent.[14] In other words, **9** is the stable tautomeric form of the bis(amino)phosphanyl-cyanamides **1**. Interestingly, **9a** reacted with elemental sulfur, in the presence of triethylamine, to afford the [bis(diisopropylamino)thioxophosphoranyl]cyanamide, Me_3SnCl adduct (**10a**) in 70% yield. This result strongly suggests that **9a** and **1** are in equilibrium since it is very unlikely that **9a** could react directly with elemental sulfur, while sulfuration of a phosphane is a classical reaction.

Compound **9a** is not deprotonated by strong bases such as DBN but, not surprisingly, is reactive towards electrophiles. In the presence of triethylamine, **9a** reacted with chlorotriisopropylsilane and bis(diisopropylamino)chlorophosphane (**6a**) affording carbodiimides **11** (93% yield)[8] and **7** (95% yield), respectively (Scheme 3). Derivative **9a** also reacted with dichlorophenylphosphane or dichlorophenyloxophosphorane but led to a mixture of unidentified polymers, rather than to the desired bis(carbodiimide) **12**.

Since phosphanylcarbodiimides are rather unstable toward polymerization, it was thus of interest to directly synthesize biscarbodiimides featuring λ^5-phosphorus substituents (**I**, X = O, S), the [bis(diisopropylamino)thioxophosphoranyl]cyanamide−Me_3SnCl adduct **10a** being the ideal precursor. The bis[bis-(diisopropylamino)thioxophosphoranylcarbodiimido]oxophosphorane (**13a**) was obtained in 82% yield by reacting **10a** with $^1/_2$ equiv of dichlorophenyloxophosphorane. The structure of **13a** was supported by the presence in the ^{31}P NMR spectrum of a triplet at −2.12 and a doublet at +48.93 (J_{PP} = 4.1 Hz), a pseudo-triplet at 125.96 (J_{PC} =10.4 Hz) in the ^{13}C NMR spectrum (NCN), and a broad absorption in the IR spectrum at 2144 cm^{-1}. Note that this bis(carbodiimide)oxophosphorane **13a** polymerized in the solid state when stored for a week, even at −30 °C under an inert atmosphere.

Using this synthetic route, the bridging phosphorus atom is introduced at the end of the reaction sequence. We found, that starting from the same building block **8**, it was also possible to introduce the bridging phosphorus atom first. Addition of half an equivalent of dichloro(diethylamino)phosphane to **8** afforded derivative **14c** in 92% yield, according to ^{31}P NMR spectroscopy. The presence of the P−H bond is obvious from the large J_{PH} coupling constant (620.8 Hz); only one signal is observed in the ^{13}C NMR spectrum for the two NCN carbon atoms (118.12 ppm, J_{PC} = 2.8 Hz), and the NH is not observed by ^1H NMR or infrared spectroscopy, clearly indicating that the NH hydrogen atom is in rapid exchange between the two nitrogen atoms. Addition of elemental sulfur to **14c**, in the presence of triethylamine, afforded bis(cyanamide)thioxophosphorane as its Me_3SnCl adduct **15c** in 75% yield (according to ^{31}P NMR spectroscopy). These two compounds **14c** and **15c** are very unstable toward polymerization, all efforts to obtain them in pure form failed. Attempts to increase the stability of such derivatives by increasing the bulk of the phosphorus substituents also failed; the bis(diisopropylamino) (**14a**) and bis(dicyclohexylamino) (**14b**) analogs of **14c** have only been characterized by ^{31}P NMR spectroscopy, while derivatives **15a** and **15b** have been characterized by multinuclear NMR and infrared spectroscopy, in solution. Bis[bis(diisopropylamino)thioxophosphoranylcarbodiimido](diethylamino)thioxophosphorane (**16c**)

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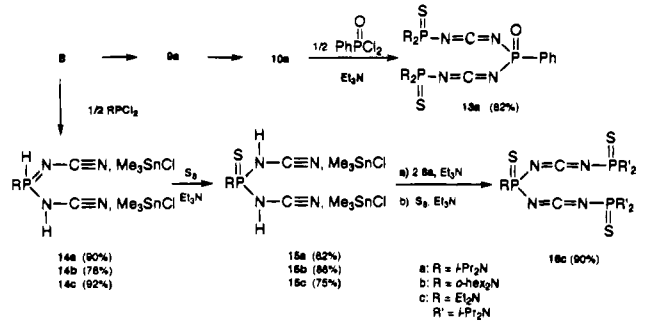
Scheme 4



was obtained in 90% isolated yield by adding 2 equiv of chlorophosphane **6a** to **15c**, followed by treatment with elemental sulfur. Note that a one-pot reaction starting from **8** afforded **16c** in 80% overall yield (Scheme 4).

In conclusion, the trimethylstannylcyanamide is an efficient and selective NH−CN transfer agent compared to the parent cyanamide. It is likely that phosphanylcyanamides exist as *N*-cyano-*P*-hydrogenoiminophosphoranes, which are powerful precursors of carbodiimides. The cross linker properties of phosphorus-substituted biscarbodiimides are under active investigation.

Experimental Section

All experiments were performed in an atmosphere of dry argon. Melting points are uncorrected. ^1H, ^{13}C, ^{31}P and ^{119}Sn NMR spectra were recorded on Brucker AC80, AC200, or WM250 spectrometers. ^1H and ^{13}C chemical shifts are reported in ppm relative to Me_4Si as external standard. ^{31}P and ^{119}Sn NMR downfield chemical shifts are expressed with a positive sign, in ppm, relative to external 85% H_3PO_4 and Me_4Sn, respectively. Infrared spectra were recorded on a Perkin-Elmer FT-IR Spectrometer 1725 X. Mass spectra were obtained on a Ribermag R10 10E instrument. Conventional glassware was used.

Bis[bis(diisopropylamino)phosphanyl]carbodiimide (7) from 4. A THF solution (10 mL) of bis(diisopropylamino)chlorophosphane (**6a**)[15] (1.00 g; 3.75 mmol) was added dropwise, at room temperature, to a THF solution (10 mL) of cyanamide (**4**) (0.079 g; 1.88 mmol) and triethylamine (0.560 mL; 4.02 mmol). The solution was stirred for 3 h at room temperature, filtered, and the solvent and excess triethylamine removed under vacuum. The residue was washed three times with pentane (3 × 5 mL), affording **7** as a white solid (0.803 g; 85%): mp 89 °C; ^1H NMR ($CDCl_3$): δ 1.08 (d, J_{HH} = 6.8 Hz, 24 H, CH_3), 1.12 (d, J_{HH} = 6.8 Hz, 24 H, CH_3), 3.45 (sept d, J_{HH} = 6.7 Hz, J_{PH} = 11.7 Hz, 8 H, CH); ^{13}C NMR ($CDCl_3$) δ 23.67 (s, CH_3), 23.79 (s, CH_3), 45.25 (d, J_{PC} = 12.8 Hz, CH), 129.02 (t, J_{PC} = 16.1 Hz, NCN); ^{31}P NMR ($CDCl_3$) +84.09; IR (THF, ν(cm^{-1})) 2126 (NCN). Anal. Calcd for $C_{25}H_{56}N_6P_2$: C, 59.80; H, 11.15; N, 16.73. Found: C, 59.76; H, 11.22; N, 16.68.

Bis[bis(diisopropylamino)phosphanyl]carbodiimide (7) from 5. A THF solution (10 mL) of chlorophosphane **6a** (0.650 g; 2.44 mmol) was added dropwise, at room temperature, to a THF solution (10 mL) of bis(trimethylstannyl)carbodiimide **5**[7,8] (0.45 g; 1.22 mmol). After the solution was stirred for 30 min at room temperature, the solvent and chlorotrimethylstannane were removed under vacuum (overnight, room temperature, 10^{-2} mmHg). **7** was obtained as a white solid (0.550 g; 90%): mp 89 °C.

Trimethylstannylcyanamide (8). A THF solution (5 mL) of chlorotrimethylstannane (1.00 g; 5.02 mmol) was added dropwise at −80 °C to a THF solution (10 mL) of cyanamide **4** (0.211 g; 5.02 mmol) and triethylamine (0.710 mL; 5.09 mmol). The solution was filtered and, for most synthetic purposes, **8**[11] could be used without any further purification. However, after removal of the solvent and treatment of the residue with pentane, **8** could be obtained as a white solid (0.940 g; 91%): mp 108 °C; ^1H NMR ($CDCl_3$): δ 0.17 (s, $J_{^{117}SnH}$ = 65.8 Hz, $J_{^{119}SnH}$ = 69.5 Hz, 9 H, $SnCH_3$), 6.60 (s, 1 H, NH); ^{13}C NMR ($CDCl_3$) δ 0.510 (s, $J_{^{117}SnC}$ = 489.9 Hz, $J_{^{119}SnC}$ = 514.7 Hz, $SnCH_3$), 123.90 (s, NCN); ^{119}Sn NMR ($CDCl_3$) −28.55 (1.6 M); IR (THF, ν(cm^{-1})): 2176 (NCN).

***N*-Cyano-*P*-hydrogenoiminophosphorane−Me_3SnCl Adduct (9a).** A THF solution (10 mL) of chlorophosphane **6a** (0.944 g; 3.54 mmol) was added dropwise at −40 °C to a THF solution (10 mL) of (trimethylstannyl)cyanamide (**8**) (0.725 g; 3.54 mmol). The solution was allowed to warm to room temperature and the solvent was removed under vacuum (overnight, room temperature, 10^{-2} mmHg). The residue was washed three times with pentane (3 × 5 mL) and **9a** was obtained as a pale yellow solid (1.502 g; 90%): mp 93 °C; ^1H NMR ($CDCl_3$): δ 0.58 (s, $J_{^{117}SnH}$ = 64.4 Hz, $J_{^{119}SnH}$ = 67.1 Hz, 9 H, $SnCH_3$), 1.21 (d, J_{HH} = 6.8 Hz, 12 H, CH_3), 1.29 (d, J_{HH} = 6.8 Hz, 12 H, CH_3), 3.55 (sept d, J_{HH} = 6.8 Hz, J_{PH} = 18.1 Hz, 4 H, CH), 7.26 (d, J_{PH} = 560.1 Hz, 1 H, PH); ^{13}C NMR ($CDCl_3$) δ 3.20 (s, $J_{^{117}SnC}$ = 487.3 Hz, $J_{^{119}SnC}$ = 509.9 Hz, $SnCH_3$), 22.05 (d, J_{PC} = 1.4 Hz, CH_3), 23.32 (d, J_{PC} = 2.2 Hz, CH_3), 45.26 (d, J_{PC} = 6.1 Hz, CH), 116.81 (d, J_{PC} = 5.6 Hz, NCN); ^{31}P NMR ($CDCl_3$) +7.75; ^{119}Sn NMR ($CDCl_3$) +9.13 (1 M), +40.1 (0.5 M); IR (THF, ν(cm^{-1})) 2183 (NCN); CIMS (*m/z*) 273 (M^+ + 1-Me_3SnCl). Anal. Calcd for $C_{16}H_{38}N_4ClPSn$: C, 40.78; H, 8.06; N, 11.89. Found: C, 40.79; H, 8.04; N, 11.89.

***N*-Cyano-*P*-hydrogenoiminophosphorane−Me_3SnCl Adduct (9b).** The procedure described for **9a** was used starting from bis(dicyclohexylamino)chlorophosphane **6b**[16] (1.00 g; 2.35 mmol), and **9b** was characterized in solution (95% yield): ^1H NMR ($CDCl_3$): δ 0.60 (s, $J_{^{117}SnH}$ = 63.8 Hz, $J_{^{119}SnH}$ = 66.2 Hz, 9 H, $SnCH_3$), 1.01−1.77 (m, 40 H, CH_2), 3.05 (m, 4 H, NCH), 7.29 (d, J_{PH} = 573.2 Hz, 1 H, PH); ^{13}C NMR ($CDCl_3$) δ 1.27 (s, $J_{^{117}SnC}$ = 450.7 Hz, $J_{^{119}SnC}$ = 471.2 Hz, $SnCH_3$), 24.46 (s, CH_2), 25.77 (s, CH_2), 32.22 (d, J_{PC} = 1.5 Hz, CH_2), 33.43 (d, J_{PC} = 2.0 Hz, CH_2), 54.28 (d, J_{PC} = 5.5 Hz, CH), 116.17 (d, J_{PC} = 6.7 Hz, NCN); ^{31}P NMR ($CDCl_3$) +8.45; ^{119}Sn NMR ($CDCl_3$) +48.83 (0.6 M), IR (CH_2Cl_2, ν(cm^{-1})) 2183 (NCN).

[Bis(diisopropylamino)thioxophosphoranyl]cyanamide−Me_3SnCl Adduct (10a). To a THF solution (10 mL) of **9a** (0.693 g; 1.47 mmol) and triethylamine (0.210 mL; 1.50 mmol), was added elemental sulfur (0.049 g; 1.53 mmol) at room temperature. The solution was stirred for 1 h at room temperature and filtered. Triethylamine and the solvent were removed under vacuum. The residue was washed three times with pentane (3 × 5 mL) and **12a** was obtained as a pale yellow solid (0.518 g; 70%): mp 70 °C dec; ^1H NMR ($CDCl_3$): δ 0.43 (s, $J_{^{117}SnH}$ = 64.2 Hz, $J_{^{119}SnH}$ = 66.9 Hz, 9 H, $SnCH_3$), 1.04 (d, J_{HH} = 6.8 Hz, 12 H, CH_3), 1.09 (d, J_{HH} = 6.8 Hz, 12 H, CH_3), 3.41 (sept d, J_{HH} = 6.8 Hz, J_{PH} = 19.2 Hz, 4 H, CH), 9.97 (broad s, 1 H, NH); ^{13}C NMR ($CDCl_3$) δ 2.13 (s, $J_{^{117}SnC}$ = 463.1 Hz, $J_{^{119}SnC}$ = 489.9 Hz, $SnCH_3$), 22.13 (d, J_{PC} = 1.7 Hz, CH_3), 22.81 (d, J_{PC} = 2.3 Hz, CH_3), 45.73 (d, J_{PC} = 6.0 Hz, CH), 127.02 (d, J_{PC} = 8.6 Hz, NCN); ^{31}P NMR ($CDCl_3$) +58.38; ^{119}Sn NMR ($CDCl_3$) +23.15; IR (CH_2Cl_2, ν(cm^{-1})) 2140 (NCN); FABMS (thioglycol) (*m/z*) 305 (M^+ + 1-Me_3SnCl). Anal. Calcd for $C_{16}H_{38}N_4ClPSSn$: C, 38.18; H, 7.55; N, 11.13. Found: C, 38.11; H, 7.49; N, 11.07.

[Bis(diisopropylamino)phosphanyl](triisopropylsilyl)carbodiimide (11).[8] A THF solution (10 mL) of chlorotriisopropylsilane (0.214 mL; 1.00 mmol) was added dropwise at room temperature to a THF solution (10 mL) of **9a** (0.470 g; 1.00 mmol) and triethylamine (0.153 mL; 1.09 mmol). The solution was stirred for 1 h at room temperature and filtered. Excess triethylamine, the solvent and trimethylchlorostannane were removed under vacuum (overnight, room temperature, 10^{-2} mmHg). The residue was washed three times with pentane (3 × 5 mL) and **10a** was obtained in 93% yield, according to ^{31}P NMR spectroscopy. After treatment with elemental sulfur the corresponding [bis(diisopropylamino)thioxophosphoranyl](triisopropylsilyl)carbodiimide[9] was isolated in 85% yield based on **9a**.

Bis[bis(diisopropylamino)phosphanyl]carbodiimide (7) from 9a. The procedure described for **10a** was used starting from chlorophosphane **6a** (0.267 g; 1.00 mmol) instead of chlorotriisopropylsilane. After three washings with pentane (3 × 5 mL) **7** was obtained as a white solid in 95% yield: mp 89 °C.

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Bis[bis(diisopropylamino)thioxophosphoranylcarbodiimido]-phenyloxophosphoranyl (13a). A THF solution (10 mL) of dichlorophenyloxophosphorane (0.056 mL; 0.39 mmol) was added dropwise at room temperature to a THF solution (10 mL) of **10a** (0.392 g; 0.78 mmol) and triethylamine (0.139 mL; 1.00 mmol). The solution was stirred for 1 h at room temperature and filtered; then the excess triethylamine, the solvent and chlorotrimethylstannane were removed under vacuum (overnight, room temperature, 10^{-2} mmHg). The residue was washed with pentane (3 × 10 mL), and **13a** was isolated as a viscous pale yellow oil (0.234 g; 82%); ^{1}H NMR ($CDCl_3$): δ 1.10 (d, J_{HH} = 6.8 Hz, 12 H, CH_3), 1.13 (d, J_{HH} = 6.8 Hz, 12 H, CH_3), 1.19 (d, J_{HH} = 6.8 Hz, 12 H, CH_3), 1.21 (d, J_{HH} = 6.8 Hz, 12 H, CH_3), 3.50 (sept d, J_{HH} = 6.8 Hz, J_{PH} = 20.8 Hz, 4 H, NCH), 3.55 (sept d, J_{HH} = 6.8 Hz, J_{PH} = 20.8 Hz, 4 H, NCH), 7.35−7.51 (m, 3 H, CH), 7.84−7.97 (m, 2 H, CH); ^{13}C NMR ($CDCl_3$) δ 21.91 (s, CH_3), 22.06 (s, CH_3), 46.50 (d, J_{PC} = 5.0 Hz, NCH), 125.96 (t-like, J_{PC} = 10.4 Hz, NCN), 128.58 (d, J_{PC} = 16.4 Hz, Caro), 130.51 (d, J_{PC} = 11.7 Hz, Caro), 132.88 (d, J_{PC} = 44.6 Hz, Cipso), 133.00 (d, J_{PC} = 2.8 Hz, Caro); ^{31}P NMR ($CDCl_3$) −2.12 (t, J_{PP} = 4.1 Hz, PO), +48.93 (d, J_{PP} = 4.1 Hz, PS); IR (CH_2Cl_2, ν(cm^{-1})) 2144 (NCN); CIMS (*m/z*) 731 (M^+ + 1). Anal. Calcd for $C_{32}H_{61}N_8OP_3S_2$: C, 52.62; H, 8.35; N, 15.34. Found: C, 52.58; H, 8.38; N, 15.29.

General Procedure for the Preparation of Derivatives 14. A THF solution (10 mL) of dialkylaminodichlorophosphane (1.90 mmol) was added dropwise at −60 °C to a THF solution (10 mL) of trimethylstannylcyanamide **8** (0.778 g; 3.80 mmol). The solution was allowed to warm to room temperature and the solvent was removed under vacuum (overnight, room temperature, 10^{-2} mmHg). The residue was washed three times with pentane (3 × 5 mL). Derivatives **14** were obtained as yellow oils, and characterized in solution.

14a: (90% yield) ^{31}P NMR ($CDCl_3$) +7.20 (J^1_{PH} = 606.4, J^3_{PH} =17.9 Hz).

14b: (78% yield) ^{31}P NMR ($CDCl_3$) +6.89 (J^1_{PH} = 607.5, J^3_{PH} =17.2 Hz).

14c: (92% yield) ^{1}H NMR ($CDCl_3$): δ 0.52 (s, $J_{^{117}SnH}$ = 64.6 Hz, $J_{^{119}SnH}$ = 67.4 Hz, 18 H, $SnCH_3$), 1.08 (t, J_{HH} = 7.2 Hz, 6 H, CH_3CH_2), 2.98 (qua d, J_{HH} = 7.2 Hz, J_{PH} = 11.4 Hz, 4 H, CH_2), 6.80 (d, J_{PH} = 620.8 Hz, 1 H, PH), the NH is not observed; ^{13}C NMR ($CDCl_3$) δ 1.05 (s, $J_{^{117}SnC}$ = 481.6 Hz, $J_{^{119}SnC}$ = 504.4 Hz, $SnCH_3$), 14.37 (d, J_{PC} = 2.5 Hz, CH_3CH_2), 39.85 (d, J_{PC} = 5.9 Hz, CH_2), 118.12 (d, J_{PC} = 2.8 Hz, NCN); ^{31}P NMR ($CDCl_3$) +12.93; ^{119}Sn NMR ($CDCl_3$) +44.10 (0.2 M); IR (CH_2Cl_2, ν(cm^{-1})) 2183 cm^{-1} (NCN).

General Procedure for the Preparation of Bis(cyanamide)-thioxophosphorane−Me_3SnCl adducts (15). To a THF solution (10 mL) of **14** (1.60 mmol), and triethylamine (0.210 mL; 1.50 mmol), elemental sulfur (0.053 g; 1.65 mmol) was added at room temperature. The solution was stirred for 1 h at room temperature and filtered. Triethylamine and the solvent were removed under vacuum. The residue was washed three times with pentane (3 × 5 mL), and derivatives **15** were obtained as pale yellow oils, and characterized in solution.

15a: (82%) ^{1}H NMR ($CDCl_3$): δ 0.42 (s, J_{SnH} = 64.2 Hz, 18 H, $SnCH_3$), 0.99 (d, J_{HH} = 6.4 Hz, 12 H, CH_3CH), 3.38 (sept d, J_{HH} = 6.4 Hz, J_{PH} = 20.8 Hz, 2 H, CH), 8.75 (broad s, 2 H, NH); ^{13}C NMR ($CDCl_3$) δ 2.21 (s, $J_{^{117}SnC}$ = 445.6 Hz, $J_{^{119}SnC}$ = 466.2 Hz, $SnCH_3$), 22.99 (d, J_{PC} = 1.9 Hz, CH_3CH), 46.78 (d, J_{PC} = 5.3 Hz, CH), 120.56 (d, J_{PC} = 2.8, NCN); ^{31}P NMR ($CDCl_3$) +44.17; ^{119}Sn NMR ($CDCl_3$) −0.55 (0.5 M); IR (CH_2Cl_2, ν(cm^{-1})) 2156 cm^{-1} (NCN).

15b: (86%) ^{1}H NMR ($CDCl_3$): δ 0.52 (s, $J_{^{117}SnH}$ = 62.0 Hz, $J_{^{119}SnH}$ = 64.8 Hz, 18 H, $SnCH_3$), 0.90−1.80 (m, 20 H, CH_2), 3.02 (m, 2 H, CH), the NH atom is not observed; ^{13}C NMR ($CDCl_3$) δ 0.48 (s, $J_{^{117}SnC}$ = 435.3 Hz, $J_{^{119}SnC}$ = 455.5 Hz, $SnCH_3$), 24.87 (s, CH_2), 26.02 (s, CH_2), 32.10 (s, CH_2), 56.02 (d, J_{PC} = 5.0, CH), 119.96 (d, J_{PC} = 2.9 Hz, NCN); ^{31}P NMR ($CDCl_3$) +43.95; IR (CH_2Cl_2, ν(cm^{-1})) 2159 cm^{-1} (NCN).

15c: (75%) ^{1}H NMR ($CDCl_3$): δ 0.47 (s, $J_{^{117}SnH}$ = 64.1 Hz, $J_{^{119}SnH}$ = 66.2 Hz, 18 H, $SnCH_3$), 0.95 (t, J_{HH} = 7.0, 6 H, CH_3CH_2), 3.00 (qua d, J_{HH} = 7.2 Hz, J_{PH} = 13.5 Hz, 4 H, CH_2), 9.45 (broad s, 2 H, NH); ^{13}C NMR ($CDCl_3$) δ 1.86 (s, $J_{^{117}SnC}$ = 451.7 Hz, $J_{^{119}SnC}$ = 471.6 Hz, $SnCH_3$), 14.26 (d, J_{PC} = 3.3 Hz, CH_3CH_2), 40.17 (d, J_{PC} = 4.0 Hz, CH_2), 122.59 (d J_{PC} = 4.3 Hz, NCN); ^{31}P NMR ($CDCl_3$) +59.10; ^{119}Sn NMR ($CDCl_3$) +75.94 (0.2 M); IR ($CDCl_3$, ν(cm^{-1})) 2153 cm^{-1} (NCN).

Bis[bis(diisopropylamino)thioxophosphoranylcarbodiimido]-(diethylamino)thioxophosphorane (16c). A THF solution (10 mL) of chlorophosphane **6a** (0.517 g; 1.94 mmol) was added dropwise at 0 °C to a THF solution (10 mL) of **15c** (0.600 g; 0.97 mmol), triethylamine (0.280 mL; 2.00 mmol) and elemental sulfur (0.064 g; 2 mmol). The solution was allowed to warm to room temperature and filtered. Excess triethylamine, the solvent and chlorotrimethylstannane were removed under vacuum (overnight, room temperature, 10^{-2} mmHg). The residue was washed with pentane (3 × 10 mL), and **16c** was isolated as a pale yellow viscous oil (0.647 g; 90%); ^{1}H NMR ($CDCl_3$): δ 1.12 (m, 54 H, CH_2CH_3, and $CHCH_3$), 3.15 (qua d, J_{HH} = 6.9 Hz, J_{PH} = 15.0 Hz, 4 H, CH_2), 3.47 (sept d, J_{HH} = 6.9 Hz, J_{PH} = 20.6 Hz, 8 H, CH); ^{13}C NMR ($CDCl_3$) δ 13.91 (d, J_{PC} = 5.0 Hz, CH_2CH_3), 21.93 (d, J_{PC} = 2.0 Hz, $CHCH_3$), 22.28 (d, J_{PC} = 2.6 Hz, $CHCH_3$), 40.66 (d, J_{PC} = 4.8 Hz, CH_2), 46.31 (d, J_{PC} = 5.6 Hz, CH), 128.21 (t-like, J_{PC} = 11.6 Hz, NCN); ^{31}P NMR ($CDCl_3$) +42.55 (t, J_{PP} = 4.9 Hz, Et_2NPS), +50.33 (d, J_{PP} = 4.9 Hz, *i*-Pr_2NPS); IR (THF, ν(cm^{-1})) 2137 (NCN); CIMS (*m/z*) 742 (M^+ + 1). Anal. Calcd for $C_{30}H_{66}N_9P_3S_3$: C, 48.59; H, 8.90; N, 17.00. Found: C, 48.58; H, 8.88; N, 16.95.

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