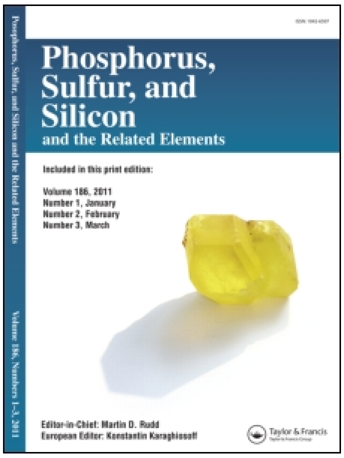

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BIS- AND TRIS-*N*-CYANO- AND *N*-SULFAMIDOPHOSPHA-λ^5-AZENES FROM A REDOX-CONDENSATION REACTION AND THE NOVEL REACTION OF SULFAMIDE WITH BIS(DIPHENYLPHOSPHINO)METHANE

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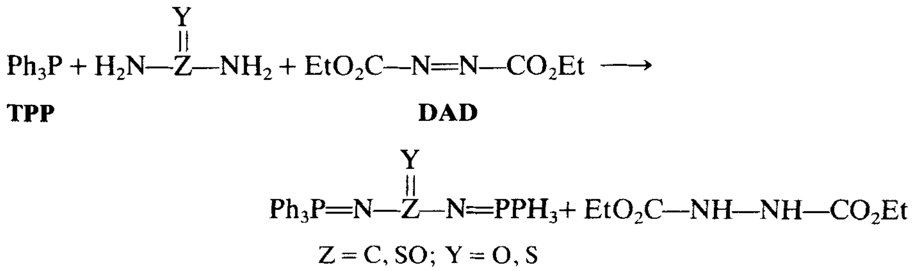
Cyanamide (**3**) has been shown to react with 1,2-bis(diphenylphosphino)ethane (**8**), 1,3-bis(diphenylphosphino)propane (**9**) and bis(2-diphenylphosphinoethyl)phenylphosphine (**10**) in the presence of diethyl azodicarboxylate (DAD) to produce, in good yields, the corresponding bis- and tris-*N*-cyanophospha-λ^5-azenes, 1,2-bis(*N*-cyanodiphenylphospha-λ^5-azeno)ethane (**11**), 1,3-bis(*N*-cyanodiphenylphospha-λ^5-azeno)propane (**12**) and *N*-cyano-bis[2-(*N*-cyanodiphenylphospha-λ^5-azeno)ethyl]phenylphospha-λ^5-azene (**13**) respectively. Sulfamide (**6**) has been shown to react with bis(diphenylphosphino)methane (**1**) and DAD to give [(*N*-sulfamidodiphenylphospha-λ^5-azeno)methyl]diphenylphosphine oxide (**14**) in 69% yield and the cyclic system, 3,3,5,5-tetraphenyl-4H-1,2,6,3λ^5,5λ^5-thiadiazadiphosphorin-1,1-dioxide (**7**), in 6% yield. It is postulated that there is a special, as yet unidentified, intramolecular effect which is operative in producing **14** and is most likely sterically related to the intramolecular effect we recently observed in the reaction of **1** with urea and DAD, which produced an anomalous product. The isolation of the cyclic molecule **7** is the first time a ring system has been observed in the oxidation-reduction condensation system involving a bis-phosphine, bis-amide and DAD. Reaction of bis- and tris-phosphines **8**, **9** and **10** with sulfamide (**6**) and DAD produce, again in good yields, the phospha-λ^5-azenes, 1,2-(bis-*N*-sulfamidodiphenylphospha-λ^5-azeno)ethane (**18**), 1,3-(bis-*N*-sulfamidodiphenylphospha-λ^5-azeno)propane (**19**) and *N*-sulfamido-bis[2-(*N*-sulfamidodiphenylphospha-λ^5-azeno)ethyl]phenylphospha-λ^5-azene (**20**), respectively.

Key words: *N*-cyanophospha-λ^5-azenes; *N*-sulfamidophospha-λ^5-azenes, cyclic bis-phospha-λ^5-azene, mono-*N*-sulfamidophospha-λ^5-azene-mono-phosphine oxide

INTRODUCTION

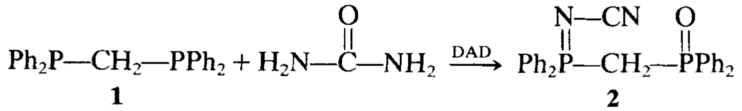
Our continuing interest in the synthesis and properties of phospha-λ^5-azene systems,[2–8] particularly the redox-condensation synthesis of such systems employing a phosphine, an amide and diethyl azodicarboxylate (DAD),[3,6–8] has recently led us to observe that urea, thiourea and sulfamide, all of which are bis-amides, could react with triphenylphosphine (TPP) and DAD to produce bis-phospha-λ^5-azenes (equation 1).[8] Further, we also showed that the reaction of urea with bis(diphenylphosphino)methane (**1**) provided an anomalous product, **2**, shown in



$$\underset{\textbf{TPP}}{Ph_3P} + H_2N-\overset{\overset{\displaystyle Y}{\|}}{Z}-NH_2 + \underset{\textbf{DAD}}{EtO_2C-N{=}N-CO_2Et} \longrightarrow$$

$$Ph_3P{=}N-\overset{\overset{\displaystyle Y}{\|}}{Z}-N{=}PPH_3 + EtO_2C-NH-NH-CO_2Et \quad (1)$$

$Z = C, SO;\ Y = O, S$



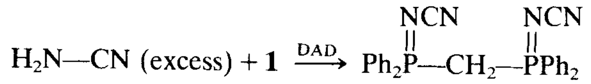
$$Ph_2P-CH_2-PPh_2 + H_2N-\overset{\overset{\displaystyle O}{\|}}{C}-NH_2 \xrightarrow{DAD} Ph_2\overset{\overset{\displaystyle N-CN}{\|}}{P}-CH_2-\overset{\overset{\displaystyle O}{\|}}{P}Ph_2 \quad (2)$$

1 **2**

equation 2.[8] In addition, we demonstrated that cyanamide (**3**) reacted readily with DAD and triphenylphosphine to give *N*-cyanotriphenylphospha-λ^5-azene

$$\underset{\mathbf{3}}{H_2N-CN} + TPP \xrightarrow{DAD} \underset{\mathbf{4}}{Ph_3P = N-CN} \quad (3)$$

(**4**; eqn. 3), and that a large excess of **3** reacted with bis-phosphine **1** and DAD to give the bis-phospha-λ^5-azene, **5** (eqn. 4).[8]

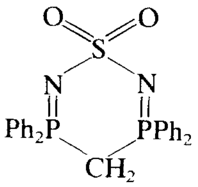


$$\underset{\mathbf{3}}{H_2N-CN} \text{ (excess)} + \mathbf{1} \xrightarrow{DAD} \underset{\mathbf{5}}{Ph_2\overset{\overset{\displaystyle NCN}{\|}}{P}-CH_2-\overset{\overset{\displaystyle NCN}{\|}}{P}Ph_2} \quad (4)$$

As a result of these observations we have now examined, and report on, the reactions of cyanamide (**3**) with other bis- and tris-phosphines to see if the reaction is general. Further, we have explored whether this reaction with bis- and tris-phosphines could be extended to sulfamide (**6**) as the bis-amide. We were particularly interested to see if the reaction of **1**, **6** and DAD would be anomalous, as it had been with urea, and also whether the cyclic bis-phospha-λ^5-azene (**7**) could be obtained. Cyclic molecules have not previously been observed in reactions of bis-phosphines with bis-amides and DAD.

$H_2N-SO_2-NH_2$

6



7

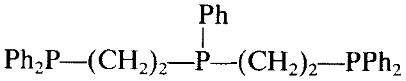
RESULTS AND DISCUSSION

Reactions of bis- and tris-Phosphines with Cyanamide (**3**) *and DAD*

1,2-bis(Diphenylphosphino)ethane (**8**), 1,3-bis(diphenylphosphino)propane (**9**) and bis(2-diphenylphosphinoethyl)phenylphosphine (**10**) were reacted with a two

$Ph_2P{-}(CH_2)_n{-}PPh_2$

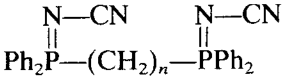
8: $n = 2$; **9**: $n = 3$



$$Ph_2P{-}(CH_2)_2{-}\underset{}{\overset{\displaystyle Ph}{\overset{|}{P}}}{-}(CH_2)_2{-}PPh_2$$

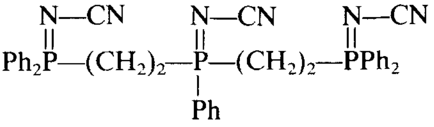
10

fold excess of cyanamide (**3**) and a somewhat lesser excess of DAD to produce in each case, the *N*-cyano bis- and tris-phospha-λ^5-azenes, 1,2-bis(*N*-cyanodiphenylphospha-λ^5-azeno)ethane (**11**), 1,3-bis(*N*-cyanodiphenylphospha-λ^5-azeno)propane (**12**) and *N*-cyano-bis[2(*N*-cyanodiphenylphospha-λ^5-azeno)ethyl]phenylphospha-λ^5-azene (**13**), respectively. The yields ranged from 68–84% and structure proofs rested on ^{1}H, ^{31}P and ^{13}C NMR and IR spectra (Table I) along with elemental analyses. Further, the spectra and melting points of compounds **11** and **12** were very similar to those reported.[9]



$$\overset{\displaystyle N{-}CN}{\overset{\|}{Ph_2P}}{-}(CH_2)_n{-}\overset{\displaystyle N{-}CN}{\overset{\|}{PPh_2}}$$

11: $n = 2$; **12**: $n = 3$



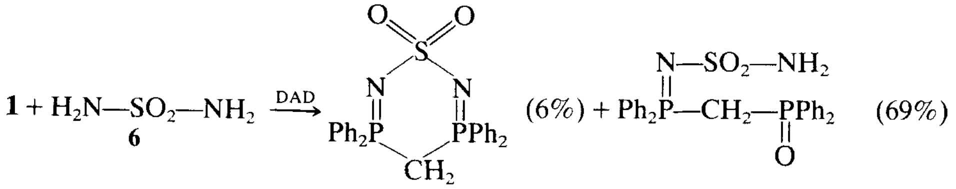
$$\overset{\displaystyle N{-}CN}{\overset{\|}{Ph_2P}}{-}(CH_2)_2{-}\underset{\displaystyle Ph}{\underset{|}{\overset{\displaystyle N{-}CN}{\overset{\|}{P}}}}{-}(CH_2)_2{-}\overset{\displaystyle N{-}CN}{\overset{\|}{PPh_2}}$$

13

Thus, the reactions of cyanamide (**3**) with DAD and phosphines appear to be straight forward in all cases. This is not, however, the situation with sulfamide.

Reactions of bis- and tris-Phosphines with Sulfamide (6) and DAD

Reaction of a two fold excess of sulfamide (**6**) with bis(diphenylphosphino)methane (**1**) and a slight excess of DAD provided two products in yields of 6% and 69%. The first was identified as the cyclic molecule, 3,3,5,5-tetraphenyl-4H-1,2,6,3λ^5,5λ^5-thiadiazadiphosphorin-1,1-dioxode (**7**) by comparison of its ^{31}P NMR and IR spectra and mp with those reported[10] (Table I). The second was shown to be the mono-phospha-λ^5-azene-mono-oxide, [(*N*-sulfamidodiphenylphospha-λ^5-azeno)methyl]diphenylphosphine oxide (**14**; eq. 5), on the basis of its ^{1}H, ^{31}P and ^{13}C NMR and IR spectra (Table I) and elemental analysis.



7 **14**

(5)

The production of these two compounds is rather interesting and unexpected. First, the formation of the cyclic molecule **7** represents the first time a cyclic system has been produced in one of these oxidation-reduction condensation reactions involving a bis-phosphine, a bis-amide and DAD. We have looked very carefully for cyclic molecules in other systems but have been unable to observe

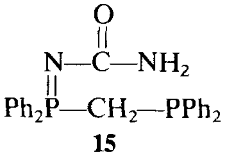
TABLE I

Spectral properties of bis- and tris-phospha-λ^5-azenes

Cmpd.	IR(cm^{-1})[a]		NMR[b]	
		^{31}P	^{1}H	^{13}C
11[c]	2175 (C≡N); 1437 (P—C); 1300 (P═N)	31.11	3.41(s, CH_2); 8.12–8.31 (m, ArH)	19.81 (p, CH_2, $^1J_{PC}+{}^2J_{PC} = 65.9$ Hz); 118.03 (s, CN); 126.08 (p, Ar-C_1, $^1J_{PC}+{}^4J_{PC} = 97.4$ Hz); 129.91 (t, Ar—C_3, $^3J_{PC}+{}^6J_{PC} = 12.5$ Hz); 131.77 (t, Ar—C_2, $^2J_{PC}+{}^5J_{PC} = 10.5$ Hz); 134.08 (s, Ar-C_4)
12[c]	2170(C≡N); 1435 (P—C); 1288 (P═N)	29.53	1.96 (m, CH_2); 2.66 (m, CH_2—P); 7.42-7.69 (m, ArH)	14.64 (t, CH_2, $^2J_{PC} = 3.5$ Hz); 27.24 (dd, CH_2—P; $^1J_{PC} = 69.6$ Hz, $^3J_{PC} = 11.1$ Hz); 118.60 (s, CN); 126.02 (d, Ar—C_1, $^1J_{PC} = 98.0$ Hz); 129.47 (d, Ar—C_3, $^3J_{PC} = 12.2$ Hz); 131.19 (d, Ar—C_2, $^2J_{PC} = 10.3$ Hz); 133.47 (Ar—C_4, $^4J_{PC} = 3.1$ Hz)
13	2180(C≡N); 1438(P—C); 1280[P═N (very br.)]	28.60 (d, Ph$_2$$P$); 37.52 (t, Ph$P$; $^3J_{PP} = 51.3$ Hz)	2.18–2.88 (m, CH_2); 7.48–7.81 (m, ArH)	20.40 (dd, CH_2, $^1J_{PC} = 67.7$, $^2J_{PC} = 4.1$ Hz); 20.71 (dm, CH_2, $^1J_{PC} = 63.7$ Hz); 122.27 (d, Ar—C_1, J = 96.3 Hz); 124.92 (dd, Ar—C_1, J = 99.8, 23.2 Hz); 129.75 (dd, Ar—C_3, J = 12.9, 7.2 Hz); 130.25 (d, Ar—C_3, J = 12.8 Hz); 131.31 (t, Ar—C_2, J = 10.5 Hz); 133.92 (dd, Ar—C_4, J = 6, 3 Hz); 134.52 (d, Ar—C_4, J = 2.6 Hz)
7[d]	1435 (P—C); 1243, 1173 (SO_2); 1115 (P═N); 820 (S—N)	10.24	4.10 (t, CH_2, $^2J_{PH} = 12$ Hz); 7.3-8.2 (m, ArH)	not obtained
14	1437 (P—C); 1290 (SO_2); 1190, 1163 (P═O, SO_2); 1114 (P═N); 837 (S—N)	10.34 (d, P = N); 25.07 (d, P = O, $^2J_{PP} = 13.1$ Hz).	4.87 (t, CH_2, $^2J_{PH} = 13.6$ Hz); 7.04 (s, NH_2); 7.6–8.4 (m, ArH)	128.91 (d, O═P—Ar—C_3, $^3J_{PC} = 12.1$ Hz); 128.94 (d, N = P—Ar—C_3, $^3J_{PC} = 12.9$ Hz); 129.20 (dd, N = P – Ar—C_1) $^1J_{PC} = 108.9$, $^3J_{PC} = 3.1$ Hz); 130.75 (d, O = P—Ar—C_2, $^2J_{PC} = 10.2$ Hz); 131.60 (d, N═P—Ar—C_2, $^2J_{PC} = 10.6$ Hz); 132.34 (d, N = P—Ar—C_4, $^4J_{PC} = 2.4$ Hz); 132.79 (d, O═P—Ar—C_4, $^4J_{PC} = 2.8$ Hz); 132.89 (dd, O═P—Ar—C_1, $^1J_{PC} = 104.8$, $J_{PC} = 2.6$ Hz).[e]
18	1439 (P—C); 1290, 1260, 1200 (SO_2); 1114 (P═N); 803 (S—N).	18.15	2.99 (br.s, CH_2); 6.20 (s, NH_2); 7.3–7.9 (m, ArH)	not obtained
19	1438 (P—C); 1275, 1260 (SO_2); 1120 (P═N); 889, 830 (S—N)	17.71	1.79 (br.s, CH_2); 2.97 (m, PCH_2); 5.95 (s, NH_2, exch. with D_2O) 7.4–7.8 (m, ArH)	14.52 (S, CH_2); 25.71(dd, PCH_2, $^1J_{PC}$═63.0 Hz, $^3J_{PC}$═13.7 Hz); 128.26 (d, Ar—C_1; $^1J_{PC}$═101.8 Hz); 128.80 (m, Ar—C_3, $^3J_{PC}$═13.2 Hz); 131.26 (m, Ar—C_2, $^2J_{PC}$═10.7 Hz); 132.36 (s, Ar—C_4).
20	1437 (P—C); 1288, 1269 (SO_2); 1135 (P═N); 885, 740.	(AB_2 System) 18.32 (dd, PPh$_2$); 28.79 (dd, PPh, $^3J_{PP} = 57.7$ Hz).	2.57 (br.s, CH_2); 2.98 (br.s, CH_2); 6.04 (s, NH_2); 6.13 (s, NH_2); 7.3–7.9 (m, ArH).	17.81, 18.49, 19.00, 19.71 (all m, CH_2); 123.25, 125.34, 126.50, 127.13, 128.60, 129.17 (sh) (all s, Ar—C_1); 129.37 (d, Ar—C_3), $^3J_{PC}$═12.7 Hz); 131.68 (m, Ar—C_2, $^2J_{PC}$═10.4 Hz); 133.10 (m, Ar—C_4)

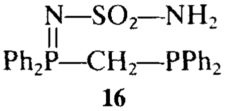
[a] KBr Pellet; b) Me_2SO-d_6 solvent except compound **12** which was in $CDCl_3$; c) Spectral properties are in reasonable agreement with those reported.[9]; d) In reasonable agreement with that reported.[10]; e) The CH_2 peaks were obscured by solvent.

any ring formation. Second, the production of the mono-phospha-λ^5-azene-mono-oxide, **14**, is unique since, except for the reaction of **1** with urea and DAD to give **2** as the major product (equation 2), this is the first time a half oxide has been observed as the major product in the reaction of a bis-phosphine. In the case of **2** (from **1**, urea and DAD) we argued that first the intermediate **15** was formed and then, in a sterically favored intramolecular reaction, the amide function was dehydrated and the phosphine moiety was concomitantly oxidized. In the case of **14**, however, the corresponding intermediate would be **16** and if this underwent



$$\mathrm{Ph_2P({=}N{-}C({=}O){-}NH_2){-}CH_2{-}PPh_2}$$

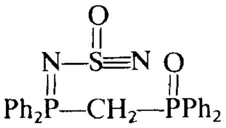
15



$$\mathrm{Ph_2P({=}N{-}SO_2{-}NH_2){-}CH_2{-}PPh_2}$$

16

intramolecular dehydration the product would be **17**, which is not what is observed. Since great care is taken to exclude moisture and oxygen, and since

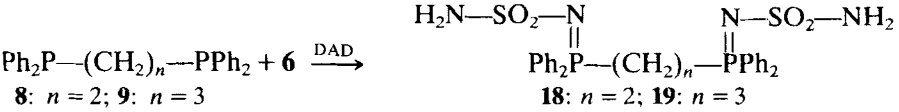


$$\mathrm{Ph_2P({=}N{-}S({=}O){\equiv}N){-}CH_2{-}P({=}O)Ph_2}$$

17

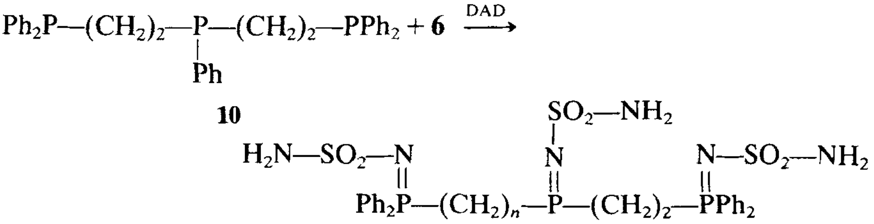
only small amounts of oxides are usually observed in these oxidation-reduction condensation reactions, including the reactions of **1** with mono-amides and DAD,[8] we must conclude that the oxide is being formed in an intramolecular process, aided in some way by the adjacent phospha-λ^5-azene group. The nature of this effect and the mechanism of this intriguing reaction must await further study.

Two other bis-phosphines, **8** and **9**, and tris-phosphine **10** were also reacted with a two fold excess of sulfamide (**6**) and a lesser excess of DAD. In these cases good yields (75–86%) of the expected products, 1,2-bis(*N*-sulfamidodiphenylphospha-λ^5-azeno)ethane (**18**), 1,3-bis(*N*-sulfamidodiphenylphospha-λ^5-azeno)-propane (**19**) and *N*-sulfamido-bis[2-(*N*-sulfamidodiphenylphospha-λ^5-azeno)-ethyl]phenylphospha-λ^5-azene (**20**; Equations 6 and 7; Table I) were obtained.



$$\mathrm{Ph_2P{-}(CH_2)_n{-}PPh_2} + \mathbf{6} \xrightarrow{\mathrm{DAD}} \mathrm{Ph_2P({=}N{-}SO_2{-}NH_2){-}(CH_2)_n{-}P({=}N{-}SO_2{-}NH_2)Ph_2} \qquad (6)$$

8: $n = 2$; **9**: $n = 3$ **18**: $n = 2$; **19**: $n = 3$



$$\mathrm{Ph_2P{-}(CH_2)_2{-}P(Ph){-}(CH_2)_2{-}PPh_2} + \mathbf{6} \xrightarrow{\mathrm{DAD}} \mathrm{Ph_2P({=}N{-}SO_2{-}NH_2){-}(CH_2)_n{-}P({=}N{-}SO_2{-}NH_2){-}(CH_2)_2{-}P({=}N{-}SO_2{-}NH_2)Ph_2} \qquad (7)$$

10 **20**

EXPERIMENTAL SECTION

General Methods. Melting points were determined on a Thomas–Hoover capillary melting point apparatus and are uncorrected. IR spectra were recorded on a Perkin–Elmer Model 599B spectrophotometer. NMR spectra were taken on a Varian EM-360 (^{1}H) or a Nicolet NT-200 WB instrument (^{1}H, ^{13}C and ^{31}P) as solutions in Me_2SO-d_6 (except where noted) using tetramethylsilane as internal standard for ^{1}H and ^{13}C. External H_3PO_4 was the standard for ^{31}P NMR spectra. ^{13}C and ^{31}P spectra were recorded using ^{1}H decoupling. Elemental analyses were determined by Texas Analytical Laboratories, Houston, TX and Tallahassee, FL. THF was distilled from $LiAlH_4$ immediately prior to use. All reactions were executed under an atmosphere of dry nitrogen or argon. Preparative chromatography was on a Harrison Research Model 7924T Chromatotron, a centrifugally accelerated, radial thin-layer chromatograph, using Si-gel 60 PF_{254} (EM Science).

General Procedure for the Reaction of the bis- and tris-Phosphines with Cyanamide (**3**) *or Sulfamide* (**6**) *and DAD.* To a stirred solution of 3.6–4 mmol of cyanamide (**3**) or sulfamide (**6**) and the bis- or tris-phosphine (0.6–1 mmol), in 20–30 mL of dry THF, at 0–5°C, under dry nitrogen or argon, was added a solution of 2.25–2.5 mmol of DAD in 5 mL of dry THF. The mixture was then stirred at room temperature for 24 h (except where noted). Workup is described below for each compound.

1,2-bis(N-Cyanodiphenylphospha-λ^5-azeno)ethane (**11**). 168 mg (4 mmol) of **3**, 398 mg (1 mmol) of 1,2-bis(diphenylphosphino)ethane (**8**) in 25 mL of THF and 435 mg (2.5 mmol) of DAD in 5 mL of THF gave 161 mg of a white solid, after filtering and washing with 5 mL of THF. After concentration of the filtrate under reduced pressure, and dissolving in a minimum amount of $CHCl_3$ it was chromatographed on the Chromatotron using EtOAc to elute. The solid obtained (182 mg) was combined with the solid obtained above and recrystallized from EtOAc to give 328 mg (68%) of **11**, mp 196–198°C (lit.[9] 204°C). Anal. Calcd. for $C_{28}H_{24}N_4P_2$: C, 70.29; H, 5.06; N, 11.71. Found: C, 70.33; H, 5.05; N, 11.73.

1,3-bis(N-Cyanodiphenylphospha-λ^5-azeno)propane (**12**). 168 mg (4 mmol) of **3**, 412 mg (1 mmol) of 1,3-bis(diphenylphosphino)propane (**9**) in 20 mL of THF and 435 mg (2.5 mmol) of DAD in 5 mL of THF gave, after stirring 4 h at room temperature and removal of the solvent under vacuum, a semi-solid which was dissolved in the minimum $CHCl_3$ and purified using the Chromatotron with 5% MeOH/95% EtOAc as eluent. Recrystallization of the product from $CHCl_3$-EtOAc gave 395 mg (80%) of **12**, mp 184–185°C (lit.[9] 186°C). Anal. Calcd. for $C_{29}H_{26}N_4P_2$: C, 70.72; H, 5.32; N, 11.38. Found: C, 70.69; H, 5.33; N, 11.37.

N-Cyano-bis[2-(N-cyanodiphenylphospha-λ^5-azeno)ethyl]phenylphospha-λ^5-azene (**13**). 151 mg (3.6 mmol) of **3**, 321 mg (0.6 mmol) of bis(2-diphenylphosphinoethyl)phenylphosphine (**10**) in 30 mL of THF and 392 mg (2.25 mmol) of DAD in 5 mL of THF gave, after 4 h of stirring, and removal of the solvent under vacuum, a yellow semi-solid. It was dissolved in $CHCl_3$, purified with the Chromatotron using 0–20% MeOH/EtOAc as eluent and recrystallized from $CHCl_3$—EtOAc to give 328 mg (84%) of **13**, mp 230–232°C. Anal. Calcd. for $C_{37}H_{33}N_6P_3$: C, 67.88; H, 5.08; N, 12.84. Found: C, 67.86; H, 5.09; N, 12.88.

[(N-Sulfamidodiphenylphospha-λ^5-azeno)methyl]diphenylphosphine Oxide (**14**) *and 3,3,5,5-Tetraphenyl-4H-1,2,6,3λ^5,5λ^5-thiadiazadiphosphorin-1,1-dioxide* (**7**). 384 mg (4 mmol) of **6**, 384 mg (1 mmol) of bis(diphenylphosphino)methane (**1**) in 30 mL of THF and 435 mg (2.5 mmol) of DAD in 5 mL of THF gave a solid precipitate which was filtered and recrystallized from MeOH to yield 27 mg (6%) of **7**, mp 248–249°C (lit.[10] 248°C). The filtrate was concentrated in vacuum, $CHCl_3$ was added and Chromatotron purification using 0–20% MeOH/EtOAc followed by recrystallization from MeOH—EtOAc gave 342 mg (69)% of **14**, mp 233–235°C. Anal. Calcd. for $C_{25}H_{24}N_2O_3P_2S$: C, 60.72; H, 4.89; N, 5.67. Found: C, 60.67; H, 4.92; N, 5.66.

1,2-bis(N-Sulfamidodiphenylphospha-λ^5-azeno)ethane (**18**). 384 mg (4 mmol) of **6**, 398 mg (1 mmol) of 1,2-bis(diphenylphosphino)ethane (**8**) in 30 mL of THF and 435 mg (2.5 mmol) of DAD in 5 mL of THF produced a white precipitate which, after filtration and washing with THF and $CHCl_3$, gave 505 mg (86%) of crude **18**, mp 224–226°C. Recrystallization from Me_2SO—EtOAc provided 441 mg (75%) of **18**, mp 228–230°C. Anal. Calcd for $C_{26}H_{28}N_4O_4P_2S_2$: C, 53.23; H, 4.81; N, 9.55. Found: C, 53.28; H, 4.83; N, 9.50.

1,3-bis(N-Sulfamidodiphenylphospha-λ^5-azeno)propane (**19**). 384 mg (4 mmol) of **6**, 412 mg (1 mmol) of 1,3-bis(diphenylphosphino)propane in 30 mL of THF and 435 mg (2.5 mmol) of DAD in

5 mL of THF gave a precipitate which after it was filtered, washed with THF and recrystallized from $CHCl_3$ gave 515 mg of **19** (86%), mp 170–171°C. Anal. Calcd for $C_{27}H_{30}N_4O_4P_2S_2$: C, 53.99; H, 5.03; N, 9.33. Found: C, 53.94; H, 5.06; N, 9.31.

N-Sulfamido-bis[2-(N-sulfamidodiphenylphospha-λ^5-azeno)ethyl]phenylphospha-λ^5-azene (**20**). 346 mg (3.6 mmol) of **6**, 321 mg (0.6 mmol) of bis(2-diphenylphosphinoethyl)phenylphosphine (**10**) in 30 mL of THF and 392 mg (2.25 mmol) of DAD gave, after removal of the solvent in vacuum, dissolving in $CHCl_3$, purifying with the Chromatotron using 0–20% MeOH/EtOAc as eluent and recrystallizing from CH_3OH—EtOAc, 385 mg (78%) of **20**, mp 221.5—222.5°C. Anal. Calcd for $C_{34}H_{39}N_6O_6P_3S_2$: C, 49.99; H, 4.81; N, 10.29. Found: C, 49.94; H, 4.80; N, 10.25.

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