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A New Rearrangement in Phosphorus Chemistry

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ABSTRACT

The oxidation of 1,5-dimethyl-2,4-bis(diethylamino)-1,5-diaza-2,4-diphosphorinan-6-one **5** *with tetrachloroorthobenzoquinone (TOB) leads to the formation of the spirophosphorane* **9**, *which is unstable and undergoes an unusual spontaneous rearrangement into the isomeric methylenephosphinophosphorane* **11**. *The sulfuration of* **9** *and* **11** *gives the stable isomers* **12** *and* **19**, *exhibiting no tendency of mutual transformation. The mechanism of the isomerization of* **9** *into* **11** *is discussed. Some chemical properties of* **9** *and* **11** *have been investigated.*

INTRODUCTION

A great variety of organophosphorus compounds and the diversity of their chemical properties are accounted for by the ability of the phosphorus atom to exist in various valence and coordination states. This fact explains the rapid growth of this field of knowledge over the last 3 decades. The presence of two phosphorus atoms in the molecule, whereby one can influence the other, frequently leads to the observation of unexpected properties. The chemistry of such compounds, however, has still been investigated only to a very small extent despite the fact that new and interesting results may be expected in this area. For example, the reaction of the chlorophosphorane 1 with the trimethylsiloxy phosphorane 2 leads not to the expected compound 3 but to the heterocyclic spirophosphorane **4** [1] (Equation 1).

Our investigations of the oxidation of 1,3-dimethyl-2,4-bis(dialkylamino)-1,3-diaza-2,4-diphosphorinan-6-ones **5** with tetrachloro-orthobenzoquinone (TOB) showed this reaction also to be unusual [2]. Instead of the expected diphosphoranes **6** the compounds **7** and **8**, containing two phosphorus atoms of opposite formal charge and different coordination number (λ^4P^+, λ^6P^-), were formed (Equation 2).

RESULTS AND DISCUSSION

In our previous work [3], on the basis of ^{31}P NMR spectral data, we suggested that the formation of compound **8** is accounted for by the rearrangement of the intermediate **9** into its isomer **10** (Equation 3). This suggestion was logical since it explained, at the same time, the formation of compound **7**, isomeric to **8**. However, more detailed investigations which form the subject of this article, only partially confirmed our earlier suggestion.

The first stage of the reaction of **5** with TOB is indeed the formation of **9**, the product of the addition of TOB to one phosphorus atom (Equation 3). The ^{31}P NMR spectrum of the reaction mixture shows an intense double doublet (δ_P = +70.60, −15.20, $^2J(PP)$ = 3.4 Hz). Compound **9**, in contrast to its homologue lacking the methylene group between the two phosphorus atoms [3], is unstable. When the reaction mixture is allowed to stand for 4d at 20°C, **9** is completely transformed, not into isomer **10** but into isomer **11**. This process is indicated in the ^{31}P NMR spectrum of the reaction mixture by the disappearance of the signals of compound **9** and the appearance and increase in intensity of a new double doublet at δ = 73.4 and −24.0 ($^2J(PP)$ = 96.3 Hz). This type of rearrange-

Dedicated to Prof. V. I. Shevchenko on the occasion of his seventy-fifth birthday.

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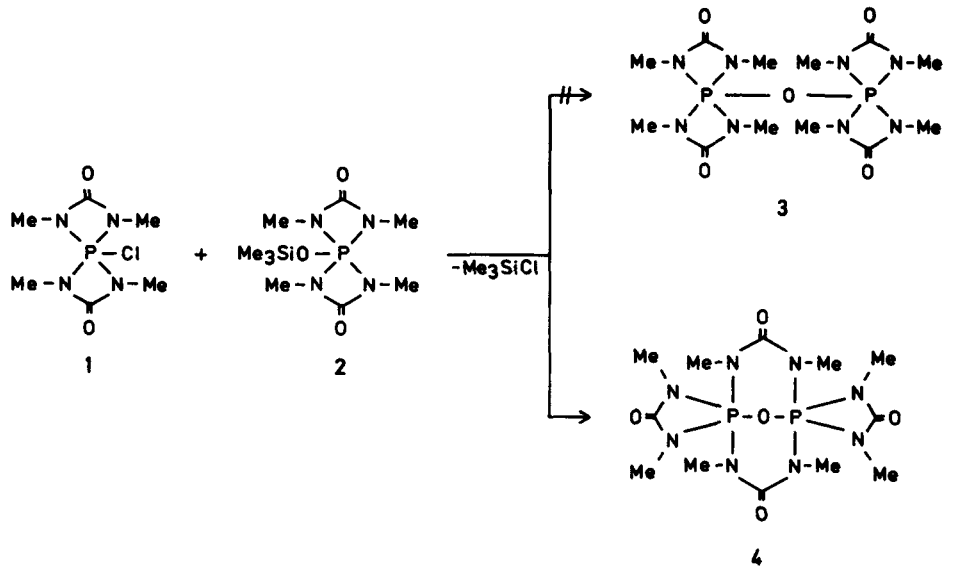

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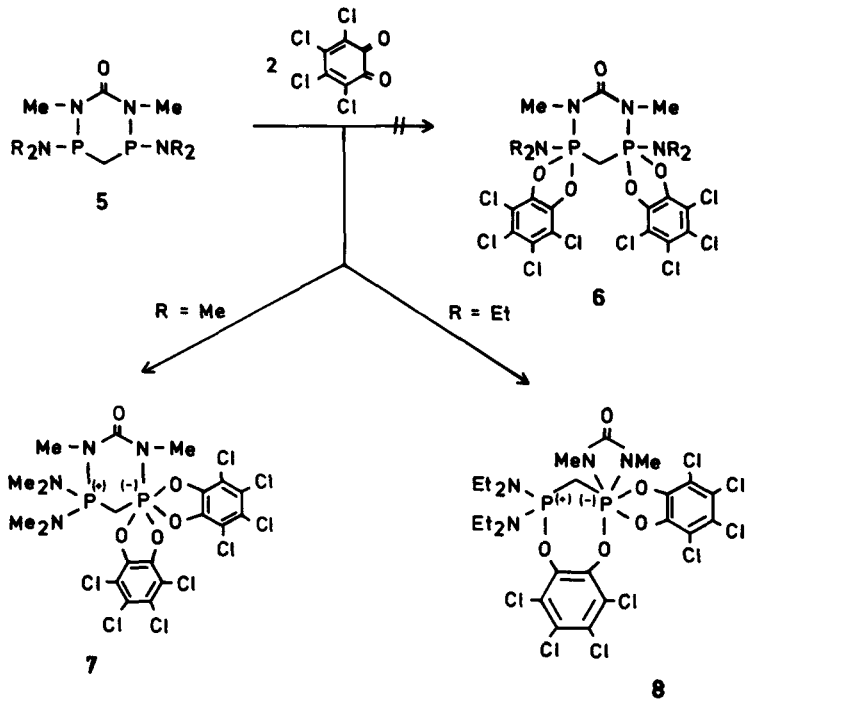
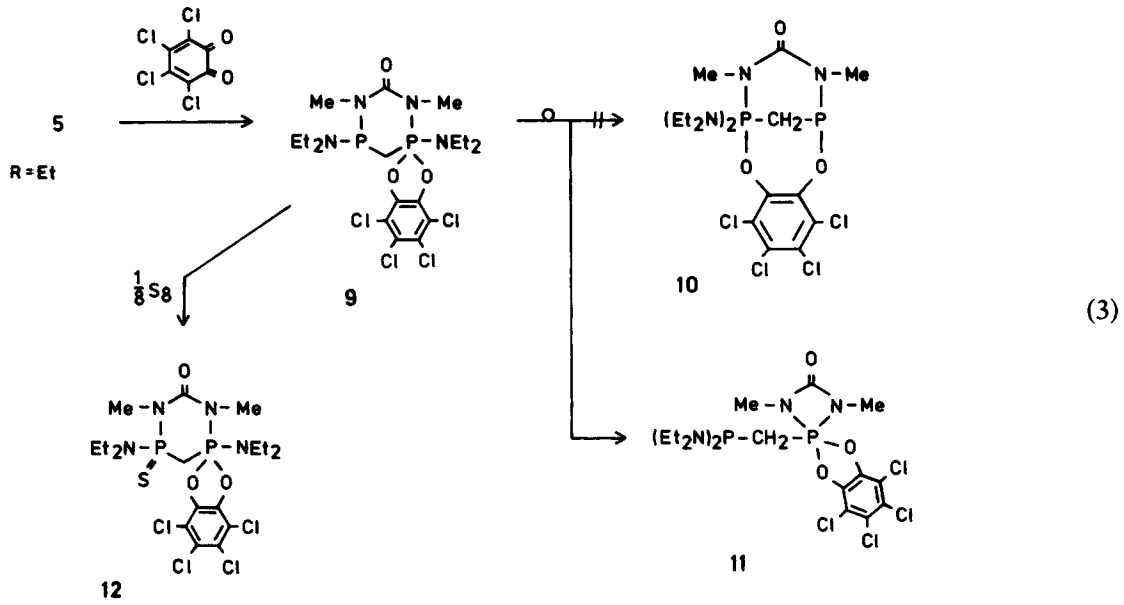


(2)

ment has not previously been observed in the chemistry of organophosphorus compounds.

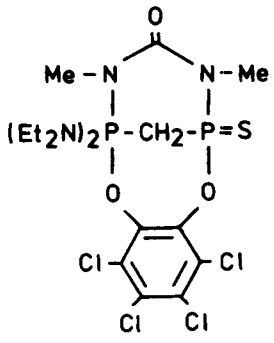
Compound **9** may be extracted from the reaction mixture with petroleum ether and is obtained in a yield of 46%. The ^{31}P NMR spectrum of the extract shows, besides the above-mentioned signals of **9**, one more double doublet at +73.98, −14.00, $^{2}J(PP)$ = 18.6 Hz, which disappears over 24 hours (at 20°C). This double doublet belongs, probably, to the second stereoisomer of **9**. In the presence of a catalytic amount of 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU), the conversion of one double doublet into another occurs during a few minutes, which confirms this assumption and testifies to the fact that the CH_2 group between the two phosphorus atoms takes part in this process. Judging by the ^{31}P NMR spectrum, the purity of **9** reaches 90%. Unfortunately, all attempts to obtain the product in crystalline form failed. Therefore, the compound was identified as its sulfur derivative, **12** (Equation 3).

Compound **12** is a colorless crystalline product, soluble in nonpolar organic solvents. Its ^{31}P-NMR spectrum shows two signals at δ = 58.2 and −29.5, with the value of the $^{2}J(PP)$ coupling constant too small to be determined precisely. In the



(3)

^{1}H NMR spectrum of **12**, the inequivalence of the methyl groups of the urea unit and of the diethylamino groups attached to the phosphorus atoms can clearly be seen. This proves the presence of the 1,3-diaza-2,4-diphosphorinan-6-one ring in the molecule. The signals were assigned by recording the spectrum with decoupling of the phosphorus-proton interaction. The ^{13}C NMR spectrum of **12** shows the equivalence in pairs of the benzene carbon atoms. All these data prove unambiguously the structure of **12** and exclude the other two conceivable isomeric structures, **13** and **14**.



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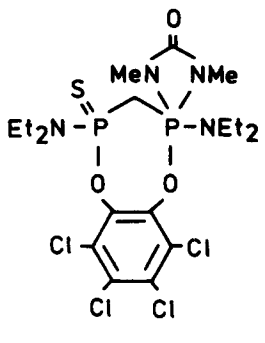

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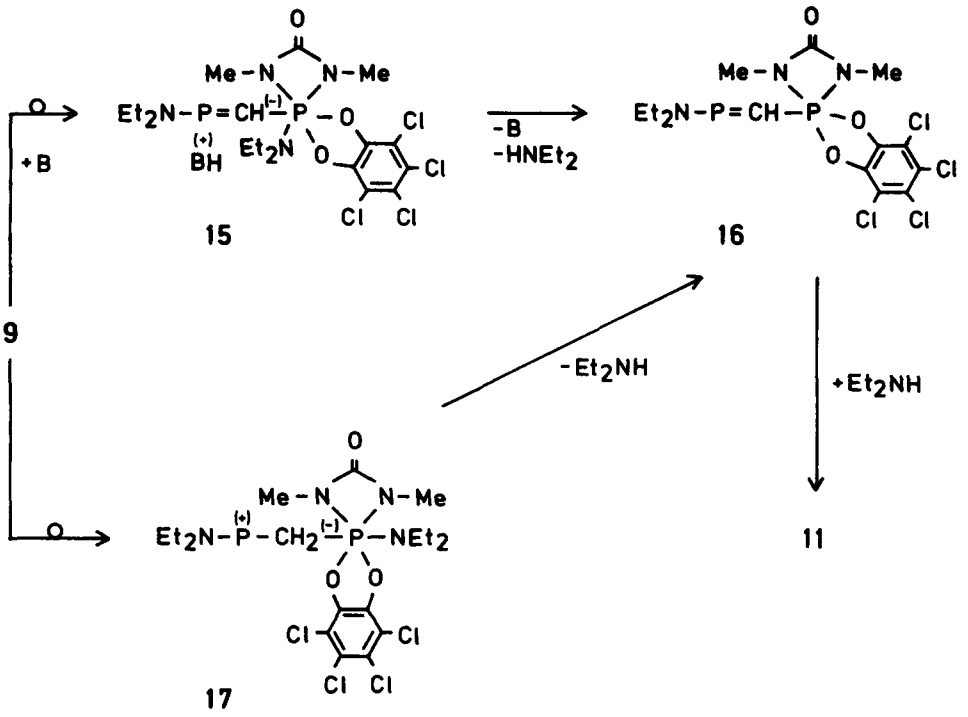
The reactivity of the trivalent phosphorus atom of **9** is markedly reduced, probably as a result of the shielding influence of bulky substituents and the electron-withdrawing effect of the phosphorane group. In comparison to the starting 1,3-diaza-2,4-diphosphorinan-6-one **5** [4], **9** reacts with sulfur slowly, without evolution of heat.

It is interesting that **9**, when extracted from the reaction mixture with petroleum ether, is substantially more stable. At room temperature, it is not converted into **11**, but, in the presence of 10% of DBU, the transformation **9** → **11** occurs slowly (3–4 days). This fact leads us to suggest a mechanism of isomerization, though we did not obtain any NMR spectral information to confirm it (Equation 4).

At first, the removal of a proton under the action of base (B), followed by the shift of the urea unit to one phosphorus atom, gives the intermediate **15**, containing two- and six-coordinate phosphorus atoms. The further transformation of **15** may proceed through elimination of diethylamine and its subsequent addition to the phosphaalkene **16**. It cannot be ruled out that, at first, the shift of the urea unit occurs with the formation of the unstable intermediate **17**, containing the phosphenium cation, involving a two-coordinate phosphorus and a six-coordinate phosphorate anion. This assumption is indirectly confirmed by the fact that dialkylamino substituents are known to stabilize the phosphenium cation [5–7].

Compound **11** is a stable crystalline product that is unchanged when heated up to 110°C in toluene. It is soluble in nonpolar organic solvents, which allows its separation from the reaction mixture by extraction with petroleum ether. The extracted product is sufficiently pure and can be used in further reactions without additional purification. The structure of **11** was established by NMR spectroscopy. In contrast to isomer **9**, the ^{1}H NMR spectrum of **11** shows the equivalence of the two methyl groups of the urea unit. The slight inequivalence of the diethylamino groups of **11** manifests itself only in the ^{13}C NMR spectrum. The analysis of this spectrum also leads to the conclusion that the tetrachlorocatechol group is attached to one phosphorus atom only.

Compound **11**, containing phosphine and phosphorane phosphorus atoms connected to each other



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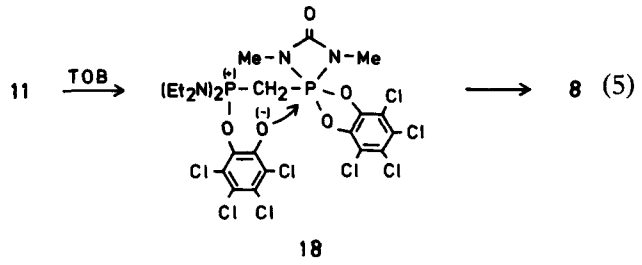

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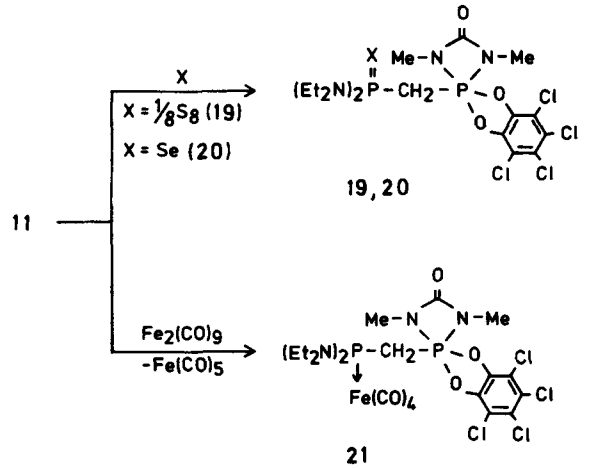

(6)

by a methylene group, constitutes a new type of compound and is an interesting synthon for further investigations. Compound **11** possesses unusual chemical properties. For example, its further oxidation with TOB leads to compound **8** [2], containing two phosphorus atoms of opposite formal charge and different coordination number. This reaction may be considered as an addition reaction of TOB to two phosphorus atoms. It cannot be excluded that this reaction proceeds via the formation of the short-lived intermediate **18** as a result of the attack of TOB on the trivalent phosphorus atom (Equation 5).

This assumption is confirmed by the fact that **11** displays other reactions typical of phosphines. For instance, it reacts readily with sulfur and selenium with formation of the derivatives **19** and **20** (Equation 6).

Compounds **19** and **20** are colorless crystalline products, whose NMR-spectroscopic and analytical data are in good agreement with the proposed structure. It should be noted that the coupling constants, $^2J(PP)$, of **19** and **20**, as well as of **12**, are very small and could not be observed in the ^{31}P NMR spectra.

Similarly to **9** and **11**, their sulfurated derivatives, **12** and **19**, are structural isomers. In contrast to their predecessors, however, they exist independently of each other and exhibit no tendency to undergo mutual isomerization, even when heated to 110°C in toluene for 6 hours. This indicates that the mechanism of rearrangement **9**→**11** is closely connected with the presence in the molecule of a trivalent phosphorus atom and partly confirms the suggested scheme (Equation 6).

The bulky diethylamino and methylenephosphorane groups of **11** strongly shield the trivalent phosphorus atom. This is probably the reason why **11** does not react with trimethylsilylazide in equimolar ratio in ether at 20°C. The reaction in toluene at 60–80°C or in trimethylsilyl azide as a solvent led to the formation of a complicated mixture of products.

The reaction of **11** with $Fe_2(CO)_9$ serves as further proof of its structure. Compound **21** is a dark-brown crystalline product whose ^{31}P NMR spectrum shows a double doublet with a characteristic low field shift of the resonance of the donor phosphorus atom (δ_P = +151.3, −30.2; $^2J(PP)$ = 14.7 Hz). The ^1H NMR spectrum and the mass spectrum of **21** offer proof of its structure.

EXPERIMENTAL

Materials and Spectroscopy

All experiments were conducted, with the exclusion of moisture, in sealed systems in an atmosphere of dried nitrogen (BASF BTS catalyst). Solvents were purified and dried according to the usual methods [8,9]. NMR spectra: spectrometer BRUKER AC 200 (^1H at 200.1 MHz; ^{13}C at 50.3 MHz; ^{31}P at 81.3 MHz). Reference substances were $SiMe_4$ (TMS) ext (^1H, ^{13}C), and 85% H_3PO_4 ext. (^{31}P). High field shifts were given a negative and low field shifts a positive sign. Materials: N,N′-dimethyl-N,N′-bis(trimethylsilyl)urea [10] and methylene-bis(diethylaminochlorophosphine) [2] were synthesized according to procedures described in the literature.

Synthesis of **9**. N,N′-Dimethyl-N,N′-bis(trimethylsilyl)urea (1.60 g, 6.87 mmol) was added to a solution of methylene-bis(diethylaminochlorophosphine) (2.0 g, 6.87 mmol) in 20 mL of CH_2Cl_2, and the mixture was stirred at room temperature for 40 minutes. The solvent was removed in vacuo (0.5 mm), and 18 mL of toluene were added. Subsequently, a solution of TOB (1.69 g, 6.87 mmol) in 18 mL toluene was added in portions of 8–10 drops at −5°C with stirring. Each portion of the TOB solution was added at an interval of 2–3 minutes. After the addition had been completed, the reaction mixture was stirred at room temperature for 30 minutes. Toluene was removed in vacuo (0.5 mm), the residue was extracted with petroleum ether 40–60°C (3 × 15 mL), and the extract was allowed to stand at 20°C for 12 hours. The solution was decanted from the small residue formed and then evaporated in vacuo (0.5 mm). The remaining viscous oil (1.74 g, 46%) was used in further experiments without purification. ^{31}P-NMR spectrum of **9** ($CDCl_3$): δ = 69.26, −16.18 [dd, $^2J(PP)$ = 3.4 Hz].

Synthesis of **11**. The reaction mixture of compound **9** in toluene (see earlier) was stirred at 20°C until the signals of **9** in the ^{31}P NMR spectrum disappeared completely (4 days). The solvent was removed in vacuo (0.5 mm), and the residue was extracted with petroleum ether (40–60°C: 3 × 15 mL). The extract was allowed to stand at 20°C for 1 hour, the solution was then decanted from the small residue formed, and the solvent was evaporated in vacuo (0.5 mm). The residue (2.06 g, 54%) was used in further reactions without purification.

For NMR-spectroscopic and analytical investigations, the residue (2.06 g) was dissolved in 20 mL of hexane and the solution was cooled to −20°C. The crystalline product formed after 3 days was separated from the mother liquor and dried in vacuo (0.05 mm). Yield 0.75 g (19.6%), mr.124–128°C. ^1H NMR ($CDCl_3$): δ = 1.00 [t, $^3J(HH)$ = 7.1 Hz, (CH_3 part of the C_2H_5 group)]; 2.46 [dd, $^2J(P^{III}H)$ = 3.3 Hz, $^2J(P^{V}H)$ = 18.4 Hz, (P-CH_2-P)]: 2.86 [d, $^3J(PH)$ = 12.1 Hz, (CH_3-N)]; 2.87–3.18 [m, (CH_2 part of the C_2H_5N group)]. ^{13}C NMR ($CDCl_3$): δ = 14.43, 14.50 (CH_3 part of the C_2H_5N group); 26.96 (CH_2 part of the C_2H_5N group); 32.42 [dd, $^1J(PC)$ = 34.7 Hz, $^1J(PC)$ = 135.0 Hz, (P-CH_2-P)]; 42.32, 46.68 (CH_3-N); 114.63 (2C, Ar); 124.90 (2C, Ar); 140.95 (2C, Ar); 156.22 (C=O). ^{13}P NMR($CDCl_3$): δ = 72.47 (d, $^2J(PP)$ = 94.5 Hz); −24.61 (d, $^2J(PP)$ = 96.3 Hz). Anal. calcd for $C_{18}H_{28}Cl_4N_4O_3P_2$: C, 39.15; H, 5.11; P, 11.22. Found: C, 39.05; H, 5.05; P, 11.06.

Synthesis of **12**. Sulfur [0.3 g (9.45 mmol)] was added to a solution of 1.74 g (3.15 mmol) of **9** (see earlier) in 10 mL of ether, and the mixture was stirred at 20°C for 1 hour. Then the reaction mixture was cooled for 12 hours to −20°C. The solution was separated from excess sulfur, and the solvent was removed in vacuo (0.5 mm). The residue was extracted with hexane (2 × 10 mL) and the extract was concentrated to a volume of 10 mL and cooled to −20°C. The colorless crystalline product formed within 3d was separated and dried in vacuo (0.05 mm). Yield 0.7 g (38%). ^1H NMR ($CDCl_3$): δ = 1.05 [t, $^3J(HH)$ = 7.1 Hz, (CH_3 part of the C_2H_5N group)]; 1.07 [t, $^3J(HH)$ = 7.1 Hz, (CH_3 part of the C_2H_5N group)]; 2.96 [d, $^3J(PH)$ = 8.3 Hz, (CH_3N)]; 3.19 [d, $^3J(PH)$ = 4.6 Hz, (CH_3N)]; 3.09 [m, (CH_2 part of the C_2H_5N group)]; 3.25 [m, (CH_2 part of the C_2H_5N group)]; 3.30–3.70 [m, (P-CH_2-P)]. ^{13}C NMR ($CDCl_3$): δ = 14.59, 14.63 (CH_3 part of the C_2H_5N group); 27.26 [d, $^2J(PC)$ = 4.8 Hz, (CH_2 part of the C_2H_5N group)]; 29.94 [d, $^2J(PC)$ = 4.6 Hz, (CH_2 part of the C_2H_5N group)]; 38.98 [d, $^2J(PC)$ = 4.5 Hz, (CH_3N)]; 44.38 [d, $^2J(PC)$ = 4.6 Hz, (CH_3N)]; 114.46 (2C, Ar); 123.91 (2C, Ar); 140.84 (2C, Ar); 157.86 [m, (C=O)]. ^{31}P NMR ($CDCl_3$): δ = 58.24, −29.47, ($^2J(PP)$ was not resolved). Anal. calcd. for $C_{18}H_{28}Cl_4N_4O_3P_2S$: C, 37.00; H, 4.83; N, 9.63. Found: C, 36.16; H, 4.78; N, 9.30.

Synthesis of **19**. Sulfur [0.12 g (3.75 mmol)]

was added to a solution of 1.0 g (1.81 mmol) of **11** (see earlier) in 8 mL of ether, and the mixture was stirred at 20°C for 30 minutes. Then the mixture was filtered and the filtrate cooled to −20°C. The colorless crystalline product formed in the course of 3d was separated and dried in vacuo (0.05 mm). Yield 0.43 g (41%); mr 178–180°C. ^{1}H NMR ($CDCl_3$): δ = 1.13 [t, ^3J(HH) = 7.1 Hz, (CH_3 part of the C_2H_5N group)]; 2.79 [m, (P-C$\underline{H}_2$-P)]; 2.90 [d, ^3J(PH) = 12.8 Hz, (CH_3N)]; 3.03 [m, (CH_2 part of the C_2H_5N group)]: 3.16 [m, (CH_2 part of the C_2H_5N group)]. ^{13}C NMR ($CDCl_3$): δ = 16.47, 16.51 (CH_3 part of the C_2H_5N group); 27.22, 27.29 (CH_2 part of the C_2H_5N group); 33.15 [dd, ^1J(PC) = 79.5 Hz, ^1J(PC) = 138.6 Hz, (P-CH_2-P)]: 39.98, 40.06 (CH_3N): 115.68 (2C, Ar): 125.52 (2C, Ar); 140.58 (2C, Ar); 155.23 [d, ^2J(PC) = 15.6 Hz, (C=O)]. ^{31}P NMR ($CDCl_3$): 68.31, −30.52, (^2J(PP) was not resolved). Anal. calcd. for $C_{18}H_{28}Cl_4N_4O_3P_2S$: P, 10.60; S, 5.49. Found: P, 10.13; S, 5.29.

Synthesis of **20**. Selenium [0.43 g (5.43 mmol)] was added to a solution of 1.0 g (1.81 mmol) of **11** (see earlier) in 10 mL of ether, and the solution was stirred at 20°C for 10 hours. The reaction mixture was filtered and the filtrate cooled to −20°C. The colorless crystalline product formed during 2d was separated and dried in vacuo (0.05 mm). Yield 0.29 g (32%); mr 154–157°C. ^{1}H NMR ($CDCl_3$): δ = 1.14 [t, ^3J(HH) = 7.1 Hz, (CH_3 part of the C_2H_5N group)]; 2.76 [m, (P-C$\underline{H}_2$-P)]: 2.90 [d, ^3J(PH) = 12.9 Hz, (CH_3N)]; 2.95–3.34 [m, CH_2 part of the C_2H_5N group]. ^{13}C NMR ($CDCl_3$): δ = 14.23, 14.31 ($\underline{C}H_3$ part of the C_2H_5N group); 27.30, 27.37 (CH_2 part of the C_2H_5N group): 34.56 [dd, ^1J(PC) = 73.3 Hz. ^1J(PC) = 146.6 Hz, (P-$\underline{C}H_2$-P)]: 40.60, 40.68 ($\underline{C}H_3N$); 115.67 (2C, Ar); 125.55 (2C, Ar); 140.49 (2C, Ar); 155.16 [d, ^2J(PC) = 15.6 Hz, ($\underline{C}$=O)]. ^{31}P NMR ($CDCl_3$): 62.8 (d, ^2J(PP) = 4.0 Hz); −30.9 (d, ^2J(PP) = 4.0 Hz). Anal. calcd for $C_{18}H_{28}Cl_4N_4O_3P_2Se$: C, 34.25; H, 4.47; P, 9.81. Found: C, 34.09; H, 4.50; P, 9.75.

Synthesis of **21**. $Fe_2(CO)_9$ [0.66 g (1.81 mmol)] was added to a solution of 1.0 g (1.81 mmol) of **11** (see earlier) in 15 mL of CH_2Cl_2, and the solution was stirred at 20°C for 4–5 hours. As soon as the $Fe_2(CO)_9$ completely dissolved, the solvents were removed in vacuo (0.5 mm) from the homogenous reaction mixture. The solid product was extracted with 25 mL of hexane, and the extract was allowed to stand at 20°C for 2 weeks. The solid product formed was collected by filtration and dried in vacuo (0.05 mm). Brown amorphous product, mp 229–232°C, yield 0.49 g (38%). All attempts to recrystallize the product failed. ^{1}H NMR ($CDCl_3$): δ = 1.16 [t, ^3J(HH) = 7.0 Hz, (CH_3 part of the C_2H_5N group)]; 2.80–2.95 [m (P-C$\underline{H}_2$P)]; 2.91 [d, ^3J(PH) = 12.7 Hz (CH_3-N)]; 3.02–3.38 [m (CH_2 part of the C_2H_5N group)]. ^{31}P NMR ($CDCl_3$): 151.33 (d, ^2J(PP) = 14.7 Hz); −30.29 (d, ^2J(PP) = 14.7 Hz). Mass spectrum: M_{calcd} = 719.95; M_{exp} (FAB) = 719 (basis peak $[M-H]^+$). Anal. calcd. for $C_{22}H_{28}Cl_4FeN_4O_7P_2$: C, 36.69; H, 3.92; N, 7.78. Found: C, 34.29; H, 3.56; N, 6.96.

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