Reaction of Terminal Phosphinidene Complexes with Acetylenic Alcohols: Intramolecular Hydrophosphination of a Phosphirene Ring

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The transient phosphinidene complex [PhP−Mo(CO)$_5$], as generated from the appropriate 7-phosphanorbornadiene complex at 110 °C in toluene, selectively reacts with the C≡C triple bond of 4-phenyl-3-butyn-1-ol to give the corresponding phosphirene complex **4**. Upon further heating, this phosphirene evolves via two pathways. The minor pathway involves the formal addition of the OH bond of the alcohol function onto the phosphirene P−C ring bond to give the 3-benzylidene-1,2-oxaphospholane complex **5**. The major pathway involves the reaction of a second molecule of [PhP−Mo(CO)$_5$] with the OH group of **4**, giving an intermediate phosphirene with an additional secondary alkoxyphosphine functionality (**7**). An intramolecular hydrophosphination of one P−C bond of the phosphirene ring then immediately takes place to give the *cis*-1,2-bis(phosphino)ethene [Mo(CO)$_4$] complex **8** as a mixture of two diastereomers. After methylation of the PH group of **8**, decomplexation can be efficiently achieved by reaction with sulfur. Structures have been ascertained by X-ray analysis for **5**, **8**, and the disulfide **10**.

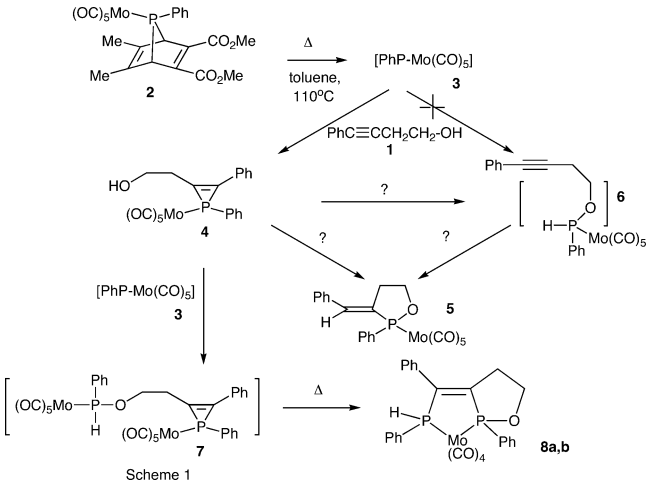
Introduction

The electrophilic terminal phosphinidene complexes [RP−M] (M = Cr, Mo, W(CO)$_5$] are now well established as powerful tools in organophosphorus synthesis.[1] A systematic investigation of their reactions with all of the basic organic functionalities has been carried out. Prominent among these are the reactions with carbon−carbon triple bonds, leading to phosphirene complexes,[2] and with alcohols, leading to secondary alkoxyphosphine complexes.[3] We wondered what would happen if two such functionalities were present in the organic reagent allowed to react with the phosphinidene species. More precisely, what functionality (OH or C≡C) would first react and what kind of secondary reaction would take place between the two installed organophosphorus functionalities? We present hereafter the results of this study, which led us to the discovery of an unprecedented hydrophosphination reaction of the P−C ring bonds of phosphirenes.

Results and Discussion

Our study has been carried out with 4-phenyl-3-butyn-1-ol (**1**) as the bifunctional organic substrate. The reaction with a 7-phosphanorbornadiene precursor (**2**)[4] of [PhP−Mo(CO)$_5$] (**3**) was performed in boiling toluene.

Scheme 1



Scheme 1

Monitoring the reaction mixture by ^{31}P NMR spectroscopy after 1.20 h showed the exclusive formation of the phosphirene ring **4** by reaction of **3** with the C≡C triple bond of **1**. The phosphirene ring displays the characteristic upfield shift of three-membered phosphorus heterocycles: $\delta(^{31}P(\mathbf{4}))$ −132.4 ppm. The transformation of **2** into **4** was complete after 18 h, but traces of other products started to appear. Product **4** was purified and completely characterized. After 4 days, compound **4** had completely disappeared and three new products had been formed. They were separated by chromatography on silica gel. The first product was identified as the 1,2-oxaphospholane complex **5** (Scheme 1). Its mass spectrum showed that it has the same molecular weight as **4** (*m*/*z* 492), but the ^{31}P NMR spectrum indicated that the three-membered ring had collapsed: $\delta(^{31}P(\mathbf{5}))$ +147

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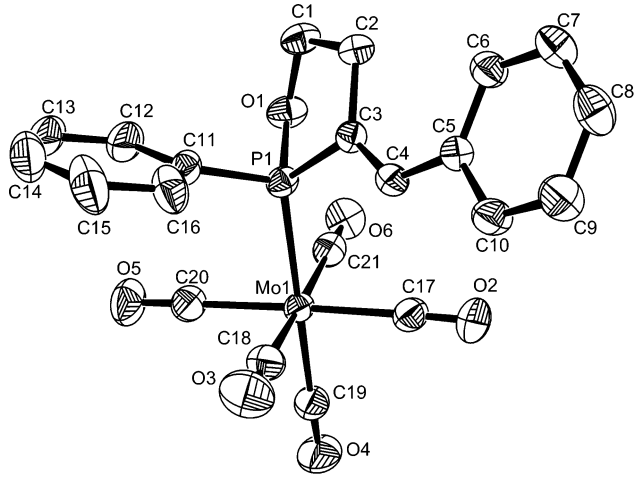

Figure 1. ORTEP drawing of one molecule of **5**. Main bond lengths (Å) and angles (deg): P(1)−Mo(1) = 2.4600(6), P(1)−O(1) = 1.6198(16), P(1)−C(3) = 1.812(2), P(1)−C(11) = 1.826(2), C(3)−C(4) = 1.341(3), C(3)−C(2) = 1.509(3), C(2)−C(1) = 1.532(3), C(1)−O(1) = 1.447(3); O(1)−P(1)−C(3) = 94.31(9), O(1)−P(1)−C(11) = 103.50(10), C(3)−P(1)−C(11) = 102.33(9), O(1)−P(1)−Mo(1) = 115.14(6), C(3)−P(1)−Mo(1) = 124.37(7), C(11)−P(1)−Mo(1) = 113.82(8).

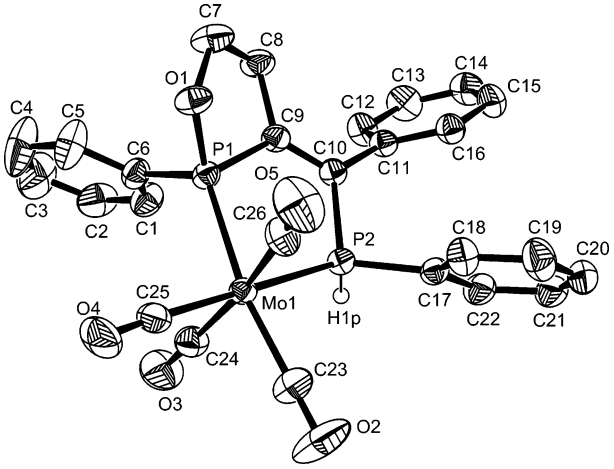

Figure 2. ORTEP drawing of one molecule of **8a**. Main bond lengths (Å) and angles (deg): P(1)−Mo(1) = 2.4355(4), P(2)−Mo(1) = 2.5047(4), P(1)−C(9) = 1.8043(16), P(1)−O(1) = 1.6268(12), P(1)−C(6) = 1.8214(17), P(2)−C(10) = 1.8494(15), P(2)−C(17) = 1.8216(17), C(9)−C(10) = 1.334(2); P(1)−Mo(1)−P(2) = 78.153(14), O(1)−P(1)−C(9) = 92.61(7), P(1)−C(9)−C(8) = 106.13(12), C(9)−P(1)−Mo(1) = 110.91(5), C(10)−C(9)−P(1) = 123.44(12), C(9)−C(10)−P(2) = 115.01(11), C(10)−P(2)−Mo(1) = 111.16(5).

ppm ($CDCl_3$). The structure was established by X-ray analysis (Figure 1). At least formally, the product results from the intramolecular hydrophosphination of the C≡C triple bond within the secondary alkoxyphosphine complex **6** (Scheme 1). We cannot establish at the moment whether our observation means that the phosphirene complex **4** equilibrates with complex **6** or not. In any event, the hydrophosphination of alkynes has been the subject of numerous recent reports and has been shown to be efficiently catalyzed by a variety of transition-metal complexes.[5] Another possible explanation for the formation of **5** relies on the fact that the methanolysis of a phosphirene complex has been shown to produce a vinylmethoxyphosphine complex.[6] Thus, an intramolecular addition of the OH group of **4** onto one P−C ring bond can also be envisaged. If the formation of **4** does not come as a complete surprise, such is not the case for the two other products of the reaction, **8a**,**b** (Scheme 1), which are, in fact, formed in much larger quantities. They appear as two AX systems: **8a** (minor), $\delta(^{31}P)$ 46.17 (P−H, $^1J_{PH}$ = 328 Hz) and 163.75, J_{AX} = 13.2 Hz; **8b** (major), $\delta(^{31}P)$ 43.35 (P−H, $^1J_{PH}$ = 321 Hz) and 169.16, J_{AX} = 13.3 Hz. As can be noticed, in both cases, the higher field resonance corresponds to a secondary phosphine complex. The mass spectrum indicates the presence of a single $Mo(CO)_4$ unit: *m/z* 572 (M^+), 516 (M − 2CO), 460 (M − 4CO). The structure was established by X-ray analysis of the minor diastereomer **8a** (Figure 2). The formation of **8a**,**b** implies that the P−H bond of **7**, transiently formed (but not detected) by reaction of a second molecule of phosphinidene complex **3** with the OH group of **4**, has added across the C−P bond of the phosphirene ring. As far as we know, this is the first time that the hydrophosphination of a P−C single bond has been reported. It must be also stressed that this P−C hydrophosphination takes place, rather than the more expected reaction at the phosphirene C=C double bond. Of course, the P−C ring bonds of phosphirenes have a great deal of π-character (Walsh orbitals) and cannot be considered as fully representative of classical P−C single bonds.

cis-1,2-Bis(phosphino)ethenes are the prototypes of rigid chelating phosphorus ligands, but the study of their coordination chemistry has been mainly restricted to the readily available *cis*-1,2-bis(diphenylphosphino)-ethene. In fact, the synthesis of dissymmetrical species of this type is not so simple, the most general route being the hydrophosphination of phosphinoalkynes in the coordination sphere of transition metals (Ni^{2+}, Pd^{2+}, Pt^{2+}).[7] The cis stereochemistry is imposed by the chelation of the transition metal, and the process is completed by a decomplexation of the ligands by cyanide ion. In such a context, it seemed interesting to investigate the possible use of the hydrophosphination of phosphirenes as a route to dissymmetrical *cis*-1,2-bis-(phosphino)ethenes. Our experiments are summarized in Scheme 2. The initial methylation leads to a mixture of two diastereomers: **9a** (minor) $\delta(^{31}P)$ 61.7 and 162.9 (THF) (J_{AX} = 13.3 Hz); **9b** (major) $\delta(^{31}P)$ 61.3 and 164.4 (J_{AX} = 13.3 Hz). The decomplexation by sulfurization is extremely efficient. This might be, in some part, explained by the destabilizing strain that exists in the metal ring of **8** (∠PMoP = 78.2°). The bis(sulfide) was obtained as a mixture of two diastereomers (major, $\delta(^{31}P)$ 39.52 and 86.04, J_{AX} = 13 Hz; minor, $\delta(^{31}P)$ 36.48 and 84.81, J_{AX} = 13 Hz). Whatever the starting product (**8a** or **8b**), we get the same 80:20 mixture of disulfides. This means that the two P anions initially obtained from **8a** and **8b** readily equilibrate at room temperature. The

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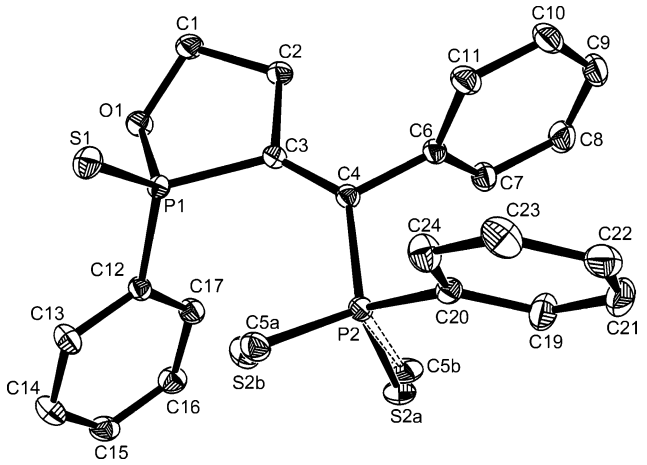
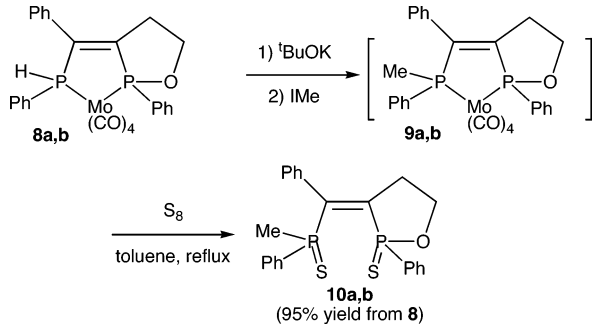


Figure 3. ORTEP drawing of one molecule of **10** showing the statistical disorder at P(2).

Scheme 2



two diastereomers syn-crystallize, and the X-ray analysis (Figure 3) shows a statistical disorder at P(2) between the sulfur atom and the methyl group. As a conclusion, the intramolecular hydrophosphination of phosphirene complexes appears as a reasonably efficient route to a series of original *cis*-1,2-bis(phosphino)ethenes with two chiral phosphorus centers.

Experimental Section

Reactions were performed under nitrogen using oven-dried glassware. Dry tetrahydrofuran was obtained by distillation from Na/benzophenone. Silica gel (70−230 mesh) was used for chromatographic separation. Nuclear magnetic resonance spectra were obtained on Bruker Avance 3000 and Varian Inova spectrometers operating at 300.13 MHz for ^{1}H, 75.45 MHz for ^{13}C, and 121.496 MHz for ^{31}P. Chemical shifts are expressed in parts per million downfield from external TMS (^{1}H and ^{13}C) and external 85% H_3PO_4 (^{31}P). Mass spectra were obtained on VG 7070 and Hewlett-Packard 5989A GC/MS spectrometers. Elemental analyses were performed by Desert Analytics Laboratory, Tucson, AZ. Starting materials were obtained from commercial suppliers.

Synthesis of 4-Phenyl-3-butyn-1-ol (1). To a solution of phenylacetylene (1.21 g, 11.6 mmol) in THF (15 mL) was added n-BuLi (7.25 mL, 1.6 M solution in hexane) at 0 °C. The reaction mixture was stirred at 0 °C for 30 min and then was cooled to −78 °C. Freshly distilled BF_3·OEt_2 (4.6 mL, 17.4 mmol) in THF (5 mL) was then added, followed by an excess of ethylene oxide (1 mL, 20 mmol), which was condensed into THF (5 mL). The mixture was stirred for 30 min at −78 °C, quenched with aqueous NH_4Cl solution, and concentrated on a rotary evaporator. The residue was taken up in Et_2O, washed with water and brine, dried (Na_2SO_4), and concentrated. The crude product was purified by column chromatography on silica gel (6:1 hexane−Et_2O) to afford 4-phenyl-3-butyn-1-ol (0.90 g, 53% yield) as a light yellow liquid.

Synthesis of the Phosphirene Complex 4. The (7-phosphanobornadiene)pentacarbonylmolybdenum complex **2** (0.77 g, 1.37 mmol) and 4-phenyl-3-butyn-1-ol (**1**; 0.2 g, 1.37 mmol) were heated at 110 °C in toluene (10 mL) for 18 h. After evaporation, the residue was chromatographed with hexane−Et_2O (1:1).

Complex **4**: $R_f \approx 0.3$; yield 0.15 g (22%); ^{31}P NMR ($CDCl_3$) δ −135.2; ^{1}H NMR ($CDCl_3$) δ 1.49 (s, br, OH), 3.20 (m, CH_2), 3.97 (t, $^{3}J_{H-H}$ = 6.3 Hz, OCH_2), 7.27−7.68 (m, Ph); ^{13}C NMR ($CDCl_3$) δ 30.58 (d, $^{2}J_{C-P}$ = 6.3 Hz, CH_2), 60.71 (s, CH_2OH), 205.43 (d, $^{2}J_{C-P}$ = 11.2 Hz, cis CO), 209.00 (d, $^{2}J_{C-P}$ = 32.5 Hz, trans CO); mass spectrum (FAB, ^{98}Mo): *m/z* 492 (M^+, 15%), 380 (M − 4CO, 100%). Anal. Calcd for $C_{21}H_{15}O_6PMo$: C, 51.45; H, 3.08. Found: C, 51.58; H, 3.12.

Synthesis of Complexes 5 and 8a,b. The (7-phosphanobornadiene)pentacarbonylmolybdenum complex **2** (1.3 g, 2.3 mmol) and 4-phenyl-3-butyn-1-ol (**1**; 0.3 g, 2.3 mmol) were heated at 110 °C in toluene (10 mL) for 4 days. After evaporation, the residue was chromatographed with hexane−Et_2O (90:10).

Complex **5**: $R_f \approx 0.8$; yield 0.06 g (6%); ^{31}P NMR ($CDCl_3$) δ 147.1; ^{1}H NMR ($CDCl_3$) δ 2.89 (m, CH_2), 4.12 (m, 1H, OCH_2), 4.43 (m, 1H, OCH_2); ^{13}C NMR ($CDCl_3$) δ 29.84 (d, $^{2}J_{C-P}$ = 12.2 Hz, CH_2), 71.75 (d, $^{2}J_{C-P}$ = 10.5 Hz, OCH_2), 205.11 (d, $^{2}J_{C-P}$ = 10.5 Hz, cis CO); mass spectrum (FAB, ^{98}Mo) *m/z* 492 (M^+, 3%). Anal. Calcd for $C_{21}H_{15}O_6PMo$: C, 51.45; H, 3.08. Found: C, 51.42; H, 2.87.

Complexes **8a**,**b**: $R_f \approx 0.7$ (minor diastereomer) and $R_f \approx 0.6$ (major diastereomer); yield 0.18 g (29%).

Complex **8a**: ^{31}P NMR ($CDCl_3$) δ 46.17 (P−H, $^{1}J_{PH}$ = 328 Hz) and 163.75, J_{AX} 13.2 Hz; ^{1}H NMR ($CDCl_3$) δ 2.44 (m, CH_2), 4.32 (m, OCH_2); ^{13}C NMR ($CDCl_3$) δ 28.07 (dd, J_{C-P} = 9.6 and 14.6 Hz, CH_2), 71.80 (d, $^{2}J_{C-P}$ = 9.5 Hz, OCH_2), 147.03 (dd, J_{C-P} = 25.6 and 32.0 Hz, =CP), 164.04 (dd, J_{C-P} = 33.5 and 45.5 Hz, =CP), 207.11 (t, CO), 208.84 (m, CO), 215.17 (t, CO), 215.58 (m, CO); mass spectrum (FAB, ^{98}Mo) *m/z* 572 (M^+, 33%), 516 (M − 2CO, 34%), 460 (M − 4CO, 42%).

Complex **8b**: ^{31}P NMR ($CDCl_3$) δ 43.35 (P−H, $^{1}J_{PH}$ = 321 Hz) and 169.16, J_{AX} 13.3 Hz; ^{1}H NMR ($CDCl_3$) δ 2.53 (m, 1H, CH_2), 2.65 (m, 1H, CH_2), 4.28 (m, OCH_2); ^{13}C NMR ($CDCl_3$) δ 28.60 (dd, J_{C-P} = 9.4 and 15.0 Hz, CH_2), 71.89 (d, $^{2}J_{C-P}$ = 11.6 Hz, OCH_2), 147.49 (dd, J_{C-P} = 28.4 and 33.4 Hz, =CP), 164.40 (dd, J_{C-P} = 33.8 and 45.2 Hz, =CP), 207.17 (dd, CO), 207.91 (t, CO), 215.58 (dd, CO), 216.05 (dd, CO). Anal. Calcd for $C_{26}H_{20}O_5P_2Mo$: C, 54.75; H, 3.53. Found: C, 54.95; H, 3.27.

Methylation−Decomplexation of Complex 8. Complex **8** (0.0096 g, 0.01 mmol) was treated with potassium *tert*-butoxide (0.0038 g, 0.034 mmol) in THF (0.6 mL). After 3 min at room temperature, methyl iodide (0.0027 mL, 0.043 mmol) was added to the reaction mixture. After 1 h of stirring, KI was removed by filtration, THF was evaporated, and the residue was heated for 4 days with sulfur (0.0016 g, 0.05 mmol) at 110 °C in toluene (0.7 mL). The reaction mixture was purified by column chromatography with dichloromethane as the eluent: $R_f \approx 0.8$; yield 0.0071 g (95%).

Sulfide **10**: ^{31}P NMR ($CDCl_3$) (major 80%) δ 39.52 (J_{PP} = 13 Hz) and 86.04, (minor 20%) δ 36.48 (J_{PP} = 13 Hz) and 84.81; ^{1}H NMR ($CDCl_3$) (major) δ 2.07 (d, $^{2}J_{HP}$ = 13.5 Hz, Me), 2.67 (m, CH_2), 4.15 (m, 1H, OCH_2), and 4.33 (m, 1H, OCH_2); ^{13}C NMR ($CDCl_3$) (major) δ 24.03 (d, $^{1}J_{CP}$ = 55.5 Hz, Me−P), 37.40 (dd, J_{CP} = 10.0 and 18.9 Hz, CH_2), 65.88 (s, OCH_2), 145.89 (dd, J_{CP} = 9.3 and 86.0 Hz, C=C), 146.51 (dd, J_{CP} = 12.9 and 67.1 Hz, C=C); mass spectrum (CI) *m/z* 441 (M + H, 100%).

X-ray Structure Determination of 5, 8a, and 10. Compounds were measured at low temperature, T = 180(2) K, on a X8-APEX Bruker Kappa four-circle X-ray diffractometer system (Mo radiation, λ = 0.710 73 Å). An optimized data

collection strategy was defined using Cosmo.[8] Frames were integrated with the aid of Bruker Saint software[9] included in the Bruker APEX2 package software[10] and using a narrow-frame integration algorithm. The integrated frames yielded the following.

Complex **5** had a total of 20 076 reflections at a maximum 2θ angle of 66.28° (0.65 Å resolution), of which 7715 were independent reflections ($R_{int} = 0.0425$, $R_{sig} = 0.0321$, completeness 97.9%) and 7320 (94.98%) reflections were greater than $2\sigma(I)$. A triclinic cell, space group $P\bar{1}$, was found, and the unit cell parameters were $a = 8.4327(6)$ Å, $b = 10.8085(8)$ Å, $c = 11.9867(10)$ Å, $\alpha = 79.068(5)°$, $\beta = 76.955(5)°$, $\gamma = 79.595(5)°$, $V = 1034.12(14)$ Å^3, $Z = 2$, and calculated density $D_c = 1.574$ Mg/m^3.

Complex **8a** had a a total of 56 946 reflections at a maximum 2θ angle of 66.34° (0.65 Å resolution), of which 9720 were independent reflections ($R_{int} = 0.0480$, $R_{sig} = 0.0577$, completeness 99.8%) and 8688 (89.38%) reflections were greater than $2\sigma(I)$. A monoclinic cell, space group $P2_1/n$, was found, and the unit cell parameters were $a = 10.3259(5)$ Å, $b = 18.5007(8)$ Å, $c = 13.7720(6)$ Å, $\beta = 104.500(3)°$, $V = 2547.2(2)$ Å^3, $Z = 4$, and calculated density $D_c = 1.487$ Mg/m^3.

Complex **10** had a total of 60 020 reflections at a maximum 2θ angle of 78.06° (0.56 Å resolution), of which 11 182 were independent reflections ($R_{int} = 0.0382$, $R_{sig} = 0.0339$, completeness 89.6%) and 8688 (77.69%) reflections were greater than $2\sigma(I)$. A monoclinic cell, space group $P2_1/n$, was found, and the unit cell parameters were $a = 12.1134(6)$ Å, $b = 12.2035(6)$ Å, $c = 15.6203(8)$ Å, $\beta = 112.104(3)°$, $V = 2139.37(19)$ Å^3, $Z = 4$, and calculated density $D_c = 1.368$ Mg/m^3.

Absorption corrections were applied for data using the SADABS program.[11] The program SIR92[12] was used for phase determination and structure solution, followed by some subsequent difference Fourier maps. From the primary electron density map most of the non-hydrogen atoms were located, and with the aid of subsequent isotropic refinement all of the non-hydrogen atoms were identified. Atomic coordinates and isotropic and anisotropic displacement parameters of all the non-hydrogen atoms were refined by means of a full-matrix least-squares procedure on F^2. The H atoms were included in the refinement in calculated positions riding on the C atoms to which they were attached. Concerning the compound **10**, a statistical disorder between carbon and sulfur atoms linked to the P(2) atom was found; the ratio of occupancy was refined and found equal to 85%/15%. The refinement converged as follows: for **5** at R1 = 0.0401 and wR2 = 0.0868 with intensity $I > 2\sigma(I)$ and with the largest peak/hole in the final difference map being 0.625 and −0.860 e/Å^3; for **8a** at R1 = 0.0296 and wR2 = 0.0660 with intensity $I > 2\sigma(I)$ and with the largest peak/hole in the final difference map being 0.535 and −0.442 e/Å^3; for **10** at R1 = 0.0355 and wR2 = 0.0892 with intensity $I > 2\sigma(I)$ and with the largest peak/hole in the final difference map being 0.596 and −0.307 e/Å^3.

Drawings of molecules were carried out using ORTEP32.[13]

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Supporting Information Available: X-ray crystal structure analyses of compounds **5**, **8a**, and **10**, as CIF files. This material is available free of charge via the Internet at http://pubs.acs.org.

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