Functionalization of Phospholide Ions: Expanding the Scope by Changing the Base

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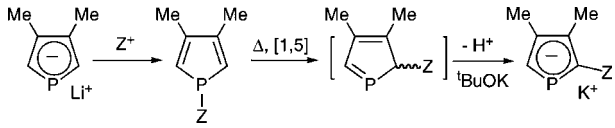
The sequence phospholide ion → 1-functional phosphole → 2-functional-2*H*-phosphole → 2-functional phospholide ion is best carried out using the starting phospholide both as a reagent and a base. Using this technique, it is possible to create in one pot α-connected phosphole−silylene−phosphole, phosphole−silylene−thiophene, and phosphole−silylene−alkyne chains. When applied to a 1,1′-biphospholyl, this technique leads to a 2-phospholylphosphole.

Introduction

Phospholes are weakly aromatic;[1] hence the central problem of their chemistry concerns their functionalization. In most of the cases, the function is introduced during the synthesis of the ring. A good recent example is provided by the preparation of phospholecarboxylic esters from the appropriate functional titanacyclopentadienes by Ti to P exchange.[2] At the moment, only two reasonably general methods afford functional from nonfunctional phospholes. The first one involves the preliminary synthesis of 2-bromophospholes that are converted into 2-lithiophospholes and then allowed to react with organic functional groups.[3] In this case, the main drawback is the lengthy synthesis of the 2-bromophospholes. The second method involves the reaction of phospholide ions with organic functionalities, followed by [1,5] sigmatropic shifts of the functions from P to the α-carbons of the ring and deprotonation of the resulting 2*H*-phospholes[4] (eq 1).

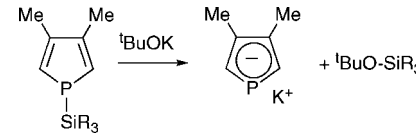


(1)

The simplicity of this one-pot synthesis of functional phospholides is quite attractive, but the yield of the process is sharply dependent on the migratory ability of Z and the compatibility of the P−Z bond with the base. Nothing can be done concerning the concerted shift, but the choice of the base remains open. We thus decided to study whether it was possible to broaden the scope of this method by changing the base.

Results and Discussion

The case of the silyl group (Z = SiR_3) appears to be quite illustrative. Silicon displays a good migratory ability,[4] but the P−Si bond is very easily cleaved by potassium *tert*-butylate (eq 2).



(2)

The P−Si bond of silylphosphines is known to be readily attacked by ^{t}BuOK.[5] In our case, the reaction is not only driven by the oxophilicity of silicon but also by the aromaticity of the phospholide. One possible solution is to increase the steric hindrance at silicon so that the nucleophilic attack at Si is slowed down and the [1,5] shift becomes competitive. This has been done with some success using the triisopropylsilyl group.[6] But this is a stopgap measure, and we felt it necessary to find a more general solution. Since most of the useful functions are electron-withdrawing, we reasoned that the starting nonfunctional phospholide is just strong enough as a base to deprotonate the functional 2*H*-phospholes. It is, of course, fully compatible with the P−Z bond. We decided to check this idea with the synthesis of a Cα−SiR_2−Cα bridge between two phosphole rings. The reaction was conducted at about room temperature in THF with 4 equiv of phospholide for 1 equiv of diphenyldichlorosilane. The reaction medium was monitored by ^{31}P NMR spectroscopy (eq 3).

Upon addition of Ph_2SiCl_2 to the excess of phospholide (**1**), the bis(phospholyl)-silane (**2**) is formed immediately and characterized by its high-field resonance at −60.5 ppm. It reacts rapidly with 1 equiv of **1** to give the monoshifted product (**3**) detected as an AX system (δ^{31}P −48.8 and +105.3 ppm, $^3J_{PP}$ = 53.3 Hz). The second shift leading to **4** (δ^{31}P +111 ppm) is much slower. It cannot be accelerated by increasing the temperature since decomposition takes place above 35 °C. The protonated phospholide **1** is recovered as the 2*H*-phosphole [4+2] dimer **5** (δ^{31}P −64.4 and −25.2 ppm, $^3J_{PP}$ = 182 Hz)[7] (eq 4).The mixture of **3** and **4** was

(1) The most recent estimate of the ASE of parent phosphole is quite low at 3.2 kcal mol^{-1}: Cyrañski, M. K.; Krygowski, T. M.; Katritzky, A. R.; Schleyer, P. v. R. *J. Org. Chem.* **2002**, *67*, 1333.

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(4) Holand, S.; Jeanjean, M.; Mathey, F. *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 98. Review: Mathey, F. *Acc. Chem. Res*. **2004**, *37*, 954.

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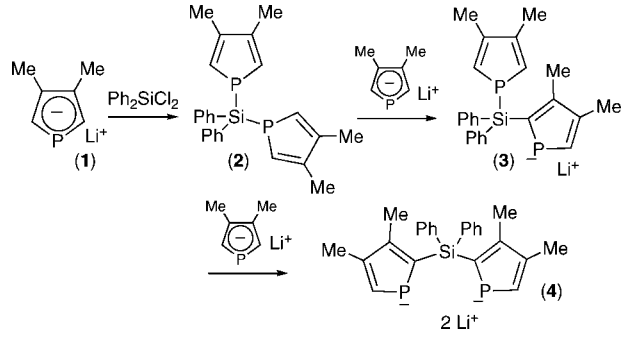
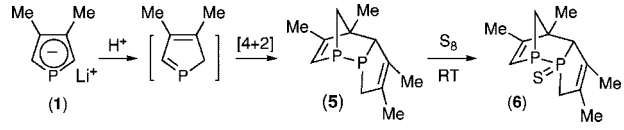


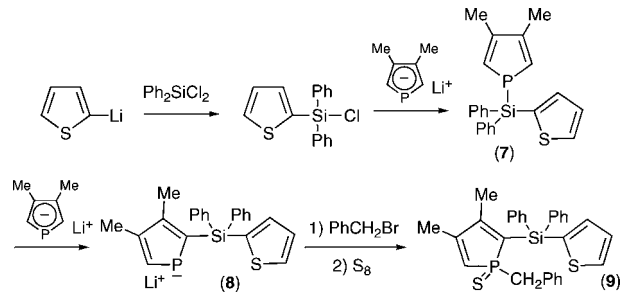
(3)

additionally characterized by anionic mass spectrometry: calcd for $C_{24}H_{25}P_2Si$ 403.1206; found 403.1215. Upon treatment by acetic acid, the phosphole−Si−phosphole bridge of **4** is cleaved and the dimer **5** is obtained. This sensitivity to hydrolysis precluded the use of **4** for synthetic purposes.



(4)

Encouraged by these initial findings, we envisaged to use silicon as a carrier for a thiophene ring. The [1,5] shift of thiophene around the phosphole ring needs strong heating,[8] and we thought that the synthesis of a α-connected phosphole−silylene−thiophene chain under mild conditions would be worthwhile. Indeed, both phosphole−thiophene[9] and thiophene−silylene[10] mixed chains have proven their worth for the manufacture of OLEDs or organic transistors. The one-pot reaction was carried out as shown in eq 5.



(5)

All of the transformations take place at room temperature. Diphenyldichlorosilane was added to the preformed 2-lithiothiophene. Lithium phospholide was then added to the crude 2-(diphenylchlorosilyl)thiophene. Silylphosphole **7** was characterized by its ^{31}P resonance at −61.4 ppm. The shift leading to **8** was performed overnight. The functional phospholide was characterized by its ^{31}P resonance at +105.4 ppm. It was fully identified as its *P*-benzyl sulfide (**9**) that was separated by chromatography from the monosulfide **6**,[7] resulting from the protonation−dimerization−sulfurization of **1** as shown in eq 4. The X-ray crystal structure of **9** is shown in Figure 1. This approach to silyl-functional phospholes can be generalized. As

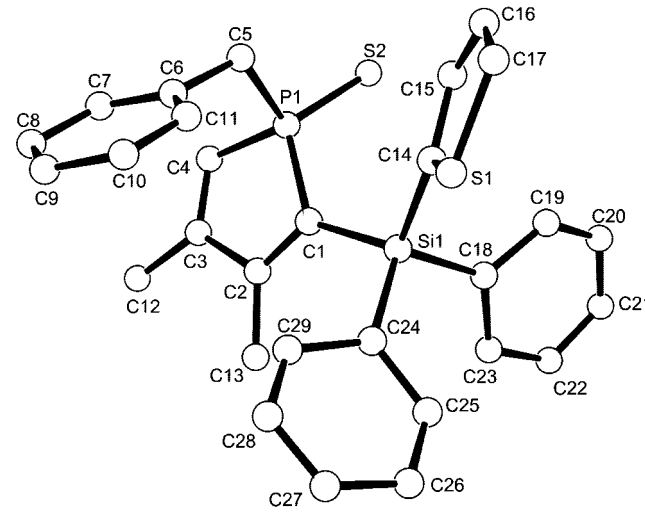
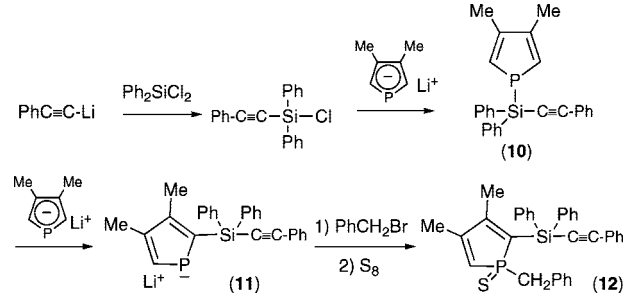


Figure 1. X-ray crystal structure of the 2-thienylsilylphosphole sulfide **9**. Main bond lengths (Å) and angles (deg): P−S 1.984(6), P−C1 1.829(13), P−C4 1.795(13), P−C5 1.852(14), C1−Si 1.905(12), C14−Si 1.888(15), C18−Si 1.914(13), C24−Si 1.897(14); C1−P−C4 93.6(6), C1−Si−C14 111.5(6).

an illustration, we also prepared an α-alkynylsilylphosphole as shown in eq 6.

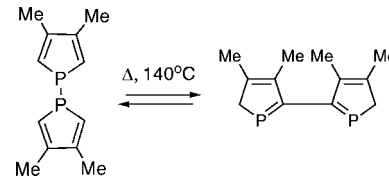


(6)

The ^{31}P resonances of **10** and **11** appear at −59.2 and +104.4 ppm, respectively. The X-ray crystal structure of **12** is shown in Figure 2.

This methodology using the starting phospholide as the base can be used with other shifting atoms than silicon. From our experiments on the synthesis of BIPNOR for asymmetric catalysis,[11] we knew that an equilibrium occurs between 1,1′-biphospholyl and 2,2′-bis(5*H*-phospholyl) at high temperature (eq 7).

The 1-phosphinophospholes have been described[12] and



(7)

display a limited chemical stability, thus preventing their use in shifting experiments with ^{t}BuOK as the base. It was tempting

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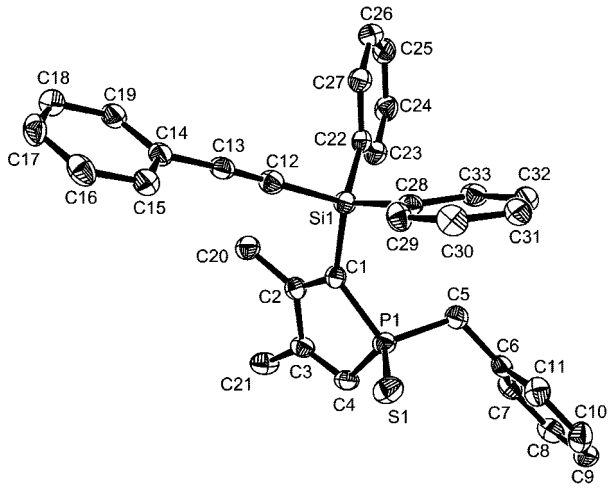


Figure 2. X-ray crystal structure of the 2-alkynylsilylphosphole sulfide **12**. Ellipsoids enclose 50% of the electronic density. Main bond lengths (Å) and angles (deg): P1−S1 1.9576(10), P−C1 1.812(3), P1−C4 1.785(3), P1−C5 1.828(3), C1−Si1 1.870(3), Si1−C12 1.828(3), C12−C13 1.207(3), C13−C14 1.445(3); C1−P−C4 93.55(12), C1−Si1−C12 109.84(11).

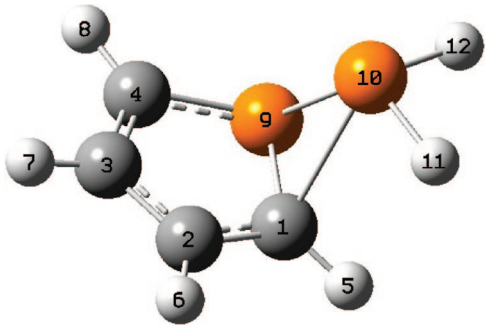
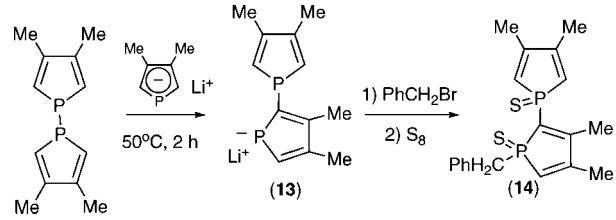


Figure 3. Structure of the transition state for the conversion of 1-phosphinophosphole into 2-phosphino-2*H*-phosphole. Main bond lengths (Å) and angles (deg): P−P 2.537, P9−C1 1.833, P10−C1 2.299, P9−C4 1.749; P9−P10−C1 44.2, C1−P9−C4 89.4.

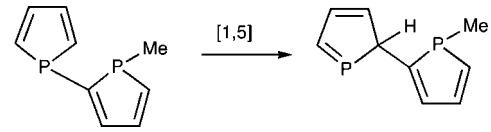
to study the shift of phosphorus-centered groups around the phosphole ring under our new mild conditions. In order to have an idea of the difficulty of this shift, we first decided to compute the barrier for the transformation of 1-phosphinophosphole into 2-phosphino-2*H*-phosphole by DFT at the B3LYP/6-311+G(d,p) level.[13] The transition state is shown in Figure 3. It lies 20.0 kcal mol^{-1} higher in energy (ZPE included) than the starting 1-phosphinophosphole. Thus the shift of P appears to be more difficult than the shift of Si (barrier for SiH_3 14.2 kcal mol^{-1})[4b] or H (barrier 18.3 kcal mol^{-1})[4b] but still rather easy. We decided to test this shift in the case of 3,3′,4,4′-tetramethylbiphospholyl.[14] The chemistry is depicted in eq 8.

The formation of **13** is monitored by the appearance of a



(8)

AX system in the ^{31}P NMR spectrum: $\delta^{31}P$ −16.3 and +93.7 ppm, $^2J_{PP}$ = 168.7 Hz. The anion was further characterized as its *P*-benzyl sulfide **14**. In **14**, the two sides of the symmetrical phosphole ring appear to be inequivalent at room temperature due to a blocked rotation around its bond with the other phosphole ring. We also wondered whether a second shift was possible in a structure like **13**. In order to evaluate the feasibilty of such a transformation, we carried out a DFT study of the reaction depicted in eq 9 at the B3LYP/6-311+G(d,p) level. The transition state is 29.6 kcal mol^{-1} higher in energy than the starting product. Thus, this second shift does not appear likely under mild conditions, and all our attempts at performing such a reaction failed even at higher temperatures.



(9)

As a conclusion, although it is hampered by relatively modest yields and separation problems, this new methodology is characterized by an extreme simplicity and significantly extends the range of functional phospholides that are accessible.

Experimental Section

Nuclear magnetic resonance spectra were obtained on a Bruker Avance 300 and Varian Inova spectrometer operating at 300.13 MHz for ^1H, 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 (^1H 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.

2-Thienylsilylphosphole Sulfide (9). In a Schlenk flask, a solution of 2-lithiothiophene was prepared by dropwise addition of nBuLi (1.66 mL, 2.66 mmol) onto thiophene (0.21 mL, 2.66 mmol) in dry THF (5 mL) at −78 °C. After stirring for 5 min, the solution was transferred dropwise via cannula onto diphenyldichlosilane (0.57 mL, 2.66 mmol) in dry THF (5 mL) at −78 °C. Lithium phospholide (5.32 mmol, in 20 mL of dry THF) was then added dropwise via cannula to the crude thienylchlorosilane still at −78 °C. The reaction was allowed to warm to room temperature and monitored by ^{31}P NMR until completion. Benzyl bromide (0.40 mL, 3.32 mmol) was added at 0 °C, and then the solution was warmed to room temperature. Then the sulfurization was performed by addition of sulfur powder (0.2 g, 6.25 mmol). After vacuum distillation of the solvent, the residue was chromatographed on

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neutral alumina with a mixture of dichloromethane−petroleum ether (70/30) and recrystallized in hexanes to yield 0.52 g (20%) of a white solid.

^{31}P NMR (CD_2Cl_2): δ + 64.0 ppm. ^{1}H NMR (CD_2Cl_2): δ 1.82 (d, ^4J(P−H) = 2.3 Hz, 3H, −C H_3), 2.03 (d, ^4J(P−H) = 1.8 Hz, −C H_3 (H)), 2.84 (m, 2H, P−C H_2), 6.15 (d, ^2J(P−H) = 31.1 Hz, 1H, C$_\alpha H$), 7.61–7.80 (m, 18H, *Ph* + *Th*). ^{13}C NMR (CD_2Cl_2): δ 17.66 (d, ^3J(P−C) = 18.36 Hz, −*C*H$_3$(H)), 20.25 (d, ^3J(P−C) = 18.36 Hz, −*C*H$_3$(Si)), 39.99 (d, ^1J(P−C) = 43.7 Hz, −*C*H$_2$), 128.96 (d, ^1J(P−C) = 76.8 Hz, −*C*$_\alpha$H), 127.5–140.1 (m, *Ph* + *Th*), 153.79 (d, ^2J(P−C) = 22.8 Hz, −*Cβ*), 165.78 (d, ^2J(P−C) = 10.8 Hz, −*Cβ*). MS: calcd for $C_{29}H_{28}PS_2Si$ *m*/*z* 499.1139, found 499.1128. Anal. Calcd for $C_{29}H_{27}PS_2Si$: C, 69.84; H, 5.46. Found: C, 69.98; H, 5.53.

2-Alkynylsilylphosphole Sulfide (12). In a Schlenk flask with phenylacetylene (2.3 mL, 21.3 mmol) in dry THF (25 mL) under nitrogen at −78 °C was added dropwise nBuLi (13.3 mL, 21.3 mmol, 1.6 M). After stirring at −78 °C for 30 min, the solution was warmed to room temperature for 30 min and then cooled to −78 °C again. This solution was transferred via cannula dropwise to another flask under nitrogen containing dichlorodiphenylsilane (4.5 mL, 21.3 mmol) in dry THF (25 mL) at −78 °C. This mixture was then allowed to warm to room temperature. Finally, a solution containing lithium phospholide (26.6 mmol) was added dropwise at room temperature and monitored by ^{31}P NMR until completion. Then benzyl bromide (1.9 mL, 16.0 mmol) was added at 0 °C, and the solution was warmed to room temperature. Sulfurization was performed by addition of sulfur powder (0.80 g, 25.0 mmol). After vacuum distillation of the solvent, the residue was purified by column chromatography on neutral alumina, using a mixture of dichloromethane/hexanes (50/50) to yield 0.78 g of a light yellow solid (11.5%).

^{31}P NMR (CD_2Cl_2): δ +63.9 ppm. ^{1}H NMR (CD_2Cl_2): δ 2.00 (s, 3H, CH_3), 2.11 (s, 3H, CH_3), 3.26 (m, 2H, P−CH_2), 6.19 (d, ^2J(P−H) = 30.8 Hz, 1H, *H*α), 7.18–8.09 (m, 20H, *Ph*). ^{13}C NMR (CD_2Cl_2): δ 17.35 (d, ^3J(P−C) = 18.4 Hz, *C*H$_3$), 19.09 (d, ^3J(P−C) = 18.4 Hz, *C*H$_3$), 40.44 (d, ^1J(P−C) = 44.3 Hz, P−*C*H2), 89.64 (s, ≡*C*−Ph), 110.55 (s, Si−*C*≡), 122.79–136.74 (m, *Ph* + =*C*−Si), 128.5 (d, ^1J(P−C) = 76.7 Hz, =*C*−H), 153.79 (d, ^2J(P−C) = 22.1 Hz, *Cβ*), 165.5 (d, ^2J(P−C) = 10.8 Hz, *Cβ*). MS: calcd for $C_{33}H_{30}PSSi$ *m*/*z* 517.1575; found 517.1563 (M^+ + H).

2-Phospholylphosphole Disulfide (14). In a flask containing lithium phospholide (10.64 mmol, in 20 mL of dry THF), iodine (1.35 g, 5.32 mmol) was added at 0 °C; the solution was then warmed to room temperature. Another solution containing lithium phospholide (5.32 mmol, in 10 mL of dry THF) was transferred dropwise to the previous solution; this mixture was then monitored by ^{31}P NMR until completion of the reaction. Benzyl bromide (0.65 mL, 5.47 mmol) was added at 0 °C, and then the solution was warmed to room temperature. Then the sulfurization was performed by addition of sulfur powder (0.51 g, 16 mmol). After vacuum distillation of the solvent, the residue was chromatographed on silica with a mixture of dichloromethane−petroleum ether (70/30) to yield 0.56 g (14%) of a yellow solid.

^{31}P NMR (CD_2Cl_2): δ +30.4 (d, ^2J(P−P) = 41.5 Hz, P_2), +56.3 (d, P_1−CH_2−Ph). ^{1}H NMR (CD_2Cl_2): δ 1.90 (dd, 3H, −CH_3 (*1*)), 2.11 (dd, 3H, −CH_3 (*2*)), 2.15 (dd, 3H, −CH_3 (*2*)), 2.31(dd, 3H, −CH_3 (*1*)), 3.39 (m, 2H, P−C H_2), 6.00 (d, ^2J(P−H) = 31.6 Hz, 1H, −C$_\alpha H$ (*1*)), 6.24 (d, ^2J(P−H) = 31.6 Hz, 1H, −C$_\alpha H$ (*2*)), 6.57 (d, ^2J(P−H) = 31.1 Hz, 1H, −C$_\alpha H$ (*2*)), 7.08–7.27 (m, 5H, *Ph*). ^{13}C NMR (CD_2Cl_2): δ 17.49–19.92 (m, −CH_3 (*1* + *2*)), 42.13 (d, ^1J(P−C) = 46 Hz, −*C*H$_2$), 123.98 (d, ^1J(P−C) = 85.2 Hz, −*C*$_\alpha$H (*2*)), 124.48 (d, ^1J(P−C) = 85.2 Hz, −*C*$_\alpha$H (*2*)), 127.165 (d, ^1J(P−C) = 78.3 Hz, −*C*$_\alpha$H (*1*)), 127.68–130.43 (−$C_{ortho\text{-}meta\text{-}para}$), 132.40 (d, ^2J(P−C) = 8.1 Hz, −C_{ipso}), 153.42 (d, ^2J(P−C) = 19.6 Hz, −*Cβ*(*2*)), 154.00 (d, ^2J(P−C) = 11.3 Hz, −*Cβ*(*1*)), 154.2 (d, ^2J(P−C) = 19.6 Hz, −*Cβ*(*2*)), 165.00 (d, ^2J(P−C) = 11.3 Hz, −*Cβ*(*1*)). MS: calcd for $C_{19}H_{23}P_2S_2$ *m*/*z* 377.0716, found 377.0711 (M^++ H). Anal. Calcd for $C_{19}H_{22}P_2S_2$: C, 60.62; H, 5.89. Found: C, 60.40; H, 5.94.

X-Ray Structure Determination for 9 and 12. The Bruker X8-APEX[15] X-ray diffraction instrument with Mo radiation was used for data collection. All data frames were collected at low temperatures (T = 100 K) using an ω, θ-scan mode (0.5° ω-scan width, hemisphere of reflections) and integrated using the Bruker SAINT-PLUS software package.[16] The intensity data were corrected for Lorentzian polarization. Absorption corrections were performed using the SADABS program.[17] SIR97[18] was used for direct methods of phase determination, and the Bruker SHELXTL software package[19] for structure refinement and difference Fourier maps. Atomic coordinates and isotropic and anisotropic displacement parameters of all the non-hydrogen atoms of two compounds were refined by means of a full matrix least-squares procedure on F^2. All H atoms were included in the refinement in calculated positions riding on the C atoms. Drawings of molecules were performed using Ortep 3.[20]

Crystal and structure parameters of 9: size 0.33 × 0.32 × 0.05 mm^3, orthorhombic, space group *P*2(1)/*n*, a = 10.27(2) Å, b = 8.806(18) Å, c = 30.09(6) Å, α = γ = 90.0°, β = 93.80(2)°, V = 2714(10) Å^3, ρ_{calcd} = 1.220 g/cm^3, Mo radiation (λ = 0.71073 Å), T = 100(2) K, reflections collected = 12 635, independent reflections = 3324 (R_{int} = 0.2617), absorption coefficient μ = 0.315 mm^{-1}; max/min transmission = 0.9844 and 0.9033, 301 parameters were refined and converged at R1 = 0.1188, wR2 = 0.2592, with intensity $I > 2\sigma(I)$; the final difference map was 0.612 and −0.743 e Å^{-3}.

Crystal and structure parameters of 12: size 0.32 × 0.17 × 0.10 mm^3, monoclinic, space group *P*2(1)/*c*, a = 11.982(2) Å, b = 11.526(2) Å, c = 20.420(4) Å, α = γ = 90.0° β = 101.671(3)°, V = 2761.8(9) Å^3, ρ_{calcd} = 1.130 g/cm^3, Mo radiation (λ = 0.71073 Å), T = 100(2) K, reflections collected = 1 3888, independent reflections = 4641 (R_{int} = 0.0491), absorption coefficient μ = 0.239 mm^{-1}; max/min transmission = 0.9765 and 0.9275, 327 parameters were refined and converged at R1 = 0.0780, wR2 = 0.1993, with intensity $I > 2\sigma(I)$; the final difference map was 0.317 and −0.327 e Å^{-3}.

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Supporting Information Available: X-ray crystal structure analysis of compounds **9** and **12**. This material is available free of charge via the Internet at http://pubs.acs.org.

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