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Stereochemistry and Some Synthetic Uses of the Heteroarylation of Phospholes

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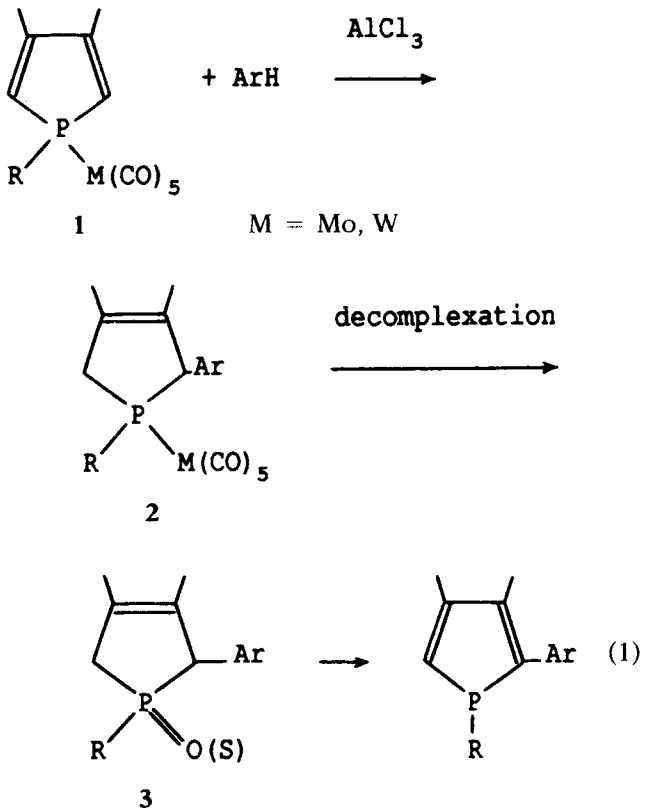
ABSTRACT

Further studies have been conducted on the condensation of electron-rich arenes or heteroarenes with the dienic system of phosphole P-*complexes. According to the X-ray crystal structure analysis of one of the resulting 2-aryl-3-phospholene* P-*complexes, the condensation takes place on the side of the diene opposite to the complexing group. The decomplexation of the phospholene P–Mo(CO)$_5$ and P–W(CO)$_5$ complexes, respectively, by reaction with sulfur or halogens and tertiary amines yields the corresponding* P-*sulfides and oxides with full retention of the stereochemistry at phosphorus. Double condensation of the phosphole* P-*complexes onto the 2 and 5 positions of thiophene and furan ultimately leads to phosphole–thiophene–phosphole and phosphole–furan–phosphole chains. The first type has been characterized by X-ray crystal structure analysis of its* P,P-*disulfide. No electronic delocalization appears to take place along the chain.*

INTRODUCTION

In a preceding paper [1], we described the arylation and heteroarylation of the phosphole ring. After a series of additional steps, this process ultimately leads to 2-aryl- or 2-heteroaryl-phospholes starting from 2-unsubstituted phospholes (Equation 1). In this paper, we wish to establish the stereochemistry of the arylation and decomplexation steps and to show how it is possible to use this methodology to build original tricyclic systems that could be used for the building of polyphosphole chains. Such chains may have some potential in the conception of new electroconducting polymers [2].



Dedicated to Marianne Baudler on the occasion of her seventieth birthday.

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RESULTS AND DISCUSSION

Stereochemistry

The initial arylation step (**1** → **2**) in all cases gives a single arylated complex **2** that is characterized by a very weak $^2J(P–CH\text{Ar})$ coupling but whose stereochemistry is unknown. Indeed, we cannot transpose to phosphine complexes the relationship that has been established between $^2J(P–CH)$ couplings and H–C–P lone pair dihedral angles in the case of free phosphines [3]. Thus, we decided to perform the X-ray crystal structure analysis of **2a** (M = W, Ar = 2-C_4H_3S, R = Ph). The structure as depicted in Figure 1 clearly shows that the aryl group points opposite to the complexing group: the Ar–CH–P–W dihedral angle is 99°. Thus, the arylation preferentially takes place on the less hindered side of the phosphole dienic system, that is, on the side opposite to the bulky complexing group. This conclusion is the opposite of what would be expected if we applied the coupling–dihedral angle relationship established for free phosphines [3]. Thus, extreme caution is needed when using NMR data to discuss the stereochemistry of phosphine complexes. A similar problem had already been encountered in the case of phosphirane complexes [4]. The two decomplexation procedures depicted in Equations 2 [5] and 3 [6] selectively convert **2** into a single isomer of the corresponding phospholene oxide or sulfide **3**. In that case, high $^2J(P–CH\text{Ar})$ coupling constants are observed and literature data [7] establish that the 2-aryl substituents of **3** are trans to the P=O or P=S groups. This result, combined with the X-ray data for **2a**, demonstrates that *the decomplexation procedures depicted in Equations 2 and 3 take place with full retention of the stereochemistry at phosphorus.*

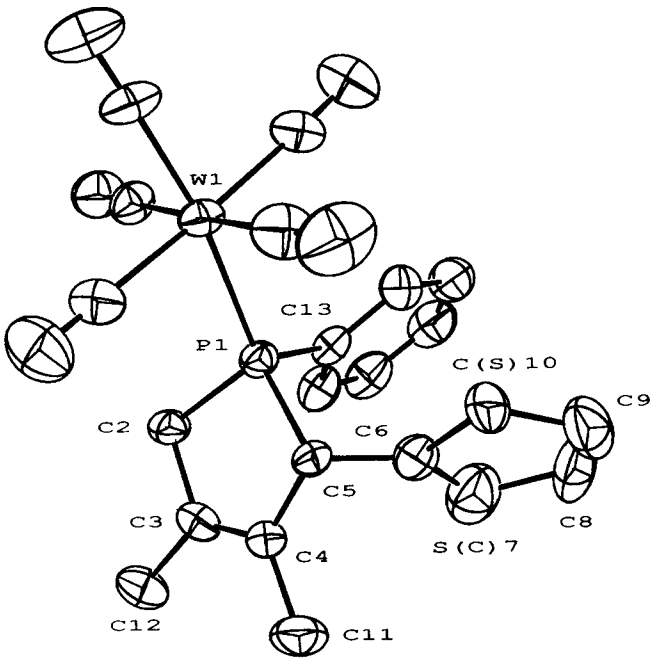


FIGURE 1 ORTEP Drawing of One Molecule of **2a** (M = W, Ar = 2-C_4H_3S, R = Ph). Vibrational ellipsoids are scaled to enclose 50% of the electron density. Hydrogen atoms are omitted for clarity. Principal bond distances (Å): $P_1–W_1$ 2.511(2); $P_1–C_{13}$ 1.813(7); $P_1–C_2$ 1.846(7); $P_1–C_5$ 1.885(6); $C_2–C_3$ 1.517(9); $C_3–C_4$ 1.301(9); $C_4–C_5$ 1.512(9); $C_5–C_6$ 1.486(9). Selected bond angles (deg): $C_2–P_1–C_5$ 93.1(3); $C_2–P_1–C_{13}$ 104.2(3); $C_5–P_1–C_{13}$ 103.9(3); $W_1–P_1–C_2$ 113.2(2); $W_1–P_1–C_5$ 118.8(2); $W_1–P_1–C_{13}$ 119.7(2); $P_1–C_2–C_3$ 104.4(5); $C_2–C_3–C_4$ 117.8(6); $C_3–C_4–C_5$ 117.5(6); $C_4–C_5–C_6$ 116.1(5); $P_1–C_5–C_4$ 103.8(4); $P_1–C_5–C_6$ 112.9(4).

$$R_3P—W(CO)_5 \xrightarrow{X_2} R_3P—W(CO)_4X_2 \xrightarrow{R_3N} R_3P{=}O \quad (2)$$

X = Br, I

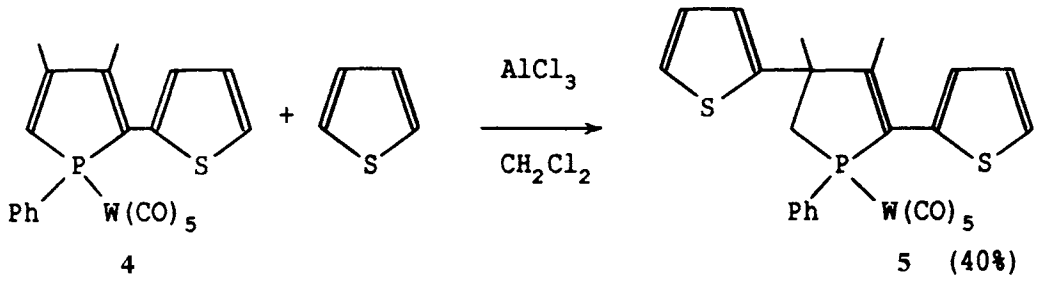
R_3N = *N*-methylimidazole, 2,2′-bipyridyl

$$R_3P—Mo(CO)_5 \xrightarrow[\Delta]{S_8} R_3P{=}S \quad (3)$$

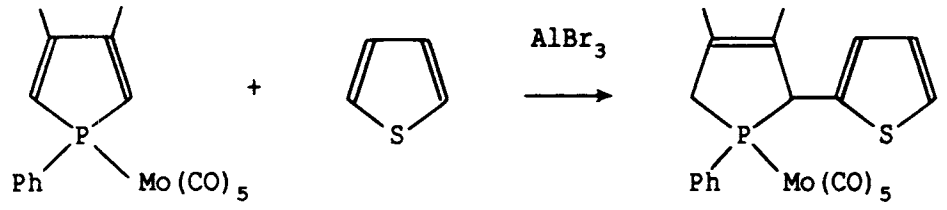
Synthesis of Tricyclic Systems

The bridging of arenes or heteroarenes with phospholes could serve to create original polycyclic chains containing phosphole units. For such a purpose, the two necessary building blocks are the arene (or heteroarene)–phosphole–arene and the phosphole–arene–phosphole units. In order to check the usefulness of our new methodology, we thus allowed the 2-thienylphosphole complex **4** to react with thiophene in the presence of aluminum trichloride (Equation 4). The condensation took place as usual but yielded the 2,4-bis(thienyl)-substituted derivative (**5**) instead of the expected 2,5-derivative. The 2,4-substitution pattern was demonstrated as follows. The ^1H NMR spectrum (C_6D_6) showed two inequivalent and uncoupled methyls at δ = 1.60 and 1.75. The CH_2 group appeared at δ = 2.69. The ^{13}C NMR spectrum ($CDCl_3$) showed two inequivalent methyls at δ = 15.80 ($^3J(C–P)$ = 8.6 Hz) and 27.94 (singlet), a CH_2 group at δ = 49.65 ($^1J(C–P)$ = 26.2 Hz) and a sp^3 carbon at δ = 56.10 (singlet). Thus, this methodology cannot serve to build arene–phosphole–arene units.

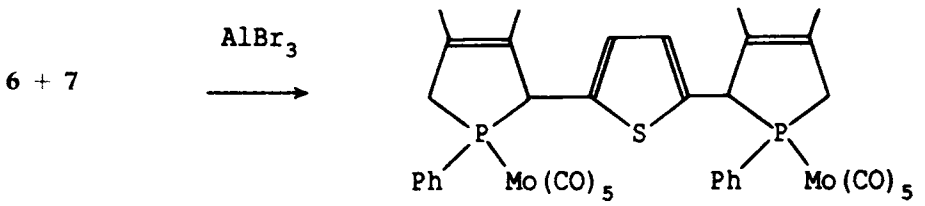
We were more fortunate with the phosphole–arene–phosphole chains. We performed the sequence of reactions shown in Equations 5–9. The



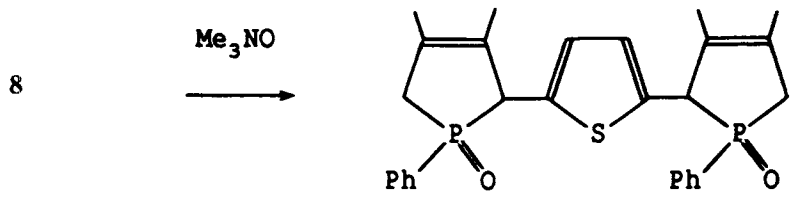
4 5 (40%) (4)



6 7 (5)



8 (6)



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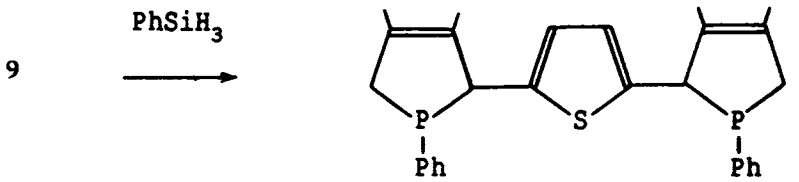

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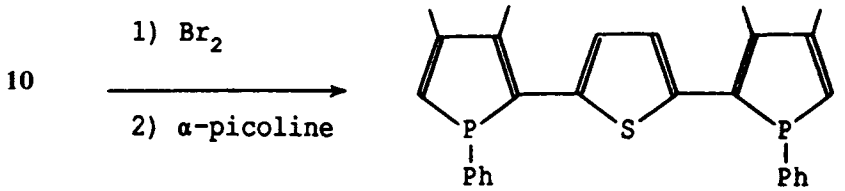
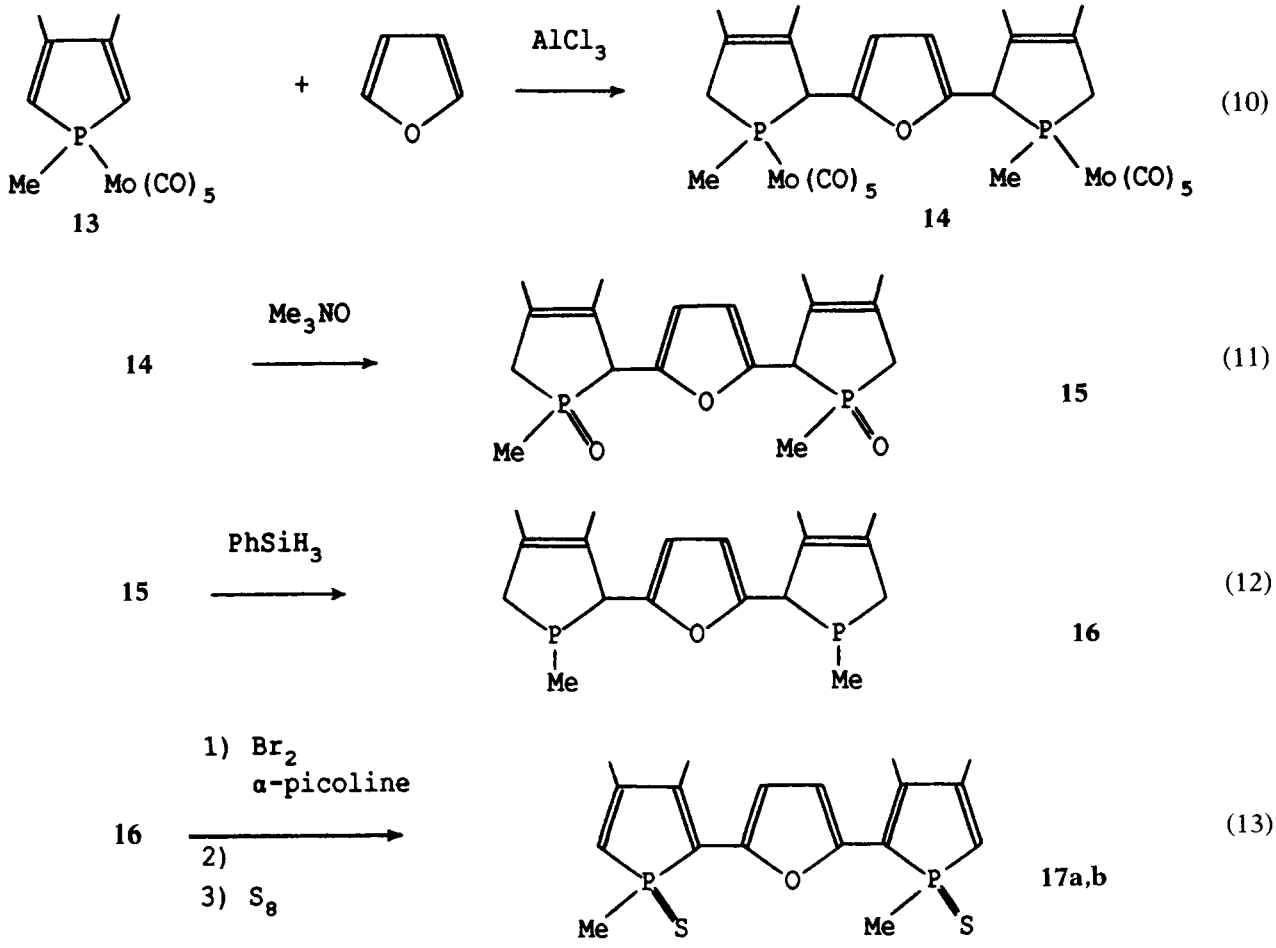


11 (9)

formation of the intermediate compounds **7–10** was monitored by ^{31}P NMR analysis. They were used as crude products without further characterization. The overall yield of the final phosphole **11** from the starting molybdenum complex **6** was a significant 40%, which means that each elementary step works quite well. By comparison with the previously described techniques [1], we have introduced some minor changes. The use of aluminum tribomide made in situ from aluminum turnings and bromine in dichloromethane proved to be beneficial (better reproducibility than with commercial anhydrous $AlCl_3$). In the oxidative decomplexation (Equation 7) we made use of trimethylamine oxide instead of sulfur because the resulting oxide **9** was easier to convert into the phosphole than the corresponding sulfide (see the preceding work [1] where a phospholene sulfide was first transformed into the corresponding oxide before conversion into the phosphole). That the central thiophene ring is 2,5-disubstituted was immediately apparent from the inspection of the ^1H NMR spectrum of **11**. The two β-protons of the thiophene ring appear as a sharp singlet at $\delta = 6.84$ ($CDCl_3$). The X-ray crystal structure analysis was carried out on the phosphole disulfide **12** (Figure 2). The geometry of the three heterocycles is absolutely normal. The phosphorus atoms are outside of the corresponding diene mean planes by only 0.0252 ± 0.0009 Å and 0.0229 ± 0.0009 Å respectively. One of the phosphole rings is almost coplanar with the thiophene ring (3.3 ± 1.6°) whereas the other significantly deviates from coplanarity (138.9 ± 0.1°). Since the C–C bridges have no double bond character, the rotation of the rings around them is probably almost free so that packing effects may be responsible for this dissymmetry.

Finally, we also attempted the synthesis of a phosphole–furan–phosphole chain as depicted in the sequence of reactions shown in Equations 10–13. The overall yield of **17** from **13** is only 23%. This may, in part, be due to the very high sensitivity toward oxidation of an intermediate such as **16**. Two significant differences appear between the thiophene and furan cases. Aluminum tribomide is excluded in the second case because it tends to destroy the furan ring. Besides, it is possible to perform simultaneously the condensation of two phosphole units on the furan ring. The resulting tricyclic dicomplex **14** was purified in order to establish this point. The mass spectrum (70 eV) shows a molec-



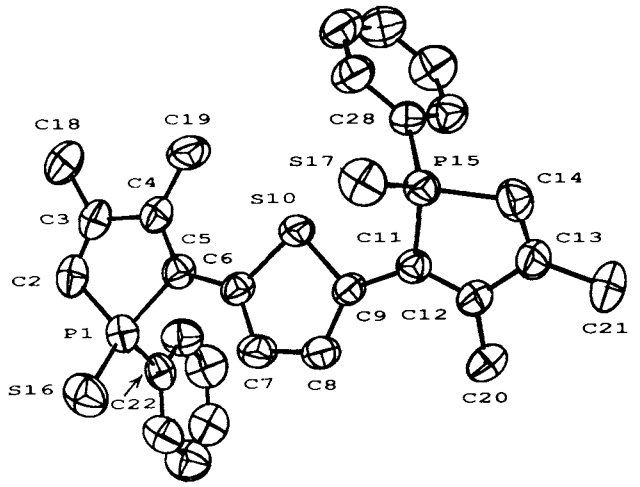


FIGURE 2 ORTEP Drawing of One Molecule of **12**. Vibrational ellipsoids are scaled to enclose 50% of the electron density. Hydrogen atoms are omitted for clarity. Principal bond distances (Å): P_1–C_2 1.774(4); P_1–C_5 1.818(3); P_1–C_{22} 1.816(3); P_1–S_{16} 1.945(1); C_2–C_3 1.326(5); C_3–C_4 1.501(4); C_4–C_5 1.354(4); C_5–C_6 1.452(4); C_6–C_7 1.370(4); C_7–C_8 1.414(4); C_8–C_9 1.364(4); C_6–S_{10} 1.724(3); C_9–S_{10} 1.722(3); C_9–C_{11} 1.461(4); C_{11}–C_{12} 1.347(4); C_{12}–C_{13} 1.499(5); C_{13}–C_{14} 1.339(5); C_{14}–P_{15} 1.779(3); C_{11}–P_{15} 1.810(3); P_{15}–C_{28} 1.816(3); P_{15}–S_{17} 1.940(1). Selected bond angles (deg): C_2–P_1–C_5 92.6(2); P_1–C_5–C_6 121.1(2); C_5–C_6–S_{10} 123.1(2); C_6–S_{10}–C_9 92.9(1); S_{10}–C_9–C_{11} 119.0(2); C_9–C_{11}–P_{15} 121.6(2); C_{11}–P_{15}–C_{14} 92.2(2).

ular peak at m/z 792. The ^{1}H NMR spectrum is especially informative since it shows a single resonance at δ = 6.10 for the two furan β protons. According to ^{1}H, ^{13}C, and ^{31}P NMR data, the two phospholene units are equivalent. Finally, if a phosphole such as **11** is obtained as a single isomer at room temperature due to the easy pyramidal inversion of phosphorus [8], a sulfide such as **17** is obtained as a ca 50:50 mixture of two isomers as expected.

Further uses of tricyclic chains such as **11** and **17** will be reported later.

EXPERIMENTAL

All reactions were performed under argon. NMR spectra were recorded on multinuclear WP 80 SY and AC 200 SY Bruker spectrometers operating at 80.13 and 200.13 (^{1}H), 20.15 and 50.32 (^{13}C), and 32.44 (^{31}P) MHz. Chemical shifts are downfield from internal TMS (^{1}H and ^{13}C) and external 85% H_3PO_4 (^{31}P), and coupling constants are in hertz. Mass spectra were recorded on as Shimadzu GC-MS QP 1000 instrument at 70 eV under electronic impact. Elemental analyses were performed by the Service Central de Microanalyse du CNRS, France.

Silica gel (70-230 mesh) was used for the chromatographic separations. All commercially available reagents were used as received from the suppliers. The experiments were carried out under argon.

Synthesis of **5**

To a solution of [1-phenyl-2-(2-thienyl)-3,4-dimethylphosphole]pentacarbonyltungsten [1] (1 g, 17 × 10^{-4} mol) in dichloromethane (10 mL) was added anhydrous aluminum trichloride (0.225 g, 2 × 10^{-3} mol), then an excess of thiophene (1.36 mL, 17 × 10^{-3} mol). The mixture was stirred at room temperature for 30 min. The resulting solution was poured onto a mixture of ice and ammonium chloride. The organic products were collected by extraction with dichloromethane. The extracts were washed with water until neutral. After evaporation of CH_2Cl_2, the organic residue was chromatographed with hexane/ether 95/5 as the eluent. Complex **5** was thus obtained as white crystals (0.46 g, 40%). ^{31}P NMR (CH_2Cl_2): δ + 27, $^1J(^{31}P-^{183}W)$ = 239 Hz; ^{1}H NMR (C_6D_6): δ 1.60 (s, 3H, Me), 1.75 (s, 3H, Me), 2.69 (m, 2H, CH_2–P), 6.50–7.94 (m, 11H, phenyl + thienyl); ^{13}C NMR ($CDCl_3$): δ 15.80 (d, ^3J(C–P) = 8.5 Hz, Me), 27.94 (s, Me), 49.65 (d, ^1J(C–P) = 26.2 Hz, CH_2–P), 56.10 (s, β, sp^3C), 153.44 (s, β sp^2C), 154.49 (d, ^1J(C–P) = 13.6 Hz, α sp^2C), 196.96 (d, ^2J(C–P) = 7 Hz, cis CO), 198.93 (d, ^2J(C–P) = 22.6 Hz, trans CO); mass spectrum (^{183}W): m/z 678 (M^+, 11%), 594 (M^+ – 3CO, 100%), 538 (M^+ – 5CO, 73%); Anal. Calcd. for $C_{25}H_{19}OPSW$: C, 44.26; H, 2.82. Found: C, 44.74; H, 2.90.

Synthesis of **11**

First Step **6** → **7** (*Equation 5*). Aluminum tribromide was first prepared in a Schlenck tube from aluminum turnings (0.6 g, 22 × 10^{-3} eq) in CH_2Cl_2 (4 mL) and dry bromine (1.7 mL, 66 × 10^{-3} eq) in CH_2Cl_2 (5 mL). The bromine solution was slowly added to the aluminum suspension with stirring and cooling of the reaction mixture in an ice bath. When the reaction mixture became colorless, a solution of complex **6** (8.28 g, 2 × 10^{-2} mol) in CH_2Cl_2 (20 mL) was quickly added followed by thiophene (3.4 mL, 42 × 10^{-3} mol). After having been stirred for 10 min. at ca 0°C, the reaction mixture was carefully poured onto a mixture of ice and ammonium chloride. The organic products were collected by extraction with dichloromethane. The extracts were washed with water until neutral and dried over anhydrous magnesium sulfate. ^{31}P NMR (CH_2Cl_2): δ (**7**) +34.

Second Step **6** + **7** → **8** (*Equation 6*). A mixture of 22 × 10^{-3} mol of $AlBr_3$ and 2 × 10^{-2} mol of **6** was prepared in 30 mL of CH_2Cl_2 as described above. The crude solution of **7** was concentrated to ca 20 mL and added to the mixture of $AlBr_3$ and **6** while stirring at ca 0°C (ice bath). After 10 min, the reaction mixture was hydrolyzed as above. The CH_2Cl_2 ex-

tracts were dried over $MgSO_4$. ^{31}P NMR (CH_2Cl_2): δ (**8**) +32.

Third Step **8** → **9** (*Equation 7*). Crude **8** obtained after evaporation of CH_2Cl_2 was dissolved in xylene (50 mL). To this solution was added Me_3NO, $2H_2O$ (35.5 g, 32×10^{-2} mol). The reaction mixture was stirred overnight at 120°C. The cooled solution was filtered through celite and dried over $MgSO_4$ after decantation of some water. ^{31}P NMR: δ (**9**) +49 (xylene): +51 (CH_2Cl_2).

Fourth Step **9** → **10** (*Equation 8*). Crude **9** obtained after evaporation of xylene was dissolved in toluene (5 mL). Phenylsilane (2.7 mL, 22×10^{-3} mol) was added and the reaction mixture was refluxed for 1 h. ^{31}P NMR (toluene): δ (**10**) −9.

Fifth Step **10** → **11** (*Equation 9*). Crude **10** obtained after evaporation of toluene was dissolved in dry CH_2Cl_2 (20 mL) and cooled at 0°C with an ice bath. Pyridinium perbromide (10.4 g, 32×10^{-3} mol) was added in aliquots under stirring. Then, freshly distilled α-picoline (6.4 mL, 66×10^{-3} mol) was added all at once. Both reactions with bromine and α-picoline were almost instantaneous. The final reaction mixture was concentrated and the organic residue was chromatographed on a degassed silica gel column with hexane/ether 95/5 as the eluent. Biphosphole **11** was thus obtained as bright yellow crystals (3.62 g, 40% overall yield from **6**). ^{31}P NMR: δ +4.0 ($CDCl_3$): +6.8 (toluene); ^1H NMR ($CDCl_3$): δ 2.13 (dd, 6H, Me), 2.25 (dd, 6H, Me), 6.39 (d, 2H, ^2J(H–P) = 39.5 Hz, =CH–P), 6.84 (s, 2H, Hβ thiophene), 7.16–7.31 (m, 10H, Ph); ^{13}C NMR ($CDCl_3$): δ 15.32 (s, Me), 18.70 (s, Me); mass spectrum: m/z 456 (M^+, 100%); Anal. Calcd. for $C_{28}H_{26}P_2S$: C, 73.67; H, 5.74. Found: C, 73.77; H, 5.69.

Synthesis of **17**

First Step **13** → **14** (*Equation 10*). To a solution of complex **13** (3.62 g, 1×10^{-2} mol) in CH_2Cl_2 (40 mL) was added anhydrous aluminum chloride (1.5 g, 1.1×10^{-2} mol) all at once. The mixture was stirred at room temperature for 10 min. Then, furan (0.8 mL, 1×10^{-2} mol) in CH_2Cl_2 (2 mL) was slowly added (ca 10 min). After 10 additional minutes, the reaction mixture was hydrolyzed (see the conversion **6** → **7**). The CH_2Cl_2 extracts were dried over $MgSO_4$. ^{31}P NMR (CH_3Cl_2): δ (**14**) +19. A pure sample of **14** was obtained by chromatography, first with hexane, then with hexane/ethyl acetate 97/3 as the eluent. ^1H NMR ($CDCl_3$): δ 1.21 (d, 6H, ^2J(H–P) = 6.3 Hz, Me–P), 1.63 (s, 6H, Me), 1.81 (s, 6H, Me), 2.69 (m, 4H, CH_2–P), 4.19 (s broad, 2H, furan–C*H*–P), 6.10 (s broad, 2H, Hβ furan); ^{13}C NMR ($CDCl_3$): δ 14.64 (s, Me), 15.45 (d, ^1J(C–P) = 19.1 Hz, Me–P), 16.88 (d, ^3J(C–P) = 5.5 Hz, Me), 42.19 (d, ^1J(C–P) = 22.6 Hz, CH_2–P), 54.46 (d, ^1J(C–P) = 21.2 Hz, CH–P), 109.69 (s, βCH furan), 129.64 (s, Cβ phospholene), 131.66 (s, Cβ phospholene), 150.52 (d, ^2J(C–P) = 5.5 Hz, αC furan), 205.77 (d, ^2J(C–P) = 9.5 Hz, cis CO), 209.85 (d, ^2J(C–P) = 23.6 Hz, trans CO); Anal. Calcd. for $C_{28}H_{26}Mo_2O_{11}P_2$: C, 42.44; H, 3.31. Found: C, 42.55; H, 3.46.

Second Step **14** → **15** (*Equation 11*). Crude **14** was oxidized by Me_3NO, $2H_2O$ (9 g, 8×10^{-2} mol) in toluene (30 mL) at reflux for 2 h. ^{31}P NMR (toluene): δ (**15**) +54.

Third Step **15** → **16** (*Equation 12*). After filtration through celite, drying over $MgSO_4$ and concentration, crude **15** was dissolved in dry toluene (5 mL) and treated with $PhSiH_3$ (1.24 mL, 1×10^{-2} mol) at reflux for 30 min. ^{31}P NMR (toluene): δ (**16**) −30.

Fourth Step **16** → **17a,b** (*Equation 13*). After evaporation of toluene under vacuum, crude **17** was dissolved in dry CH_2Cl_2 (30 mL) and cooled at 0°C (ice bath). Pyridinium perbromide (2.7 g, 8×10^{-3} mol) was added, then α-picoline (1.6 mL, 16×10^{-3} mol), then sulfur (0.32 g, 1×10^{-2} eq). ^{31}P NMR: tervalent phosphole, δ −12, disulfide (**17**): δ +47. After the usual workup, the crude organic residue was chromatographed with hexane/ether 60/40. Compound **17** was thus obtained as orange crystals (0.45 g, 23% from **13**). ^{31}P NMR ($CDCl_3$): δ 44.73 and 45.03 (2 isomers); ^1H NMR ($CDCl_3$) 1.90 (d, ^2J(H–P) = 13.5 Hz, Me–P, **a** isomer), 1.98 (d, ^2J(H–P) = 13.6 Hz, Me–P, **b** isomer), 2.12 (m, Me, **a** + **b** isomers), 2.36 (d, ^4J(H–P) = 1.8 Hz, Me, **b** isomer), 2.41 (d, ^4J(H–P) = 1.7 Hz, Me, **a** isomer), 6.11 (d, ^2J(H–P) = 32.5 Hz, =CH–P, **a** + **b** isomers), 7.00 (s, βH furan, **a** isomer), 7.03 (s, βH furan, **b** isomer); mass spectrum: m/z 380 (M^+, 100%); Anal. Calcd. for $C_{18}H_{22}OP_2S_2$: C, 56.83; H, 5.83. Found: C, 56.88; H, 5.65.

X-ray Structure Determination for **2a**

Crystals of **2a**, $C_{21}H_{17}O_5PSW$, were grown at 4° C from a dichloromethane–hexane solution of the compound. Data were collected at 23° ± 1° on an Enraf Nonius CAD4 diffractometer. The crystal structure was solved and refined using the Enraf Nonius supplied SDP package. The compound crystallizes in space group *P*-1, a = 12.067(1), b = 12.660(1), c = 16.564(1) Å, α = 97.47(1)°, β = 106.32(1)°, γ = 109.30(1)°; V = 2221.40 (93) Å^3; Z = 4; Dc = 1.792 g/cm^3; MoKα radiation (λ = 0.71073 Å) graphite monochromator; μ = 55.0 cm^{-1}; $F(000)$ = 1164. A total of 5384 unique reflections were recorded in the range $2° \leq 2\theta \leq 44.0°$ of which 816 were considered as unobserved ($F^2 < 3.0\,\sigma(F^2)$), leaving 4568 for solution and refinement. The structure was solved by Patterson methods, yielding a solution for the tungsten atoms. The hydrogen at-

oms were not included. The thiophene ring occupies both the syn and anti orientation relative to the phosphorus as is evidenced by the isotropic temperature factors of the atoms at the ortho position of the thiophene ring and the obviously wrong distances that result from attempts to refine these atoms as carbon or sulfur. Because of the close proximity of the disordered sites, it proved impossible to refine the structure with two independent rings, both having an occupancy factor of 0.5. The disorder was accounted for by using a composite diffusion factor computed with 50% contribution from the carbon and sulfur atoms. Anisotropic temperature factors were used for all atoms. A non-poisson weighting scheme was applied with a p factor equal to 0.08. The final agreement factors were $R = 0.030$, $R_w = 0.048$, GOF = 1.14.

X-ray Structure Determination for **12**

Crystals of **12**, $C_{28}H_{26}P_2S_3$ were grown at 4° C from a dichoromethane–hexane solution of the compound. Data collection and structure resolution was conducted as above. The compound crystallizes in space group $P\text{-}1$, $a = 8.830(1)$, $b = 12.706(1)$, $c = 14.144(1)$ Å, $\alpha = 61.52(1)°$, $\beta = 76.14(1)°$, $\gamma = 78.02(1)°$; $V = 1345.96(15)$ Å^3; $Z = 2$; $Dc = 1.285$ g/cm^3; MoKα radiation ($\lambda = 0.71073$ Å) graphite monochromator; $\mu = 4.0$ cm^{-1}; $F(000) = 544$. A total of 6162 unique reflections were recorded in the range $2° \leq 2\theta \leq 55.0°$ of which 2911 were considered as unobserved ($F^2 < 3.0\,\sigma(F^2)$), leaving 3251 for solution and refinement. The structure was solved by direct methods, yielding a solution for the phosphole and thiophene rings. The hydrogen atoms were included as fixed contribution in the final stages of least-squares refinement while using anisotropic temperature factors for all other atoms. A non-poisson weighting scheme was applied with a p factor equal to 0.08. The final R factors were $R = 0.041$, $R_w = 0.059$, GOF = 1.14.

SUPPLEMENTARY MATERIAL AVAILABLE

Further details of the structures are available from the Cambridge Crystallographic Data Centre, Lensfield Road, Cambridge CB2 1EW.

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