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Synthesis and Structure of 1-Phospholyl- and Di(1-phospholyl)acetylenes and the Corresponding Sulfides

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ABSTRACT: *The acetylenes possessing one and two 1-phospholyl groups were synthesized by reaction of the alkynyl Grignard reagents with the 1-chlorophosphole and converted to the corresponding phosphole sulfides. Reaction of the 1-phenylethynylphosphole sulfide with $CpCo(CO)_2$ resulted in η^4-complexation on the phosphole moiety. The structures of the di(1-phospholyl)acetylene disulfide and the [η^4-(1-phenylethynylphosphole sulfide)]cobalt(I) complex were characterized by X-ray crystallography.* © 2006 Wiley Periodicals, Inc. Heteroatom Chem 17:344–349, 2006; Published online in Wiley InterScience (www.interscience.wiley.com). DOI 10.1002/hc.20230

INTRODUCTION

Phospholes [1] have attracted considerable attention due to their unique structures, reactivities, and potential applications such as ligands for transition metal catalysts [2] and key synthetic intermediates for phosphorus functional molecules [3]. On the other hand, acetylenes possessing phosphorus functional groups have been reported to undergo reaction or complexation with transition metals not only at the phosphorus [4] but at the acetylene unit [5] to afford a variety of products. Phospholylacetylenes and the related compounds are expected to exhibit interesting properties and diverse reactivities due to three reactive sites, i.e., phosphole, phosphorus, and acetylene. There have been several reports on 1-ethynylphospholes such as the 3,4-dimethyl derivatives, which undergo [4 + 2] cycloaddition and further reactions [3b], and cyclic diphospholylacetylenes [2a]. Recently, we have been interested in construction of the cyclic π-conjugated systems carrying array of the phosphorus functional groups by reaction of the phosphorus-substituted acetylenes [6]. (η^5-Cyclopentadienyl)-[η^4-tetrakis(diethoxyphosphoryl)cyclobutadiene]cobalt(I) (**1**) and the related compounds were synthesized by reaction of the diphosphorylacetylenes with $CpCo(CO)_2$ and **1** was found to act as bis(bidentate) ligands to form one-dimensional coordination polymer. The ethynylphospholyl compounds can be regarded as one of the candidates for the substrates for integration of the phosphorus functional groups in this manner. However, synthesis, structure, and reactivity of simple 1-ethynylphospholes have been not so much explored as compared with the conventional ethynylphosphorus compounds. In this report, we describe synthesis and structure of acetylenes possessing one and two 1-phospholyl groups and the corresponding sulfides. Reaction of 1-alkynylphosphole sulfides with $CpCo(CO)_2$ is also reported.

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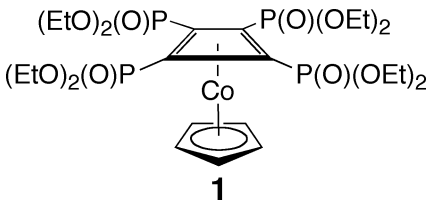

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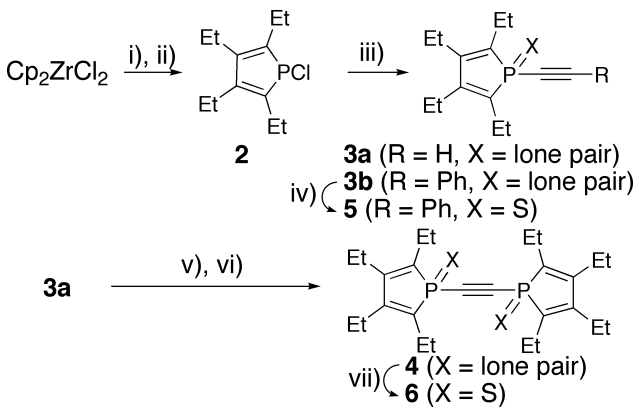
RESULTS AND DISCUSSION

Synthesis

The phospholylacetylenes were synthesized by reaction of the alkynyl Grignard reagents with 1-chloro-2,3,4,5-tetraethylphosphole (**2**) [7], which was prepared by reaction of the zirconacyclopentadiene with phosphorus trichloride (Scheme 1). Addition of ethynyl and phenylethynyl Grignard reagents to **2** in tetrahydrofuran at 0°C afforded ethynylphospholes **3a** and **3b**, respectively. Ethynylphosphole **3a** was converted to the corresponding alkynyl Grignard reagent and allowed to react with **2** to give diphospholylacetylene **4**. Phospholes **3b** and **4** were treated with elemental sulfur in the presence of triethylamine and isolated as more stable sulfides **5** and **6**.

Structure

The phospholylacetylenes and the corresponding sulfides were characterized by conventional spectroscopy. The ^{31}P NMR chemical shifts of **3a** (δ −32), **3b** (δ −32), and **4** (δ −29) are observed in a significantly high field as a result of substitution of the alkynyl group. The ^{13}C NMR signals of **4** reflect significant magnitude of J_{PP} as compared with J_{PC} and $J_{P'C}$ and are observed as typical AXX′ patterns [8], where alkenyl and alkynyl, and alkyl carbons appear as six and five lines, respectively. On the other hand, the ^{13}C signals of **6** except for the alkyl carbons do not show typical AXX′ patterns due to considerably larger J_{PC} for the alkenyl and the alkynyl carbons than J_{PP}. The alkenyl and alkynyl carbons of **6** appear as simple doublets and a doublet of doublet, respectively. The structure of **6** was further investigated by X-ray crystallography (Fig. 1). The bond lengths and angles of the phosphole rings and the acetylenic carbons are within the range of typical values, which suggests negligible π-conjugation effect. The two thiophosphole rings are planar with the mean deviation from the least-squares plane as 0.0024 and 0.0097 Å and take *trans* configuration with the torsion angle of the two P=S bonds as 164.7°, which is larger than the value reported for $Ph_2P(S)C{\equiv}CP(S)Ph_2$ (120°) [9]. The angle between the two planes is 17.2°. The thiophosphole rings lie with acute C(sp^2)–P–C(sp) bond angles ranging from 103.91(6) to 107.31(6)°. Thus, the acetylenic carbons are shielded by the thiophospholyl groups as well as the ethyl groups at the 2,5-positions, suggesting limited reactivity to some extent.



SCHEME 1 Synthesis of phospholylacetylenes. Reagents and conditions: (i) 3-hexyne, *n*-BuLi, THF; (ii) PCl_3, dichloromethane, 0°C (63%); (iii) ethynylmagnesium bromide (**3a**: 53%) or phenylethynylmagnesium bromide (**3b**: 67%), THF; (iv) S_8, triethylamine, toluene, 0°C (**5**: 58%); (v) ethylmagnesium bromide; (vi) **2**, THF, 0°C (**4**: 63%); (vii) S_8, triethylamine, toluene, 0°C (**6**: 80%).

Reaction with $CpCo(CO)_2$

Reaction of **6** with the transition metal complexes such as $PdCl_2(CH_3CN)_2$, $Co_2(CO)_8$, $Ni(CO)_2(PPh_3)_2$,

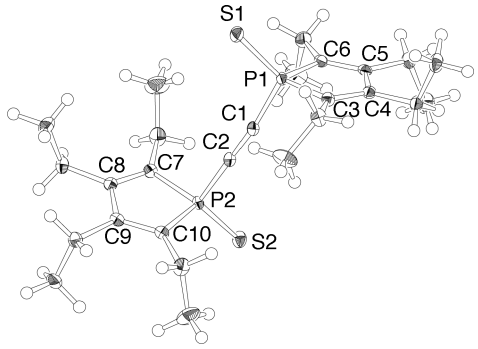
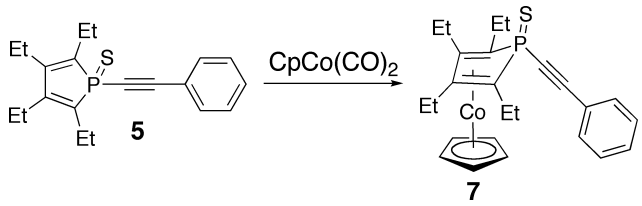


FIGURE 1 ORTEP drawing of **6** with 50% probability thermal ellipsoids. Selected bond lengths (Å) and angles (deg): S1–P1, 1.940(1); P1–C3, 1.794(1), C3–C4, 1.343(2); C4–C5, 1.509(2); C5–C6, 1.339(2); P1–C6, 1.796(1); P1–C1, 1.769(1); C1–C2, 1.203(2); S2–P2, 1.944(1); P2–C7, 1.794(2); C7–C8, 1.342(2); C8–C9, 1.508(2); C9–C10, 1.340(2); P2–P10, 1.791(1); P2–C2, 1.765(1); S1–P1–C1, 110.94(5); S1–P1–C3, 118.46(5); S1–P1–C6, 119.61(5); C1–P1–C3, 107.31(6); C1–P1–C6, 104.00(6); C3–P1–C6, 94.48(7); S2–P2–C2, 111.52(5); S2–P2–C7, 119.05(6); S2–P2–C10, 118.89(5); C2–P2–C7, 103.91(6); C2–P2–C10, 106.78(6); C7–P2–C10, 94.49(7).



SCHEME 2 Reaction of phosphole sulfide with $CpCo(CO)_2$. Conditions: xylene, reflux (**7**: 39%).

and $CpCo(CO)_2$ resulted in recovery of **6**, probably because of steric hindrance around the reactive sites, i.e., the acetylenic carbons and the *syn* face of phosphole to acetylene as indicated by X-ray crystallography. On the other hand, reaction of **5** with $CpCo(CO)_2$ afforded [η^4-(phosphole sulfide)]cobalt(I) complex **7** in 39% yield (Scheme 2). The ^{31}P NMR and mass spectra of the remaining products suggested formation of a (η^5-cyclopentadienyl)cobalt(I) complex carrying the η^4-cyclobutadiene ligand resulting from [2 + 2] addition of acetylene **5**, although the detailed regioselectivity has not been clear. Structure of **7** was confirmed by X-ray crystallography (Fig. 2), where the CpCo moiety attached on the phosphole ring to the same face as the phenylethynyl group. The cobalt and phosphorus atoms are 1.572 and 0.703 Å apart from the plane defined by C3—C4—C5—C6, respectively. Similar structure was reported for the (η^5-cyclopentadienyl)(η^4-phosphole oxide)cobalt(I) complexes [10]. Difference of the reactivity of **5** and **6** toward $CpCo(CO)_2$ is consistent with the steric environment of the reactive sites. The two reactive sites of **5**, one face of the phosphole sulfide *syn* to the acetylene and acetylenic carbons,

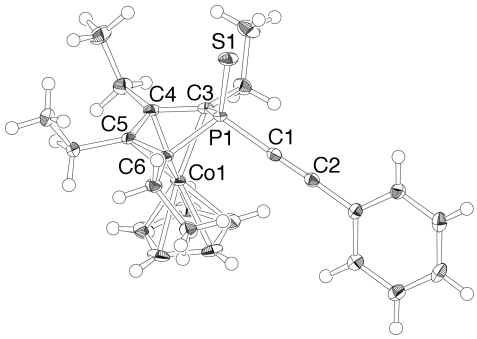


FIGURE 2 ORTEP drawing of **7** with 50% probability thermal ellipsoids. Selected bond lengths (Å) and angles (deg): S1–P1, 1.9627(6); P1–C3, 1.781(2); C3–C4, 1.438(2); C4–C5, 1.443(2); C5–C6, 1.442(2); P1–C6, 1.781(2); P1–C1, 1.757(2); C1–C2, 1.201(2); S1–P1–C1, 109.56(6); S1–P1–C3, 122.81(6); S1–P1–C6, 119.84(6); C1–P1–C3, 106.15(8); C1–P1–C6, 107.88(8); C3–P1–C6, 88.22(7).

can be accessed by the cobalt reagent. Introduction of two thiophospholyl moieties at the acetylenic carbons makes the both reactive sites inaccessible. Although the other face of the phosphole sulfide is unexpectedly inert, the remaining reactive sites, the phosphorus, or sulfur, are expected to coordinate to metals. Further investigation on the integration of the phospholylacetylenes and the related compounds is in progress.

EXPERIMENTAL

General

^{1}H, ^{13}C, and ^{31}P NMR spectra were measured on a Bruker AC200P or an AM600 spectrometer. ^{1}H and ^{13}C NMR chemical shifts are expressed as δ downfield from external tetramethylsilane. ^{31}P NMR chemical shifts are expressed as δ downfield from external 85% H_3PO_4. Infrared spectra and ultraviolet-visible spectra were collected on a Horiba FT-300 spectrometer and a Hitachi U-3210 spectrophotometer, respectively. Mass spectra were measured on a Hitachi M-2500S with electron impact (EI) ionization at 70 eV or a JEOL HX-110 with fast atom bombardment (FAB) ionization using *m*-nitrobenzyl alcohol matrix. Melting points were measured on a Yanagimoto MP-J3 apparatus without correction. Microanalyses were performed at the Instrumental Analysis Center for Chemistry, Graduate School of Science, Tohoku University. Tetrahydrofuran and diethyl ether were distilled from sodium diphenylketyl under argon just prior to use.

Synthesis

2,3,4,5-Tetraethyl-1-ethynylphosphole **3a**. To a solution of Cp_2ZrCl_2 (2.0 g, 6.84 mmol) in tetrahydrofuran (40 mL) was added butyllithium (1.5 M in hexane, 9.12 mL, 13.7 mmol) at −78°C, and the resultant yellow solution was stirred for 30 min. 3-Hexyne (1.55 mL, 13.7 mmol) was added, and the mixture was warmed to room temperature to give a reddish orange solution. After stirring at room temperature for 4 h, tetrahydrofuran was removed under reduced pressure and dichloromethane (30 mL) was added. Phosphorus trichloride (0.65 mL, 6.50 mmol) was added at 0°C and the mixture was stirred for 15 min. Dichloromethane was removed under reduced pressure and hexane (60 mL) was added. The insoluble salts were removed by filtration through Celite under argon, and the filtrate was concentrated under reduced pressure to afford crude 1-chloro-2,3,4,5-tetraethylphosphole. The residue was dissolved in tetrahydrofuran (30 mL), and ethynylmagnesium bromide (0.5 M in THF, 12.0 mL, 6.0 mmol)

was added at 0°C. The solution was stirred for 1 h at room temperature, and the solvent was evaporated. Hexane (40 mL) was added, and the insoluble salts were removed by filtration through Celite under argon. The filtrate was concentrated under reduced pressure, and the resultant brown oil was purified by flash column chromatography (Al_2O_3/hexane) followed by distillation under reduced pressure to give **3a** (772 mg, 3.61 mmol, 53%). **3a**: colorless oil; bp 85–100°C/2 mmHg (Kugelrohr); ^{1}H NMR (200 MHz, C_6D_6) δ 2.71 (d, $^3J_{PH} = 1.44$ Hz, 1H, CCH), 2.65–2.35 (m, 4H, CH_2), 2.29–1.99 (m, 4H, CH_2), 1.22 (t, $J_{HH} = 7.55$ Hz, 6H, CH_3), 0.85 (t, $J_{HH} = 7.57$ Hz, 6H, CH_3); ^{13}C NMR (50 MHz, C_6D_6) δ 148.9 (d, $^1J_{PC} = 13.7$ Hz, C2, 5), 140.0 (d, $^2J_{PC} = 3.8$ Hz, C3, 4), 96.8 (d, $^2J_{PC} = 1.51$ Hz, PC*C*), 78.1 (d, $^1J_{PC} = 23.3$ Hz, P*C*C), 21.6 (d, $^2J_{PC} = 18.7$ Hz, *C*H_2), 21.1 (d, $^3J_{PC} = 3.5$ Hz, *C*H_2), 16.6 (d, $^3J_{PC} = 7.2$ Hz, *C*H_3), 14.8 (d, $^4J_{PC} = 3.4$ Hz, *C*H_3); ^{31}P NMR (81 MHz, C_6D_6) δ −32.2 (quintet, $^3J_{PH} = 11.2$ Hz); LRMS (EI, 70 eV) *m/z* (relative intensity) 220 (M^+, 100), 191 (M^+–Et, 61); HRMS (EI, 70 eV) *m/z* Calcd for $C_{14}H_{20}P$: 220.142, Found: 220.138; UV–Vis (hexane) λ_{max} (log ε) 279 (3.68) nm; IR (NaCl) 3294 ν(CC—H), 2031 ν(CC) cm^{-1}.

2,3,4,5-Tetraethyl-1-(phenylethynyl)phosphole **3b**. 1-Chloro-2,3,4,5-tetraethylphosphole was prepared similarly to the procedure for **3a** from Cp_2ZrCl_2 (1.00 g, 3.41 mmol), butyllithium (1.5 M in hexane, 4.55 mL, 6.82 mmol), 3-hexyne (0.78 mL, 6.82 mmol), and phosphorus trichloride (0.34 mL, 3.38 mmol). Ethylmagnesium bromide (1.02 M in tetrahydrofuran, 2.23 mL, 2.27 mmol) was added to a solution of ethynylbenzene (0.25 mL, 2.27 mmol) in tetrahydrofuran (10 mL) at 0°C, and the mixture was warmed to 20°C. The resultant solution was added to the tetrahydrofuran (20 mL) solution of 1-chloro-2,3,4,5-tetraethylphosphole at 0°C, and the mixture was stirred at 20°C for 1 h. The resultant brown suspension was concentrated under reduced pressure. Hexane (30 mL) was added to the residue, and the insoluble material was removed by filtration through Celite. The filtrate was concentrated under reduced pressure, and the resultant brown oil was purified by flash column chromatography (Al_2O_3/hexane) and distillation under reduced pressure to give **3b** (680 mg, 2.30 mmol, 67%). **3b**: pale yellow oil; bp 135–145°C/2 mmHg (Kugelrohr); ^{1}H NMR (200 MHz, C_6D_6) δ 7.38–7.21 (m, 2H, arom.), 6.93–6.75 (m, 3H, arom.), 2.72–2.35 (m, 4H, CH_2), 2.30–2.01 (m, 4H, CH_2), 1.28 (t, $J_{HH} = 7.54$ Hz, 6H, CH_3), 0.89 (t, $J_{HH} = 7.57$ Hz, 6H, CH_3); ^{13}C NMR (50 MHz, C_6D_6) δ 148.5 (d, $^1J_{PC} = 13.7$ Hz, C2, 5), 140.4 (d, $^2J_{PC} = 3.9$ Hz, C3, 4), 131.9 (d, $^3J_{PC} = 0.74$ Hz, *ipso*-arom.), 128.5 (s, *o*-arom.), 128.5 (s, *m*-arom.), 123.9 (s, *p*-arom.), 108.8 (s, PC*C*), 82.6 (d, $^1J_{PC} = 18.8$ Hz, P*C*C), 21.8 (d, $^2J_{PC} = 18.8$ Hz, *C*H_2), 21.2 (d, $^3J_{PC} = 3.5$ Hz, *C*H_2), 16.8 (d, $^3J_{PC} = 6.9$ Hz, *C*H_3), 15.0 (d, $^4J_{PC} = 3.5$ Hz, *C*H_3); ^{31}P NMR (81 MHz, C_6D_6) δ −31.7 (quintet, $^3J_{PH} = 11.8$ Hz); LRMS (EI, 70 eV) *m/z* (relative intensity) 296 (M^+, 29), 281 (M^+−Me, 28), 267 (M^+−Et, 100).

2,3,4,5-Tetraethyl-1-(phenylethynyl)phosphole sulfide **5**. A mixture of phosphole **3b** (680 mg, 2.30 mmol), sulfur (147 mg, 0.57 mmol), and triethylamine (0.1 mL, 0.72 mmol) in toluene (15 mL) was stirred for 20 h at room temperature. The mixture was concentrated under reduced pressure and purified by flash column chromatography (Al_2O_3/hexane, hexane/ether = 3/1) to afford **5** (436 mg, 1.33 mmol, 58%). **5**: yellow oil; ^{1}H NMR (200 MHz, C_6D_6) δ 7.20–7.05 (m, 2H, arom.), 6.86–6.65 (m, 3H, arom.), 2.90–2.60 (m, 2H, CH_2), 2.58–2.28 (m, 2H, CH_2), 1.90 (q, $J_{HH} = 7.59$ Hz, 4H, CH_2), 1.38 (t, $J_{HH} = 7.57$ Hz, 6H, CH_3), 0.72 (t, $J_{HH} = 7.59$ Hz, 6H, CH_3); ^{31}P NMR (81 MHz, C_6D_6) δ 25.1 (quintet, $^3J_{PH} = 18.5$ Hz); LRMS (EI, 70 eV) *m/z* (relative intensity) 328 (M^+, 100), 313 (M^+−Me, 22), 299 (M^+−Et, 22).

Bis(2,3,4,5-tetraethyl-1-phospholyl)acetylene **4**. 1-Chloro-2,3,4,5-tetraethylphosphole was prepared similarly to the procedure for **3a** from Cp_2ZrCl_2 (1.50 g, 5.13 mmol), butyllithium (1.5 M in hexane, 6.83 mL, 10.2 mmol), 3-hexyne (1.17 mL, 10.2 mmol), and phosphorus trichloride (0.51 mL, 5.07 mmol). Ethylmagnesium bromide (1.02 M in tetrahydrofuran, 3.34 mL, 3.40 mmol) was added to a solution of **3a** (728 mg, 3.40 mmol) in tetrahydrofuran (10 mL) at 0°C, and the mixture was warmed to 20°C and stirred for 3 h. The resultant solution was added to the tetrahydrofuran (30 mL) solution of 1-chloro-2,3,4,5-tetraethylphosphole at 0°C and the mixture was stirred at 20°C for 2 h. The resultant brown suspension was concentrated under reduced pressure. Hexane (40 mL) was added to the residue, and insoluble material was removed by filtration through Celite. The filtrate was concentrated under reduced pressure, and the resultant yellow oil was purified by flash column chromatography (Al_2O_3/hexane) and distillation under reduced pressure to give **4** (1.16 g, 2.80 mmol, 82%). **4**: yellow oil; bp 100 C/2 mmHg (Kugelrohr); ^{1}H NMR (200 MHz, C_6D_6) δ 2.70–2.31 (m, 8H, CH_2), 2.31–1.90 (m, 8H, CH_2), 1.20 (t, $J_{HH} = 7.54$ Hz, 12H, CH_3), 0.84 (t, $J_{HH} = 7.55$ Hz, 12H, CH_3); ^{13}C NMR (50 MHz, C_6D_6) δ 148.4 (AXX′, $^1J_{PC} + {}^4J_{P'C} = 14.1$ Hz, C2, 5), 139.8 (AXX′, $^2J_{PC} + {}^5J_{P'C} = 4.9$ Hz, C3, 4), 103.2 (AXX′, $^1J_{PC} + {}^2J_{P'C} = 103.2$ Hz, acetylene), 21.7 (AXX′,

$^2J_{PC} + {}^5J_{P'C} = 18.9$ Hz, CH_2), 21.1 (AXX′, $^3J_{PC} + {}^6J_{P'C} = 3.6$ Hz, CH_2), 16.6 (AXX′, $^3J_{PC} + {}^6J_{P'C} = 6.8$ Hz, CH_3), 14.9 (AXX′, $^4J_{PC} + {}^7J_{PC} = 3.3$ Hz, CH_3); ^{31}P NMR (81 MHz, C_6D_6) δ −28.5 (quintet, $^3J_{PH} = 11.0$ Hz); LRMS (EI, 70 eV) m/z (relative intensity) 414 (M^+, 100), 399 (M^+–CH_3, 47), 385 (M^+−Et, 93), 194 ($Et_4C_4P + 1$, 41); UV–Vis (hexane) λ_{max} (logε) 280 (4.09), 237 (4.10) nm; IR (NaCl) 3294 ν(CC—H), 2100 ν(CC) cm^{-1}.

Bis(2,3,4,5-tetraethyl-1-phospholyl)acetylene Disulfide **6**. A mixture of phosphole **4** (953 mg, 2.30 mmol), sulfur (287 mg, 1.12 mmol), and triethylamine (0.1 mL, 0.72 mmol) in toluene (20 mL) was stirred for 40 h at room temperature. The mixture was concentrated under reduced pressure and purified by flash column chromatography (Al_2O_3/hexane) and recrystallization from hexane to afford **6** (880 mg, 1.84 mmol, 80%). **6**: colorless prisms, mp 110–112°C; ^{1}H NMR (200 MHz, C_6D_6) δ 2.71–2.40 (m, 4H, CH_2), 2.40–2.10 (m, 4H, CH_2), 1.82 (q, $^3J_{HH} = 7.57$ Hz, 8H, CH_2), 1.24 (t, $J_{HH} = 7.58$ Hz, 12H, CH_3), 0.66 (t, $J_{HH} = 7.57$ Hz, 12H, CH_3); ^{13}C NMR (50 MHz, C_6D_6) δ 151.5 (d, $^1J_{PC} = 29.1$ Hz, C3,4), 134.3 (d, $^2J_{PC} = 88.6$ Hz, C2,5), 93.1 (dd, $^1J_{PC} = 95.1$, $^2J_{PC} = 8.9$ Hz, acetylene), 20.3 (AXX′, $^2J_{PC} + {}^5J_{P'C} = 16.8$ Hz, CH_2), 19.0 (AXX′, $^3J_{PC} + {}^6J_{P'C} = 13.0$ Hz, CH_2), 15.0 (brs, CH_3), 14.0 (AXX′, $^4J_{PC} + {}^7J_{P'C} = 2.5$ Hz, CH_3); ^{31}P NMR (81 MHz, C_6D_6) δ 25.4 (quintet, $^3J_{PH} = 17.7$ Hz); LRMS (EI, 70 eV) m/z (relative intensity) 478 (M^+, 100), 445 (M^+–S–1, 33), 251 (M^+–C_4Et_4PS, 28); HRMS (EI, 70 eV) m/z Calcd for $C_{26}H_{40}P_2S_2$: 478.216, Found: 478.204.

Reaction of **5** *with CpCo(CO)$_2$*. A mixture of **5** (340 mg, 1.04 mmol) and $CpCo(CO)_2$ (118 mL, 1.04 mmol)) in xylene (15 mL) was refluxed for 10 h. The resultant black suspension was concentrated under reduced pressure, and the residue was purified by flash column chromatography (Al_2O_3/hexane, ether) to give [η^4-{2,3,4,5-tetraethyl-1-(phenylethynyl)phosphole sulfide}](η^5-cyclopentadienyl)cobalt(I) (**7**) (182 mg, 0.40 mmol, 39%). Recrystallization from ether gave crystals suitable to X-ray crystallography. **7**: reddish brown prisms; mp 144–147°C; ^{1}H NMR (200 MHz, C_6D_6) δ 7.55–7.42 (m, 2H, arom.), 7.00–6.89 (m, 3H, arom.), 4.26 (s, 5H, Cp), 2.42–2.18 (m, 2H, CH_2), 2.10–1.70 (m, 6H, CH_2), 1.51 (t, $J = 7.39$ Hz, 6H, CH_3), 1.09 (t, $J = 7.57$ Hz, 6H, CH_3); ^{31}P NMR (81 MHz, C_6D_6) δ 24.3 (q, $^3J_{PH} = 19.8$ Hz); LRMS (EI, 70 eV) m/z (relative intensity) 452 (M^+, 70), 419 (M^+−S−1, 36), 319 (M^+−PhCC−S, 100); IR (KBr) 2173 ν(CC) cm^{-1}. A mixture containing [η^4-diphenylbis(2,3,4,5-tetraethylthiophospholyl)cyclobutadiene](η^5-cyclopentadienyl)cobalt(I) was also obtained as a dark green oil (113 mg): ^{31}P NMR (81 MHz, C_6D_6) δ 44.8, (m, $J_{PH} = 15.2$ Hz); FAB MS m/z (rel. intensity) 781 ($M^+ + 1.4$).

X-ray crystallography

Crystal data: **6**: $C_{26}H_{40}P_2S_2$, $M = 478.67$, monoclinic, $P2_1/n$ (#14), $a = 17.26(1)$ Å, $b = 9.463(2)$ Å, $c = 18.313(5)$ Å, $\beta = 113.79(3)°$, $V = 2737(2)$ Å^3, $Z = 4$, $D_{calc} = 1.161$ gcm^{-3}, 5375 collected, 5058 unique ($R_{int} = 0.030$, $I > 0.00\sigma(I)$), $T = 115$ K, $R_1/R/R_w = 0.030/0.034/0.047$. **7**: $C_{25}H_{30}PSCo$, $M = 452.48$, monoclinic, $P2_1/c$ (#14), $a = 8.961(1)$ Å, $b = 19.560(5)$ Å, $c = 13.540(3)$ Å, $\beta = 94.154(7)°$, $V = 2295.6(8)$ Å^3, $Z = 4$, $D_{calc} = 1.309$ gcm^{-3}, 4353 collected, 4215 unique ($R_{int} = 0.027$, $I > 0.00\sigma(I)$), $T = 115$ K, $R_1/R/R_w = 0.026/0.034/0.037$. Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Data Centre as supplementary publication nos. CCDC-180564 (**6**) and 180565 (**7**). Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB21EZ, UK (Fax: (+44)1223-336-033; E-mail: deposit@ccdc.cam.ac.uk).

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