Synthesis and Crystal Structure of the First 6a-Thiathiophthen Metal Complex $[Mo(CO)_5PPh_2]_2(\mu\text{-}C_5H_2S_3)$

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The first 6a-thiathiophthen metal complex was prepared by treating $M(CO)_5[PPh_2CS_2CH_2C{\equiv}CH]$ with a catalytic amount of secondary amine or tertiary amine; the structure of the 6a-thiathiophthen molybdenum complex is confirmed by an X-ray diffraction analysis.

With their unusually long S–S distances and possible aromatic properties of the two fused five-membered rings, the 6a-thiathiophthen (3,3a,4-trithiopentalene) derivatives[1] have attracted considerable attention. Methods for the synthesis of 6a-thiathiophthen[2] and arylthio- or alkylthio-derivatives[3] using various thionation reagents such as S, H_2S and P_2S_5 have been reported. Furthermore, much work has been done on the bonding,[4] structure,[5] reactions[6] and electron density deformation[7] studies on 6a-thiathiophthen and its derivatives. However, no 6a-thiathiophthen metal complex has been reported. Here we report the high yield synthesis and the structure determination of the first 6a-thiathiophthen metal complex, which was prepared from the metal complex containing the diphenyl(*S*-prop-2-ynyl-dithioformato)phosphine ligand.[8]

Treatment of $M(CO)_5[PPh_2(CS_2CH_2C{\equiv}CH)]$ (M = Mo, **1a**; W, **1b**) with a catalytic amount of Et_3N in CH_2Cl_2 yields the 6a-thiathiophthen metal complexes $[M(CO)_5PPh_2]_2(\mu\text{-}C_5H_2S_3)$ (M = Mo, **2a**; W, **2b**) at room temperature (Scheme 1). Complex **2a** is isolated as a red microcrystalline powder by recrystallization from hexane–CH_2Cl_2 in *ca.* 85% yield. The spectroscopic† and analytical data of **2a** are in agreement with the formulation. The FAB mass spectrum of **2a** shows a base peak at *m*/*z* 721, corresponding to $[MoPPh_2]_2(\mu\text{-}C_5H_2S_3)^+$, formed by loss of the ten CO groups from **2a**. The IR spectrum of **2a** shows two terminal carbonyl stretches at 2073 and 1924 cm^{-1}, a typical pattern for a $LM(CO)_5$ unit in octahedral geometry. The ^1H NMR spectrum of **2a** exhibits a doublet at δ 7.90 ($^3J_{P-H}$ = 7.2 Hz) attributed to the two equivalent methyne protons, and the corresponding ^{13}C NMR signal is a doublet at δ 177.95 ($^2J_{P-C}$ = 11.3 Hz). The low field ^1H chemical shift is regarded as evidence for a strong ring current. The ^{13}C NMR resonance of the 3a-carbon exhibits a triplet at δ 177.21 ($^3J_{P-C}$ = 8.3 Hz). The ^1H and ^{13}C NMR spectra clearly imply C_{2v} symmetry in **2a**. The molecular structure of this unusual complex **2a** is confirmed by an X-ray diffraction study.‡ An ORTEP drawing of **2a** is shown in Fig. 1. The coordination geometry about the two molybdenum atoms can be described as distorted octahedral. Two metal atoms were bridged by two phosphorus atoms connected by a 6a-thiathiophthen unit. The two S–S distances [2.318(2) and 2.330(2) Å] in complex **2a** are significantly longer than the expected S–S single bond lengths (2.05 Å) but considerably shorter than sum of the sulfur van der Waals radii (3.7 Å).[9] Interestingly, in the crystal, **2a** does not exhibit C_{2v} symmetry and the $P_2C_5H_2S_3$ unit is not planar. To our

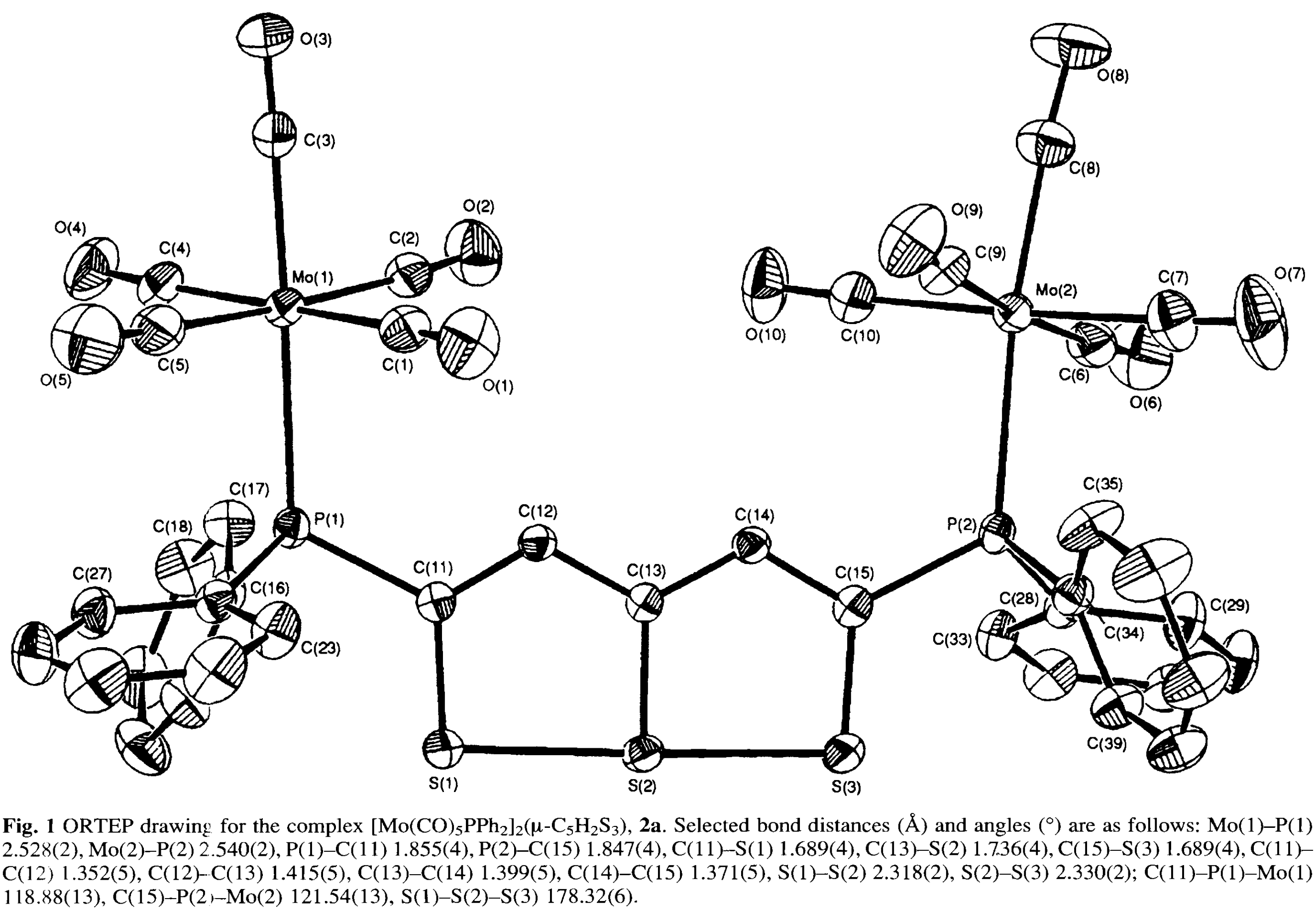
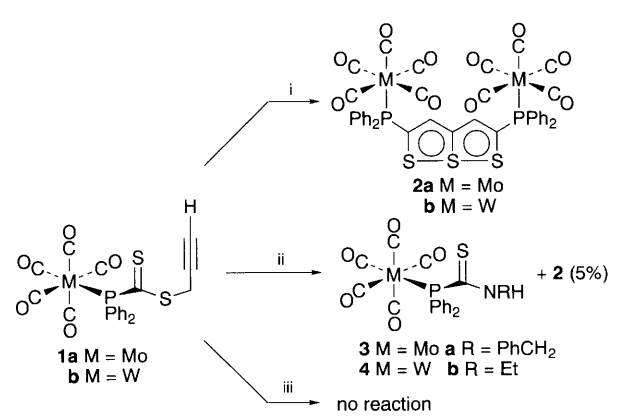


Fig. 1 ORTEP drawing for the complex $[Mo(CO)_5PPh_2]_2(\mu\text{-}C_5H_2S_3)$, **2a**. Selected bond distances (Å) and angles (°) are as follows: Mo(1)–P(1) 2.528(2), Mo(2)–P(2) 2.540(2), P(1)–C(11) 1.855(4), P(2)–C(15) 1.847(4), C(11)–S(1) 1.689(4), C(13)–S(2) 1.736(4), C(15)–S(3) 1.689(4), C(11)–C(12) 1.352(5), C(12)–C(13) 1.415(5), C(13)–C(14) 1.399(5), C(14)–C(15) 1.371(5), S(1)–S(2) 2.318(2), S(2)–S(3) 2.330(2); C(11)–P(1)–Mo(1) 118.88(13), C(15)–P(2)–Mo(2) 121.54(13), S(1)–S(2)–S(3) 178.32(6).



Scheme 1 *Reagents and conditions*: i, Et_3N or Pr^i_2NH or Et_2NH or F^-, CH_2Cl_2, 25 °C, 10 min; ii, RNH_2 (R = $PhCH_2$, Et), CH_2Cl_2, 25 °C, 1 min; iii, Bu^nLi or Bu^tOK or $PhNH_2$, THF, 25 °C, 1 h

knowledge, complex **2a** is the first example of metal-derivative of 6a-thiathiophthen.

In order to study the role of Et_3N in the formation of **2a**, other amines and Bu_4NF were used to replace Et_3N in the reaction. Complexes **1a** and **1b** were reacted with secondary amine (Pr^i_2NH, Et_2NH) or Bu^n_4NF to give **2a** and **2b**, respectively, both in high yield. The rate of formation of **2** depends on the amine used and decreases in the order $Et_3N > Pr^i_2NH > Et_2NH > Bu^n_4NF$. No reaction was observed when **1** was reacted with Bu^nLi, Bu^tOK or $PhNH_2$. But the reactions of **1** with several primary aliphatic amines (RNH_2; R = $PhCH_2$, Et) give $M(CO)_5PPh_2CSNHR$ (M = Mo, R = $PhCH_2$, Et; **3a–b**; M = W, R = $PhCH_2$, Et; **4a–b**) and $HC{\equiv}CCH_2SH$ in high yield, Scheme 1. Interestingly, complex **3** (or **4**) is not the precusor that leads to **2**. On the basis of the above-mentioned experiments, one can conclude that secondary or tertiary amines catalyse the formation of **2** but primary amines or strong bases do not. To probe the origin of the two methyn protons of **2a** (from the terminal or the methylene of **1a**), ^2H-labelling experiment was carried out. Treatment of the terminally labelled [$^2H_1$]**1a** with Et_3N afforded **2a** with *no* ^2H-labelling. In addition, when the reaction was monitored by the ^{31}P and ^1H NMR spectra, complex **2a** was observed as the only product (yield 95% from integration of the ^{31}P NMR spectrum) and no intermediate was observed. Attempts to trap possible intermediates by separate addition of PPh_3, CS_2, TCNE, MeI or cyclopentadiene into the reaction of **1** with Et_3N failed to produce any product other than **2**. The metal carbonyl fragment is crucial for the formation of **2**, since treatment of the analogous organic species $Et_2NC(S)SCH_2C{\equiv}CH$ with Et_3N or $PhCH_2NH_2$ resulted in no reaction under the same reaction conditions. In the absence of R_3N, dimerization of **1** gave a five-membered ring consisting of a C=S unit and the propynyl moiety.[10]

The reactivity of the 6a-thiathiophthen metal complexes and the mechanism for their formation are currently under investigation.

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Footnotes

† *Selected spectroscopic data*: ^1H (300 MHz) and $^{13}C\{^1H\}$ (75 MHz) NMR (298 K, $CDCl_3$, relative to $SiMe_4$, multiplicity, assignment, *J* in Hz) ^{31}P (121.5 MHz) NMR (H_3PO_4 external standard).

1a: IR (CH_2Cl_2, ν_{CO}/cm^{-1}): 2075(m), 1942(vs). ^{31}P NMR: δ 76.76. ^1H NMR: δ 2.18 (t, 1H, ≡C*H*, $^4J_{H-H}$ = 2.68), 3.98 (d, 2H, S-CH_2, $^4J_{H-H}$ = 2.68), 7.47 (m, 6H, Ph), 7.67 (m, 4H, Ph). ^{13}C NMR: δ 26.36 (S-CH_2), 72.60 (≡*C*H), 75.77 (*C*≡CH), 128.55 (d, *meta*-C of Ph, $^3J_{P-C}$ = 9.60), 131.03 (s, *para*-C of Ph), 133.69 (d, *ortho*-C of Ph, $^2J_{P-C}$ = 11.77), 133.67 (d, *ipso*-C of Ph, J_{P-C} = 30.70), 205.35 (d, *C*O, $^2J_{P-C}$ = 8.48), 209.84 (d, CS_2, J_{P-C} = 26.10). MS (FAB, NBA, *m*/*z*): 539 (M^+), 483 ($M^+ - 2CO$).

[$^2H_1$]**1b** (^2H 98%): IR (CH_2Cl_2, ν_{CO}/cm^{-1}): 2072(m), 1940(vs). ^{31}P NMR: δ 59.95 (J_{W-P} = 237.0). ^1H NMR: δ 3.96 (s, 2H, S-CH_2), 7.45 (m, 6H, Ph), 7.69 (m, 4H, Ph).

2a: IR (KBr, ν_{CO}/cm^{-1}): 2073(m), 1924(vs). ^{31}P NMR: δ 46.59. ^1H NMR: δ 7.41 (m, 6H, Ph), 7.52 (m, 4H, Ph), 7.90 (d, 2H, C*H*, $^3J_{P-H}$ = 7.2). ^{13}C NMR: δ 128–134 (Ph), 177.21 (t, HC*C*, $^3J_{P-C}$ = 8.3), 177.95 (d, *C*H, $^2J_{P-C}$ = 11.3), 205.22 (d, *cis*-*C*O, $^2J_{P-C}$ = 9.0), 209.67 (d, P*C*S, J_{P-C} = 24.8). MS (FAB, NBA, *m*/*z*): 1000.9 (M^+), 972.9 ($M^+ - CO$), 945 ($M^+ - 2CO$), 916.9 ($M^+ - 3CO$), 721.0 ($M^+ - 10CO$).

2b: IR (KBr, ν_{CO}/cm^{-1}): 2068(m), 1931(vs). ^{31}P NMR: δ 28.54 (J_{W-P} = 249.6). ^1H NMR: δ 7.41 (m, 6H, Ph), 7.52 (m, 4H, Ph), 7.91 (d, 2H, C*H*, $^3J_{P-H}$ = 8.0). ^{13}C NMR: δ 128–134 (Ph); 177.21 (t, HC*C*, $^3J_{P-C}$ = 8.3), 177.30 (d, *C*H, $^2J_{P-C}$ = 11.3), 196.80 (d, *cis*-*C*O, $^2J_{P-C}$ = 9.0). MS (FAB, NBA, *m*/*z*): 1176.2 (M^+), 1148.0 ($M^+ - CO$), 1064.0 ($M^+ - 4CO$), 1036.8 ($M^+ - 5CO$), 1008.2 ($M^+ - 6CO$), 952.1 ($M^+ - 8CO$), 925.2 ($M^+ - 9CO$), 896.2 ($M^+ - 10CO$).

3a: ^{31}P NMR: δ 63.47. ^1H NMR: δ 4.87 (s, 2H, CH_2), 7.14–7.65 (m, 15H, Ph). MS (FAB, NBA, *m*/*z*): 571.4 (M^+), 543.4 ($M^+ - CO$).

3b: ^{31}P NMR: δ 62.38. ^1H NMR: δ 1.14 (t, 6H, CH_3, J_{H-H} = 7.3), 3.68 (q, 4H, CH_2, J_{H-H} = 7.3), 2.42 (b, 1H, N*H*), 7.43–7.67 (m, 10H, Ph).

4a: ^{31}P NMR: δ 47.14 (J_{W-P} = 256.4). ^1H NMR: δ 4.86 (s, 2H, CH_2), 7.29–7.68 (m, 15H, Ph), 7.91 (d, 2H, C*H*, $^3J_{P-H}$ = 8.0). MS (FAB, NBA, *m*/*z*): 659.3 (M^+), 631.3 ($M^+ - CO$).

4b: ^{31}P NMR: δ 46.30 (J_{W-P} = 257.6). ^1H NMR: δ 1.19 (t, 6H, CH_3, J_{H-H} = 7.3), 3.95 (q, 4H, CH_2, J_{H-H} = 7.3), 7.30–7.63 (m, 10H, Ph).

‡ *Crystal data* for **2a**: $C_{39}H_{22}O_{10}P_2S_3Mo_2$, space group $P\bar{1}$, a = 9.042(7), b = 15.175(6), c = 16.554(8) Å, α = 112.02(4), β = 96.38(4), γ = 92.92(4)°, V = 2082.2(21) Å^3, Z = 2, D_{calcd} = 1.596 g cm^{-3}, μ = 8.603 cm^{-1}, observed reflections 4298, $2\theta_{max}$ = 45.0°. An absorption correction has been carried out. The structure was solved by Patterson synthesis then refined *via* standard least-squares and difference Fourier techniques. Non-hydrogen atoms were refined by using anisotropic thermal parameters. Total number of parameters: 506. R = 0.028, R_w = 0.029; GOF = 1.36, ΔF = 0.51, −0.48 e Å^3; Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Information for Authors, Issue No. 1.

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