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

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The first 6a-thiathiophthen metal complex was prepared by treating  $M(CO)_5[PPh_2CS_2CH_2C=CH]$  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 6athiathiophthen (3,3a,4-trithiopentalene) derivatives<sup>1</sup> have attracted considerable attention. Methods for the synthesis of 6athiathiophthen<sup>2</sup> and arylthio- or alkylthio-derivatives<sup>3</sup> using various thionation reagents such as S, H<sub>2</sub>S and P<sub>2</sub>S<sub>5</sub> have been reported. Furthermore, much work has been done on the bonding,<sup>4</sup> structure,<sup>5</sup> reactions<sup>6</sup> and electron density deformation<sup>7</sup> 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.<sup>8</sup>

Treatment of  $M(CO)_5[PPh_2(CS_2CH_2C\equiv CH)]$  (M = Mo, 1a; W, 1b) with a catalytic amount of Et<sub>3</sub>N in CH<sub>2</sub>Cl<sub>2</sub> yields the 6athiathiophthen metal complexes  $[M(CO)_5PPh_2]_2(\mu-C_5H_2S_3)$  (M = Mo, 2a; W, 2b) at room temperature (Scheme 1). Complex 2a is isolated as a red microcrystalline powder by recrystallization from hexane-CH<sub>2</sub>Cl<sub>2</sub> 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  $[MoPPh_2]_2(\mu$ -C<sub>5</sub>H<sub>2</sub>S<sub>3</sub>)+, 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)<sub>5</sub> unit in octahedral geometry. The <sup>1</sup>H NMR spectrum of **2a** exhibits a doublet at  $\delta$  7.90 ( ${}^{3}J_{P-H} = 7.2$ Hz) attributed to the two equivalent methyne protons, and the corresponding <sup>13</sup>C NMR signal is a doublet at  $\delta$  177.95 (<sup>2</sup>J<sub>P-C</sub> = 11.3 Hz). The low field <sup>1</sup>H chemical shift is regarded as evidence for a strong ring current. The <sup>13</sup>C NMR resonance of the 3a-carbon exhibits a triplet at  $\delta$  177.21 ( ${}^{3}J_{P-C} = 8.3$  Hz). The <sup>1</sup>H and <sup>13</sup>C NMR spectra clearly imply  $C_{2\nu}$  symmetry in **2a**. The molecular structure of this unusual complex 2a is confirmed by an X-ray diffraction study.<sup>‡</sup> 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).<sup>9</sup> Interestingly, in the crystal, **2a** does not exhibit  $C_{2\nu}$ symmetry and the P<sub>2</sub>C<sub>5</sub>H<sub>2</sub>S<sub>3</sub> unit is not planar. To our



Fig. 1 ORTEP drawing for the complex  $[Mo(CO)_5PPh_2]_2(\mu-C_5H_2S_3)$ , **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<sub>2</sub>, Et),  $CH_2Cl_2$ , 25 °C, 1 min; iii,  $Bu^nLi$  or  $Bu^iOK$  or PhNH<sub>2</sub>, 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<sub>4</sub>NF were used to replace Et<sub>3</sub>N in the reaction. Complexes 1a and 1b were reacted with secondary amine (Pr<sup>i</sup><sub>2</sub>NH, Et<sub>2</sub>NH) or Bu<sup>n</sup><sub>4</sub>NF 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  $Et_3N > Pr_2^iNH > Et_2NH$ >  $Bu^{n_4}NF$ . No reaction was observed when 1 was reacted with Bu<sup>n</sup>Li, Bu<sup>t</sup>OK or PhNH<sub>2</sub>. But the reactions of 1 with several primary aliphatic amines (RNH<sub>2</sub>; R = PhCH<sub>2</sub>, Et) give  $M(CO)_5PPh_2CSNHR$  (M = Mo, R = PhCH<sub>2</sub>, Et; **3a-b**; M = W, R = PhCH<sub>2</sub>, Et; 4a-b) and HC=CCH<sub>2</sub>SH 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), <sup>2</sup>H-labelling experiment was carried out. Treatment of the terminally labelled [2H1]1a with Et3N afforded 2a with no 2H-labelling. In addition, when the reaction was monitored by the <sup>31</sup>P and <sup>1</sup>H NMR spectra, complex 2a was observed as the only product (yield 95% from integration of the <sup>31</sup>P NMR spectrum) and no intermediate was observed. Attempts to trap possible intermediates by separate addition of PPh3, CS2, TCNE, MeI or cyclopentadiene into the reaction of 1 with Et<sub>3</sub>N 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<sub>2</sub>NC(S)SCH<sub>2</sub>C=CH with Et<sub>3</sub>N or PhCH<sub>2</sub>NH<sub>2</sub> resulted in no reaction under the same reaction conditions. In the absence of R<sub>3</sub>N, dimerization of 1 gave a fivemembered 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

<sup>†</sup> Selected spectroscopic data: <sup>1</sup>H (300 MHz) and <sup>13</sup>C{<sup>1</sup>H} (75 MHz) NMR (298 K, CDCl<sub>3</sub>, relative to SiMe<sub>4</sub>, multiplicity, assignment, *J* in Hz) <sup>31</sup>P (121.5 MHz) NMR (H<sub>3</sub>PO<sub>4</sub> external standard).

**1a**: IR (CH<sub>2</sub>Cl<sub>2</sub>,  $v_{CO}/cm^{-1}$ ): 2075(m), 1942(vs). <sup>31</sup>P NMR:  $\delta$  76.76. <sup>1</sup>H NMR:  $\delta$  2.18 (t, 1H,  $\equiv$ CH, <sup>4</sup>J<sub>H-H</sub> = 2.68), 3.98 (d, 2H, S-CH<sub>2</sub>, <sup>4</sup>J<sub>H-H</sub>)

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= 2.68), 7.47 (m, 6H, Ph), 7.67 (m, 4H, Ph). <sup>13</sup>C NMR:  $\delta$  26.36 (S-*C*H<sub>2</sub>), 72.60 (=*C*H), 75.77 (*C*=CH), 128.55 (d, *meta*-C of Ph, <sup>3</sup>*J*<sub>P-C</sub> = 9.60), 131.03 (s, *para*-C of Ph), 133.69 (d, *ortho*-C of Ph, <sup>2</sup>*J*<sub>P-C</sub> = 11.77), 133.67 (d, *ipso*-C of Ph, *J*<sub>P-C</sub> = 30.70), 205.35 (d, *C*O, <sup>2</sup>*J*<sub>P-C</sub> = 8.48), 209.84 (d, CS<sub>2</sub>, *J*<sub>P-C</sub> = 26.10). MS (FAB, NBA, *m*/*z*): 539 (M<sup>+</sup>), 483 (M<sup>+</sup> - 2CO).

[<sup>2</sup>H<sub>1</sub>]**1b** (<sup>2</sup>H 98%): IR (CH<sub>2</sub>Cl<sub>2</sub>, ν<sub>CO</sub>/cm<sup>-1</sup>): 2072(m), 1940(vs). <sup>31</sup>P NMR: δ 59.95 ( $J_{W-P}$  = 237.0). <sup>1</sup>H NMR: δ 3.96 (s, 2H, S-CH<sub>2</sub>), 7.45 (m, 6H, Ph), 7.69 (m, 4H, Ph).

**2a**: IR (KBr,  $v_{CO}/cm^{-1}$ ): 2073(m), 1924(vs). <sup>31</sup>P NMR:  $\delta$  46.59. <sup>1</sup>H NMR:  $\delta$  7.41 (m, 6H, Ph), 7.52 (m, 4H, Ph), 7.90 (d, 2H, CH, <sup>3</sup>J<sub>P-H</sub> = 7.2). <sup>13</sup>C NMR:  $\delta$  128–134 (Ph), 177.21 (t, HCC, <sup>3</sup>J<sub>P-C</sub> = 8.3), 177.95 (d, CH, <sup>2</sup>J<sub>P-C</sub> = 11.3), 205.22 (d, *cis*-CO, <sup>2</sup>J<sub>P-C</sub> = 9.0), 209.67 (d, PCS, J<sub>P-C</sub> = 24.8). MS (FAB, NBA, *m*/z): 1000.9 (M<sup>+</sup>), 972.9 (M<sup>+</sup> - CO), 945 (M<sup>+</sup> - 2CO), 916.9 (M<sup>+</sup> - 3CO), 721.0 (M<sup>+</sup> - 10CO).

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

**3a**: <sup>31</sup>P NMR: δ 63.47. <sup>1</sup>H NMR: δ 4.87 (s, 2H, CH<sub>2</sub>), 7.14–7.65 (m, 15H, Ph). MS (FAB, NBA, *m*/*z*): 571.4 (M<sup>+</sup>), 543.4 (M<sup>+</sup> - CO).

**3b**: <sup>31</sup>P NMR:  $\delta$  62.38. <sup>1</sup>H NMR:  $\delta$  1.14 (t, 6H, CH<sub>3</sub>, J<sub>H-H</sub> = 7.3), 3.68 (q, 4H, CH<sub>2</sub>, J<sub>H-H</sub> = 7.3), 2.42 (b, 1H, NH), 7.43–7.67 (m, 10H, Ph).

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

**4b**: <sup>31</sup>P NMR:  $\delta$  46.30 ( $J_{W-P}$  = 257.6). <sup>1</sup>H NMR:  $\delta$  1.19 (t, 6H, CH<sub>3</sub>,  $J_{H-H}$  = 7.3), 3.95 (q, 4H, CH<sub>2</sub>,  $J_{H-H}$  = 7.3), 7.30–7.63 (m, 10H, Ph).

‡ Crystal data for **2a**: C<sub>39</sub>H<sub>22</sub>O<sub>10</sub>P<sub>2</sub>S<sub>3</sub>Mo<sub>2</sub>, space group  $P\overline{1}$ , a = 9.042(7), b = 15.175(6), c = 16.554(8) Å,  $\alpha = 112.02(4)$ ,  $\beta = 96.38(4)$ ,  $\gamma = 92.92(4)^\circ$ , V = 2082.2(21) Å<sup>3</sup>, Z = 2,  $D_{calcd} = 1.596$  g cm<sup>-3</sup>,  $\mu = 8.603$  cm<sup>-1</sup>, observed reflections 4298,  $2\theta_{max} = 45.0^\circ$ . 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,  $\Delta F = 0.51$ , -0.48 e Å<sup>3</sup>; 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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