# Synthesis and Crystal Structure of the First 6a-Thiathiophthen Metal Complex [Mo(CO)5PPh2]2(μ-C5H2S3)

## Kuang-Hway Yih, Ying-Chih Lin,* Gene-Hsiang Lee and Yu Wang

*Department of Chemistry, National Taiwan University, Taiwan 106, Republic of China*

The first 6a-thiathiophthen metal complex was prepared by treating M(CO)5[PPh2CS2CH2C≡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, H2S and P2S5 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[PPh2(CS2CH2C≡CH)] (M = Mo, 1a; W, 1b) with a catalytic amount of Et3N in CH2Cl2 yields the 6a-thiathiophthen metal complexes [M(CO)5PPh2]2(μ-C5H2S3) (M = Mo, 2a; W, 2b) at room temperature (Scheme 1). Complex 2a is isolated as a red microcrystalline powder by recrystallization from hexane–CH2Cl2 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 [MoPPh2]2(μ-C5H2S3)+, 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 13C 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 13C NMR resonance of the 3a-carbon exhibits a triplet at δ 177.21 ($^3J_{P-C}$ = 8.3 Hz). The 1H and 13C 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 P2C5H2S3 unit is not planar. To our
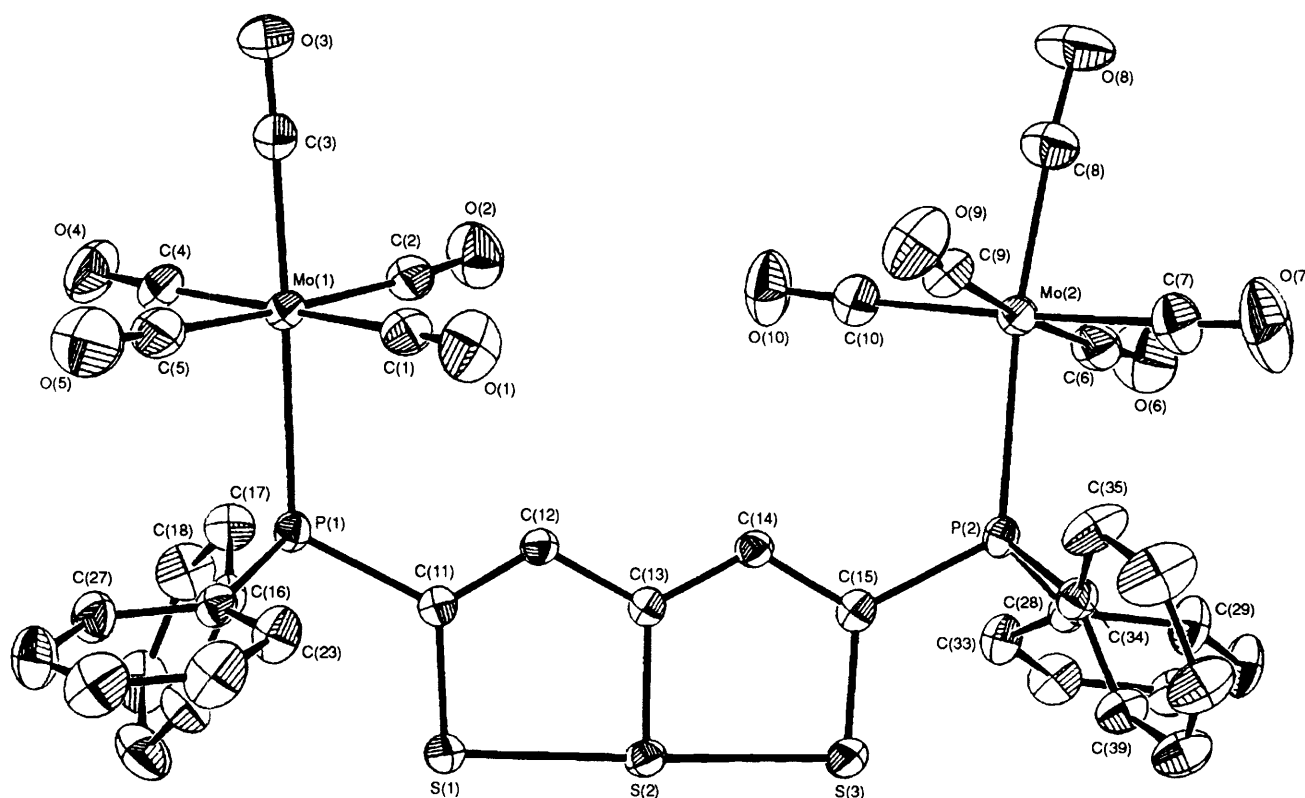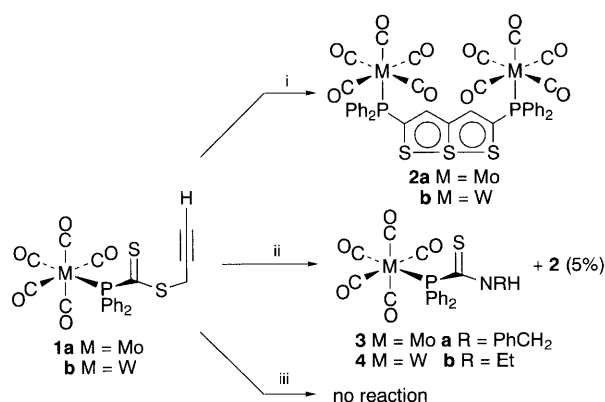


Fig. 1 ORTEP drawing for the complex [Mo(CO)5PPh2]2(μ-C5H2S3), 2a. Selected bond distances (Å) and angles (°) are as follows: Mo(1)–P(1) 2.528(2), Mo(2)–P(2) 2.540(2), P(1)–C(11) 1.855(4), P(2)–C(15) 1.847(4), C(11)–S(1) 1.689(4), C(13)–S(2) 1.736(4), C(15)–S(3) 1.689(4), C(11)–C(12) 1.352(5), C(12)–C(13) 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.

## 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 ($CH_2Cl_2$, $v_{CO}/cm^{-1}$): 2075(m), 1942(vs). $^{31}P$ NMR: δ 76.76. $^1H$ NMR: δ 2.18 (t, 1H, $\equiv CH$, $^4J_{H-H}$ = 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 ($\equiv CH$), 75.77 ($C\equiv CH$), 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, *CO*, $^2J_{P-C}$ = 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 ($CH_2Cl_2$, $v_{CO}/cm^{-1}$): 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, $v_{CO}/cm^{-1}$): 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, $CH$, $^3J_{P-H}$ = 7.2). $^{13}C$ NMR: δ 128–134 (Ph), 177.21 (t, HCC, $^3J_{P-C}$ = 8.3), 177.95 (d, $CH$, $^2J_{P-C}$ = 11.3), 205.22 (d, *cis*-CO, $^2J_{P-C}$ = 9.0), 209.67 (d, PCS, $J_{P-C}$ = 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, $v_{CO}/cm^{-1}$): 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, $CH$, $^3J_{P-H}$ = 8.0). $^{13}C$ NMR: δ 128–134 (Ph); 177.21 (t, HCC, $^3J_{P-C}$ = 8.3), 177.30 (d, $CH$, $^2J_{P-C}$ = 11.3), 196.80 (d, *cis*-CO, $^2J_{P-C}$ = 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, $CH$, $^3J_{P-H}$ = 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) Å³, *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, Δ*F* = 0.51, −0.48 e Å³; 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.

## References

1 Y. Wang, S. K. Yeh, S. Y. Wu, C. T. Pai, C. R. Lee and K. J. Lin, *Acta Crystallogr., Sect. B: Struct. Sci.*, 1991, **47**, 298; L. K. Hansen and A. Hordvik, *Acta. Chem. Scand.*, 1973, **27**, 411; Q. Shen and K. Hedberg, *J. Am. Chem. Soc.*, 1974, **96**, 289.
2 R. Gleiter and R. Gygax, *Top. Curr. Chem.*, 1976, **63**, 1.
3 K. T. Potts, S. A. Nye and K. A. Smith, *J. Org. Chem.*, 1992, **57**, 3895; U. Chiacchio, A. Corsaro, A. Rescifina, M. G. Testa and G. Purrello, *Heterocycles*, 1993, **36**, 223; H. G. Marei and M. M. Mishrikey, *Phosphorus, Sulfur and Silicon*, 1992, **73**, 229.
4 K. Maeda, *Bull. Chem. Soc. Japan*, 1961, **34**, 785; R. Cimiraglia and H.-J. Hofmann, *J. Am. Chem. Soc.*, 1991, **113**, 6449; A. S. Brown and V. H. Smith, *J. Chem. Phys.*, 1993, **99**, 1837.
5 H. Behringer, M. Ruff and R. Wiedenmann, *Chem. Ber.*, 1964, **97**, 1732; A. Hordvik, E. Sletten and J. Sletten, *Acta Chem. Scand.*, 1966, **20**, 2001; R. J. S. Beer, D. Cartwright and D. Harris, *Tetrahedron Lett.*, 1967, 953.
6 R. J. S. Beer, D. Cartwright, D. Harris and R. J. Gait, *J. Chem. Soc. C*, 1971, 963; G. Duguay, D. H. Reid, K. O. Wade and R. G. Webster, *J. Chem. Soc. C*, 1971, 2829.
7 Y. Wang, M. J. Chen and C. H. Wu, *Acta Crystallogr., Sect. B: Struct. Sci.*, 1988, **44**, 179; K. J. Lin and Y. Wang, *J. Phys. Chem.*, 1993, **97**, 3176.
8 K. H. Yih, Y. C. Lin, M. C. Cheng and Y. Wang, *J. Chem. Soc., Chem. Commun.*, 1993, 1380.
9 L. Pauling, *The Nature of the Chemical Bond*, 3rd ed., Cornell University Press, New York, 1960.
10 K. H. Yih, Y. C. Lin, M. C. Cheng and Y. Wang, *Organometallics*, 1994, **13**, 1561.