

# Novel synthesis of a dicationic thiopyrylium salt: bis(2,4,6-triphenylthiopyrylium)dicarbonylmolybdenum perchlorate

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## Abstract

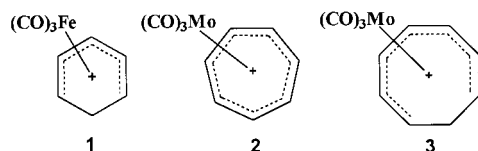
In this work formation of a dicationic thiopyrylium salt, bis(2,4,6-triphenylthiopyrylium)dicarbonylmolybdenum perchlorate, by the reaction of 2,4,6-triphenylthiopyrylium perchlorate and hexacarbonylmolybdenum in diglyme/benzene solvent is reported. © 1999 Elsevier Science S.A. All rights reserved.

*Keywords:* Hexacarbonylmolybdenum; Molybdenum; Thiopyrylium; Thiopyrylium cation

## 1. Introduction

Tricarbonylcyclohexadienyliron tetrafluoroborate,  $[(\eta^5\text{-C}_6\text{H}_7)\text{Fe}(\text{CO})_3][\text{BF}_4]$  (**1**) and its substituted derivatives which contain a cationic ring system have been reported in the literature [1]. It is also known that the reaction of cycloheptatriene with hexacarbonylmolybdenum in diglyme at reflux temperature gives a new complex, tricarbonylcycloheptatrienemolybdenum(0) [2], which on treatment with triphenylmethyl perchlorate turns into tropyliumtricarbonylmolybdenum cation [3],  $[(\eta^7\text{-C}_7\text{H}_7)\text{Mo}(\text{CO})_3]^+$  (**2**). Similar complexes are also synthesized for vanadium and chromium, namely  $[(\eta^7\text{-C}_7\text{H}_7)\text{V}(\text{CO})_3]^+$  [4] and  $[(\eta^7\text{-C}_7\text{H}_7)\text{Cr}(\text{CO})_3]^+$  [3].

Larger cationic ring systems are found in  $[\text{C}_8\text{H}_9\text{-Mo}(\text{CO})_3]^+$  (**3**) [5,6] and bicyclic  $[\text{C}_8\text{H}_9\text{Fe}(\text{CO})_3]^+$  [7].



In view of the fact that these cationic ring systems are stabilized by coordination to a carbonyl–metal moiety, it seemed of considerable interest to examine the reac-

tion of 2,4,6-triphenylthiopyrylium perchlorate (**4**), a relatively stable salt [8], with  $\text{Mo}(\text{CO})_6$  in diglyme, where a dicationic stable compound was isolated and identified as bis(2,4,6-triphenylthiopyrylium)dicarbonylmolybdenum perchlorate **5**.

## 2. Experimental

Instruments used for identification of the novel compound were: Bruker AC 80 FT-NMR spectrometer, Shimadzu 4300 FT-IR spectrophotometer, Finnigan Mat 8430 magnetic sector mass spectrometer and Varian-A5 atomic absorption spectrophotometer.

The complex 2,4,6-triphenylthiopyrylium perchlorate (**4**) was prepared according to the method described in the literature [8]. In a round-bottom flask equipped with a magnetic stirrer, a condenser and gas inlet, 2,4,6-triphenylthiopyrylium perchlorate (10 mmol) and hexacarbonylmolybdenum (8 mmol) were mixed in dry diglyme (50ml) and dry benzene (15 ml) under argon atmosphere. This mixture was stirred and refluxed at 124°C for 12 h. At this stage the color of the solution was greenish yellow. The reaction mixture was cooled and filtered. The greenish yellow filtrate was concentrated by evaporation in a rotary evaporator. Preparative layer chromatography (PLC) of this residue on alumina using a 5:1 mixture of  $\text{CH}_2\text{Cl}_2$  and  $(\text{C}_2\text{H}_5)_2\text{O}$  showed three bands with orange, yellow and green

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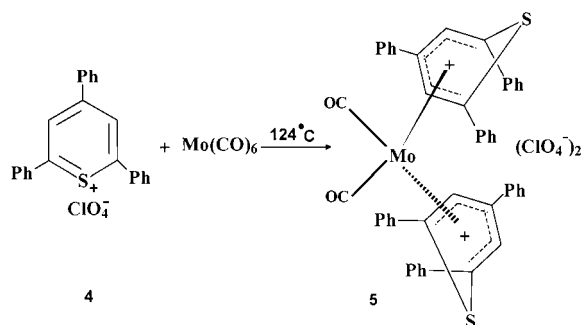
E-mail address: pirelahi@khayam.ut.ac.ir (H. Pirelahi)

colors from top to bottom. The major orange band was extracted with a 5:1 mixture of  $\text{CH}_2\text{Cl}_2$  and  $(\text{C}_2\text{H}_5)_2\text{O}$ . Removal of the solvent under reduced pressure, followed by crystallization of the residue from ether, gave pink needles with 21% yield which were characterized as bis(2,4,6-triphenylthiopyrylium)dicarbonylmolybdenum perchlorate (**5**). M.p. 109–110°C. Anal. Calc.  $\text{C}_{48}\text{H}_{34}\text{O}_{10}\text{S}_2\text{Cl}_2\text{Mo}$  (MW 1001): Mo, 9.58; S, 6.40; Cl, 7.08%. Found: Mo, 9.61; S, 6.60; Cl, 7.50%. Mass spectrum,  $m/z$ : 1001 (M, 0.7%), 847 (M – 2Ph, 1.16), 387 ( $[\text{M} - \text{CO} - 2\text{ClO}_4]^{2+}$ , 1.5), 340 (M – 6Ph –  $2\text{ClO}_4$ , 2), 325 (triphenylthiopyrylium, 40), 310 ( $[\text{M} - \text{CO} - 2\text{Ph} - 2\text{ClO}_4]^{2+}$ , 100), 142 ( $[\text{M} - 2\text{CO} - 6\text{Ph} - 2\text{ClO}_4]^{2+}$ , 2). IR spectrum (KBr)  $\nu$ : 1969 (b, 2CO), 1090 (b,  $\text{ClO}_4$ ).  $^1\text{H-NMR}$  spectrum ( $\text{CDCl}_3$ )  $\delta$ : 4.85 (4H, rather br s, H-3,-5S), 7.23–8.11 (30H, m, ArH).  $^{13}\text{C-NMR}$  spectrum ( $\text{CDCl}_3$ )  $\delta$ : 124.43, 127.57, 129.05, 129.36, 129.51 and 130.07 (various aromatic carbons), 133.43 and 133.62 (allylic C-3,-5S), 137.89, 139.59 and 142.30 (*ipso*-carbons of Ph), 153.45 (C-4S), 191.52 (CO), 196.81 (CO), 305.01 (C-2,-6S). Attempts failed to prepare single crystals of **5** suitable for X-ray analysis.

The yellow band of PLC was also extracted with a 5:1 mixture of  $\text{CH}_2\text{Cl}_2$  and  $(\text{C}_2\text{H}_5)_2\text{O}$ . The resulting orange residue crystallized from ethanol gave the starting 2,4,6-triphenylthiopyrylium perchlorate (**4**) as orange crystals, having the same m.p. and  $^1\text{H-NMR}$  spectrum reported in the literature for an authentic sample [8]. Moreover, when the green band from the PLC was extracted the  $^1\text{H-NMR}$  spectrum of the resulting unidentified green residue did not show any upfield protons characteristic of coordination of the heteroatom ring to molybdenum.

### 3. Results and discussion

Hexacarbonylmolybdenum reacts with 2,4,6-triphenylthiopyrylium perchlorate (**4**) in diglyme/benzene as solvent at 124°C. It is assumed that in this process some of the carbonyl groups are replaced by diglyme and since diglyme is not capable of  $d_{\pi}-p_{\pi}$  bond formation with the metal, this ligand is easily replaced by 2,4,6-triphenylthiopyrylium ion to produce a novel compound, bis(2,4,6-triphenylthiopyrylium)dicarbonylmolybdenum perchlorate (**5**).



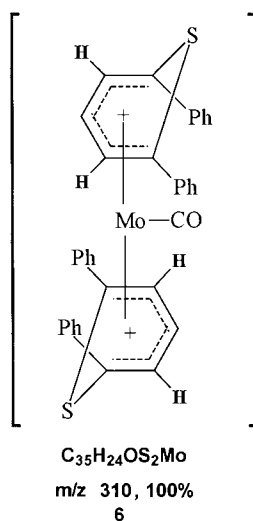
The reaction mixture was separated into three bands using PLC on alumina. The orange band was extracted using dichloromethane/ether (5:1) as solvent and the extract was crystallized from ether as pink needles.

Elemental analysis and mass spectrum of the product corresponds with the molecular formula  $\text{C}_{48}\text{H}_{34}\text{O}_{10}\text{S}_2\text{Cl}_2\text{Mo}$  (MW 1001). Characteristic features of the mass spectrum results are the molecular ion at  $m/z$  1001 and the most abundant fragment ions at different masses which could be formed by the loss of Ph, CO and  $\text{ClO}_4$  groups from the molecular ion as shown below (Table 1). These fragments are consistent with the molecular formula and indicate that the formation of S-containing doubly charged ions is highly favored. Since the sulfur atom is capable of  $d_{\pi}-p_{\pi}$  bonding, it seems that the nonbonding electrons of sulfur atoms could have an effective role in the stability of doubly charged ions. The base peak at  $m/z$  310 could be due to the doubly charged ion **6** where the centers are so remote from each other that the positive charges are easily accommodated by the fragment. The infrared spectrum in KBr disc shows two overlapping broad bands centered at  $1969\text{ cm}^{-1}$  for carbonyl groups as well as an intense broad band at  $1090\text{ cm}^{-1}$  characteristic of the perchlorate anion [9]. In agreement with the molecular formula, the  $^1\text{H-NMR}$  spectrum of this compound in  $\text{CDCl}_3$  shows a rather broad singlet at  $\delta = 4.85$  ppm for the protons of the sulfur ring at 3-, 5-positions and a multiplet in the range of  $\delta = 7.23$ – $8.11$  ppm due to the protons of phenyl groups at 2-, 4-, 6-positions in the ratios 4:30, respectively. The resonance shift due to the protons of 3-,5-positions in the free ligand, which appears at  $\delta = 8.90$  ppm, to higher field at 4.85 ppm in **5** is consistent with the bond formation of the sulfur ring with molybdenum.

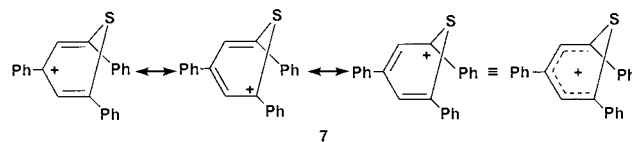
Table 1

| $m/z$ | %      | Fragment ion                                  |
|-------|--------|---|
| 1001  | 0.70   | M   |
| 847   | 1.16   | M – 2Ph                                       |
| 387   | 1.50   | M – (Xo, $2\text{ClO}_4$ ) <sup>a</sup>       |
| 340   | 2.00   | M – (6Ph, $2\text{ClO}_4$ )                   |
| 325   | 40.00  | Triphenylthiopyrylium                         |
| 310   | 100.00 | M – (CO, 2Ph, $2\text{ClO}_4$ ) <sup>a</sup>  |
| 142   | 2.00   | M – (2CO, 6Ph, $2\text{ClO}_4$ ) <sup>a</sup> |

<sup>a</sup> Doubly charged ions.



By coordination of the heteroatom ring to molybdenum, the aromatic character of the S-containing ring is lost and hydrogen atoms in the 3-,5-positions of the ring appear as conjugated allylic forms. Birch has shown [1] that in substituted tricarbonylcyclohexadienyliron salts, nucleophilic attack occurs at the ring and therefore the positive charge is located in the ring system. In our case it can also be concluded that the positive charge is part of a delocalized  $4\pi-\eta^5$  moiety of the heteroatom ring system **7**. In accordance with the delocalized structures, the  $^{13}C$ -NMR spectrum of compound **5** in  $CDCl_3$  exhibits downfield resonances at  $\delta$ : 305.01 (C-2,-6S), 153.45 (C-4S), 133.62 and 133.43 (allylic C-3,-5S) ppm indicative of a coordinated sulfur ring with molybdenum. Unlike the carbon atom at the 4-position, the lowest peak at 305.01 ppm reveals a highly stabilized carbocation [10] at the 2-,6-positions as shown in **7**. The presence of two carbonyl groups was also reconfirmed by the two singlets at  $\delta = 196.81$  and 191.52 ppm along with aromatic carbon atoms in the range of  $\delta = 124.43$ –142.30 ppm.



#### 4. Conclusions

Considering the  $^1H$ - and  $^{13}C$ -NMR spectra of compound **5** it is concluded that the sulfur atom has no effective contribution to the metal–ring bonding in the ground state; hence the ring is not planar and takes on a nonaromatic character in this compound as indicated in the formula **5**, where in this way the metal atom retains an 18-electron configuration.

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