

## A SIMPLE SYNTHESIS OF THIOKETONEMOLYBDENUM CARBONYL COMPLEXES. AN EXAMPLE OF GEOMETRIC ISOMERISM

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### Summary

Thioketones react with molybdenum hexacarbonyl in tetrahydrofuran (60–65°C, 2–3 h) to give molybdenum pentacarbonyl complexes in 52–80% yield. Geometric isomers were isolated in the case of thiocamphor.

### Introduction

Recently, one of us [1] reported the isolation of the first analytically pure thioketonemolybdenum carbonyl complex (III), obtained in 26% yield by reaction of the chlorine bridged molybdenum carbonyl trianion (I) with 4,4'-

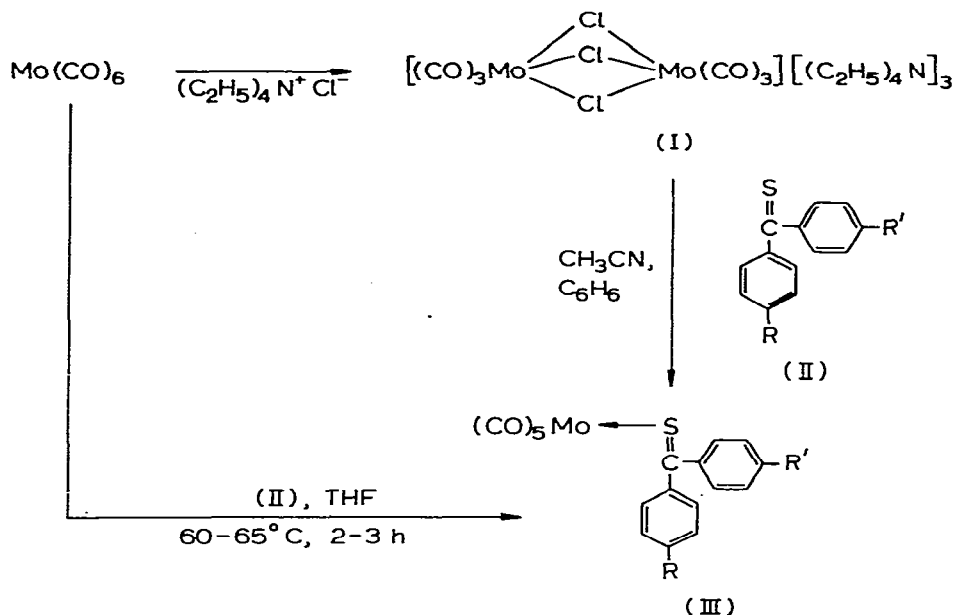


TABLE 1

YIELDS, MELTING POINTS, AND ANALYTICAL DATA FOR THE THIOKETONEMOLYBDENUM COMPLEXES

Complex	Reaction time (h)	Yield <sup>a</sup> (%)	M.p. (°C)	Analyses (Found (Calcd.) (%))		
				C	H	S
III, R = R' = OCH <sub>3</sub>	3	76	81–82 <sup>b</sup>			
III, R = OCH <sub>3</sub> , R' = H	2	62	oil	48.67 (49.16)	3.02 (2.61)	7.11 (6.91)
III, R = R' = CH <sub>3</sub>	2	52	56–58	52.36 (51.96)	3.14 (3.05)	6.66 (6.94)
III, R = R' = N(CH <sub>3</sub> ) <sub>2</sub>	2	69	110–112	51.20 (50.78)	4.08 (3.87)	5.77 (6.16)
V	.3	57	78–80	44.51 (44.56)	4.23 (3.99)	8.00 (7.93)
VI		23	63–65	45.03 (44.56)	3.94 (3.99)	7.72 (7.93)
VIII	3	72	oil	44.88 (44.56)	3.83 (3.99)	7.79 (7.93)

<sup>a</sup> Yield is base on thioketone. <sup>b</sup> Lit. m.p. 81–82°C [1].

dimethoxythiobenzophenone (II, R = R' = OCH<sub>3</sub>) in benzene containing acetonitrile. The trianion I was prepared from molybdenum hexacarbonyl. We now report a superior and direct synthesis of thioketonemolybdenum carbonyl complexes, and the isolation of the first geometric isomers of thioketone complexes.

### Results and discussion

Treatment of 4,4'-dimethoxythiobenzophenone (II, R = R' = OCH<sub>3</sub>) with an equimolar amount of molybdenum hexacarbonyl in dry tetrahydrofuran for 2–3 h, at 60–65°C, affords the molybdenum complex III in 76% yield. The yield is significantly higher than that reported previously [1], and good yields of analytically pure complexes were also realized from other thiobenzophenones (II, R = R' = CH<sub>3</sub>, N(CH<sub>3</sub>)<sub>2</sub>; R = OCH<sub>3</sub>, R' = H) \*. The yields and analytical data for the complexes are listed in Table 1. The infrared, proton magnetic resonance, and mass spectral results (Table 2) are in good agreement with data reported for III, R = R' = OCH<sub>3</sub> and for other thioketonemetal pentacarbonyl complexes [3].

When the thermal complexation reaction was applied to thiocamphor (IV) two isomeric molybdenum carbonyl complexes, V and VI, were formed in 57 and 23% yield, respectively. Complexes V and VI showed similar, but distinct, terminal metal carbonyl stretching bands in the infrared region. While the chemical shifts for the protons of the three methyl groups of complex VI were almost identical to those for the free ligand (IV), those for V were different. In addition, the carbon magnetic resonance spectrum for the thiocamphor ligand

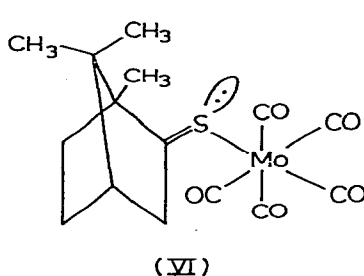
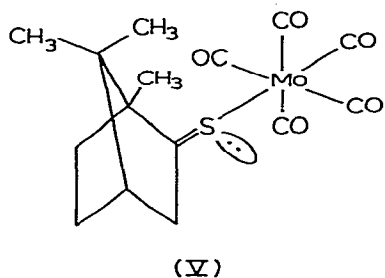
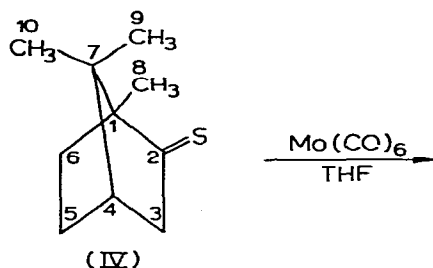
\* Molybdenum pentacarbonyl complexes of thiobenzophenone and adamantanethione have also been prepared by irradiation of the organosulfur ligand with Mo(CO)<sub>6</sub>. However, definitive yields were not given and the complexes were inadequately characterized (e.g., no analytical data) [2].

TABLE 2

## PERTINENT SPECTRAL DATA FOR THE THIOKETONEMOLYBDENUM COMPLEXES

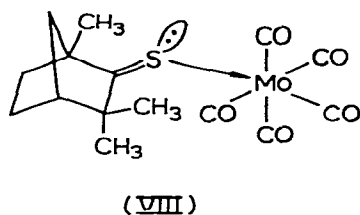
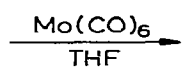
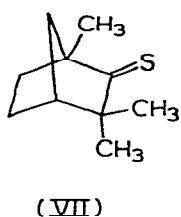
Complex	IR, $\nu(\text{CO})$ [solvent] ( $\text{cm}^{-1}$ )	Mass spectrum ( $m/e$ )	$^1\text{H}$ NMR ( $\delta$ , ppm) <sup>a</sup>	$^{13}\text{C}$ NMR ( $\delta$ , ppm) <sup>a,b</sup>
III, R = R' = OCH <sub>3</sub>	2070m, 1962vs, 1937s [C <sub>6</sub> H <sub>14</sub> ] 2042m, 1949vs, 1915m [THF]	494	3.91 (s, 6 H, OCH <sub>3</sub> ), 6.97 (d, 4 H, J 9 Hz, protons <i>ortho</i> to methoxy bearing carbons), 7.61 (d, 4 H, protons <i>meta</i> to methoxy bearing carbons) 3.90 (s, 3 H, OCH <sub>3</sub> ), 6.92 (d, 2 H, J 9 Hz, protons <i>ortho</i> to methoxy bearing carbons) 7.25-7.90 (m, 7 H, other aromatic protons)	13.1 (C(8)), 19.5, 19.6 (C(9), C(10)), 26.8 (C(5)), 34.0 (C(6)), 45.4 (C(4)), 50.6 (C(7)), 55.1 (C(3)), 70.9 (C(1)), 204.5 (carbonyl carbons <i>cis</i> to the thioketone ligand), 213.0 (carbonyl carbon <i>trans</i> to thioketone), 267.8 (C(2))
III, R = OCH <sub>3</sub> , R' = H	2078m, 1963vs, 1940s [C <sub>6</sub> H <sub>14</sub> ]		2.28 (s, 6 H, CH <sub>3</sub> ), 6.98 (d, 4 H, J 8 Hz, protons <i>ortho</i> to methyl bearing carbons), 7.40 (d, 4 H, protons <i>meta</i> to methyl bearing carbons)	13.1 (C(8)), 19.6, 19.8 (C(9), C(10)), 27.1 (C(5)), 33.9 (C(6)), 45.3 (C(4)), 48.9 (C(7)), 55.3 (C(3)), 69.5 (C(1)), 206.0 (carbonyl carbons <i>cis</i> to the thioketone ligand), 214.1 (carbonyl carbon <i>trans</i> to the thioketone ligand), 271.8 (C(2))
III, R = R' = CH <sub>3</sub>	2075m, 1964vs, 1938s [C <sub>6</sub> H <sub>14</sub> ]		0.73 (s, 3 H, CH <sub>3</sub> ), 1.00 (s, 3 H, CH <sub>3</sub> ), 1.15 (s, 3 H, CH <sub>3</sub> ) <sup>c</sup>	
III, R = R' = N(CH <sub>3</sub> ) <sub>2</sub> V	2040m, 1944vs, 1915m [THF] 2077m, 1959vs, 1940s [C <sub>6</sub> H <sub>14</sub> ]	520 404		
VI	2075m, 1953vs, 1940s [C <sub>6</sub> H <sub>14</sub> ]	404	0.78 (s, 3 H, CH <sub>3</sub> ), 1.02 (s, 3 H, CH <sub>3</sub> ), 1.08 (s, 3 H, CH <sub>3</sub> ) <sup>c</sup>	
VIII	2084m, 1968vs, 1940s [C <sub>6</sub> H <sub>14</sub> ]	404	1.13 (s, 3 H, CH <sub>3</sub> ), 1.17 (s, 3 H, CH <sub>3</sub> ), 1.31 (s, 3 H, CH <sub>3</sub> ) <sup>d</sup>	

<sup>a</sup> CDCl<sub>3</sub> with tetramethylsilane as internal standard. <sup>b</sup> Results obtained with the FT-80 spectrometer operating in the fully decoupled mode. Partially decoupled spectra were also recorded so as to aid in the assignments of signals. <sup>c</sup> Thiocamphox, <sup>1</sup>H NMR:  $\delta$  0.78 (s, 3 H, CH<sub>3</sub>), 1.03 (s, 3 H, CH<sub>3</sub>), 1.09 ppm (s, 3 H, CH<sub>3</sub>); <sup>13</sup>C NMR:  $\delta$  13.1 (C(8)), 19.6, 19.8 (C(9)), C(10)), 27.2 (C(5)), 33.9 (C(6)), 45.1 (C(4)), 48.9 (C(7)), 55.5 (C(3)), 69.2 (C(1)), 271.1 ppm (C(2)), <sup>d</sup> Thiofenchone, <sup>1</sup>H NMR:  $\delta$  1.13 (s, 3 H, CH<sub>3</sub>), 1.17 (s, 3 H, CH<sub>3</sub>), 1.32 (s, 3 H, CH<sub>3</sub>).



of VI was essentially the same as that for free thiocamphor, with the thiocarbonyl carbon occurring at 0.3 ppm lower field in VI. In complex V, the thiocarbonyl carbon resonance appeared at 3.7 ppm higher field than that of IV. More than fractional changes were observed for carbons 1 and 7 on conversion of IV to V. The chemical shifts for the carbonyl carbons of V and VI were also different. Structures V and VI are suggested for this pair of geometric isomers, since complexation of the  $\text{Mo}(\text{CO})_5$  group as in VI would be expected to have a less pronounced effect, when compared to V, on the proton and carbon magnetic resonance chemical shifts of thiocamphor. Note that  $\pi$ -complexation did not occur as a large upfield shift of the thiocarbonyl carbon resonance should have been observed [4,5].

Thiofenchone (VII) reacted with molybdenum carbonyl to give a single complex whose NMR spectrum was virtually identical to that of the sulfur ligand.



The complex probably has structure VIII, although the isomeric structure cannot be ruled out, since we did not have both isomers available for the comparative purposes. Fluxionality cannot be ruled out here.

In conclusion, thioketonemolybdenum carbonyl complexes can now be synthesized in an efficient manner. We are searching for other systems (e.g. sulfine complexes) capable of existing as geometric isomers.

## Experimental

### General

Melting points were determined using a Fisher—Johns apparatus, and are uncorrected. Elemental analyses were performed by M-H-W Laboratories, Phoenix, Arizona, and by Butterworth Microanalytical Consultancy Ltd., Teddington, Great Britain. Proton NMR spectra were obtained using a Varian T60 or HA100 spectrometer, with tetramethylsilane as the internal standard. Carbon magnetic resonance spectra were recorded in the fully and partially decoupled modes using a Varian FT-80 spectrometer. An infrared Unicam SP1100 spectrophotometer was used for infrared spectral determinations. Mass spectra were recorded on an AEI MS902 spectrometer.

Molybdenum hexacarbonyl was purchased from Pressure Chemical Co., and was used as received. The thioketones were either commercial products (II, R = R' = OCH<sub>3</sub>, Aldrich Chemical Co.) or prepared as described in the literature [6–8].

### General procedure for the reaction of thioketones (II) with Mo(CO)<sub>6</sub>

A dry tetrahydrofuran solution (30–45 ml) containing equimolar amounts of Mo(CO)<sub>6</sub> and the thioketone (5–10 mmol) was heated at 60–65°C for 2–3 h. The reaction mixture was cooled, concentrated, and the residue was then chromatographed on silica gel. Elution with hexane gave recovered Mo(CO)<sub>6</sub> (if any). The molybdenum pentacarbonyl complex III was eluted from the column with hexane/benzene (usually 3/1). In the case of thiocamphor, complex V was eluted off the column ahead of VI.

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### References

- 1 H. Alper and H.N. Paik, *J. Organometal. Chem.*, 155 (1978) 47.
- 2 J.A. Gladysz and R.W. Avakian, *Syn. React. Inorg. Metal. Org. Chem.*, 5 (1975) 247.
- 3 R.G.W. Gingerich and R.J. Angelici, *J. Organometal. Chem.*, 132 (1977) 377.
- 4 B.E. Mann, *J. Chem. Soc., Dalton Trans.*, (1973) 2012.
- 5 H. Alper and N.D. Silavwe, unpublished results.
- 6 M.M. Campbell, G.M. Anthony and C.J.W. Brooks, *Org. Mass Spectrom.*, 5 (1971) 297.
- 7 J.W. Scheeren, P.H.J. Ooms and R.J.F. Nivard, *Synthesis*, (1973) 149.
- 8 J.W. Griedanus, *Can. J. Chem.* 48 (1970) 3530.