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Preliminary communication

SELECTIVE π-COMPLEXATION REACTIONS OF DIENE THIONES WITH DICYCLOPENTADIENYLHEXACARBONYLDIMOLYBDENUM

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Summary

Diene thiones react with dicyclopentadienylhexacarbonyldimolybdenum to give complexes of structural type $L(CO)_4Mo_2(\eta^5\text{-}C_5H_5)_2$ (L = diene thione), in which the less substituted double bond and the thiocarbonyl group are π-bound to the metal.

There has been considerable recent interest in transition metal carbonyl complexes of thioketones, particularly with respect to their interesting structures [1] and their application as intermediates in synthesis [2]. In 1975, Barton and co-workers [3] reported the preparation of cyclohexa-1,4-diene-3-thiones. It was of interest to determine whether metal carbonyls would complex with the thiocarbonyl function or with one, or both, of the double bonds of the unsaturated thione. Tautomerism of the thione to the thioenol, followed by complexation, was also conceivable. This communication describes the first examples of metal carbonyl complexes of diene thiones.

Treatment of thiosantonin (I) with dicyclopentadienylhexacarbonyldimolybdenum in refluxing benzene gave the binuclear tetracarbonyl complex II (m.p. 134°C dec., 54% yield, work-up by chromatography on 80—200 mesh Fisher alumina with $CHCl_3$), identified on the basis of analytical* and spectral data. The infrared spectrum ($CHCl_3$) displayed terminal metal carbonyl stretching bands at 1957m, 1931vs, 1864s, and 1819w cm^{-1}. Similar absorptions were reported for μ-allenedicyclopentadienyltetracarbonyldimolybdenum [4]. The lactone carbonyl stretching band of II occurred at 1780 cm^{-1}, and the thiocarbonyl band (1141 cm^{-1}) of I shifted to lower frequency on complexation. The methyl group attached to the unsaturated carbon of II gave a singlet signal in the nuclear magnetic resonance (NMR, $CDCl_3$) spectrum at δ 1.90 ppm,

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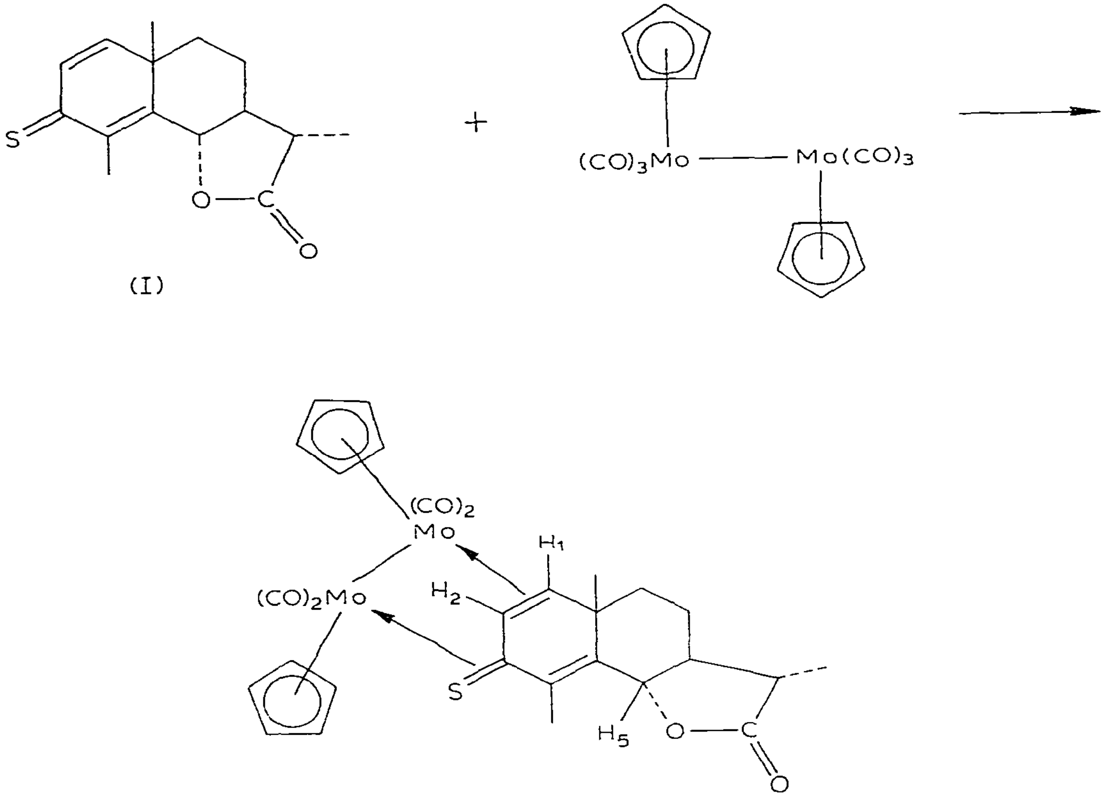
*Satisfactory C, H, S, and Mo analyses, and molecular weights (osmometry) were obtained for the new complexes.

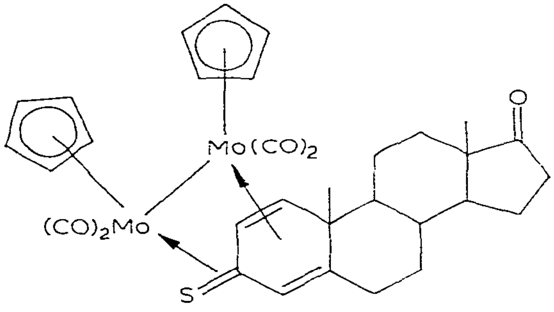


(I)

(II)

similar to that of the free ligand (other methyls at δ 1.19, 1.30 ppm). The unsaturated protons of thiosantonin (H1, δ 6.37 ppm; H2, δ 7.03 ppm (J = 8 Hz)) experienced a significant upfield shift on complexation (II; H1, δ 4.07 ppm; H2, δ 5.15 ppm (J = 8 Hz)) clearly indicating attachment of that double bond to molybdenum. Other noteworthy NMR absorptions include signals at δ 4.87 ppm (H5) and at δ 5.36, 5.39 ppm (η^5-C_5H_5 rings).

Similar reaction of androsta-1,4-diene-17-one-3-thione with $[\eta^5\text{-}C_5H_5Mo(CO)_3]_2$ afforded III (m.p. 161°C dec., 41% yield)*, in which the least-substituted double bond was again complexed to the metal.



(III)

We are currently investigating the applications of complexes II and III in organic synthesis.

Acknowledgments

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