

NITRATO, NITRITO AND NITRO COMPLEXES OF DICYCLOPENTADIENYLMOLYBDENUM(VI) AND DIINDENYL- MOLYBDENUM(VI)

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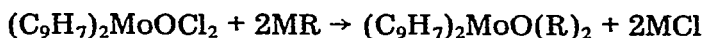
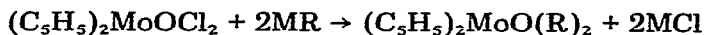
(Received May 20th, 1975)

Summary

Dicyclopentadienyloxodichloromolybdenum(VI) and bisindenylloxodichloromolybdenum(VI) react with sodium nitrite, silver nitrite or silver nitrate in tetrahydrofuran to yield complexes of the type $(C_5H_5)_2MoO(R)_2$ and $(C_9H_7)_2MoO(R)_2$ in which R is nitro (NO_2), nitrito (ONO), nitrato (ONO_2), respectively. The nitro and nitrato are more stable than the nitrito complexes, which change into nitro complexes on storage.

Introduction

Dicyclopentadienyloxodichloromolybdenum(VI) and diindenylloxodichloromolybdenum(VI) [1] have been prepared by treatment of oxotetrachloromolybdenum [2] with sodium salts of cyclopentadiene and indene, respectively, in tetrahydrofuran. Alkyl [3], aryl [3], alkoxy [1,4], borohydride [5], β -diketonic ester [6], pseudohalide [7] and phenoxy [8] derivatives of dicyclopentadienyl- and diindenyl-oxodichloromolybdenum(VI) have been reported. We describe below the preparation of nitro, nitrito, and nitrato derivatives of dicyclopentadienyl- and bisindenyl-oxodichloromolybdenum(VI) by treatment with sodium nitrite, silver nitrite or silver nitrate in tetrahydrofuran.



R = NO_2 , ONO or ONO_2 , M = Na or Ag

These compounds vary from light brown, through red brown to dark brown in colour, are extremely sensitive to moisture, but stable in a dry, inert atmosphere; they decompose above $100^\circ C$ without melting. They are nonvolatile, do not sublime even in vacuum, are soluble in common organic solvents.

TABLE 1

DETAILS OF THE PREPARATION OF $(C_5H_5)_2MoO(R)_2$ AND $(C_9H_7)_2MoO(R)_2$ ($R = NO_2, ONO$ or ONO_2)

Compound	Solvent used (ml)	Reaction time (h)	Colour	Yield (%)	Analysis Found (calcd.)		
					Mo	C	H
$(C_5H_5)_2MoO(NO_2)_2$	THF (100)	8	Brown	58	28.61 (28.75)	35.93 (35.80)	2.84 (2.99)
$(C_5H_5)_2MoO(ONO)_2$	THF (120)	3	Light brown	42	28.58 (28.75)	35.93 (35.76)	2.80 (2.99)
$(C_5H_5)_2MoO(ONO_2)_2$	THF (120)	6	Chocolate	60	26.08 (26.23)	32.61 (32.78)	2.61 (2.73)
$(C_9H_7)_2MoO(NO_2)_2$	THF (110)	5-6	Dirty brown	48	49.61 (49.77)	21.98 (22.12)	3.07 (3.22)
$(C_9H_7)_2MoO(ONO)_2$	THF (100)	3-4	Red-brown	46	49.59 (49.77)	22.0 (22.12)	3.05 (3.22)
$(C_9H_7)_2MoO(ONO_2)_2$	THF (110)	7-8	Brown	56	20.48 (20.60)	46.31 (46.35)	2.81 (2.99)

They are insoluble in water, but are readily hydrolysed when heated with water or on treatment with dilute acids and alkalis. Analytical data and some properties are given in Tables 1 and 2.

Experimental

Special precautions were taken to exclude moisture. Solvents were dried and purified before use by standard methods. Tetrahydrofuran was refluxed over potassium hydroxide and then distilled in the presence of lithium aluminium hydride. Silver nitrite used was obtained as a white precipitate by mixing

TABLE 2

IR SPECTRA OF $(C_5H_5)_2MoO(R)_2$ AND $(C_9H_7)_2MoO(R)_2$ ($R = NO_2, ONO$ or ONO_2)

Compound	Bands (cm^{-1})
$(C_5H_5)_2MoO(NO_2)_2$	3050s, 1610w, 1540w, 1480s, 1440m, 1360m, 1140m, 1060w, 955m, 820m, 785m
$(C_5H_5)_2MoO(ONO)_2$	3040m, 1640w, 1600m, 1480m, 1440m, 1330w, 1145w, 1050m, 1030w, 945m, 850w, 830m, 795w
$(C_5H_5)_2MoO(ONO_2)_2$	3020m, 1630m, 1540w, 1510m, 1480s, 1305w, 1260m, 1180w, 1030m, 960m, 840m, 810w, 785m
$(C_9H_7)_2MoO(NO_2)_2$	3040m, 1630m, 1550w, 1460m, 1430w, 1360m, 1310m, 1140w, 1035m, 955m, 830m, 750w, 710m
$(C_9H_7)_2MoO(ONO)_2$	3020s, 1700m, 1640w, 1610s, 1540w, 1470s, 1410m, 1360m, 1140w, 1065s, 1050w, 945m, 840m, 790w, 720m
$(C_9H_7)_2MoO(ONO_2)_2$	3010s, 1710m, 1640m, 1600w, 1530m, 1440m, 1360m, 1280m, 1210w, 1160w, 1045m, 960m, 840w, 825m, 790m, 720w

saturated solutions of silver nitrate and sodium nitrite. Infrared spectra (in KBr) were recorded on Perkin—Elmer Model-137 spectrophotometer. Molybdenum was determined as the 8-hydroxyquinolate and carbon and hydrogen by micro-analytical methods. The presence of cyclopentadienyl, indenyl, nitro, nitrito and nitrate groups was inferred from the IR spectra.

Preparation of dicyclopentadienyloxodinitromolybdenum(VI)

Sodium nitrite (0.140 g, 0.002 mol) was added to dicyclopentadienyloxodichloromolybdenum(VI) (0.313 g, 0.001 mol) in tetrahydrofuran (100 ml). The mixture was stirred for 2-3 h and then heated under reflux for 5 h at 70°C. The solution was filtered through a G-4 sintered disc and the residue was washed with tetrahydrofuran. The combined filtrate and washings were evaporated under reduced pressure (15-20 mmHg) to yield a brown paste. This was recrystallised from petroleum ether (60-80°C) and dried under reduced pressure to give brown crystals of $(C_5H_5)_2MoO(NO_2)_2$ in 58% yield.

Diindenylloxodinitromolybdenum(VI) was obtained analogously.

Preparation of dicyclopentadienyloxodinitritomolybdenum(VI)

Silver nitrite (0.308 g, 0.002 mol) was added to dicyclopentadienyloxodichloromolybdenum(VI) (0.313 g, 0.001 mol) in tetrahydrofuran (120 ml). The mixture was stirred and heated under reflux at 40°C for 3 h. The resulting solution, light brown in colour, was filtered through a G-4 sintered disc and the residue was washed with tetrahydrofuran. The combined filtrate and washings were evaporated under reduced pressure to leave a brown paste, which was repeatedly crystallised from petroleum ether (40-60°C) to give light brown crystals of $(C_5H_5)_2MoO(ONO)_2$, in 52% yield.

Diindenylloxodinitritomolybdenum(VI) was prepared analogously.

Preparation of dicyclopentadienyloxodinitratomolybdenum(VI)

To silver nitrate (0.340 g, 0.002 mol) was added dicyclopentadienyloxodichloromolybdenum(VI) (0.313 g, 0.002 mol) in tetrahydrofuran (120 ml). The mixture was stirred and warmed at 60°C for 3-4 h and then refluxed for 2 h until it became dark brown. The solution was filtered through a G-4 sintered disc and washed with tetrahydrofuran. The filtrates and washings were evaporated under reduced pressure to leave a dark brown paste, which was repeatedly crystallised from petroleum ether (60-80°C) to give chocolate brown crystals of $(C_5H_5)_2MoO(ONO_2)_2$ in 60% yield.

Diindenylloxodinitratomolybdenum(VI) was prepared analogously.

Results and discussion

The above preparations of the nitrate, nitrito and nitro derivatives are analogous to those of alkyl and aryl [3], alkoxy [4], bisborohydride [5], pseudohalide [7], and phenoxy [8] derivatives of dicyclopentadienyl- and bisindenyl-oxodichloromolybdenum(VI).

The presence of the cyclopentadienyl group is indicated by the usual bonds [9], viz.: the C—H stretching frequencies around 3010 cm^{-1} , a C—C stretching band at $\sim 1440\text{ cm}^{-1}$, the C—H in-plane bending $\sim 1040\text{ cm}^{-1}$ and the C—H out-

of-plane bending around 840 cm^{-1} . The indenyl group shows the same bands for C_5H_5^- groups, and in addition the bands of the phenyl group, viz.: the C—H stretch at 1375 cm^{-1} , the C—C stretch at $\sim 1565\text{ cm}^{-1}$, the C—H out-of-plane bending at 765 cm^{-1} , and also the methylene rocking vibration at $\sim 720\text{ cm}^{-1}$. Indene [10] itself shows an absorption band at $\sim 700\text{ cm}^{-1}$.

The presence of the nitro group (NO_2) is indicated by asymmetric and symmetric NO stretching vibrations at $\sim 1440\text{ cm}^{-1}$ and $1300\text{--}1350\text{ cm}^{-1}$, and that of the nitrito group (ONO) by NO stretching bands at $\sim 1470\text{ cm}^{-1}$ and 1060 cm^{-1} [11,12]. The nitrito derivatives are less stable, and change into nitro derivatives on storage as indicated by the IR spectrum of an aged sample of a nitrito complex. The presence of the nitrate group is indicated by asymmetric and symmetric stretching vibrations in the region $1530\text{--}1480$ and $1280\text{--}1240\text{ cm}^{-1}$. The spectra also show an intense band in the region $930\text{--}960\text{ cm}^{-1}$ due to $\text{M}=\text{O}$ linkage [13].

The IR spectra suggest that the cyclopentadienyl or indenyl ring are attached to the metal atom by delocalised π -bonds, and the ONO, NO_2 , ONO_2 groups by σ -bonds. This is consistent with the behaviour of other π -cyclopentadienyl-transition metal complexes [14,15].

Acknowledgement

One of the authors (M.S.B.) is grateful to the Council of Scientific and Industrial Research, India for a fellowship.

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