The Silver and Molybdenum Metal Complexes of *cis,cis,cis*-1,4,7-Cyclononatriene

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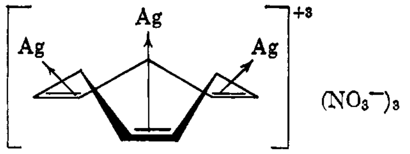
The preparations and properties of the silver nitrate–*cis,cis,cis*-1,4,7-cyclononatriene adduct and *cis,cis,cis*-1,4,7-cyclononatriene molybdenum tricarbonyl are described. The data for making the structural assignments of the two metal complexes are presented. In these assigned structures, the silver nitrate adduct of the title hydrocarbon has the silver ions associated with the outer (divergent) π-orbital lobes; the molybdenum tricarbonyl complex has the molybdenum bonded to the inner (convergent) π-orbital lobes of the title hydrocarbon.

Recently we reported the synthesis of *cis,cis,cis*-1,4,7-cyclononatriene (I).[1] Our isolation and purification procedure employed the formation of its silver nitrate complex (II). The silver nitrate complex of I forms with extreme ease. Either pure I or a solution of I (carbon tetrachloride, cyclohexane, isooctane) gives a quantitative yield of the salt when shaken with excess aqueous silver nitrate. The ligand does not rearrange during the complex formation since I is quantitatively regenerated from II with ammonium hydroxide. The complex II is an air-stable, white crystalline solid (m.p. 248° dec.) and is only slowly changed (days) when exposed to light. It exhibits a high degree of crystal stability, since it decomposes at a temperature significantly higher than silver nitrate itself (m.p. 212°). It is also noteworthy that ligand I can be recovered after thermal decomposition of II.

The elemental analyses and molecular weight determination of the complex show it has the formula $C_9H_{12}(AgNO_3)_3$. The infrared spectrum of II exhibits major absorptions at 7.14, 7.20 sh, 7.69, 7.74 sh, and 7.97 μ. The proton n.m.r. spectrum shows clearly that the ligand I is present in the salt. The typical nine-lined pattern of the olefinic hydrogens of I[1] is seen at τ 4.08 (area = 2) and two separate multiplets for the methylene hydrogens at *ca.* τ 6.3 and 7.5 (area = 1), respectively. The conformation of ligand I has already been indicated to be the crown[2] and preliminary results of an X-ray structural determination of II show that the required C_{3v} symmetry is present. In addition, the conformation of I has been proven to be the crown by proton–proton spin decoupling experiments (this laboratory).[3]

From the above data, we assign the following structure to the complex II.



II

In this structure, the silver ions are bicoordinate and associated with the outer, or divergent, π-bond lobes. The symmetrical structure which has the silver ions bonded to the inner, or convergent, π-orbital lobes, we believe, is ruled out, since it would be sterically impossible to accommodate three silver ions in the space necessary for bonding along these directed π-lobes. Also, the silver ions would be as far apart as possible, due to the repulsion of their residual like charge. Our assigned structure (II) satisfies this requirement as well. This complex is the most stable cyclic triene–silver nitrate adduct thus far reported,[4] based on its ease of formation, high decomposition temperature, stability to oxygen and light, and its low dissociation constant (a sample of II, when subjected to a pressure of 0.1 mm. for 14 hr., showed no weight loss).

Because of the unique geometry of I, which results in half of the π-orbital lobes converging on one side of the plane of the double bonds, it was thought that metal complexes would easily form utilizing these converging lobes. Attempts to form such metal complexes were made with both molybdenum and chromium hexacarbonyls. It was thought that little change in the metal–ligand bonding angles would be necessary in order to form such complexes since both the molybdenum and chromium hexacarbonyls are bipyramidal with CO–M–CO angles of 90°. Aside from many other possible products, two likely pairs are *cis,cis,cis*-1,4,7-cyclononatrienemolybdenum or chromium tricarbonyl and di-*cis,cis,cis*-1,4,7-cyclononatrienemolybdenum or -chromium.

Despite this expected favorable situation, our attemps to complex I with chromium hexacarbonyl were unsuccessful. However, I readily forms a single product with molybdenum hexacarbonyl in refluxing isooctane or cyclohexane. The crude product precipitates out of solution in approximately 40% yield. Nearly all of the unchanged I can be recovered as II by treating the filtrate with aqueous silver nitrate. The molybdenum complex (III) is a lemon yellow, air-stable, crystalline solid which can be recrystallized from methylene chloride–cyclohexane or sublimed with accompanying decomposition at 140° (0.01 mm.). The compound does not exhibit a discrete melting point, but rather decomposes at various temperatures dependent upon the conditions employed, *e.g.*, slow decomposition beginning at 155° in a capillary open to the atmosphere, 185° in a sealed evacuated capillary. The complex is unstable in polar solvents (acetonitrile). Even acetone displaces the ligand from the molybdenum complex.

The elemental analysis of III gives it an empirical formula of $C_{12}H_{12}O_3Mo$. Its molecular weight was determined to be 310 (theory, 300). The infrared spectrum (KBr) exhibits strong absorptions at 5.14 and 5.44 μ and weak absorptions at *ca.* 3.4, 6.38, 6.66, 6.96, 7.74, 8.05, 8.11, and 13.02 μ. The ultraviolet spectrum shows

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(1) K. G. Untch, *J. Am. Chem. Soc.*, **85**, 345 (1963).

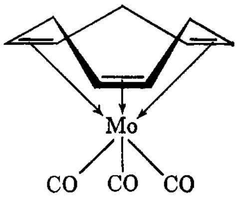
(2) K. G. Untch and R. J. Kurland, *ibid.*, **85**, 346 (1963).

(3) K. G. Untch and R. J. Kurland, unpublished results.

(4) (a) For cyclooctatrienes see, A. C. Cope and F. A. Hochstein, *J. Am. Chem. Soc.*, **72**, 2515 (1950); W. O. Jones, *J. Chem. Soc.*, 1808 (1954); (b) for cyclododecatrienes, see L. I. Zakharkin and V. V. Korneva, *Dokl. Akad. Nauk SSSR*, **132**, 1078 (1960).

absorptions at λ_{max} 257 mμ (ϵ 18,000) and 352 (14,000) in cyclohexane at 5.3×10^{-5} mole/l.

The new molybdenum carbonyl complex is assigned structure III based on the above data. The structure of III was proved when its proton n.m.r. spectrum was obtained. Despite the compound's low solubility in chloroform, enough did dissolve to provide a satisfactory spectrum using a Varian 100-Mc. spectrometer. The proton n.m.r. absorption patterns of III were somewhat unexpected. It was thought that the molybdenum tricarbonyl complex would display an n.m.r. spectrum quite similar to that of the "frozen" hydrocarbon (except for chemical shift differences).[2] The same nine-lined pattern of the parent triene is observed for the olefinic hydrogens of the metal complex (τ 6.09), thus showing the ligand to be intact and unrearranged. However, the methylene hydrogens absorb at nearly the same magnetic field (multiplet centered at *ca.* τ 6.95), unlike the two absorptions of the inner and outer methylene hydrogens of the "frozen" parent triene, which are separated by nearly 100 c.p.s. (60 Mc.).[2] In order to verify that the conformation of the ligand is a fixed crown, the olefinic protons were irradiated and the methylene hydrogen multiplet was observed. A typical AB quartet is observed for them which demonstrates the magnetic equivalence of the three inner and that of the three outer methylene hydrogens.



III

It is interesting that the proton n.m.r. absorptions of the inner and outer methylene hydrogens of III appear as one multiplet. Either the two types of methylene hydrogens are chemically shifted to approximately the same value accidentally, or the hydrocarbon portion of the metal complex is more nearly planar than the parent I. X-Ray structural determinations of I and III would decide between these alternatives and both are currently being undertaken.

Experimental

Infrared spectra were obtained from Nujol and halocarbon mulls and recorded with Beckman spectrophotometers, Models IR-4 and IR-9. Ultraviolet spectra were obtained on a Cary spectrophotometer, Model 15. Proton n.m.r. spectra were obtained on either a Varian Associates Model A-60 or HR-100 n.m.r. spectrometer.[5] Chemical shifts are given in p.p.m. downfield from tetramethylsilane. Melting and decomposition points were determined in capillary tubes and are uncorrected.

***cis,cis,cis*-1,4,7-Cyclononatriene–Silver Nitrate Complex (II).**—A solution of 24 mg. (0.2 mmole) of *cis,cis,cis*-1,4,7-cyclononatriene and 3.0 ml. of carbon tetrachloride was shaken with a solution of 159 mg. (0.9 mmole) of silver nitrate and 1.0 ml. of water. The resulting white precipitate was collected by suction filtration. Recrystallization of the crude salt from acetonitrile and diethyl ether at room temperature gave 126 mg. (quantitative yield) of II as white needles, m.p. 248° dec.

Anal. Calcd. for $C_9H_{12}O_9N_3Ag_3$: C, 17.16; H, 1.92; Ag, 51.38; mol. wt., 629.8. Found: C, 17.46; H, 2.06; Ag, 51.40; mol. wt., $146 \times 4 = 584$ (H_2O) and $162 \times 4 = 648$ (CH_3CN) (Mechrolab Model 301A osmometer).

A saturated deuterium oxide solution of II containing sodium 2,2-dimethyl-2-silapentane-5,5-sulfonate as an internal reference was used to obtain its proton n.m.r. spectrum.

A solution of 126 mg. (0.2 mmole) of II and 5.0 ml. of water was treated with 3.0 ml. of *ca.* 8 *N* ammonium hydroxide solution. The resulting suspended precipitate was extracted into carbon tetrachloride, which was washed with water until neutral. The carbon tetrachloride layer was treated with 159 mg. (0.9 mmole) of silver nitrate dissolved in 1.0 ml. of water. The resulting precipitate was collected and recrystallized as above to yield 125 mg. of white needles, m.p. 248° dec.

***cis,cis,cis*-1,4,7-Cyclononatrienemolybdenum Tricarbonyl.**—A solution of 76.2 mg. (0.635 mmole) of I (obtained from 400 mg. of purified II treated with ammonium hydroxide solution) and 15.0 ml. of isooctane was placed in a 50-ml. three-necked flask equipped with a magnetic stirrer, condenser, and gas inlet. After purging the system with nitrogen[6] 370 mg. (0.70 mmole) of molybdenum hexacarbonyl was added. The flask was immersed into a preheated (110°) oil bath and refluxed under a nitrogen atmosphere for 20 hr. During the course of this period a yellow solid precipitated from solution. The reaction mixture was cooled and the crude solid (90 mg., 47% yield) was collected by suction filtration. Recrystallization from methylene chloride–cyclohexane gave 63 mg. of yellow platelets. Melting point determinations were carried out on a sample that had been sublimed at 140° (0.01 mm.). Slow decompositions beginning at 155° in an open capillary tube and 185° in a sealed evacuated capillary tube were observed.

Anal. Calcd. for $C_{12}H_{12}O_3Mo$: C, 48.03; H, 4.00; O, 16.00; mol. wt., 300.1. Found: C, 48.22; H, 4.37; O, 16.14; mol. wt., 310 (benzene) (Mechrolab Model 301A osmometer).

The proton n.m.r. spectra were obtained from a saturated chloroform-*d* solution of III containing tetramethylsilane as the internal reference.

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(5) We thank Mr. L. F. Johnson of Varian Associates for the undecoupled and decoupled spectra obtained on the 100-Mc. spectrometer.

(6) Complete elimination of oxygen is necessary for the reaction to proceed. We have had several experiments fail to give any product due to traces of oxygen.