

The Crystal and Molecular Structure of the Silver Nitrate Complex of *cis,cis,cis*-1,4,7-Cyclononatriene, $C_9H_{12}(AgNO_3)_3$

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Abstract: The structure of the silver nitrate π complex of *cis,cis,cis*-1,4,7-cyclononatriene, $C_9H_{12}(AgNO_3)_3$, has been determined by a three-dimensional single-crystal X-ray diffraction investigation. The complex crystallizes in space group $R\bar{3}c$; cell dimensions for the triply primitive hexagonal cell are $a = 16.258$ and $c = 9.556$ Å at approximately -125° . The cyclononatriene ring is in the crown configuration and shows little or no distortion due to the complex formation. Each silver is associated with only one ethylenic bond at divergent ends of the π -bonded p orbitals. The silver ions are distorted 17° in the direction of the *cis* hydrogens.

The structure of *cis,cis,cis*-1,4,7-cyclononatriene, C_9H_{12} ,²⁻⁴ is known to have a crown configuration.^{5,6} Silver complexes of olefins are well known⁷ and several⁸⁻¹³ have been investigated by X-ray diffraction techniques. The present study was undertaken to further elucidate the geometry of the nine-membered ring system and to compare the bonding in the olefin with that of its silver complex.

Experimental Section

Data Collection. White needles of $C_9H_{12}(AgNO_3)_3$ were prepared¹⁴ and supplied to us by Dr. Karl Untch. Irregular single crystals approximately $0.2 \times 0.2 \times 0.3$ mm were cleaved and mounted, the first of these with the needle axis along the goniometer head axis. Preliminary Weissenberg and precession photographs indicated a rhombohedrally centered hexagonal unit cell, the hexagonal c axis corresponding to the needle axis. The conditions for nonextinction, $-h + k + l = 3n$ for hkl and $l = 2n$ for $hk0l$, required the space group to be $R\bar{3}c$ or $R\bar{3}c$. Cell dimensions obtained from film measurements and an approximate density (by flotation) of 2.9 g/cm³ indicated six molecules in the hexagonal unit cell. It was assumed, and later verified, that the molecule had the same symmetry, $3m-C_{3v}$, as its parent compound. This symmetry condition restricted the space group to $R\bar{3}c$, since $R\bar{3}c$ would have required the molecule to have $\bar{3}-C_{3i}$ or $32-D_3$ symmetry.

Two sets of three-dimensional, low-temperature intensity data were collected: initially (a) integrated Weissenberg multiple film data, using $Cu K\alpha$ radiation, of levels $hki0-hki3$ and $0kil-8kil$, and for later refinement (b) counter-diffractometer data, collected manually with $Mo K\alpha$ radiation on a General Electric spectrogoniometer equipped with a single-crystal orienter and scintillation counter. Threefold redundant data were measured for 483 unique film intensities and 364 unique counter intensities. The integrated films were measured with a Nonius Model I densitometer. Both sets of data were collected at low temperature using a conventional nitrogen vapor cold stream in order to reduce thermal motion and to inhibit a gradual surface decomposition of the crystals. Improved hexagonal cell dimensions, obtained by least-squares fit

with diffractometer 2θ data, were $a = 16.258 \pm 0.005$ and $c = 9.556 \pm 0.003$ Å at approximately -125° .

Computations. All calculations were performed on a CDC 3600 computer. The raw data were correlated and corrected for Lorentz and polarization effects using a program written at this laboratory. Standard errors for the film intensities were based on observed deviations during film correlation with a minimum error of $0.05I_{obsd}$ to avoid accidental agreement. Standard errors for the counter data were based on counting statistics as described by Johnson.¹⁵ Cell dimensions and errors were determined using the least-squares program by Heaton, Gvildys, and Mueller.¹⁶ Patterson and electron-density maps were computed using the Gvildys Fourier summation program.¹⁷ The Busing and Levy full-matrix least-squares program¹⁸ was used for the structure refinement, and their function and error program¹⁹ was used for calculation of bond distances, angles, anisotropic parameters, and their respective standard deviations.

Structure Determination. The structure was solved by the heavy-atom method. The x and y silver atom coordinates were determined from a two-dimensional Patterson map calculated from 40 $hki0$ film intensities. Since there was only one silver atom in the asymmetric unit and the position of the origin along the c axis was arbitrary, we proceeded directly to a three-dimensional least-squares refinement. Two cycles, varying the silver coordinates and the absolute scale factor, decreased the residual, $R = \Sigma ||F_o| - |F_c|| / \Sigma |F_o|$, from 0.41 to 0.22. A three-dimensional Fourier map revealed the approximate positions of the carbon ring atoms. After two least-squares cycles refining silver and carbon coordinates, another difference map was computed and the nitrate group atoms were located. Further refinement of all coordinates (except hydrogen), scale factor, and isotropic temperature factors failed to lower R below 0.185. The relatively high value of R at this stage of refinement led us to make a correction for systematic errors in the form of artificial temperature factors. The film data were collected over an extended period of time involving more than one crystal and several interruptions in the operation of the cold stream. It was therefore suspected that the various film packs may have been exposed at somewhat different temperatures and that this would constitute the major systematic error. The original intensities were corrected according to the relation $I_{scaled} = k_i I_{obsd} \exp(-B_i \sin^2 \theta / \lambda^2)$, where I_{obsd} 's are the observed intensities for a given film pack, k_i is the correlation scale factor for that pack, and B_i is the individual film pack temperature factor which was fitted by least squares. Two cycles of isotropic refinement with the corrected intensities, followed by two cycles with anisotropic tempera-

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Table I. Observed and Calculated Structure Factors^a

hk0										hk7									
3	0	2949	2901	859	2771					6	5	1317	1357	1332	258				
6	0	5444	5761	-2983	4928					9	5	1465	1513	268	148				
9	0	3080	3008	-1191	-2762					12	5	1216	1248	-850	610				
12	0	2083	2107	-1325	-1638					15	5	2022	2120	-595	2035				
15	0	1469	1464	1394	448					18	4	1624	1550	-872	1282				
1	1	2425	2469	-2469	0					21	6	2602	2679	-1968	-1817				
4	1	2247	2193	1061	-1919					24	6	704	676	252	-627				
7	1	771	864	633	588					27	7	2151	2204	-507	-2145				
10	1	1635	1663	36	1662					30	7	3558	148	147	14				
13	1	1938	1969	-800	-1350					33	8	1087	1168	1035	61				
16	1	430	407	-84	-398					36	8	937	1088	707	569				
2	2	657	595	-545	0					39	8	707	1002	-114	996				
5	2	3053	2953	-220	-2945					42	8	871	876	-672	-563				
8	2	1367	1330	955	-926					45	8	417	169	166	31				
11	2	1511	1534	1506	293					48	9	737	677	650	-188				
14	2	657	753	-88	748					51	9	1580	1646	1610	-341				
17	2	2815	2703	-2703	0					54	9	1144	1123	-389	1054				
2	3	2924	2917	2859	580					57	10	1288	1338	-1069	99				
5	3	800	656	-461	-468					60	10	799	995	633	646				
8	3	1848	1811	14	1611					63	10	841	817	341	-743				
11	3	406	534	427	-320					66	11	2162	2236	-1262	-1846				
14	3	4242	343	-343	0					69	11	1487	1468	-1237	-790				
17	3	2530	2586	-1644	1980					72	11	1373	1438	-519	-1341				
2	4	521	557	-327	-451					75	12	874	904	894	-136				
5	4	1251	1276	-464	-1189					78	12	4412	461	450	-136				
8	4	1681	1607	-1607	0					81	13	1107	1168	-133	131				
11	4	683	707	-455	-541					84	13	1324	1340	1322	-320				
14	4	499	457	785	-533					87	15	991	909	-878	-235				
17	4	2111	2071	2071	0														
2	5	2393	2429	-1548	1872														
5	5	593	458	142	435														
8	5	1928	1991	1991	0														
11	5	1716	1708	1700	167														
14	5	1447	1391	-1391	0														
17	5	1038	1047	-117	-1040														
2	6	412	236	-236	0														

observed structure factors are listed in Table I which, in addition, includes 70 unobserved intensities estimated (at the raw-data level) as half the minimum observed intensity. The unobserved data were not used in the least-squares refinements.

Results

Atom coordinates, isotropic temperature factors, and their standard deviations are given in Table II. Interatomic distances and angles and their errors are given in Table III.

Table II. Atomic Coordinates and Isotropic Temperature Factors

Atom	x/a_1	y/a_2	z/c	$B, \text{\AA}^2$
Ag	0.8717 (1) ^a	0.2823 (1)	0.2441 ^b	...
C ₁	0.7969 (10)	0.3549 (11)	0.3657 (14)	1.08 (28)
C ₂	0.7306 (11)	0.2589 (11)	0.3624 (12)	1.34 (27)
C ₃	0.6398 (12)	0.2111 (12)	0.2741 (14)	0.87 (29)
O ₁	0.2868 (7)	0.3018 (8)	0.1806 (10)	2.03 (22)
O ₂	0.2928 (7)	0.1792 (7)	0.2521 (12)	1.46 (23)
O ₃	0.3825 (8)	0.2645 (8)	0.0805 (11)	2.56 (24)
N	0.3217 (8)	0.2483 (8)	0.1690 (11)	1.24 (22)

^a Standard deviations are $\times 10^4$ for coordinates and $\times 10^3$ for B 's. ^b The position of the origin along the c axis is arbitrary and was chosen for convenience in computing a suitable unit in the electron-density maps. ^c See Table IV for the anisotropic thermal parameters for silver.

Table III. Distances and Angles for $\text{C}_9\text{H}_{12}(\text{AgNO}_3)_3$

Bonded Distances (Å) and Angles			
C ₂ -C ₃	1.532 ± 0.020	C ₂ -C ₃ -C ₄	107.6 ± 1.1°
C ₃ -C ₄	1.542 ± 0.019	C ₁ -C ₂ -C ₃	126.4 ± 1.2°
C ₁ -C ₂	1.384 ± 0.020	C ₃ -C ₄ -C ₅	122.9 ± 1.4°
Ag ₁ -C ₁	2.379 ± 0.015	Ag ₁ -C ₁ -C ₂	74.5 ± 0.9°
Ag ₁ -C ₂	2.411 ± 0.014	Ag ₁ -C ₂ -C ₁	71.9 ± 0.9°
N-O ₁	1.259 ± 0.015	O ₁ -N-O ₂	117.7 ± 1.1°
N-O ₂	1.259 ± 0.014	O ₂ -N-O ₃	121.9 ± 1.3°
N-O ₃	1.225 ± 0.013	O ₁ -N-O ₃	120.4 ± 1.2°
Midpoint of C ₁ -C ₂ to Ag ₁ 2.300 ± 0.014			
Nonbonded Distances (Å)			
C ₂ -C ₄	2.480 ± 0.020	O ₁ -O ₂	2.155 ± 0.016
C ₃ -C ₅	3.133 ± 0.027	O ₁ -O ₃	2.156 ± 0.015
Ag ₁ -C ₃	3.357 ± 0.016	O ₂ -O ₃	2.172 ± 0.016
Ag ₁ -C ₅	3.281 ± 0.017		
Distances (Å) and Angles in Silver Environment			
Ag ₂ -O ₂	2.438 ± 0.012	Ag ₂ -O ₉	3.190 ± 0.011
Ag ₂ -O ₃	2.927 ± 0.011	Ag ₂ -O ₁₂	3.240 ± 0.011
Ag ₂ -O ₄	2.484 ± 0.010	O ₂ -Ag ₂ -O ₄	97.7 ± 0.4°
Ag ₂ -O ₅	2.771 ± 0.012	O ₂ -Ag ₂ -O ₇	111.5 ± 0.3°
Ag ₂ -O ₇	2.474 ± 0.010	O ₄ -Ag ₂ -O ₇	86.3 ± 0.2°
(Midpoint of C ₄ -C ₅)-Ag ₂ -O ₇ 109.9 ± 0.2°			
(Midpoint of C ₄ -C ₅)-Ag ₂ -O ₂ 108.8 ± 0.2°			
(Midpoint of C ₄ -C ₅)-Ag ₂ -O ₄ 140.1 ± 0.2°			
Distances (Å) in Nitrate Environment			
Ag ₂ -O ₂	2.430 ± 0.012	Ag ₄ -O ₁	2.474 ± 0.010
Ag ₂ -O ₃	2.927 ± 0.011	Ag ₄ -O ₃	3.190 ± 0.011
Ag ₂ -O ₃	3.240 ± 0.011	Ag ₅ -O ₁	2.484 ± 0.009
Ag ₂ -O ₁	4.711 ± 0.010	Ag ₅ -O ₂	2.771 ± 0.012
Dihedral Angles between Planes Each Defined by Three Atoms			
C ₂ -C ₃ -C ₄ and C ₁ -C ₂ -C ₃	73.0 ± 1.7°		
Ag ₁ -C ₁ -C ₂ and C ₁ -C ₂ -C ₃	107.8 ± 1.5°		
Ag ₁ -C ₁ -C ₂ and C ₁ -C ₂ -C ₃	106.4 ± 1.5°		
C ₁ -C ₂ -C ₃ and a, b plane	49.3 ± 0.4°		
O ₁ -O ₂ -O ₃ and a, b plane	42.4 ± 0.8°		
Ag ₂ -Ag ₄ -Ag ₅ and O ₁ -O ₂ -O ₃	8.3 ± 1.0°		

As proposed,¹⁴ the cyclononatriene ring retains the crown configuration on complex formation with silver nitrate. The rings are stacked along the threefold axes

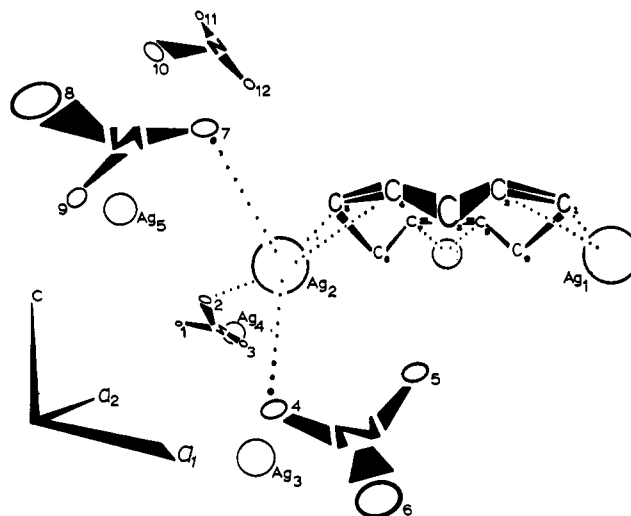


Figure 1. The environment of a silver ion (Ag_2) showing all neighboring oxygen atoms. Ag_1 and Ag_2 are related by a threefold axis; Ag_3 , Ag_4 , and Ag_5 are related by a 3_1 screw axis. A 3_2 screw axis relates the NO_3 groups 4-5-6, 7-8-9, and 10-11-12. Oxygens O_2 , O_3 , O_4 , O_5 , O_7 , O_9 , and O_{12} are within 4.0 Å of the silver ion. Ag_2 - O_2 , Ag_2 - O_4 , Ag_2 - O_7 , and Ag_2 -(midpoint of C_4 - C_5) are the shortest distances and are in a roughly tetrahedral configuration (dotted lines).

of the crystal at intervals of $c/2$, each ring being rotated 35.7° from its nearest neighbors above and below. Each silver ion interacts with only one double bond, all other double bonds directionally feasible being greater than 5 Å distant. The closest approach of any two silver ions is 4.5 Å. Several nitrate groups surround the silver ions (Figure 1); five oxygen atoms approach within 3 Å, and three of these are close enough to 2.46, the sum of the atomic radii, to suggest some degree of covalency.⁸ These three oxygens together with the midpoint of the interacting double bond form a roughly tetrahedral arrangement around silver.

The average N-O bond length of 1.25 Å compares well with values determined in other silver nitrate complexes^{8,10} and in AgNO_3 itself.²⁰ It is slightly greater than the value of 1.218 ± 0.004 Å reported²¹ for NaNO_3 . The average O-N-O bond angle is 120° , and the group is planar within experimental error.

The local environment of the nitrate group consists of three silver ions (Ag_2 , Ag_4 , and Ag_5) within 3.25 Å of the nitrogen atom which describe a plane somewhat above and parallel to the NO_3 plane. Ag_3 lies below and at a distance of 4.25 Å from the nitrogen atom. As is indicated by the Ag-O bond lengths in Table III, the silver-oxygen coordination is not simple. It appears as if each silver ion above the NO_3 group interacts with two oxygens and that Ag_3 is coordinated only to O_3 .

Silver anisotropic temperature parameters, U_{ij} 's, are given in Table IV. Also tabulated are the direction cosines (ϕ , ψ , and ω corresponding to the cell edges a_1 , a_2 , and c , respectively) and root-mean-square displacements of the principal axes of the ellipsoid of vibration. The errors in the directions of the principal axes are large. The only general conclusion drawn is that the most extensive thermal vibration is approximately along the c axis but is tilted slightly so that principal axis P

(20) P. F. Lindley and P. Woodward, *J. Chem. Soc., Sect., A*, 123 (1966).

(21) R. L. Sass, R. Vidale, and J. Donohue, *Acta Cryst.*, 10, 567 (1957).

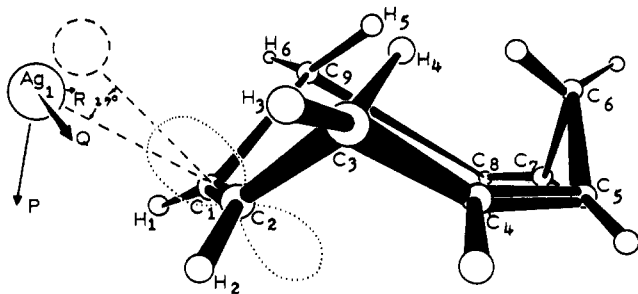


Figure 2. The cyclononatriene ring with assumed hydrogen positions. The silver ion is shown interacting with carbons C_1 and C_2 and distorted 17° from the normal position (dotted lines) along the perpendicular bisector of the ethylene group. P , Q , and R are the principal axes of thermal motion for the silver ion. One π -bonded p orbital is shown in its normal position. The lower lobe is convergent with five other lobes below the ring.

(Figure 2) lies almost parallel to the plane $C_9-C_1-C_2-C_3$. Therefore the silver motion is perpendicular to the direction of the p orbitals and allows the silver to remain approximately equidistant from the double bond throughout the vibration.

Table IV. Anisotropic Thermal Motion Parameters^a

U_{11}	Values of U_{ij} for Silver					U_{13}
	U_{22}	U_{33}	U_{12}	U_{23}	U_{13}	
0.01898 (0.00075)	0.01829 (0.00073)	0.03493 (0.00046)	0.00968 (0.00072)	0.00066 (0.00051)	0.00299 (0.00051)	
Direction Cosines and Root-Mean-Square Values of Principal Axes						
Axis	ϕ	ψ	ω	$\sqrt{\mu^2}$ (Å)		
P	-0.84	0.87	0.17	0.1283 (31)		
Q	-0.50	-0.49	0.17	0.1365 (29)		
R	0.24	-0.07	0.97	0.1904 (14)		

^a Anisotropic temperature factors were calculated and refined in the form $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)]$ and were converted [D. W. J. Cruickshank, *Acta Cryst.*, **19**, 153 (1965)] to U_{ij} 's according to $U_{11} = \beta_{11}/a^2 \cdot 2\pi^2$, etc.

Discussion

The carbon ring geometry is almost identical with that of the uncomplexed *cis,cis,cis*-1,4,7-cyclononatriene.⁶ The only possibly significant change is a stretching of the C_1-C_2 bond from 1.34 to 1.38 Å which would indicate a weakening due to the silver interaction as is also indicated by infrared studies of other silver π complexes.²² The increase in the normal trigonal angles to an average of 124° has the effect of separating the intraannular hydrogen atoms as discussed previously.⁶ It would appear, therefore, that the structure of the cyclic olefin is changed little, if at all, with silver complex formation.

At the request of a referee, an attempt was made to observe the effect of the hydrogen atoms on the ring geometry. The hydrogen positions (Table V) were not apparent in the difference Fourier maps and were therefore estimated using standard criteria. Two cycles of least-squares refinement resulted in a shortening of the C_1-C_2 , C_2-C_3 , and C_3-C_4 bond lengths to 1.372, 1.514, and 1.536 Å, respectively. The angle $C_2-C_3-C_4$ is

(22) H. Hosoya and S. Nagakura, *Bull. Chem. Soc. Japan*, **37**, 249 (1964).

increased to 109.4° , $C_1-C_2-C_3$ to 126.9° , and $C_3-C_4-C_5$ to 123.8° . These values generally show poorer agreement with normal bond lengths and angles than those previously obtained (Table III). Also, with the exception of the angle $C_2-C_3-C_4$, all shifts were within one standard deviation. Therefore the shifts were considered meaningless and Tables II-IV, which are based on the final refinement without the hydrogen atoms, were retained.

Table V. Estimated Hydrogen Coordinates

Atom	x/a_1	y/a_2	z/c
H ₁	0.859	0.383	0.434
H ₂	0.741	0.210	0.427
H ₃	0.625	0.141	0.242
H ₄	0.648	0.254	0.182

The Ag-C distances of 2.379 and 2.411 Å are within error of those obtained for the humulene-silver nitrate adduct,^{10,11} $C_{15}H_{24}(AgNO_3)_2$, and the silver nitrate adduct of norbornadiene,¹³ $C_7H_8(AgNO_3)_2$. Corresponding values for the silver nitrate adduct of cyclooctatetraene,⁸ $C_8H_8AgNO_3$, and its dimer,⁹ $C_{16}H_{16}AgNO_3$, are approximately 0.1 Å longer due to the interaction of two or more ethylenic bonds with each silver ion.

The slight difference in the two Ag-C distances has been observed in all the silver π complexes thus far studied in detail. Turner and Amma²³ have explained the discrepancy for silver aromatic complexes in terms of molecular orbital theory. The 5s orbital of silver is expected to accept electrons from the bonding π orbital (e_1) and the filled d orbitals to donate electrons to the antibonding π orbital (e_2). The silver ion seeks a position allowing maximum overlap, which is directly above one of the carbon p lobes for the 5s, but is above and symmetrically between two carbon atoms for the d orbital. It is postulated that the equilibrium is a compromise somewhat off center, hence the difference in bond lengths. The same argument can be applied to Ag-olefin complexes although the observed discrepancy is considerably less than in Ag-aromatic complexes.

Several considerations enter a rationale for the fact that in $C_9H_{12}(AgNO_3)_3$ the plane $Ag_1-C_1-C_2$ is not perpendicular to the $C_1-C_2-C_3-C_9$ plane but rather forms an angle of 107° with it (Figure 2). This distortion of 17° from the normal silver position which would assure maximum overlap with the π orbital can be explained by (a) steric repulsions between the silver ion and the intraannular hydrogens or carbon atoms C_3 and C_9 ; (b) a twisting of the π -bonded p orbitals themselves so that silver is, in fact, in the optimum position for overlap; or (c) homoconjugation.

That steric effects play an important role in forcing the silver ion away from the ring is unlikely since in the normal position silver is encircled by a nearly symmetrical ring of hydrogen atoms (Table VI). Carbon atoms C_9 and C_3 would be too far away (3.3 Å) and in unfavorable directions to exert much steric influence. Also there is no evidence of twisting of the

(23) R. W. Turner and E. L. Amma, *J. Am. Chem. Soc.*, **88**, 1877 (1966).

Table VI. Estimated Hydrogen to Silver Distances (Å)

Ag ₁ -H ₁	2.53	Ag _n -H ₁ ^a	2.78
Ag ₁ -H ₂	2.54	Ag _n -H ₂	2.78
Ag ₁ -H ₃	3.49	Ag _n -H ₃	3.26
Ag ₁ -H ₄	3.49	Ag _n -H ₄	3.04
Ag ₁ -H ₅	3.40	Ag _n -H ₅	2.94
Ag ₁ -H ₆	3.40	Ag _n -H ₆	3.15

^a Ag_n refers to silver in the normal position estimated at $x/a_1 = 0.850$, $y/a_2 = 0.289$, $z/c = 0.187$.

C₈ and C₉ atoms about the C₁-C₂ bond. The dihedral angle between C₁-C₂-C₈ and C₂-C₁-C₉ is $1.8 \pm 2.3^\circ$.

That the divergent lobes of the p orbitals are twisted outward from their normal positions (assuming sp² hybridization) is consistent with the argument²⁴ that in *cis*-ethylenic systems the π -bonded carbon p orbitals are distorted in order to relieve strain due to bond oppositions. (It is noteworthy that for the *trans* double bond in the humulene-silver nitrate adduct the silver ion is distorted only 5° from the normal position, whereas for the *cis* double bonds in the norbornadiene adduct, the distortion is approximately 24°.)

Finally, a distortion of the p orbitals could be attributed to a rotation of the p orbitals about the C₁-C₂

(24) P. D. Gardner, R. L. Brandon, and N. J. Nix, *Chem. Ind.* (London), 1363 (1958).

axis affecting a further spreading of the divergent lobes and a congestion of those which are convergent. The driving force for such a distortion would be a stabilization due to increased overlap of the convergent lobes and resulting homoconjugation. It is unlikely that homoconjugation is a very important factor in the bonding of the complex. Homoaromaticity in cyclononatriene itself is expected to be small according to simple LCAO-MO calculations,^{3,4} and it would seem reasonable that the silver ion would tend to withdraw electrons during complex formation, thus further decreasing any existing p-orbital overlap. Also, increases in the trigonal carbon angles and a decrease in the tetrahedral angles of the ring, which would be expected to accompany significant homoconjugation, are small and can be explained by the intraannular hydrogen interactions.

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Proton and Phosphorus-31 Nuclear Magnetic Resonance Studies of Tetraalkoxyphosphonium Hexachloroantimonates and Related Compounds^{1a}

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Abstract: Tetramethoxyphosphonium hexachloroantimonate (Ia) was obtained in moderate yield from the reaction between trimethyl phosphite and methyl hypochlorite in the presence of antimony pentachloride (reaction ii, X = O). Proton and phosphorus-31 nuclear magnetic resonance (nmr) and infrared and conductivity studies support this formulation. Evidence was also obtained for the formation of the triethoxymethoxy- and triphenoxymethoxyphosphonium cations. These results confirm that such salts are intermediates in the reaction between phosphite triesters and alkyl hypochlorites. The control reaction (iii) between trimethyl phosphite and antimony pentachloride gave a minor product which was shown to be trimethoxymethylphosphonium hexachloroantimonate (II), the intermediate from intermolecular transmethylation.

Current advances in the understanding of the mechanisms of phosphorus reactions owe much to the detection and characterization of four- and five-covalent intermediates resulting from valency expansion of phosphorus(III) compounds.²⁻¹¹ While stable pentaalkoxy-

phosphoranes² and trialkoxyalkylphosphonium salts^{3,4} have been isolated, the tetraalkoxyphosphonium salts have only been tentatively identified as transient intermediates. Denney and Relles¹² observed their formation using proton nmr in the reactions between trialkyl phosphites and neopentyl hypochlorite (reaction i).

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