Journal of Organometallic Chemistry
Elsevier Sequoia S.A., Lausanne
Printed in The Netherlands

PRELIMINARY COMMUNICATION

1,2,6-CYCLONONATRIENE-METAL COMPLEXES

G. NAGENDRAPPA and D. DEVAPRABHAKARA
Department of Chemistry, Indian Institute of Technology, Kanpur (India)

(Received January 27th, 1969; in revised form February 22nd, 1969)

We report a study on the reaction of 1,2,6-cyclononatriene with Ag(I) and Cu(I) salts, the first investigation of metal-allene complexes involving a cyclic allene.

Under conditions similar to those used for the preparation of other medium-size cyclic diene-metal complexes[1], treatment of 1,2,6-cyclononatriene[2] with aqueous silver nitrate solution caused immediate precipitation of 1:1 complex (Found: C, 37.24; H, 4.14; $C_9H_{12}AgNO_3$ Calcd: C, 37.23; H, 4.28%). The complex decomposes and darkens slowly in the atmosphere, but is fairly stable when kept in a sealed tube in the dark. It darkens at 145° and melts at 150–152° with decomposition. It is insoluble in most common organic solvents.

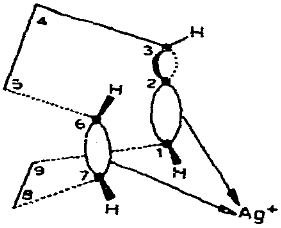
The triene did not give a Cu(I) complex with Cu_2Cl_2 under the conditions used for the preparation of Cu(I)-1,5-cyclononadiene complex[1]. This is consistent with the fact that Cu(I)-diene complexes are generally much less stable than the corresponding Ag(I)-diene complexes.

The 1900 cm^{-1} band can be assigned to the free allenic bond in the complex; it possibly corresponds with that at 1950 cm^{-1} in the non-coordinated allene, assigned to the antisymmetrical $C{=}C{=}C$ stretching vibration[3]. The band at 1740 cm^{-1}, which is absent in the free allene, may be attributed to the coordinated allenic bond. The 1595 cm^{-1} band is assigned to the coordinated isolated $C_6{=}C_7$ bond which appears as a very weak band around 1650 cm^{-1} in free allene. This assignment seems to be reasonable since the two π-bonds of the allene are perpendicular to each other and the *p*-orbitals of only one of them can have the correct orientation to coordinate with the metal ion (*cf.* ref.4).

1,2-Cyclononadiene did not give an isolable silver(I) complex even when the reaction mixture was kept for over a long time. This indicates that the isolated $C_6{=}C_7$ double bond is involved in the formation of a stable complex in the case of 1,2,6-cyclononatriene.

Even though the complex is stable, the bonding seems not to be strong enough to bring about changes in the structure of the ligand molecule, since the allene was regenerated without any isomerization, when the complex was treated with aqueous potassium cyanide.

The most probable structure of 1,2,6-cyclononatriene-Ag(I) complex seems to be:



1,2,6-Cyclononatriene undergoes isomerization when treated with rhodium or palladium salts, and studies on this are in progress.

REFERENCES

1 G. Nagendrappa and D. Devaprabhakara, *J. Organometal. Chem.*, 15 (1968) 225.
2 K.G. Untch, D.J. Martin and N.T. Castellucci, *J. Org. Chem.*, 30 (1965) 3572.
3 J.H. Wotiz and D.E. Mancuso, *J. Org. Chem.*, 22 (1957) 207.
4 M.A. Bennett, in F.G.A. Stone and R. West (Eds.), *Advances in Organometallic Chemistry*, Vol. 4, Academic Press, New York, 1966, p.353.