---

## 385. *The Possible Existence of Transition-metal Complexes of* cyclo*Butadiene.*

By H. C. LONGUET-HIGGINS and L. E. ORGEL.

The possibility that the unstable *cyclo*butadiene molecule can be stabilised by combination with a suitable transition-metal ion is investigated by use of molecular-orbital theory. It is suggested that complexes of the type $M^{II}X_2(C_4H_4)$, where M is nickel, palladium, or platinum and X is a univalent ligand, may be stable, and that $Ni(CN)_2(C_4H_4)$ is an intermediate in the Reppe synthesis of *cyclo*octatetraene.

ALTHOUGH the *cyclo*pentadienyl radical $C_5H_5$ is unstable, very stable transition-metal *cyclo*pentadienyls are known.[1,2] All attempts to prepare *cyclo*butadiene $C_4H_4$ having failed, the question arises whether it is possible to stabilise it by combination with a transition metal. We believe that such stabilisation can be achieved; the literature indicates the existence of *cyclo*butadiene complexes, if only as transitory intermediates.

Our reasons for postulating the existence of *cyclo*butadiene complexes may be understood by considering the transition-metal *cyclo*pentadienyls, the carbonyls, and their mixed complexes. A complex of this type will, as a rule, be most stable if the valency shell of the metal contains 18 electrons, it being postulated that a carbonyl contributes two, and a *cyclo*pentadienyl radical five electrons to the valency shell.[2,3] The chemical bond between the metal atom and a neighbouring $C_5H_5$ group is partly $\sigma$ with respect to the 5-fold axis, but mostly $\pi$, with possibly a little $\delta$ bonding.[4,5,6] The $\pi$ bonding is particularly strong because the doubly degenerate $e_{1g}$ orbital of a *cyclo*pentadienyl radical contains only three electrons, of which one is unpaired and can be used for covalent bonding.

[1] Piper, Cotton, and Wilkinson, *J. Inorg. Nuclear Chem.*, 1955, **1**, 165, and earlier papers.
[2] Fischer and H. Leipfinger, *Z. Naturforsch.*, 1955, **10b**, 353, and earlier papers.
[3] Dunitz and Orgel, to be published.
[4] *Idem, Nature*, 1953, **171**, 121.
[5] *Idem, J. Chem. Phys.*, 1955, **23**, 954.
[6] Moffitt, *J. Amer. Chem. Soc.*, 1954, **76**, 3386.

*cyclo*Butadiene would have, according to molecular-orbital theory, a doubly degenerate non-bonding $e_g$ orbital containing only two electrons. In this molecule both $e_g$ electrons should be unpaired (which, incidentally, is a possible explanation of its instability) and both these electrons could therefore be used in forming covalent $\pi$ bonds to a metal. There would also be a weak co-ordinate $\sigma$ bond to the metal from the $a_{1u}$ orbital of the ring, and a weak co-ordinate $\delta$ bond from the metal atom to the $a_{2u}$ orbital of the ring. *cyclo*Butadiene therefore differs from *cyclo*pentadienyl in three respects: first, in having four mobile electrons rather than five; secondly, in being able to form two $\pi$ bonds to a metal atom rather than one; and thirdly, in forming only one $\delta$ bond by back co-ordination.

Were there no other differences between *cyclo*butadiene and *cyclo*pentadiene one might therefore expect the former to form even more stable complexes than the latter. There is, however, the further important difference that *cyclo*butadiene can dissociate into a pair of acetylene molecules. We must therefore enquire whether a *cyclo*butadiene complex would be more or less stable than the corresponding complex containing two acetylene molecules.

In acetylene the four unsaturated electrons all occupy a very stable doubly degenerate $\pi_u$ orbital. The lowest unoccupied orbital, of symmetry $\pi_g$, has a high energy, which reduces its acceptor capacity. It is for this reason that transition-metal complexes of acetylene (and also of olefins) are relatively unstable. In *cyclo*butadiene, on the other hand, the doubly degenerate $e_g$ orbital is of intermediate energy, being effectively non-bonding. The presence of two unpaired electrons in this orbital would therefore, in combination with a suitable metal, favour a *cyclo*butadiene complex rather than one containing two acetylene molecules. This extra stability of the metal–carbon bonds might well more than compensate for the mild strain present in the four-membered ring.

The metals, and their valency states, which will be most likely to form *cyclo*butadiene complexes are most easily predicted by considering the conditions under which a metal forms stable complexes of any sort. Two important cases must be distinguished; that in which the metal atom is completely surrounded by ligands and that in which the ligands lie in a plane. In the former type of complex there will be a stable molecular orbital arising from each of the *d*, *s*, and *p* valency orbitals of the transition metal, making nine orbitals in all, so that 18 electrons are required to form a closed shell. In the planar complexes, on the other hand, the *p* orbital which is antisymmetrical with respect to the molecular plane is of higher energy and there are no stable ligand orbitals to combine with it. There are thus only 8 stable molecular orbitals instead of 9, and 16 electrons are sufficient to fill these.

To illustrate these cases we may consider the known molecules $(C_5H_5)Mn(CO)_3$ and $Pt(CO)Cl_3^-$. In the former, which is non-planar, the manganese atom contributes seven electrons, each CO group contributes two, and five are available from the $C_5H_5$ group; together these electrons form a closed shell of 18, the number required for stability. In the latter, the $Pt^{++}$ ion contributes 8 electrons, and each ligand, CO or $Cl^-$, contributes 2, so that there are in all 16 electrons in the valency shell of the platinum atom; this is why the complex is stable in the planar configuration.

By analogy with *cyclo*pentadiene, *cyclo*butadiene should contribute four electrons to the valency shell of a transition metal; one might therefore expect the existence of "non-planar" complexes such as $(C_4H_4)Ni(CO)_2$ with 18 electrons, or "planar" complexes such as $(C_4H_4)AuCl_2$ with 16. The geometrical configurations of these two hypothetical complexes are virtually identical, and it is therefore necessary to consider their electronic structures in order to decide whether the maximum stability is obtained with 16 or 18 electrons.

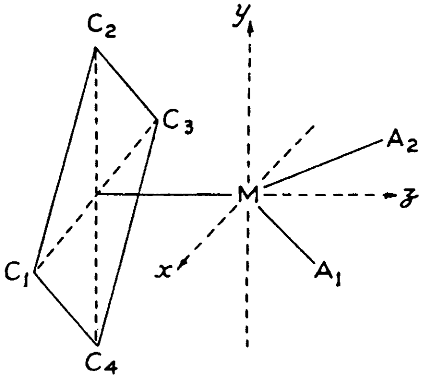
We will set up co-ordinate axes as shown in the Figure. The four $\pi$ orbitals of *cyclo*butadiene have the forms

$$\psi_1 = \tfrac{1}{2}(\phi_1 + \phi_2 + \phi_3 + \phi_4)$$

$$\psi_2 = \sqrt{\tfrac{1}{2}}(\phi_1 - \phi_3), \psi_3 = \sqrt{\tfrac{1}{2}}(\phi_2 - \phi_4)$$

$$\phi_4 = \tfrac{1}{2}(\phi_1 - \phi_2 + \phi_3 - \phi_4)$$

where $\phi_i$ denotes the $2p_z$ atomic orbital of $C_i$. Of these, $\psi_1$ is stable, $\psi_2$ and $\psi_3$ are of intermediate stability, and $\psi_4$ has a relatively high energy. These orbitals, together with the valency orbitals of the metal and the $\sigma$ orbitals, $\chi_1$ and $\chi_2$, of $A_1$ and $A_2$, respectively,



*The hypothetical structure of a* $[MA_2(C_4H_4)]$ *complex.*

are classified in the Table according to their behaviour upon reflection in the *xz* and *yz* planes.

*Symmetry classification of orbitals in* $(C_4H_4)MA_2$.

| $\sigma_{xz}$ | $\sigma_{yz}$ | *cyclo*Butadiene | $A_1$, $A_2$ | M |
|---|---|---|---|---|
| + | + | $\psi_1$ | $\frac{1}{2}\sqrt{}(\chi_1 + \chi_2)$ | $s$, $p_z$, $d_{z^2}$, $d_{x^2-y^2}$ |
| + | − | $\psi_2$ | $\frac{1}{2}\sqrt{}(\chi_1 - \chi_2)$ | $p_x$, $d_{xz}$ |
| − | + | $\psi_3$ | — | $p_y$, $d_{yz}$ |
| — | — | $\psi_4$ | — | $d_{xy}$ |

The last row in the Table is the simplest; by combining $\psi_4$ and $d_{xy}$ we obtain one orbital more stable and one less stable than either separately. The stable combination consists mainly of $d_{xy}$ and must be doubly occupied in a stable complex. The other combination will be unstable and antibonding.

If, in the second row of the Table, we replace $p_x$ and $d_{xz}$ by their sum and difference, it becomes clear that one of these combinations will overlap strongly with $\psi_2$ and the other with $\sqrt{\frac{1}{2}}(\chi_1 - \chi_2)$, so that we obtain two bonding and two antibonding orbitals from the four. Of these, the two bonding orbitals can contain four electrons.

Next we consider the totally symmetric orbitals. If the orbitals $d_{z^2}$ and $d_{x^2-y^2}$ were not present, one of the hybrid orbitals $\sqrt{\frac{1}{2}}(s \pm p_z)$ would combine strongly with $\psi_1$ and the other with $\sqrt{\frac{1}{2}}(\chi_1 + \chi_2)$, giving two strongly bonding and two strongly antibonding orbitals. Similarly, in the absence of the ligands, the $d_{z^2}$ and $d_{x^2-y^2}$ orbitals would be stable. In the actual molecule, the six orbitals will all mix; though the finer details of this mixing cannot be determined from a qualitative discussion, it seems almost certain that of the six resulting molecular orbitals four will be stable and two unstable.

Lastly we consider the orbitals $\psi_3$, $p_y$, and $d_{yz}$. If we form from $p_y$ and $d_{yz}$ an additive and a subtractive combination, the latter will overlap strongly with $\psi_3$ and the former hardly at all. We may therefore expect there to be one bonding and one antibonding combination of the three orbitals, and a third, effectively non-bonding, orbital of approximate form $\sqrt{\frac{1}{2}}(p_y + d_{yz})$. The bonding orbital must be doubly occupied, and the antibonding unoccupied; the condition of the non-bonding orbital is more difficult to decide. Indeed, the distinction between the 18- and 16-electron structures consists solely in whether this hybrid atomic orbital is occupied or not, because the stable molecular orbitals number 8 in all.

The stability of the critical orbital $\sqrt{\frac{1}{2}}(p_y + d_{yz})$ depends, among other things, on the amount of energy required to promote an electron from the $d$ to the next $p$ shell. If this energy is large, we would expect the 18-electron structure to be unstable relative to the 16-electron structure. This situation will arise in complexes derived from positive ions, since the $nd$–$(n-1)p$ separation increases with the positive charge on the metal ion. On the other hand, if the $d$–$p$ separation is small, the 18-electron structure should be favoured. The 18-electron structure is therefore most likely to appear in formally zero-valent metal complexes.

In the *cyclo*pentadienyl series a neutral 18-electron complexes $(C_5H_5)Co(CO)_2$ and a positively charged 16-electron complex $[(C_5H_5)Fe(CO)_2]^+$ have both been prepared;[1] they are structurally analogous to the hypothetical complexes $(C_4H_4)Ni(CO)_2$ and $[(C_4H_4)Co(CO)_2]^+$ respectively.

Makowka,[7] repeating work by Erdmann and Koethner,[8] reported that when acetylene is passed into an aqueous solution of palladous chloride, a brown-red precipitate, $PdC_4H_5OCl$, is slowly deposited, which on decomposition with alkali gives a product containing butyraldehyde, and Makowka concluded that a $C_4$ skeleton was present as a structural unit. It seems likely on his evidence that the first compound was $(C_4H_4)PdCl_2$, which subsequently hydrolysed to give $(C_4H_4)PdCl(OH)$. Both of these substances would be 16-electron *cyclo*butadiene complexes, of the type described above. Bivalent palladium is peculiarly reluctant to form any 18-electron complexes.

Solutions of auric chloride also react with acetylene, as indicated by the appearance of a deep colour.[8] It is not inconceivable that this might be due to formation of a *cyclo*butadiene complex such as $[(C_4H_4)AuCl_2]^+$.

Reppe showed that acetylene polymerises in a non-aqueous solution of $Ni(CN)_2$ to give *cyclo*octatetraene;[9] very little benzene is formed, despite its greater thermodynamic stability. An attractive hypothesis to explain the predominance of *cyclo*octatetraene is that this molecule is formed in a bimolecular reaction, both molecules in which contain a $C_4H_4$ unit. We suggest that the intermediate is $(C_4H_4)Ni(CN)_2$, which would be a 16-electron *cyclo*butadiene complex.

*Added, May 9th,* 1956.—The stable monomeric complex $C_7H_4O_3Fe$ prepared by Reppe is most reasonably formulated as $Fe(CO)_3(C_4H_4)$, since its reactions suggest that it is a substituted iron carbonyl. It may be an example of an 18-electron complex.

UNIVERSITY CHEMICAL LABORATORY, CAMBRIDGE. [*Received, November 29th,* 1955.]

[7] Makowka, *Ber.*, 1908, **41**, 824.

[8] Erdmann and Koethner, *Z. anorg. Chem.*, 1898, **18**, 48.

[9] See Bigelow and Copenhaver, " Acetylene and Carbon Monoxide Chemistry," Reinhold, New York, 1949.