The Structure of Cyclo-octenylnickel(II) Acetylacetonate

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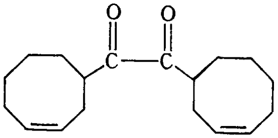
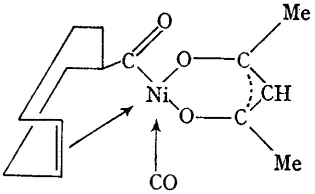
WILKE *et al.*[1] have described the preparation and properties of bis(cyclo-octa-1,5-diene)nickel(0) (I). Reaction of (I) with acetylacetone yields (II) of stoicheiometry (COD)(Hacac)Ni. Treatment of (II) with three moles of carbon monoxide leads to formation of the diketone (III) in a two-stage process, the first of which involves the addition of two moles of carbon monoxide.



(III)

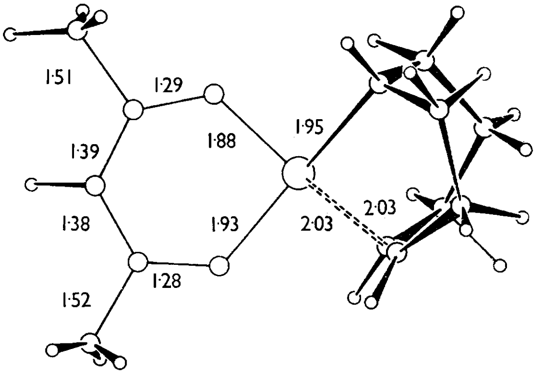


(IV)

We have examined the structure of (II) in the hope that we might find detail suggestive of the mechanism of the formation of (III) as well as the geometry and mode of co-ordination of the eight-membered ring and acetylacetone. We conclude that the complex is correctly represented as cyclo-octenylnickel(II) acetylacetonate.

A sample of (II) was kindly provided by Professor Wilke. Since the crystals are very unstable in air, the X-ray photographs were taken of a sample sealed in a thin-walled tube filled with nitrogen. The crystals are triclinic with $a = 8{\cdot}38$, $b = 8{\cdot}98$, $c = 9{\cdot}55$ Å, $\alpha = 68{\cdot}67°$, $\beta = 79{\cdot}59°$, and $\gamma = 71{\cdot}83°$ ($C_{13}H_{20}O_2Ni$). The unit-cell contains two molecules and the structure has been determined with the assumption that the space group is $P\bar{1}$.

The structure was solved by conventional methods and has been refined to an R-value of 7·8% for 1173 reflexions. All the hydrogen atoms have been detected and the positional co-ordinates of most have been successfully refined by least-squares methods. The conformation of the complexed cyclo-octene ring has thus been determined. The structure is shown in the Figure. It is clear that the acetylacetone co-ordinates as the usual bidentate ligand. This group is found to be symmetrical. Three atoms of the eight-membered ring, C-1, C-2, and C-5, lie 2·03 Å or less from the nickel atom; the next closest approach is 2·80 Å. The structure clearly involves a single bond between the nickel and C-5 with π-bonding between C-1=C-2 and the metal. The bond length C-1–C-2 is, to us, surprisingly large (1·42 Å), although it is 0·07 Å shorter than any other in the ring and is undoubtedly the location of the double bond. The attachment of the ring to the nickel is thus similar to that found in PtCl(OMe)-(dicyclopentadiene).[2] However, in contrast with the considerable lengthening of the Pt–Cl bond *trans* to the σ-bonded carbon (0·17 Å) reported for the platinum complex, we find at most an increase of $0{\cdot}04_5$ Å in the Ni–O distance in the *trans*-position. The co-ordination of the nickel is essentially square planar; the angle subtended at the nickel by the acetylacetonate group is 92·5° and by the σ-bond and centre of the double bond 87·7°.



FIGURE

Average standard deviation of Ni–C = 0·02 Å.
Average standard deviation of C–C = 0·03 Å.

The arrangement thus involves a 34-electron structure. From this, and the observed geometry, it seems reasonable to suggest that on treatment with carbon monoxide, one mole co-ordinates to the metal to yield a square-pyramidal five-co-ordinate system which is followed by insertion into the σ-bond (Ni–C-5) with further uptake of another mole of carbon monoxide[3] (IV). The reaction of acetylacetone with (I) thus involves a proton transfer from the acetylacetone to the ring atom C-6 with concomitant change of oxidation number of the nickel from zero to two. Although en-yl attachments of the kind suggested in the Figure for (II) have been suggested for platinum and palladium, this is the first time that it has been observed in the case of nickel.

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[1] G. Wilke, personal communication and in the press; M. Kroner, Thesis, Technische Hochschule, Aachen, 1961.

[2] W. A. Whitla, H. M. Powell, and L. M. Venanzi, *Chem. Comm.*, 1966, 310.

[3] T. H. Coffield, J. Kozikowski, and R. D. Closson, *J. Org. Chem.*, 1957, **22**, 598.