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NOTE

DIPENTADIENYLCHROMIUM

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While extensive publications have appeared dealing with several classes of transition metal complexes containing unsaturated organic groups, very little is known about the pentadienyl derivatives of transition metals. The only example reported in the literature concerns a cation $[C_5H_7Fe(CO)_3]^+$ prepared by extraction of a hydride ion from *cis*-1,3-pentadienyliron tricarbonyl by means of the triphenylmethyl cation[1].

This paper describes the preparation and the properties of a pentadienyl derivative of chromium which we obtained from pentadienylsodium (C_5H_7Na)[2] and chromium(II) chloride in tetrahydrofuran at −30°, yields were 60% based on the Cr used.

The green-coloured complex obtained after crystallization from n-heptane melts at 122–123°, seemingly without any decomposition; it is very soluble in aromatic hydrocarbons and chlorinated solvents.

The analytical data and cryoscopic measurements in benzene indicate the empirical formula $C_{10}H_{14}Cr$. (Found: C, 63.96; H, 7.58; Cr, 27.85; mol.wt., 190. $C_{10}H_{14}Cr$ calcd.: C, 64.49; H, 7.58; Cr, 27.93%; mol.wt., 186.23.)

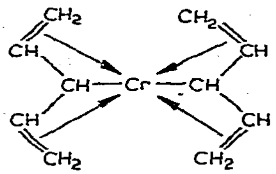
The measurement of the magnetic moment (2.74 BM) shows the presence of two unpaired electrons.

The chemical behaviour of the complex is similar to that of triallyl chromium: it is highly sensitive to air and reacts easily with protic solvents evolving 2 moles of pentadiene (40% 1,4-pentadiene, 50% *trans*-1,3-pentadiene, 10% *cis*-1,3-pentadiene) per mole of complex; it reacts with hydrogen very slowly also in the presence of colloidal Ni or Pd giving rise to the formation of n-pentane.

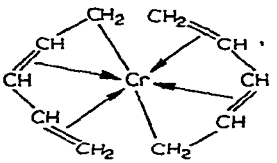
The IR spectrum shows the complete absence of the absorptions characteristic of non complexed double bonds, and the presence of absorptions at 1455 cm^{-1}, 1480 cm^{-1} and 1490 cm^{-1} which may be attributed to the C=C stretching of the unsaturated bonds coordinated to metal atoms.

The chemical-physical data and the results of the above reactions may be interpreted by assuming that the complex is a Cr^{II} derivative, in which two pentadienyl groups are bound to the metal.

The reactivity of the complex with water or alcohols is consistent with a structure of type (I) or type (II), characterized by the presence of a σ-bond between



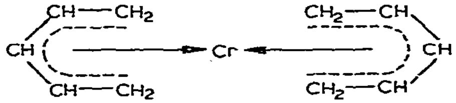
(I)



(II)

chromium and a carbon atom of the pentadienyl ligand and by the simultaneous coordination of the unsaturated bonds with chromium.

However, in our opinion, the available data are not completely sufficient to definitely establish the structure of $Cr(C_5H_7)_2$. In fact, formula (III), in which a π-bond is present between the chromium atom and the pentadienyl groups, could also be suggested.



(III)

Although the Cr atom in the complex lacks two electrons to reach the electronic structure of Kr, it does not give rise to stable etherates and does not react at room temperature with $P(C_6H_5)_3$. On the other hand, it reacts slowly with CO at room temperature and pressure in hydrocarbon solution. Along with the $Cr(CO)_6$, a green-coloured diamagnetic complex is formed (yield 60%), insoluble in aliphatic hydrocarbons, slightly soluble in aromatic hydrocarbons, chlorinated solvents, acetone, dimethylsulphoxide, or dimethylformamide. It may be crystallized from toluene, decomposes on heating and is slightly soluble in alcohols. Unlike dipentadienylchromium, it is not decomposed by alcohols.

The analytical data and cryoscopic measurements in benzene indicate the empirical formula $[Cr(C_{10}H_{14})CO]_2$. (Found: C, 60.67; H, 6.65; CO, 12.9; Cr, 23.9; mol.wt., 418. $C_{22}H_{28}Cr_2O_2$ calcd.: C, 61.67; H, 6.58; CO, 13.07; Cr, 24.28%; mol.wt., 428.48.)

The complex reacts slowly with hydrochloric acid evolving CO and pentadiene (40% 1,4-pentadiene, 50% *trans*-1,3-pentadiene, 10% *cis*-1,3-pentadiene). On the basis of this reaction, and of the results of mass spectroscopic analysis which exclude the presence of hydrocarbon fragments above C_5, we may reasonably assign to the complex the formula $[Cr(C_5H_7)_2CO]_2$.

Furthermore, the IR spectrum of this complex reveals the absence of absorptions characteristic of non-complexed double bonds, and the presence of absorptions at 1927 cm^{-1} and 1935 cm^{-1} (sh) characteristic of metal carbonyls and of absorptions at 1450 cm^{-1}, 1455 cm^{-1} (sh), 1485 (sh), and 1490 cm^{-1}, which may be attributed to the C=C stretchings of the unsaturated bonds coordinated to metal atoms.

Further characterization of this compound as well as an X-ray analysis of the compound $Cr(C_5H_7)_2$ are in progress.

REFERENCES

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2 J. G. Berger, E. L. Stogryn and A. A. Zimmerman, *J. Org. Chem.*, 29 (1964) 950.