

Preliminary communication

η^5 -CYCLOPENTADIENYL- η^5 -SYN-1-METHYLPENTADIENYLIRIDIUM
 AND IRIIDIUM CATIONS - PREPARATION AND REACTIONS WITH
 NUCLEOPHILES

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SUMMARY

η^5 -cyclopentadienyl- η^5 -syn-1-methylpentadienyliridium(I) hexafluorophosphate, a novel complex containing an open chain pentadienyl ligand, has been prepared *via* protonation of η^5 -cyclopentadienyl- η^4 -hexa-2,4-dien-1-ol iridium. It and the corresponding rhodium salt are attacked by methoxide ion at the central 3-position of the dienyl group to give 1,4-diene complexes. This contrasts with nucleophilic attack on pentadienyltricarbonyliron cations which occurs at the terminal positions of the dienyl group.

Recently we reported the preparation of cobalt and rhodium salts of the cations $[M(\eta^5-C_5H_5)(\eta^5-CH_3C_5H_6)]^+$ which contain open chain 1-methylpentadienyl ligands.¹ Apart from the well known tricarbonyliron complexes, coordination of an acyclic η^5 -pentadienyl ligand to a transition element is rare.^{2,3} In this paper the synthesis of the analogous iridium salt (Ib) is described. The method used for this preparation also affords an improved route to the rhodium complex (Ia).

Reduction of the sorbaldehyde complexes IIa, IIb¹ with sodium borohydride in aqueous methanol gave the sorbyl alcohol derivatives IIIa,

hexafluorophosphate solution. The stability to hydrolysis of our salts contrasts sharply with that of the corresponding tricarbonyliron complex which is readily attacked by water.^{4,5}

The novel iridium complex was characterised by elemental analysis and by proton n.m.r. spectroscopy.

¹H n.m.r. (T scale, J-coupling constants in Hz)

(CD₂Cl₂) CH₃, 8.21(d), J 6.5;
 H^{1a}, 7.5 (dq) J 6.5, 9; H² 4.3 (m);
 H³ 3.31 (t), J 7; H⁴, 4.3 (m);
 H^{5s}, 5.75 (dd), J 3.5, 8.5; H^{5a}, 8.2 (dd)
 (partly obscured by CH₃): C₅H₅, 4.01 (s).

When Ia or Ib was treated with sodium methoxide in methanol, methoxy derivatives IVa, IVb could be isolated. These were readily hydrolysed; addition of water followed by ammonium hexafluorophosphate produced the original salts. On the basis of ¹H n.m.r. results the methoxy-complexes are considered to have structures IVa, IVb, in which the nucleophile has become attached to the central 3-position of the pentadienyl group. This contrasts with the behaviour of open chain pentadienyltricarbonyliron cations, which are attacked by nucleophiles at the terminal positions^{4,5} and also with that of certain cyclic dienyl cations, for which attack at the 2-position has sometimes been observed.^{6,7} Moreover cyclohexadienyl-cyclopentadienylrhodium tetrafluoroborate reacts with methoxide ion to give (cyclopentadienyl)(5-methoxycyclohexa 1,3-diene) rhodium, i.e. at the terminal positions of the dienyl group.⁸

Ia was similarly reduced by aqueous sodium borohydride to a complex V in which attack at the 3-position has also occurred. This structural assignment is again based largely on the ¹H n.m.r. spectrum, which closely resembles those of similar 1,4-diene complexes of rhodium.⁹

¹H n.m.r. IVa: CH₃, 8.55(d), J 6; H^{1a}, H^{5s} ~ 7.6 (m); H², H⁴, ~ 6.6(m);
 H³, 5.74(t), J 6.5; H^{5a}, ~ 8.7(m) (under CH₃);
 C₅H₅, 4.71(s); OCH₃, 6.90(s).

IVb: CH_3 , 8.52(s); H^{1a} , 8.5 (obscured by CH_3); H^2 , $\text{H}^4 \sim 6.9$
 (under OCH_3); H^3 , 5.73(t), J 6.5; H^{5s} , 7.88 (dd),
 J 9, 2.5; H^{5a} , 9.43(dd), J 9, 2.5; C_5H_5 , 4.72 (s); OCH_3 , 6.94(s)
 V: CH_3 , 8.58(d), J 6.5; H^2, H^4 , 6.9(m); H^3 , $\text{H}^{3'}$, H^{5s} , 7.7(m);
 H^{1a} , H^{5a} , 8.8(m) (partly obscured by CH_3).

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