An Iridium(V) Organometallic Compound; Synthesis and *X*-Ray Crystal Structure of Tetramethyl(η^5-pentamethylcyclopentadienyl)iridium

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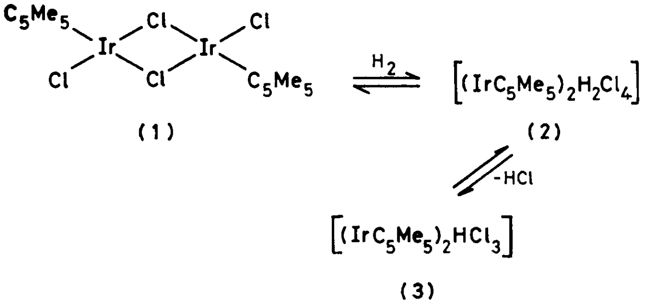
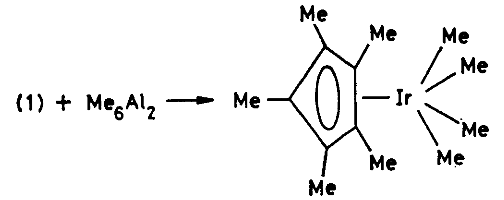
Summary Reaction of $[Ir_2(C_5Me_5)_2Cl_4]$ with Al_2Me_6 gives $[Ir^V(\eta^5\text{-}C_5Me_5)Me_4]$, characterised by spectroscopy and an *X*-ray structure determination.

IN our development of the chemistry of pentamethylcyclopentadienyl-iridium and -rhodium complexes,[1] we have been aware of the possibility that such complexes containing the metal in an oxidation state higher than +III could have reasonable stability. For example, the heterolytic activation of hydrogen by the iridium(III) complex (**1**) giving the μ-hydrido-iridium(III) complex (**3**)[2] could well proceed *via* a higher-oxidation-state species such as (**2**). A related scheme has been shown to apply to the heterolytic activation of hydrogen by some Ru^{II} complexes.[3]



Attempts to obtain stable complexes of iridium in a higher oxidation state by reaction of iridium(III) complexes with conventional oxidising agents such as halogens were unsuccessful.[4]

However, we now find that complex (**1**) reacts with methylating agents such as hexamethyldialuminium in a complex redox reaction. From the product the volatile (80 °C at 0·2 mmHg) and pentane-soluble $[(IrC_5Me_5)Me_4]$ (**4**) could be isolated as pale yellow crystals in 11% yield.



(4)

The complex was characterised by elemental analysis and mass spectrometry [M^+, m/e 386 (^{191}Ir, 37%) and 388 (^{193}Ir, 63%)]. The ^{1}H n.m.r. spectrum (60 MHz, CD_2Cl_2) shows two singlets, at δ 1·28 and 0·47 in the (measured) ratio of 5·00 : 4·02; the two resonances may therefore with confidence be ascribed to the C_5Me_5 and the Me_4Ir methyl groups respectively. The ^{13}C n.m.r. spectrum (100 MHz, CD_2Cl_2) shows the expected three singlet resonances at δ −3·4 (Me_4Ir), +6·3 ($C_5\mathit{Me}_5$), and +97·8 (C_5Me_5) p.p.m.

The structure of (**4**) was confirmed by an *X*-ray structure determination. *Crystal data:* $C_{14}H_{27}Ir$; M = 387·6, orthorhombic; a = 15·381(2), b = 7·018(1), c = 13·980(5) Å; U = 1509·1 Å^3, Z = 4, D_c = 1·71 g cm^{-3}, $F(000)$ = 752. Systematic absences indicate the space group to be either $Pca2_1$ (C^5_{2v}, No. 29) or $Pcam$ (D^{11}_{2h}, *bac* setting of No. 57); Mo-K_α radiation (graphite monochromator), λ = 0·71069 Å, μ(Mo-K_α) 87·89 cm^{-1}.

Single-crystal *X*-ray data in the range 3·5 < 2θ < 50° were collected on a Nicolet–Syntex R3 4-circle diffractometer. 624 independent reflections with $I > 3\sigma(I)$ (corrected for Lorentz, polarisation, decay, and absorption) were used for the structure solution by Patterson and Fourier methods. Full-matrix least-squares refinement was used in the centric space group with the cyclopentadienyl ring restricted to its idealised geometry. With anisotropic thermal parameters for all atoms R has converged to 0·058.†

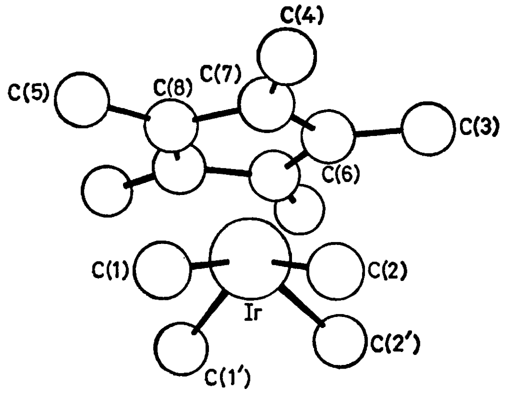


FIGURE. View of the molecule of $[(IrC_5Me_5)(CH_3)_4]$. Bond lengths: Ir–C(1) 2·13(5), Ir–C(2) 2·03(5), Ir–C(6) 2·23(2), Ir–C(7) 2·24(2), Ir–C(8) 2·25(2) Å. Bond angles: C(1)–Ir–C(2) 76(2), C(1)–Ir–C(1′) 67(2)°, C(1)–Ir–C(2′) 113(2), C(2)–Ir–C(2′) 70(2)°.

The structure may be described as a four-legged piano stool (Figure) and has a mirror plane through the metal, C-6, and C-3. The pentamethylcyclopentadienyl ring is η^5-bonded [mean Ir–C (ring) 2·24(2) Å], and the four methyl groups are at a mean distance of 2·08(5) Å from the metal.

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† The atomic co-ordinates for this work are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Rd., Cambridge CB2 1EW. Any request should be accompanied by the full literature citation for this communication.

The high e.s.d.s reflect the high thermal vibrations, especially of the metal-bonded methyl groups, at ambient temperature.

Although Ir^V is known in fluoro-complexes[5] (*e.g.* $[IrF_6]^-$) and in the hydrides $IrH_5(PR_3)_2$,[6] (**4**) appears to be the first organometallic complex in this oxidation state.

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