Synthesis and *X*-Ray Structure of an Unusual Iridium Ylide or Carbene Complex

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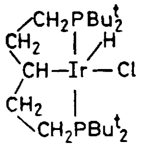
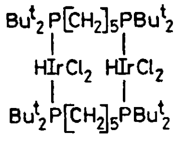
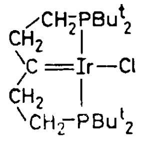
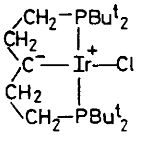
Summary $\mathrm{IrCl_3}$ reacts with $\mathrm{Bu^t_2P[CH_2]_5PBu^t_2}$ to give $\mathrm{[IrHCl\{Bu^t_2P[CH_2]_2CH[CH_2]_2PBu^t_2\}]}$ which loses dihydrogen reversibly to give $\mathrm{[IrCl\{Bu^t_2P[CH_2]_2C[CH_2]_2PBu^t_2\}]}$, the structure of which has been determined by *X*-ray diffraction.

Treatment of hydrated $\mathrm{IrCl_3}$ with $\mathrm{Bu^t_2P[CH_2]_5PBu^t_2}$ in boiling isopropyl alcohol for 3 days gives a mixture of three iridium-containing species: an orange red metallated hydride $\mathrm{[IrHCl\{Bu^t_2P[CH_2]_2CH[CH_2]_2PBu^t_2\}]}$ (I), a reddish-purple binuclear hydride $\mathrm{[IrHCl_2\{Bu^t_2P[CH_2]_5PBu^t_2\}]_2}$ (II), and an insoluble red-brown material which we have not characterized. The mononuclear complex (I) shows the expected n.m.r. hydride resonance at τ_H (C_6D_6) 53·33 [^2J(P–H) 12 and ^3J(H–CH) 5 Hz] and two 1 : 2 : 1 t-butyl triplets, and a singlet ^{31}P resonance at δ 76·1 p.p.m. ($CDCl_3$) (relative to 85% H_3PO_4). In the i.r. spectrum a strong peak at 267 cm^{-1} is assigned to ν(Ir–Cl) but no peak due to ν(Ir–H) could be observed. In several other 5-co-ordinate iridium(iii) hydrides of similar type the band due to ν(Ir–H) is either weak or not observed.[1] With carbon monoxide, the pale-yellow co-ordinatively saturated carbonyl hydride $\mathrm{[IrHCl(CO)\{Bu^t_2P[CH_2]_2CH[CH_2]_2PBu^t_2\}]}$ is formed.


(I)


(II)


(III)


(IV)

When the hydride (I) is heated at *ca.* 170 °C and 15 mmHg, it partially decomposes to give a dark brown (almost black), highly crystalline sublimate. The hydride tends to co-sublime with this dark product but after resublimation (sometimes three times more) small quantities of a very dark red-brown complex could be obtained pure. On the basis of microanalyses, molecular weight measurements (osmometrically and mass spectrometrically), and i.r. and ^{1}H, ^{13}C, and ^{31}P n.m.r. spectroscopy (see later), and particularly the structural determination by *X*-ray diffraction (below), the product is formulated as $\mathrm{[IrCl\{Bu^t_2P[CH_2]_2C[CH_2]_2PBu^t_2\}]}$ with a structure somewhere between the extremes of an iridium(i) carbene (III) and an iridium(iii) ylide (IV). The loss of dihydrogen from (I) is reversible since a benzene solution of $\mathrm{[IrCl\{Bu^t_2P[CH_2]_2C[CH_2]_2PBu^t_2\}]}$ under dihydrogen at 20 °C slowly turns orange-red over 3 h to give back the hydride (I), identified by its ^{1}H n.m.r. spectrum. We suggest that in (I) the two hydrogen atoms, Ir–H and C–H, are mutually *cis*.

Crystals of the dark red-brown complex, $C_{21}H_{44}ClIrP_2$, *M* 585·7, are monoclinic, space group $P2_1/c$, with a = 12·326(2), b = 14·362(3), c = 14·807(2) Å, β = 104·87(1)°, and Z = 4. The structure analysis employed 2229 independent, absorption-corrected reflections having $I > 3\sigma(I)$ and $5° < 2\theta < 40°$. Measurements were made using a Syntex $P2_1$ diffractometer with graphite monochromatised Mo-K_α radiation (λ = 0·71069 Å). Least-squares refinement of atomic co-ordinates, anisotropic vibration parameters for non-hydrogen atoms, and isotropic vibration parameters for hydrogen atoms gave a final R of 0·016. The molecular structure is shown in the Figure.†

In the structure C(3) lies 0·30 Å from the plane of Ir–C(2)–C(4) whereas for tetrahedrally directed bonds of the

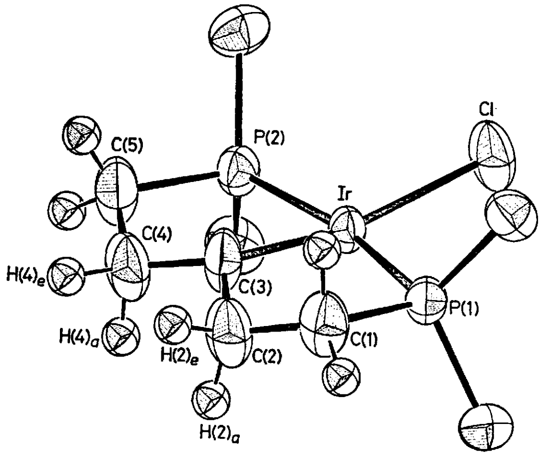


Figure. ORTEP drawing of the molecular structure of $\mathrm{[IrCl\{Bu^t_2P[CH_2]_2C[CH_2]_2PBu^t_2\}]}$. For clarity, the methyl groups of Bu^t have been omitted and hydrogen atoms have been given artificial temperature factors of U_{iso} = 0·02 Å^2. Principal dimensions are: Ir–P, 2·303 and 2·304(1); Ir–Cl, 2·414(1); Ir–C(3), 2·006(4); C(2)–C(3), 1·504(6); and C(3)–C(4), 1·502(6) Å; ∠P–Ir–Cl, 96·1 and 95·8(1); ∠P–Ir–C, 84·0 and 84·3(1); ∠Ir–C–C 119·1 and 118·4(3); and ∠C(2)–C(3)–C(4), 112·9(3)°.

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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 Road, Cambridge CB2 1EW. Any request should be accompanied by the full literature citation for this communication.

same length in the purely ylide structure (IV) one would expect a displacement of 0·55 Å. The Ir–C bond length of 2·006(4) Å is shorter than that found (2·16[2] and 2·10[3] Å) in octahedral iridium(III) complexes having a saturated carbon atom *trans* to Cl, but similar to the 1·99[4] and 2·01[5] Å found in compounds having trigonal carbon bonded to iridium(III). No complexes having square-planar co-ordination of iridium(III) have been characterized nor are there data available for comparable Ir(I)–C bond lengths. The average of the C(2)–C(3) and C(3)–C(4) bond lengths [1·503(6) Å] is in the range expected for bonds between trigonal and tetrahedral carbon atoms.

The i.r. spectrum of the ylide (carbene) complex shows a band at 279 cm^{-1} due to ν(Ir–Cl) and the ^{31}P n.m.r. spectrum shows a singlet at δ 83·4 p.p.m. (relative to 85% H_3PO_4). The ^{13}C n.m.r. spectrum shows the expected number and multiplicity of peaks, in particular the unique (carbene or ylide) carbon absorbs at δ (C_6D_6) 66·6 [^2J(P–C) 18 Hz]; there is no resonance at a larger δ-value than this. Usually carbene carbons attached to metals absorb at $\delta > 220$ p.p.m. (relative to Me_4Si[6,7]). One might expect an ylide carbon to be more shielded than a carbene carbon.[8] In $Me_3P{=}CH_2$ the methylene (ylide) carbon is even more shielded than the methyl carbon.[9] Thus the ^{13}C n.m.r. evidence is also against a pure carbene structure (III) and favours a substantial contribution from the ylide form (IV). We suggest that the very dark colour is due to a charge-transfer absorption (carbon to iridium). A feature of the ^{1}H n.m.r. spectrum is a quintet of *ca.* 1 : 4 : 6 : 4 : 1 relative intensities at τ 12·77 (apparent *J* 7·1 Hz) due to two protons. We assign this resonance with the remarkably high τ value to two of the chemically equivalent hydrogen atoms on C(2) and C(4) and shielded by the negative charge. We cannot say whether the hydrogen atoms giving rise to this pattern are the pseudo-axial $H(2)_a$ or $H(4)_a$ or the pseudo-equatorial $H(2)_e$ or $H(4)_e$ (Figure). The quintet pattern presumably arises because these hydrogens are on carbon atoms β to two strongly coupled and chemically equivalent P nuclei (H–H geminal coupling is presumably small). In complexes of the type *trans*-$[MX_2(PEt_3)_2]$ (M = Ni, Pd, or Pt; X = halogen) the methyl hydrogen resonance pattern is an apparent 1 : 4 : 6 : 4 : 1 quintet.[10,11] The ^{1}H n.m.r. pattern of the remaining methylene protons of $[IrClBu_2{}^tP\text{-}[CH_2]_2C[CH_2]_2PBu_2{}^t]$ is extremely complex and partially buried under the intense t-butyl triplet.

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