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Preliminary communication

A TERMINAL METHYLENE COMPLEX OF IRIDIUM(I), $Ir(=CH_2)I(CO)(PPh_3)_2$, AND REARRANGEMENT TO AN *ortho*-METALLATED PHOSPHORUS YLIDE COMPLEX, $Ir(CH_2PPh_2C_6H_4)HI(CO)(PPh_3)$

G.R. CLARK, W.R. ROPER* and A.H. WRIGHT
Department of Chemistry, University of Auckland, Auckland (New Zealand)

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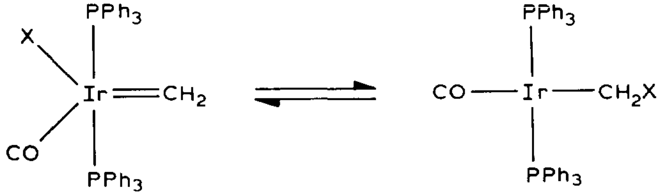
Summary

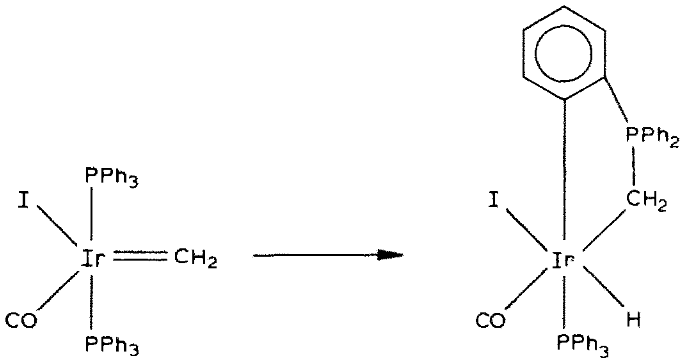
Diazomethane addition to $IrI(CO)(PPh_3)_2$ at −50°C gives $Ir(=CH_2)I(CO)(PPh_3)_2$, an orange crystalline solid with m.p. 110°C. Solutions of this complex at room temperature rearrange to a phosphorus ylide complex which undergoes intramolecular hydrogen transfer to iridium (an oxidative addition), forming the *ortho*-metallated complex $Ir(CH_2PPh_2C_6H_4)HI(CO)(PPh_3)$ the structure of which is confirmed by X-ray crystal structure determination.

The recent isolation of the stable methylene complex, $Os(=CH_2)Cl(NO)(PPh_3)_2$ [1] from reaction of $OsCl(NO)(PPh_3)_3$ with CH_2N_2 suggests that similar complexes should exist with iridium(I), viz., $Ir(=CH_2)X(CO)(PPh_3)_2$, X = anionic ligand. However, the experiments of Mango and Dvoretzky [2] indicate that for X = Cl, and for CH_2N_2 addition to an ether suspension of the iridium(I) complex, the only isolable complex is the rearranged chloromethyl species, $Ir(CH_2Cl)(CO)(PPh_3)_2$:



Left to right the above reaction is a "migratory-insertion" and right to left an "α-elimination". The position of equilibrium between methylene and substituted methyl species should be dependent on X and in the expectation of the weaker C—I bond favouring the methylene form we have examined the reaction between $IrI(CO)(PPh_3)_2$ and CH_2N_2 in THF at –50°C. An orange crystalline solid, ν(CO), 1940 cm^{-1}, m.p. 110°C, which has some air-stability at room temperature, can be isolated in 93% yield by addition of hexane to the THF solution. The ^1H NMR spectrum of this compound measured at –50°C in CD_2Cl_2 reveals a triplet signal at δ 12.88 ppm (J(PH) 19 Hz), which unambiguously indicates that the structure is $Ir({=}CH_2)I(CO)(PPh_3)_2$. $Os({=}CH_2)Cl(NO)(PPh_3)_2$ has a similar triplet at δ 13.81 ppm [1]. No signal attributable to an iodomethyl ligand is observed.

In many respects the chemistry of $Ir({=}CH_2)I(CO)(PPh_3)_2$ parallels that of $Os({=}CH_2)Cl(NO)(PPh_3)_2$ [1]. With HCl, $IrCH_3ClI(CO)(PPh_3)_2$ is formed and with $(Et_4N)(AuI_2)$, $\overline{Ir(CH_2Au}I)I(CO)(PPh_3)_2$ results. However, whereas $Os({=}CH_2)Cl(NO)(PPh_3)_2$ is stable in solution indefinitely at room temperature, the ^1H NMR spectrum of a solution of $Ir({=}CH_2)I(CO)(PPh_3)_2$ at room temperature shows loss of the low-field triplet and appearance of a high-field signal, a doublet of doublets, at δ –15.39 ppm, indicating that two chemically inequivalent phosphorus atoms are coupling with a hydride ligand. A colourless crystalline product, ν(CO), 1995; ν(IrH), 2178 cm^{-1}, can be isolated in quantitative yield. The spectroscopic data suggests that this rearranged product is an *ortho*-metallated phosphorus ylide complex and this was confirmed by X-ray crystal structure determination.



Single crystals suitable for X-ray study were grown from THF/Et_2O. Crystal data: $C_{38}H_{32}IIrOP_2$, M = 885.73, triclinic, space group $P1$ a 11.626(1), b 12.073(1), c 13.011(1) Å, α 97.53(1), β 93.25(1), γ 108.50(1)°, U 1707.51 Å^3, Z = 2, D_c 1.722, D_O 1.72 g cm^{-3}, μ(Mo-K_α) 47.08 cm^{-1}. The structure was solved using Patterson and electron density syntheses, and refined by full-matrix least-squares methods to R = 0.051, using 7105 observed reflections ($I > 3\sigma(I)$, θ_{max} 29°, absorption corrected) recorded on an Enraf—Nonius CAD-4 diffractometer.

The geometry of $\overline{Ir(CH_2PPh_2C}_6H_4)HI(CO)(PPh_3)$ is depicted in Fig. 1. The structure is regular in all respects. The hydride ligand was not located but must occupy the position *trans* to I which is also suggested by the very high-field chemical shift found for this ligand. The probable mechanism for formation of this product would involve phosphine migration to the methylene ligand in $Ir({=}CH_2)I(CO)(PPh_3)_2$ forming a four coordinate Ir(I) ylide complex which undergoes an oxidative addition reaction via *ortho*-metallation of the ligated CH_2PPh_3.

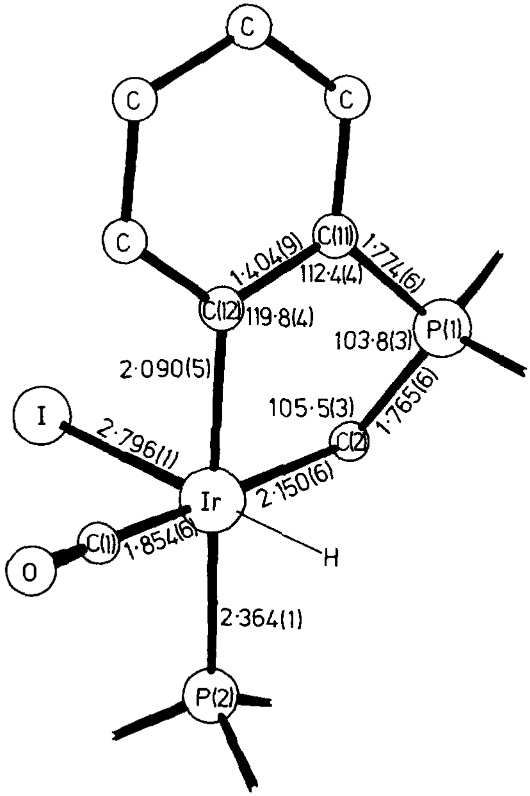


Fig. 1. Molecular structure of $Ir(CH_2PPh_2C_6H_4)HI(CO)(PPh_3)_2$ with phenyl groups omitted for clarity. Bond lengths in Angstrom units.

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References

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