Novel Routes to Alkynyl and Vinylidene Iridium Complexes. The First Example of :C=CH$_2$ Ligand Transfer from a 4d to a 5d Transition Metal Atom

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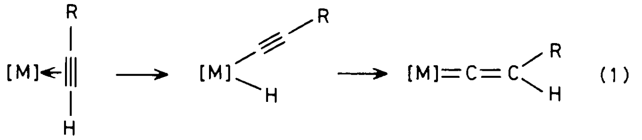
Square-planar vinylidene iridium(I) complexes *trans*-[IrCl(=C=CHR)(PPr$^i_3$)$_2$] (R = H, Me, Ph, SiMe$_3$, CO$_2$Me) are prepared from IrH$_2$Cl(PPr$^i_3$)$_2$ and alk-1-ynes HC$_2$R, *via* IrH(C$_2$R)Cl(PPr$^i_3$)$_2$ as intermediates; the parent member of the series with R = H has also been obtained from C$_5$H$_5$Rh(=C=CH$_2$)PPr$^i_3$ and IrCl(PPr$^i_3$)$_2$, *i.e.* by transfer of a :C=CH$_2$ ligand from a 4d to a 5d transition metal atom.

We have recently shown that the co-ordinatively unsaturated 14-electron species RhCl(PPr$^i_3$)$_2$ [1] and IrCl(PPr$^i_3$)$_2$ [2] are useful starting materials for the synthesis of various square-planar alkyne rhodium and iridium complexes,[3] and that with alk-1-ynes the derivatives *trans*-[MCl(HC$_2$R)(PPr$^i_3$)$_2$] rearrange in two consecutive steps to give first the alkynyl(hydrido) and then the isomeric vinylidene metal derivatives, equation (1).[4] However, while the rhodium compound RhCl(PPr$^i_3$)$_2$ (although extremely air-sensitive) has been isolated,[1b] the analogous iridium complex has only been obtained *in situ* from [IrCl(C$_8$H$_{14}$)$_2$]$_2$ by using an excess of PPr$^i_3$,[2] which reacts with alk-1-ynes such as HC$_2$CO$_2$Me to produce stable adducts[5] and thus prevents the preparation of alkyne and subsequently vinylidene iridium derivatives *trans*-[IrCl(=C=CHR)(PPr$^i_3$)$_2$] with functional R groups such as CO$_2$Me. We have therefore developed an alternative route to these derivatives starting from the five-co-ordinate dihydridoiridium compound IrH$_2$Cl(PPr$^i_3$)$_2$ (**1**), formed on addition of H$_2$ to IrCl(PPr$^i_3$)$_2$.[1b,6]

Reaction of (**1**) with equimolar amounts of HC$_2$CO$_2$Me in pentane at room temperature leads to the formation of the alkynyl(hydrido)metal complex (**2a**) in almost quantitative yield.† The proposed configuration shown in Scheme 1 is mainly supported by the unusual chemical shift of the Ir–H resonance in the ^{1}H n.m.r. spectrum which is observed at δ



[M] = RhCl(PPr$^i_3$)$_2$, IrCl(PPr$^i_3$)$_2$; R = H, Me, Ph

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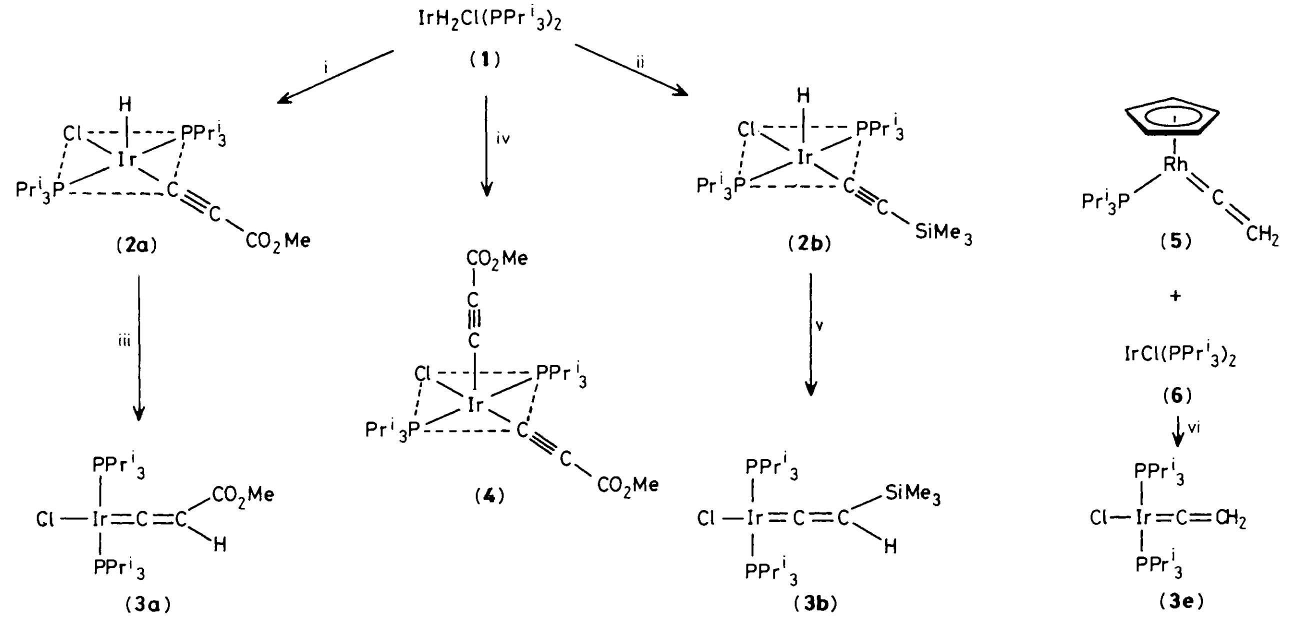
† All new compounds gave analytical data, including mass spectra, consistent with their structures: (**2a**) red, air-sensitive crystals, m.p. 93 °C (decomp.); (**2b**) red, air-sensitive crystals; (**3a**) red, relatively air-stable crystals, m.p. 133 °C (decomp.); (**4**) red, air-sensitive crystals, m.p. 108 °C (decomp.).



Scheme 1. *Reagents and yields:* i, HC_2CO_2Me, hexane, 25 °C, 10 min, 97%; ii, HC_2SiMe_3, hexane, 25 °C, 5 min, 90%; iii, benzene, 80 °C, 24 h, 91%; iv, HC_2CO_2Me (molar ratio 1:2), hexane, 25 °C, 2 h, 81%; v, toluene, 110 °C, 2 h; vi, benzene, 50 °C, 2 h, 77%.

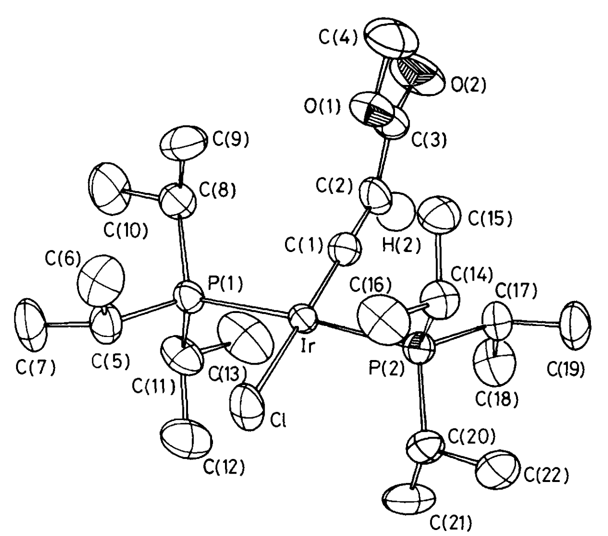


Figure 1. The *X*-ray structure of (**3a**).

−44.35,[‡] *i.e.* in a high-field region typical for five-co-ordinate square-pyramidal hydrido iridium(III) compounds.[1b] On heating in benzene, (**2a**) rearranges to give quantitatively the vinylidene complex (**3a**).[†‡] If in the reaction of (**1**) with HC_2CO_2Me two equiv. of the alkyne are used, the main product is the bis(alkynyl) compound (**4**),[†‡] which possibly also has a square-pyramidal structure.

Alkynes such as HC_2SiMe_3, HC_2Me, and HC_2Ph behave similarly to HC_2CO_2Me towards (**1**) and produce the corresponding alkynyl(hydrido)iridium complexes $IrH(C_2R)Cl(PPr^i_3)_2$ [R = $SiMe_3$ (**2b**), Me (**2c**), Ph (**2d**)]. Whereas (**2c**) and (**2d**) have recently been prepared by thermal rearrangement of *trans*-$[IrCl(HC_2R)(PPr^i_3)_2]$,[4] the trimethylsilyl compound (**2b**) is not accessible by this route. Compound (**2b**) can only be isolated under rigorous anhydrous conditions as it reacts with even slight traces of water (or alcohol) to form *trans*-$[IrCl(=C=CH_2)(PPr^i_3)_2]$ (**3e**),[4] probably *via* $IrH(C_2H)Cl(PPr^i_3)_2$ as intermediate. Under similar conditions used for the preparation of (**3a**), (**2b**) also rearranges to give (**3b**),[‡] which like (**2b**) is extremely sensitive to proton sources and has not yet been isolated in analytically pure form.

The result of the *X*-ray structure analysis of (**3a**) is shown in Figure 1.[§] The metal is co-ordinated in a square-planar arrangement with the phosphine ligands in *trans* positions. The Ir–C(1)–C(2) linkage is almost linear; together with C(3), O(1), and O(2) it forms a plane that is nearly perpendicular (angle 96.4°) to the best plane containing the atoms Ir, P(1), P(2), Cl, and C(1). This structural feature together with the short Ir–C(1) distance {compared, *e.g.*, with the Ir=C bond

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[‡] *Selected spectroscopic data:* i.r. in KBr (ν in cm^{-1}); ^1H n.m.r. (δ) in C_6H_6 at room temperature (*J* and *N* in Hz). (**2a**) ^1H n.m.r., 3.43(3H, s, CO_2Me), 3.03(6H, m, PCH), 1.23[18H, dvt, *J*(H-H) 7.1, *N* 14.1, PCH*Me*], 1.18[18H, dvt, *J*(H-H) 7.2, *N* 13.8, PCH*Me*], −44.35[1H, t, *J*(H-P) 11.9, IrH]. (**2b**) ^1H n.m.r., 3.25(6H, m, PCH), 1.36[18H, dvt, *J*(H-H) 7.1, *N* 13.9, PCH*Me*], 1.34[18H, dvt, *J*(H-H) 7.1, *N* 13.9, PCH*Me*], 0.34(9H, s, $SiMe_3$), −42.39[1H, t, *J*(H-P) 12.5, IrH]. (**3a**) I.r., 1692 (C=O), 1616 (C=C); ^1H n.m.r., 3.52(3H, s, CO_2Me), 2.87(6H, m, PCH), 1.25[36H, dvt, *J*(H-H) 7.1, *N* 13.9, PCH*Me*], −2.27[1H, t, *J*(H-P) 2.3, =C*H*R]. (**3b**) ^1H n.m.r., 3.12(6H, m, PCH), 1.31[36H, dvt, *J*(H-H) 7.1, *N* 14.0, PCH*Me*], 0.58(9H, s, $SiMe_3$), −5.01[1H, t, *J*(H-P) 2.7, =C*H*R]. (**4**) I.r., 2092 (C≡C), 1684 (C=O); ^1H n.m.r., 3.43(6H, s, br, CO_2Me), 3.13(6H, m, PCH), 1.15(18H, dvt, *J*(H-H) 7.3, *N* 14.0, PCH*Me*], 1.12[18H, dvt, *J*(H-H) 7.0, *N* 13.8, PCH*Me*].

[§] *Crystal data* for (**3a**): Violet plates (from hexane), *M* = 623.21; triclinic, space group $P\bar{1}$, *a* = 8.943(4), *b* = 10.087(5), *c* = 15.909(8) Å, α = 78.41(4), β = 84.65(4), γ = 75.74(4)°, *U* = 1361.0 Å^3, *Z* = 2; Syntex $P2_1$ diffractometer, Mo-K_α radiation, graphite monochromator, $5° \leq 2\theta \leq 52°$, 5353 reflections, Patterson method (Syntex XTL), H-positions from difference Fourier syntheses, full matrix least squares refinement, H-atoms refined isotropically; *R* = 0.025, R_w = 0.039 for 5185 structure factors; $F_o > 3.92\ \sigma(F_o)$, 437 variables. Atomic co-ordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.

length of 1.868(9) Å in Ir(=CH_2)[N($SiMe_2CH_2PPh_2$)$_2$]}[7] supports the formal analogy between vinylidene metal complexes and allenes.[8] It is worth mentioning that the Ir–C(1) distance is slightly shorter [1.764(6) *vs.* 1.775(6) Å] than that in the structurally related rhodium compound, *trans*-[RhCl(=C=CHMe)(PPr^i_3)$_2$].[4]

The parent member of the square-planar vinylidene iridium complexes, (**3e**), has also been obtained by a completely unexpected route. Following the discovery that the 14-electron compound RhCl(PPr^i_3)$_2$ reacts with C_5H_5Rh(=C=CH_2)PPr^i_3 (**5**) to produce a dinuclear hydrido-bridged Rh_2 product,[9] we were interested to find out whether the analogous iridium species IrCl(PPr^i_3)$_2$ (**6**) behaves similarly. The reaction of (**5**) with (**6**) leads, however, to the formation of complex (**3e**), *i.e.* a transfer of the vinylidene ligand from Rh to Ir takes place. The composition of the rhodium containing product was not elucidated. To the best of our knowledge, there is only one example in the literature of a transfer of a substituted vinylidene, :C=CHPh, from one metal (Mn) to another (Re),[10] but this reaction does not occur cleanly and gives only a low yield (4%) of the product.

In the reaction of (**5**) with (**6**), we assume that a dinuclear vinylidene bridged compound [C_5H_5(PPr^i_3)Rh(μ-C=CH_2)IrCl(PPr^i_3)$_2$] is formed as an intermediate which in contrast with related dinuclear Rh–Mn and Rh–Cr complexes such as [C_5H_5(PPr^i_3)Rh(μ-C=CH_2)(μ-CO)Mn(CO)C_5H_5] and [C_5H_5(PPr^i_3)Rh(μ-C=CH_2)(μ-CO)Cr(CO)C_6H_6],[11] reacts further to give (**3e**). It should be mentioned that :C=CH_2 transfer from (**5**) to cyclopentadiene has also been achieved thus allowing the characterization of bicyclo[3.1.0]hex-2-ene as a new C_7H_8 isomer.[12]

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