

Iridium(I), -(III), and -(V) Complexes of an O-Donor Ligand in Alkyne Hydrosilylation

Robin S. Tanke and Robert H. Crabtree

Yale Chemistry Department, 225 Prospect St., New Haven, CT 06511, USA

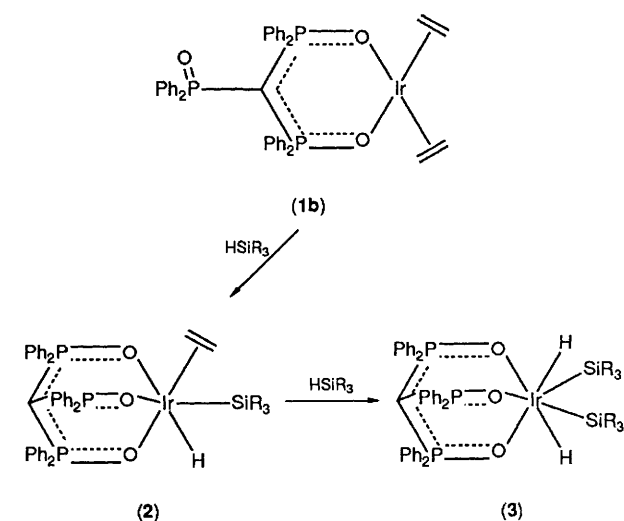
The O-donor ligand $C(Ph_2PO)_3^-$ (triso) stabilises iridium(I), -(III), and -(V) species such as $[(triso)IrH_2(SiMePh_2)_2]$; the complexes catalyse the net *anti*-addition of silanes to alkynes.

P- and C-Donor ligands dominate organometallic chemistry and homogeneous catalysis. The harder O-donor ligands are rarely able to stabilise organometallic compounds,¹ or promote catalytic activity,² even though metal crystallites and organometallic precursors supported on metal oxide surfaces are often catalytically active.³

We find that Grim's⁴ $Na[C(Ph_2PO)_3]$ (= Na[triso]) reacts with $[Ir(coe)_2Cl]_2$ (coe = cyclo-octene) in tetrahydrofuran (THF) at 25 °C for 4 h to give $[(triso)Ir(coe)_2]$ (**1a**) (76%).[†] Complex (**1a**) in hexanes reacts with C_2H_4 (1 atm; 1 h) to give $[(triso)Ir(C_2H_4)_2]$ (**1b**) (65%), isolated by cooling to -10 °C. Complexes (**1a**) and (**1b**) probably have the η^2 -triso structure shown in Scheme 1 [³¹P NMR (CD_2Cl_2 ; 85% H_3PO_4 reference): δ 45 (2P, d, J_{PP} 21 Hz) and 26 (1P, t, J 21 Hz)].

Complex (**1b**) reacts with Ph_3SiH in CH_2Cl_2 for 30 min to give $[(triso)Ir(C_2H_4)H(SiPh_3)]$ (**2**)⁵ (42%). ¹H NMR shows the hydride at δ -24.8 [³¹P NMR (CD_2Cl_2): δ 23.5 (2P) and 48.5 (1P, br)]. The triso is probably η^3 because Ir^{III} hydrides are usually 18 electron. The less bulky and more donating silane Ph_2MeSiH reacts with (**1b**) to give $[(triso)IrH_2(SiPh_2Me)_2]$ (**3**) (48%). Such double oxidative additions are rare. Complex (**3**) has a classical 7-co-ordinate structure because the ¹H NMR of $[(triso)IrHD(SiPh_2Me)_2]$ shows no HD coupling, ruling out (η^2 -H₂) structures,⁵ and (**3**) shows no SiH coupling ruling out (η^2 -HSiR₂R') structures.⁶ Complex (**3**) is fluxional, showing only one ³¹P NMR resonance at δ 23.6. Ir^V species are rare, although the pentamethylcyclopentadienyl analogue of (**3**) is known.⁷

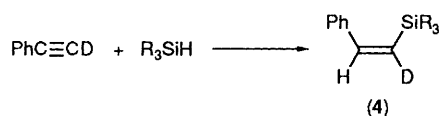
Complexes (**1**)–(**3**) are all catalytically active, even at ambient temperatures. For example, they catalyse the hydrosilylation of $PhC\equiv CH$ with Et_3SiH [70 turnovers/h at 25 °C for (**1a**) in CH_2Cl_2]. Unexpectedly, the vinylsilane (**4**) is formed by a net *anti*-addition of SiH to the $C\equiv C$ bond to give the thermodynamically less stable *cis*-isomer (99.2% *cis*). Prolonged contact with the catalyst leads to isomerisation to the more stable *trans*-isomer. Net *trans*-addition to an alkyne has been observed previously⁸ but in no case has a *cis/trans* ratio greater than 5 been reported.[‡] Isotope labelling (Scheme 2) showed that the methyne CH is not scrambled in the reaction.



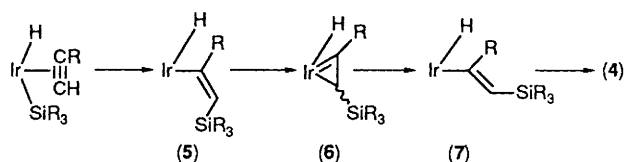
Scheme 1

[†] The compounds were characterized by microanalytical and ¹H, ¹³C, and ³¹P NMR and IR spectral data: (**1a**) ¹H NMR ($CDCl_3$; 250 MHz) δ 7.9–7.7 (m, 8H, Ph), 7.4–7.0 (m, 22H, Ph), and 1.2–2.0 (m, 28H, coe); (**1b**) ¹H NMR δ 7.75–7.55 (m, 8H, Ph), 7.4–7.0 (m, 22H, Ph), and 2.5 (s, 8H, ethylene); (**2**) ¹H NMR ($CD_3C_6D_5$) δ 7.95–7.70 (m, 18H, Ph), 7.0–6.8 (m, 27H, Ph), 3.31 (m, 2H, ethylene), 2.30 (m, 2H, ethylene), and -24.78 (s, 1H, Ir-H); (**3**) ¹H NMR (C_6D_6) δ 8.0 (br., 4H, Ph), 7.64–7.61 (m, 16H, Ph), 7.06–7.03 (m, 13H, Ph), 7.02–6.7 (m, 17H, Ph), 0.88 (s, 6H, Me), and -20.96 (s, 2H, Ir-H).

[‡] I. Ojima (Stony Brook) has unpublished data on a system which gives ca. 95% *anti*-addition (personal communication, 1990).



Scheme 2



Scheme 3

One mechanism (Scheme 3) is consistent with all the observations and resembles one proposed previously.⁹ In an intermediate like (2), the alkyne inserts into the M–Si bond. The resulting 16-electron vinyl (5) rearranges to the sterically less hindered isomer (7), which leads to the observed product on reductive elimination. Green¹⁰ has noted that 16e vinyls rearrange readily to the η^2 -form and so (6) provides a reasonable intermediate for the conversion of (5) to (7). Further work will be required to test this proposal.

O-Donor ligands can thus stabilise iridium-(I), -(III), and -(V) and promote high catalytic activity. The almost exclusive net *anti*-addition of silane to the C≡C bond should be synthetically useful.

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