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

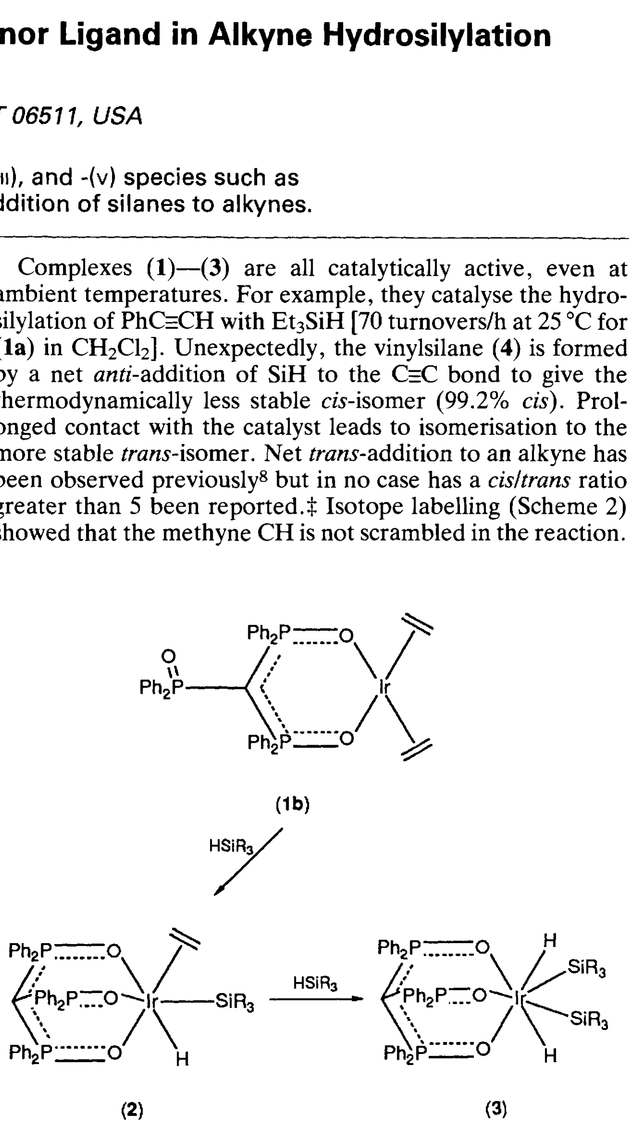
The *O*-donor ligand $C(Ph_2PO)_3^-$ (triso) stabilises iridium-(I), -(III), and -(V) species such as $[(triso)IrH_2(SiMePh_2)_2]$; the complexes catalyse the net *anti*-addition of silanes to alkynes.

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's[4] $Na[C\{Ph_2PO\}_3]$ (= 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 [^{31}P 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%). ^{1}H NMR shows the hydride at δ −24.8 [^{31}P 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 ^{1}H NMR of $[(triso)IrHD(SiPh_2Me)_2]$ shows no HD coupling, ruling out (η^2-H_2) structures,[5] and (**3**) shows no SiH coupling ruling out (η^2-$HSiR_2R'$) structures.[6] Complex (**3**) is fluxional, showing only one ^{31}P 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≡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≡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 previously[8] 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.

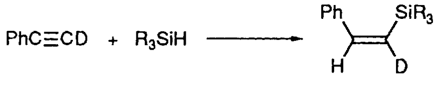


Scheme 1

---

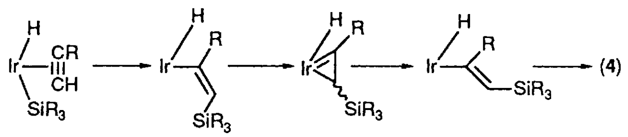
† The compounds were characterized by microanalytical and ^{1}H, ^{13}C, and ^{31}P NMR and IR spectral data: (**1a**) ^{1}H NMR ($CDCl_3$; 250 MHz) δ 7.9—7.7 (m, 8H, Ph), 7.4—7.0 (m, 22H, Ph), and 1.2—2.0 (m, 28H, coe); (**1b**) ^{1}H NMR δ 7.75—7.55 (m, 8H, Ph), 7.4—7.0 (m, 22H, Ph), and 2.5 (s, 8H, ethylene); (**2**) ^{1}H 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**) ^{1}H 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).



(4)

Scheme 2



(5) (6) (7)

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. Green[10] 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.

We thank the NSF for funding and P. Demou for experimental assistance.

Received, 12th April 1990; Com. 0/01645D

References

1 R. E. LaPointe, P. T. Wolczanski, and G. D. Van Duyne, *Organometallics*, 1985, **4**, 1810; M. H. Chisholm, D. M. Hoffman, and J. Huffman, *Chem. Soc. Rev.*, 1985, **14**, 69; C. J. Besecker and W. G. Klemperer, *J. Am. Chem. Soc.*, 1980, **102**, 7598; V. W. Day, C. J. Besecker, and W. G. Klemperer, *ibid.*, 1982, **104**, 6158; V. W. Day, C. W. Earley, W. G. Klemperer, and D. Maltbie, *ibid.*, 1985, **107**, 8261; D. J. Edlund, R. J. Saxton, D. K. Lyon, and R. G. Finke, *Organometallics*, 1988, **7**, 1692; W. Kläui, A. Müller, W. Eberspech, R. Boese, and I. Goldberg, *J. Am. Chem. Soc.*, 1987, **109**, 164; F. J. Feher, *ibid.*, 1986, **108**, 3851; V. W. Day, C. J. Besecker, and W. G. Klemperer, *Organometallics*, 1985, **4**, 564; C. J. Besecker and W. G. Klemperer, *J. Organomet. Chem.*, 1981, **205**, C31.

2 Except in cases where dissociation of *O*-donor ligand is evident and homogeneity ambiguous: A. J. Cornish, M. F. Lappert, G. L. Filatos, and T. A. Nile, *J. Organomet. Chem.*, 1979, **172**, 153.

3 Yu. I. Yermarkov, B. N. Kuznetsov, and V. Zakharov, 'Catalysis by Supported Complexes,' Elsevier: Amsterdam, 1981; D. G. H. Ballard, *Adv. Catal.*, 1973, **23**, 263; J. Schwartz, *Acc. Chem. Res.*, 1985, **18**, 302 and references cited; B. C. Gates and H. H. Lamb, *J. Mol. Catal.*, 1989, **52**, 1.

4 S. O. Grim, S. A. Sangokoya, I. J. Colquhoun, W. McFarlane, and R. K. Khanna, *Inorg. Chem.*, 1986, **25**, 2699.

5 A few other ethylene silylhydrides are known: G. Bellachioma, G. Cardaci, E. Colomer, R. J. P. Corriu, and A. Vioux, *Inorg. Chem.*, 1989, **28**, 519; J. Ruiz, P. O. Bentz, B. E. Mann, C. M. Spencer, B. F. Taylor, and P. M. Maitlis, *J. Chem. Soc., Dalton Trans.*, 1987, 2709; S. B. Duckett, D. M. Haddleton, S. A. Jackson, R. N. Perutz, M. Poliakoff, and R. K. Upmacis, *Organometallics*, 1988, **7**, 1526.

6 G. J. Kubas, R. R. Ryan, B. I. Swanson, P. J. Vergamini, and H. J. Wasserman, *J. Am. Chem. Soc.*, 1984, **106**, 451.

7 U. Shubert, J. Müller, and H. G. Att, *Organometallics*, 1987, **6**, 469.

8 M.-J. Fernandez and P. M. Maitlis, *J. Chem. Soc., Dalton Trans.*, 1984, 2063.

9 K. A. Brady and T. A. Nile, *J. Organomet. Chem.*, 1981, **206**, 299; H. M. Dickers, R. N. Haszeldine, A. P. Mather, and R. V. Parish, *ibid.*, 1978, **161**, 91; I. Ojima, M. Kumagai, and Y. Nagai, *ibid.*, 1974, **66**, C14; D. C. Apple, K. A. Brady, J. M. Chance, N. E. Heard, and T. A. Nile, *J. Mol. Catal.*, 1987, **42**, 195.

10 S. R. Allen, R. G. Beevor, M. Green, N. C. Norman, A. G. Orpen, and I. D. Williams, *J. Chem. Soc., Dalton Trans.*, 1985, 435.