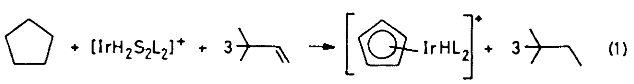
π-Arene Complexes as Unexpected Deactivation Products in Alkane Activation and Alkene Hydrogenation Reactions

By Robert H. Crabtree,* Michelle F. Mellea, and Jennifer M. Quirk

(*Sterling Chemistry Laboratory, Yale University, New Haven, CT* 06511)

Summary Styrene reacts with complexes $[IrH_2S_2L_2]BF_4$ to give $[Ir(\eta^6\text{-}PhEt)L_2]BF_4$ (S = H_2O or Me_2CO; L = PPh_3): this accounts for the failure of styrene to act as a hydrogen acceptor in our related alkane activation system, and may account for the anomalously low hydrogenation rates observed for styrene using $[Ir(cod)(PMePh_2)_2]PF_6$ as catalyst precursor.

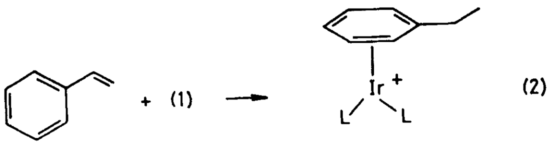
We have recently described the first system in which simple alkanes can be selectively dehydrogenated under mild conditions, equation (1).[1] The choice of hydrogen acceptor (2) is critical. An alkene containing an allylic hydrogen is dehydrogenated in preference to the alkane; for example, cyclo-octane gives $[Ir(cod)L_2]^+$ (cod = cyclo-octa-1,5-diene). Styrene, however, has no allylic hydrogens, but still fails to act as a hydrogen acceptor in this reaction. We set out to understand why this is so, and have discovered the first example of an unexpected reaction in which complex (**1**) reacts with styrene and its derivatives, but not with other arenes, to give π-arene complexes.



(1) (2) (3)

(S = Me2CO or H2O; L = PPh3)

Styrene (10 mol. equiv.) reacts with the tetrafluoroborate salt of (**1**) in CH_2Cl_2 at 25 °C over 5 min to give an orange solution, from which the orange, microcrystalline complex (**4**) (as its BF_4^- salt) can be isolated with Et_2O, equation (2).



(4)

Recrystallisation from CH_2Cl_2–Et_2O gives 94% of an analytically pure material.

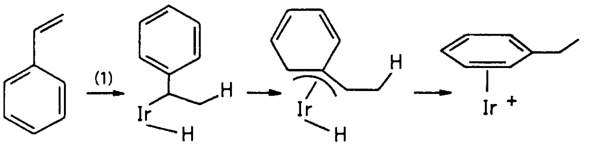
The ^1H n.m.r. spectrum (25 °C, $CDCl_3$) of (**4**) is as follows: δ 1·2 (t, *J* 8 Hz, CH_3), 2·5 (q, *J* 8 Hz, CH_2), 5·0 (d, *J* 6 Hz, *ortho*-H), 5·4 (t, *J* 8 Hz, *meta*-H), 7·1 (t, *J* 6 Hz, *para*-H), and 7·2 (complex, PPh_3). Decoupling experiments confirmed these assignments.

The reaction seems to be intramolecular because (**4**), not the corresponding toluene complex, is formed when reaction (2) is carried out in the presence of toluene. The deuterium analogue of (**1**), $[IrD_2S_2L_2]^+$, reacts with styrene to give $[Ir(\eta^6\text{-}C_6H_5CHDCH_2D)L_2]^+$ even in the presence of 10 mol. equiv. $CH_3CH_2C_6H_5$. ^2H N.m.r. spectroscopy confirms that the deuterium is equally distributed between the 1- and 2-positions of the side chain.

In contrast with rhodium–arene complexes,[2] the arene in (**4**) is not labile; for example, the ethylbenzene is not substituted by benzene (100 mol. equiv.) after 4 h at 25 °C. It is therefore not surprising that styrene is inactive as a hydrogen acceptor in reaction (**1**).

Other arenes behave similarly, stilbene and α-methylstyrene giving the analogous products in similar yields.

The mechanism, equation (3), presumably involves the intermediacy of an η^3-benzyl complex, of which several examples are known.[3]



(3)

These observations probably also explain the anomalously low hydrogenation rates we observed for styrene using $[Ir(cod)L_2]PF_6$ (L = $PMePh_2$) as catalyst.[4] We have detected (^1H n.m.r.) an η-ethylbenzene complex analogous to (**4**) as the product of hydrogenation of (**1**) in the presence of styrene, but have not yet been able to isolate it in a pure state. Styrene and its derivatives may therefore not always be a good choice of substrate for catalytic studies.

We thank the Petroleum Research Fund and the National Science Foundation for funding, and the A. P. Sloan Foundation for a Fellowship (to R. H. C.).

(*Received*, 10*th August* 1981; *Com.* 966.)

---

[1] R. H. Crabtree, J. M. Mihelcic, and J. M. Quirk, *J. Am. Chem. Soc.*, 1979, **101**, 7738.

[2] J. Halpern, D. P. Riley, A. S. C. Chan, and J. J. Pluth, *J. Am. Chem. Soc.*, 1977, **99**, 8055.

[3] J. S. Roberts and J. K. Klabunde, *J. Organomet. Chem.*, 1975, **85**, C13.

[4] G. E. Morris, Thèse, Orsay, 1976; R. H. Crabtree, H. Felkin, and G. E. Morris, *J. Organomet. Chem.*, 1977, **141**, 205.