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# Neighboring Group Participation of Halo and Aryl Groups in the Stoichiometric and Catalytic Reactions of Olefins with Transition-Metal Hydrides and a New Route to Arene Complexes

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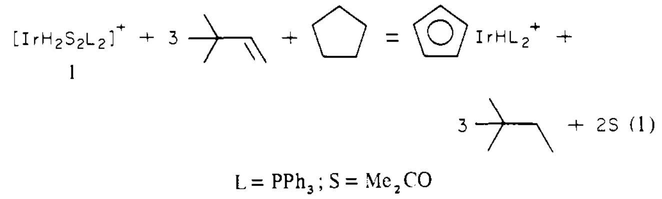
**Abstract:** $[IrH_2(Me_2CO)_2(PPh_3)_2]BF_4$ (**1**) reacts with $ArCH{=}CH_2$ to give $[Ir(\eta^6\text{-}ArEt)L_2]BF_4$ (**2**, Ar = Ph, 2,6-$Me_2C_6H_3$, *p*-$MeOC_6H_4$, $PhCH_2$, $Ph(CH_2)_2$, 2,6-$Cl_2C_6H_3$, and 2-$XC_6H_4$ {X = Cl, or Br}). For the first three substrates, a neighboring group participation of the aryl group via an $\eta^3$-benzyl intermediate is proposed. For the next two, isomerization takes place to give a styrene derivative which then reacts as above. For the halogen-containing substrates the unusual intermediates $[IrH_2(\eta^3\text{-}XC_6H_4CH{=}CH_2)L_2]BF_4$ are observed, in which the substrate chelates to the metal via the (C═C) and halo groups. These are rare examples of both a halocarbon complex and an olefin dihydrido complex. The high branched:linear isomer ratios generally observed in the hydroformylation and hydrosilation of styrene are interpreted in terms of neighboring group participation via an $\eta^3$-benzyl intermediate. Halo and aryl groups are suggested as candidtates for study in connection with directing effects and asymmetric induction in homogeneous catalysis.

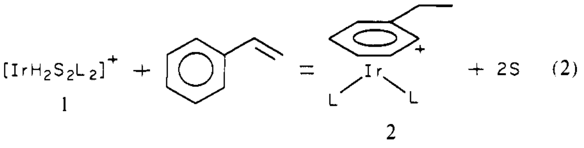
One of the most persuasive cases for the use and study of homogeneous rather than heterogeneous catalysts is the superior selectivity often shown by homogeneous systems. This is an important property in a variety of applications because it makes expensive or tedious purification steps unnecessary and avoids the loss of product inherent in an unselective process. The question that arises is whether the factors leading to high selectivity can be understood, to help in what might otherwise be an empirical search for selective homogeneous catalysts.

The purpose of this paper is to emphasize the importance of a neighboring group participation in determining selectivity and to describe this effect for halo and aryl groups, which up to now might now have been considered unpromising candidates. We shall first describe the chemistry and then discuss its implications.

## Results

During attempts to dehydrogenate alkanes with $[IrH_2S_2L_2]BF_4$[1] (**1**, S = $Me_2CO$; L = $PPh_3$) we screened a large number of olefins as hydrogen acceptors for the reaction (eq 1). The most successful hydrogen acceptor was *tert*-butylethylene, but a number of apparently equally suitable alkenes failed, e.g., styrene. In order to find out why this was so, we looked at the reaction of various vinylarenes with **1** and found the unexpected reaction[2] shown in eq. 2, which constitutes a novel route to arene complexes. The new complexes **2** were ineffective in alkane dehydrogenation under the conditions of eq 1, accounting for the failure of vinylarenes as hydrogen acceptors.





The reactions of eq 2 generally went in $CH_2Cl_2$ at room temperature over 30 s in 80–97% yield. They were accompanied by a color change from colorless to orange. The addition of $Et_2O$ at this stage led to the isolation of the new complexes. These air-stable microcrystalline orange fluoroborate salts were readily recrystallized from $CH_2Cl_2/Et_2O$.

The identity of the products followed from the spectroscopic data in Table I. Taking the example of $[Ir(\eta^6\text{-}PhEt)L_2]BF_4$ (**2**), the IR spectrum ($CDCl_3$ solution) showed aliphatic C–H vibrations at 2927 $cm^{-1}$ and the B–F vibrations at 1061 $cm^{-1}$. The $^1H$ NMR spectrum showed strong coordination shifts of the $\eta^6$-ring protons but only minor shifts in the ethyl side chain.[3] The resonance positions ($\delta$) of the PhEt group together with the coordination shifts (ppm) (in parentheses) from free PhEt were as follows: 1.3 (+0.005) Me; 2.6 (−0.08) $CH_2$; 5.0 (2.2) *o*-CH; 5.4 (1.8) *m*-CH; 6.9 (−0.3) *p*-CH. The identity of each resonance was confirmed by decoupling experiments. The low coordination shifts we observe for the ethyl side chain suggest this group is not interacting with the metal. The other $\eta^6$-arene complexes gave similar spectra.

**Mechanism.** In order to check that the hydrogen incorporated in the styrene really does come from **1**, we studied the reaction using $[IrD_2S_2L_2]BF_4$ ($d^2$-**1**). The product was entirely $d^2$-**2** as confirmed by $^2H$ NMR and IR. In particular, the $^2H$ NMR of $d^2$-**2** showed two peaks of equal intensity at $\delta$ 1.2 and 2.5 as expected.

An external arene did not interfere with the reaction; for example, no $\eta^6$-styrene complex was ever seen even though reaction 2 was run in a large excess of styrene, nor was any $\eta^6$-toluene complex seen in the presence of a large excess of toluene in the solvent medium. Finally, no $\eta^6$-ethylbenzene complex was formed from **1**, *tert*-butylethylene, and ethylbenzene under similar conditions. The aryl and vinyl groups must be present in the same molecule for the reaction to occur, therefore this is an authentic example of neighboring group participation.[4]

**Other Vinylarenes.** We were interested to know how far the side chain could be extended and still give the $\eta^6$-arene product. Allylbenzene, $PhCH_2CH{=}CH_2$, reacts under the same conditions as styrene to give the analogous $\eta^6$-propylbenzene product. At first sight, therefore, the reactions might seem to go via $PhCH_2CH(CH_3)[Ir]$ (where [Ir] represents the metal and asso-

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[1] Crabtree, R. H.; Mihelcic, J. M; Quirk, J. M. *J. Am. Chem. Soc.* **1979**, *101*, 7738; **1982**, *104*, 107.

[2] Crabtree, R. H.; Mellea, M. F.; Quirk, J. M. *J. Chem. Soc., Chem. Commun.* **1981**, 1217.

[3] Haines, L. M. *Inorg. Chem.* **1971**, *10*, 1685.

[4] Page, M. I. *Chem. Soc. Rev.* **1973**, *2*, 295.

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Table I. Spectral, Analytical, and Yield Data for the New Complexes

| arene[a] | product[b] complexes | time,[c] temp (°C) | yield,[d] % | $^1$H NMR[e] | analysis,[f] % C | analysis,[f] % H | solvent of cryst[g] |
|---|---|---|---|---|---|---|---|
| $PhCH{=}CH_2$ | 2 | 30 s | 97 | 1.3, t (8), Me: 2.6, q (8), $CH_2$; 5.0, d (6), *o*-H: 5.4, dd (6, 8), *m*-H; 6.9, dd (6, 8) *p*-H[h] | 58.57<br>(58.72) | 4.56<br>(4.45) | |
| $PhCH_2CH{=}CH_2$ | 2 | 30 s | 93 | 0.9, t (7), Me: 1.5, c, $\beta$-$CH_2$: 2.5, t (8), $\alpha$-$CH_2$: 5.0, d (6.5), *o*-H; 5.5, dd (5.3, 6.6), *m*-H: 6.9, t (5.3), *p*-H | 56.54<br>(56.63) | 4.61<br>(4.46) | 0.5 |
| $Ph(CH_2)_2CH{=}CH_2$ or $PhCH_2CH{=}CHCH_3$ | 2 | 30 s | 91 | 1.09, t (8), Me: 1.35, c, $\beta$- and $\gamma$-$CH_2$; 2.45, c, $\alpha$-$CH_2$: 4.94, d (5.4), *o*-H; 5.41, t (7), *m*-H | 56.10<br>(56.06) | 4.78<br>(4.55) | 0.75 |
| *trans*-$PhCH{=}CHPh$ or<br>*cis*-$PhCH{=}CHPh$ | 2 | 30 s<br>2 h | 88<br>85 | 2.67, c, $CH_2$; 4.85, d (6.8), *o*-H; 5.39, dd (6, 8), *m*-H; 6.96, t (6.8), *p*-H | *j* | | |
| 2,6-$Me_2C_6H_3CH{=}CH_2$ | 2 | 30 s | 94 | 1.03, t (8.1), Me: 2.55, q (8.1), $CH_2$: 2.17, s, *o*-Me; 5.17, d (7.5), *m*-H: 5.45, t (7.5), *p*-H | 57.49<br>(57.61) | 4.62<br>(4.62) | 0.33 |
| $PhC(Me){=}CH_2$ | 2 | 30 s | 93 | 1.49, c, Me; 2.84, c, $\alpha$-CH; 5.08 and 5.37, c, *o*- and *m*-H | 56.99<br>(57.20) | 4.52<br>(4.48) | 0.33 |
| *p*-$MeOC_6H_4CH{=}CH_2$ | 2 | 5 min | 80 | 1.09, t (8), Me; 2.49, q (8), $CH_2$: 3.78, s, MeO; 4.53, d (6.5), *m*-H; 5.4, d (6.6), *o*-H[k] | 53.86<br>(54.49) | 4.51<br>(4.34) | 1.0 |
| 2,6-$Cl_2C_6H_3CH{=}CH_2$ | 5 | 15 min | 83 | −26.3, dt (7.2,[l] 14.4[m]), $IrH_F$;[n] −8.5, dt (7.2,[l] 16.9[m]), $IrH_G$; 3.09, dt (6.4,[m] 10[p]), $H_A$; 3.68, d (10[q]), $H_B$; 5.45, ddd (10,[p] 10,[q] 10[m]), $H_C$: 6.75, d (8), $H_D$; 7.09, t (8), $H_E$ | *j* | | |
| 2,6-$Cl_2C_6H_3CH{=}CH_2$ | 2 | 1 h, 40 | 80 | 1.09, t (7), Me; 2.80, q (7), $CH_2$; 5.21, c, *m*-H; 5.6, c, *p*-H | *j* | | |
| 2-$ClC_6H_4CH{=}CH_2$ | 5 | 20 min, −13 | (quant.) | −26.7, dt (6.6,[l] 13.2,[m]), $IrH_F$;[n] −8.7, dt (6.6,[l] 19[m]), $IrH_G$; 3.13, c, $H_A$: 3.67, d (9.9),[q] $H_B$; 5.21, ddd (10,[p] 10,[q] 10[m]), $H_C$: 6.7, d (8.24), and 6.9, c, $H_D$, and $H_Y$; 7.03, c, $H_D$ or $H_E$ | *j* | | |
| 2-$ClC_6H_4CH{=}CH_2$ | 2 | 20 min | 95 | 1.25, t (8.3), Me; 2.77, q (8.3), $CH_2$: 4.39, d (5), and 4.5, d (6.6), $H_{D'}$, and $H_Y$;[n] 6.8, c, $H_D$ | *j* | | |
| 2-$BrC_6H_4CH{=}CH_2$ | 5 | 20 min, 7 | (quant.) | −25, dt (6.6,[l] 13.2[m]), $IrH_F$;[n] −8.85 dt (6.6,[l] 18.1[m]), $IrH_G$; 3, c, $H_A$; 3.7, dd (3.3,[s] 9[q]), $H_B$; 5.15, ddd (11,[p] 11,[q] 11[m]), $H_C$; 6.8, d (6.6), and 6.9, c, $H_{D'}$. and $H_Y$; 7.06, c, $H_D$ or $H_E$ | *j* | | |
| 2-$BrC_6H_4CH{=}CH_2$ | 2 | 2 h | 90 | 1.24, t (6.6), Me; 2.78, q (6.6), $CH_2$; 4.4, d (6.6), and 4.5, d (6.6), $H_{D'}$, and $H_Y$;[n] 6.8, c, $H_D$ | | | |
| 2-$IC_6H_4CH{=}CH_2$ | 5 | 20 min, 10 | (quant.) | −21.3, dt (6.6,[l] 13.2[m]), $IrH_F$;[n] −9.14, dt (6.6,[l] 18.1[m]), $IrH_G$; 2.9, dd (5,[s] 11.5[p]), $H_A$; 3.7, c, $H_B$; 5.12, c, $H_C$; 6.7, d (6.6), and 7.0, c, $H_D$ and $H_Y$; 7.15, c, $H_D$ or $H_E$ | *j* | | |
| $PhCH{=}CH_2$[t] | 6 | 5 min | (quant.) | 1, t (10.3), Me; 2.3, q (10.3), $CH_2$; 5.1, ct[t] (8.2), *o*-H; 5.52, c, *m*-H;[u] 6.78, c, *p*-H[t] | *j* | | |

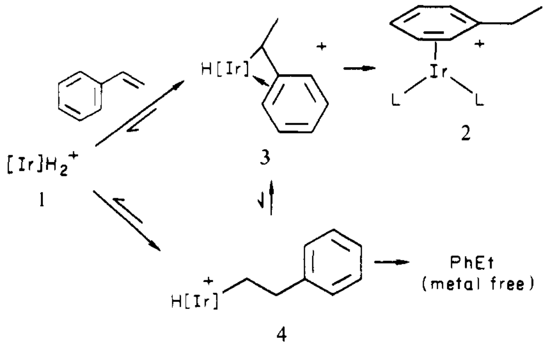
[a] Used in the reaction with 1. [b] Type of complex formed. The colors of the complexes were as follows: 2, orange; **5**, colorless: 6, yellow-orange. [c] Conditions of the formation reaction (at 15 °C unless stated). When the temperature shown was below 15 °C, this was also the temperature at which the $^1$H NMR was recorded. [d] Of purified product, or, when the yield is shown in parentheses, the yield in solution estimated by integration of the appropriate $^1$H NMR spectrum. [e] In $CDCl_3$ at 20 °C (but see footnote *c*). Reported as–position ($\delta$), multiplicity (coupling constant (Hz)), assignment. [f] Calculated values in parentheses. [g] Mol of $CH_2Cl_2$ per iridium atom, by microanalysis and confirmed by $^1$H NMR. [h] $^{13}$C NMR: 15, Me; 27, $CH_2$; 93.6 and 95.4, *p*- and *m*-C; 98.5, ipso-C; 120.7, *o*-C; 128, 128, 130.5, and 134.1, $PPh_3$. [i] $PhCH{=}CHCH_3$ gave comparable results. [j] Not analyzed. In 6 and cases involving haloarenes, the products were not very stable. [k] Spectrum recorded at -60 °C. [l] $^2J(H,H)$. [m] $^2J(H,P)$, confirmed by $^{31}$P decoupling in the case of 2,6-dichlorostyrene. [n] See Figure 1 for assignment key. [p] $^3J(H_A,H_B)$. [q] $^3J(H_B,H_C)$. [r] At 40 °C. [s] $^2J(H_A,H_B)$. [t] Reaction with $]RhH_2(EtOH)_2(PPh_3)_2]PF_6$. [u] Additional couplings identified as $^2J(Rh,H)$ by comparison with the analogous iridium complex.

ciated ligands). A variable-temperature $^1$H NMR study showed that this was not in fact so. $^1$H NMR studies from 160 to 300 K in an NMR tube show that the reaction proceeds via free propenylbenzene, $PhCH{=}CHCH_3$. On warming a mixture of allylbenzene (10 molar equiv) and **1**, the first sign of reaction is seen at 183 K. The hydride resonances of **1** disappear and are replaced by new peaks, including a triplet at −13.6 $\delta$ which may well arise from $[IrH_2(PhCH_2CH{=}CH_2)_2L_2]^+$, since the corresponding styrene complex[2] has almost identical resonances. At 240 K, peaks due to free propenylbenzene appear in the spectrum, and by the time 245 K is reached the whole of the allylbenzene present has been catalytically converted to free propenylbenzene. Only at 290 K do the characteristic peaks of the product $[(\eta^6\text{-}PhPr)IrL_2]^+$ begin to appear. The same product is formed directly when propenylbenzene reacts with **1**.

$Ph(CH_2)_2CH{=}CH_2$ also reacts with **1** to give an analogous complex. Detailed study showed that, as in the case of allylbenzene, isomerization preceded the formation of **2**. This was first observed at 215 K and at 265 K only $\beta$-ethyl styrene was present. Complex **2** was formed above 290 K.

We decided to examine allyl phenyl ether, because in this compound the vinyl group cannot move into conjugation with the ring. At −60 °C the isomerization of the compound to propenyl phenyl ether is so fast that it is complete before the first NMR spectral data can be collected at 215 K. Related isomerizations at higher temperatures have been reported.[5] At room temperature, the acetone complex **1** hydrogenated allyl propenyl ether to give uncharacterizable iridium-containing materials; no trace

Scheme I. The Reactions of $[IrH_2S_2L_2]BF_4$ (1) with Vinylarenes[a]



[a] [Ir] refers to the metal and associated ligands.

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(5) Baudry, D.; Ephritkine, M.; Felkin, H. *Nouv. J. Chim.* **1978**, *2*, 355.

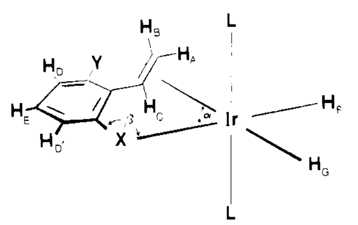


**Figure 1.** The conformation adopted by **5** suggested by studies on molecular models (X = Y = Cl; or X = Cl, Br, I, Y = $H_Y$, L = $PPh_3$).

of an arene complex was observed.

These results give us useful mechanistic information. An iridium attached to a benzylic carbon gives high yields of $\eta^6$-arene complex, but an iridium at a more remote site, as would be the case in the hydrogenation of allyl phenyl ether, gives no $\eta^6$-arene product. It is therefore likely that the intermediate that leads to the arene complex **2** is an $\eta^3$-benzyl complex[6] of type **3**, not a homobenzylic complex of type **4** (Scheme I). This is discussed in more detail below.

Stilbene reacts entirely analogously, but while reaction with the trans isomer is fast (30 s), the cis isomer reacts much more slowly (2 h). 2,6-Dimethylstyrene reacts rapidly (30 s) even though this substrate is hindered. α-Methylstyrene also behaves in the same way. β-Methoxystyrene reacts more slowly (5 min). Either the metal tends to bind unproductively to the methoxy group[7] or it undergoes slower insertion.

**Halostyrenes.** Styrenes substituted with halogens in the 2 position behave very differently from all the others we have studied. For example, 2,6-dichlorostyrene reacts rapidly with **1** at 25 °C but gives a solid on workup which does not have the orange color of the other π-arene complexes. The structure we propose for the product (**5**) is shown in Figure 1. The ${}^1$H NMR spectrum of complex **5** (Table I) shows two inequivalent hydride resonances, which are both mutually coupled ($J_{H_F,H_G}$ = 7.2 Hz) and also coupled to two phosphorus nuclei ($J$(H,P) = 14–17 Hz). The three protons of the coordinated vinyl group can also be seen; two of these are coupled to two phosphorus nuclei (confirmed by ${}^{31}$P decoupling). The aromatic resonances near 7 δ are also observed. Furthermore, the chemical shifts of the IrH groups δ −26.3 ($H_F$) and −8.5 ($H_G$) are consistent with these hydrogens being trans to aryl halide[8] and olefin,[9a] respectively.

The 2-halostyrenes, $o$-$XC_6H_4CH{=}CH_2$, are available for all three halogens (X = Cl, Br, and I). On the ideas presented above, these might well also give complexes of type **5**.

2-Chlorostyrene reacts with **1** at 260 K in $CDCl_3$ in an NMR tube to give a complex of type **5** quantitatively, as judged by the appearance of a spectrum (Table I) closely related to that observed in the case of dichlorostyrene. Similarly, the bromo and iodo analogues at 280 K also gave a high yield of **5**.

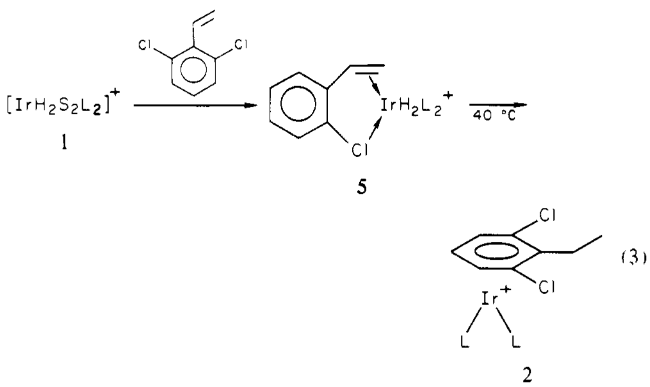
The alternative structure for **5**, $[IrH_2(\eta^4\text{-}ArCHCH_2)L_2]^+$, in which the vinylarene binds via four contiguous carbon atoms, is ruled out by the following considerations. The hydride ligand trans to the vinyl group, $H_G$, changes its resonance position very little ($C_8H_6Cl_2$, δ −8.5; $C_8H_7Cl$; δ −8.7; $C_8H_7Br$, δ −8.85; $C_8H_7I$, δ −9.14) and has a chemical shift close to that observed in other cases where C=C groups are trans to H in Ir(III) complexes (typical range: δ 9–14). The hydride resonance trans to X is in a quite different position; this would not be expected on the basis of the alternative structure mentioned. The exact resonance position varies as a function of the nature of the trans group X ($C_8H_6Cl_2$ (X = Cl), δ −26.3; $C_8H_7Cl$ (X = Cl), δ −26.7; $C_8H_7Br$ (X = Br), δ −25; $C_8H_7I$ (X = I), δ −21.3) and is close to the range observed for halocarbon ligands (δ 16.5–23). The $o$-chloro groups hinder the vinyl group to such an extent that the planar conformer of free 2,6-dichlorostyrene is expected to be very unfavorable. If it were to act as an $\eta^4$-ligand, dichlorostyrene would have to be nearly planar. Finally, no trace of an intermediate was observed in our studies on any other vinylarene including 2,6-Dimethylstyrene.

These are very unusual examples of isolable dihydrido olefin complexes. At the same time they are also complexes of a halocarbon, of which we recently reported the first crystallographically demonstrated examples[8] in this same iridium system.

As we have pointed out elsewhere[8a] the positive charge on the metal probably prevents oxidative addition of the C–Cl bond to the metal by inhibiting electron transfer. Halocarbons are probably weak σ donors, but some back-bonding into the C–Cl σ* orbital probably helps stabilize the complex.[8b]

More surprising perhaps is the fact that **5** is a dihydrido olefin complex. We and others have described other examples,[9] but only those containing the 1,5-cyclooctadiene and related ligands have previously been thermally stable[9a,g] at room temperature. Dichlorostyrene is a monoolefin, and its dihydride complex (**5**) is stable to 40 °C.[10] We imagine this is due to the conformation that must be adopted by the vinylarene (Figure 1). Models show that both the RCl and C=C groups can chelate to the metal if β = 100° (close to the values of 99.9° and 101.8° we have observed[8] in the related structure of $[IrH_2(C_6H_4I_2)(PPh_3)_2]BF_4$) and α = 92° (as expected for octahedral coordination). In addition, the C=C vector may have a ca. 40° inclination to the $IrH_FH_G$ plane. This is probably the reason for the stability of the compound because we have shown that M(C=C)H coplanarity (angle of inclination: 0°) is required for rapid insertion.[9a] Alternatively, the chelating character of the ligand may inhibit insertion.

On heating to 40 °C for 15 min, the dichlorostyrene complex **5** is smoothly converted to the normal $\eta^6$-arene complex **2**. **5** therefore seems to be an intermediate in the conversion if **1** to **2** (eq 3).



(3)

2-Chlorostyrene, on the other hand, completely converts **1** to the $\eta^6$-arene complex after only 20 min at 20 °C. For bromostyrene this takes 2 h at 20 °C. For iodostyrene, in contrast, no complex of type **2** was ever observed. This reactivity order (Cl > Br > I) parallels the stability order of Ir(III) RX complexes that we have previously established.[8] The conversion of the intermediate to the arene complex may perhaps require the dissociation of the halo ligand to give a normal $\eta^2$ metal olefin complex. This would have free rotation of the C=C group so that M(C=C)H coplanarity can be attained. Alternatively, insertion may take place within the chelated intermediate **5**.

In view of these results we closely reexamined the reactions of the other vinylarenes not containing halogen groups. No trace

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(6) Roberts, J. S.; Klabunde, J. K. *J. Am. Chem. Soc.* **1977**, *99*, 2509.

(7) Crabtree, R. H.; Demou, P. C.; Eden, D.; Mihelcic, J. M.; Parnell, C.; Quirk, J. M.; Morris, G. E. *J. Am. Chem. Soc.* **1982**, *104*, 6994.

(8) (a) Crabtree, R. H.; Faller, J. W.; Mellea, M. F.; Quirk, J. M. *Organometallics* **1982**, *1*, 1361. (b) Involvement of a σ* orbital also explains the bent M-Hal-C arrangement found in these complexes,[8a] because this gives better overlap with filled metal d orbitals. (c) A complex Wilkinson[8d] suggested contained a coordinated MeI, now seems only to contain solvent of crystallization and is not a true complex.[8e] (d) Lawson, D. N.; Osborn, J. A.; Wilkinson, G. W. *J. Chem. Soc. A* **1966**, 1733. (e) Troughton, P. G. H.; Skapski, A. C. *J. Chem. Soc., Chem. Commun.* **1968**, 575.

(9) Crabtree, R. H.; Felkin, H.; Khan, T.; Morris, G. *J. Organomet. Chem.* **1978**, *144*, C15; **1979**, *168*, 183. (b) A complex Pennella[9c] suggested was $[RuH_2(C_5H_{10})(PPh_3)_2]$ has now been shown[9d] to be $[RuH_4(PPh_3)_3]$. (c) Pennella, F. *Coord. Chem. Rev.* **1975**, *16*, 51. (d) Cole-Hamilton, D. J.; Wilkinson, G. *Chem. Commun.* **1977**, 59. (e) Hietkamp, S.; Stufkens, D. S.; Vrieze, K. *J. Organomet. Chem.* **1978**, *152*, 347. Clark, G. R.; Clark, P. W.; Jones, A. J.; Mazid M. A.; Russell, D. R. *Ibid* **1979**, *166*, 109. (g) Anton, D. R.; Crabtree, R. H. *Organometallics* **1983**, *2*, 261.

(10) Suitable crystals for X-ray crystallography have not yet been obtained.

of any chelated intermediate was observed by $^1H$ NMR at low temperatures. In the case of styrene, for example, only $[IrH_2(\eta^2\text{-}PhCH{=}CH_2)SL_2]^+$ was observed at low temperature. There was no sign of an $\eta^4$-$PhCH{=}CH_2$ complex nor of an $\eta^3$-$PhCH{=}CH_2$ in which an *o*-CH group could be bonded to the metal.

**Rhodium Analogues.** $[RhH_2S_2L_2]PF_6$ (S = EtOH; L = $PPh_3$) behaves similarly. On warming with styrene in $CDCl_3$ from 213 K, reaction sets in at 233 K and when 293 K is reached the only product present is $[Rh(\eta^6\text{-}PhEt)L_2]PF_6$ (**6**). This was identified by the close analogy of its $^1H$ NMR spectrum (Table I) with that of the iridium analogue **2**. Coupling of the aromatic protons to the rhodium was also detected. The complex was far less stable, however, and was never isolated pure. It decomposes readily to liberate free PhEt. This suggests that **6** may be involved in the $[Rh(cod)L_2]BF_4$-catalyzed hydrogenation of styrene,[11] although we do not know whether there are other paths, not involving the arene complex, which may be faster under catalytic conditions. No rhodium complex of type **5** was ever observed.

**Implication for Catalysis.** One of the most dramatic examples of selectivity in homogeneous catalysis is asymmetric hydrogenation.[12] Hydrogen is added with great selectivity to one side of a prochiral olefin substrate by a chiral catalyst to give a chiral product. A key feature of the process is the presence of a group on the substrate, which, with the C=C group, chelates to the metal. This provides sufficient rigidity and structure to the intermediate to allow efficient interaction of the chiral catalyst with the chiral coordinated substrate.

Brown et al.[13] demonstrated that an OH group can efficiently direct hydrogen to attack one side of a chiral substrate when an achiral rhodium catalyst is used. We and others[14] showed that the more efficient iridium catalyst based on complex **1** could also do this (eq 4) in a wider variety of olefin substrates.

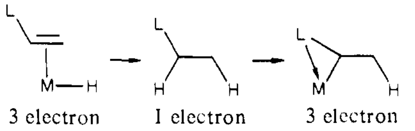
The results described in this paper suggest that under suitable conditions, aryl and halo groups may also be able to play the same role in asymmetric hydrogenation and in directed hydrogenation. We are currently studying these possibilities.

In the insertion reaction of **1** with styrene, there is no evidence for participation of the aromatic ring prior to insertion. Probably the benzylic species **3** is in a fast preequilibrium with the homobenzylic species **4**, the latter being more stable due to its $\eta^3$ structure. The second H transfer would then be slow and probably rate determining (Scheme I). This picture is consistent with the rapid catalytic isomerization of allylbenzene at a temperature 50 C lower than that required to give **2**.

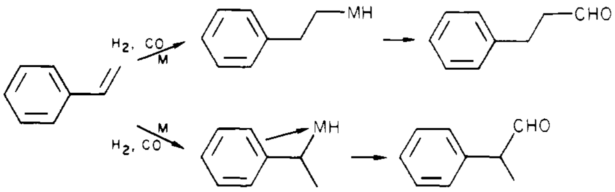
The conversion of an MH(olefin) system to an M(alkyl) system by insertion leaves the metal with two fewer valence electrons. A neighboring arene ring is therefore always permitted by the 18-electron rule to bind to the metal in $\eta^2$ fashion, since this restores the 2-electron deficiency caused by the insertion. Hydrogenation and hydroformylation of vinylarenes by a variety of rhodium complexes probably goes by this route.

This may also account for the anomalous isomer ratios observed in the hydroformylation of styrene.[15] In this reaction, CO insertion labels the carbon to which the metal was attached in the alkyl intermediate (eq 5). The $[Rhcod(PPh_3)_2]PF_6/NEt_3$ catalyst we reported recently[16] hydroformylates *n*-$BuCH{=}CH_2$ to give mostly linear product (branched:linear ratio = 0.33). Styrene gives mostly branched product (ratio = 100). Other catalysts show the same general patern of isomer ratios.[15]

Hydrosilation with $(EtO)_3SiH$ catalyzed by chloroplatinic acid behaves similarly. From 1-hexene essentially only linear product is formed; from styrene the branched:linear ratio is 7.[17]



(4)



(5)

Neighboring group effects may also occur when other substituents are present; $EtOCH{=}CH_2$ also gives an isomer ratio of 7 when subjected to hydrosilation. The addition of 10 molar equiv of certain ligands, such as $PPh_3$ or pyridine, in both of the above cases leads to the formation of linear silanes only.[17] This can be understood in terms of competition between the added ligand and the substrate neighboring group (EtO or Ph) for the metal. The differing electronic effects of Ph, EtO, and Bu groups no doubt play a role; it is difficult to judge the magnitude of this factor,[18] but it is clearly not dominant or the addition of ligands would not reverse the selectivities. Very recently, Tolman et al.[19] have independently developed a similar argument to account for anomalous isomer ratios in the hydrocyanation of styrene.

As discussed in our preliminary note[2], these observations also help explain the anomalously low hydrogenation rates observed in the hydrogenation of styrene with $[Ir(cod)(PMePh_2)_2]PF_6$[20] and the failure of vinylarenes to act as hydrogen-acceptors in eq. 1.[1]

## Conclusion

The reaction of eq 2 constitutes a new route to arene complexes. The proposed mechanism via an $\eta^3$-benzyl species casts light on the abnormal isomer ratios in styrene hydroformylation and hydrosilation. This is an example of neighboring group participation in the olefin insertion reaction. 2-Halostyrenes give an unusual intermediate in which both the C=C and C—Hal groups are coordinated to the metal. These results suggest that aryl and halo groups may be useful neighboring groups for directed and asymmetric hydrogenation.

## Experimental Section

**Reagents.** Ammonium chloroiridate was obtained from Englehard Industries and Johnson Matthey Inc. Ligands were purchased from Aldrich Chemical Co. and distilled before use.

**Spectroscopy.** NMR spectra were recorded on a Bruker 270-MHZ instrument and IR spectra on a Nicolet 7000 series FT model.

**Synthesis.** Starting materials were synthesized by published procedures.[1,11]

**($\eta^6$-Ethylbenzene)bis(triphenylphosphine)iridium(I) Tetrafluoroborate.** To a solution of $[IrH_2(Me_2CO)_2L_2]BF_4$ (100 mg) in $CH_2Cl_2$ (15 mL) was added an excess (0.5 ml) of the arenes shown in Table I. After being stirred 25 °C for the times shown, the $CH_2Cl_2$ was removed in vacuo, the oily product washed with ether/pentane (1:1) to remove the excess arene, and the resulting powder dried in vacuo. Recrystallization from $CH_2Cl_2/Et_2O$ gave the products shown. Spectral and analytical data are also given in Table I. In the case of 2,6-dichlorostyrene, this product was only obtained on heating (1 h, 40 °C).

**Mechanistic Studies.** Reactions run as above but in the presence of toluene (1.1 mmol) gave identical results. In particular, no $[(\eta^6\text{-}PhCH_3)Ir(PPh_3)_2]BF_4$[21] was seen. Reaction of styrene with $d^2$-**1**, as above, gave the complexes $d^2$-**2**, in which the D was evenly distributed between the $CH_2$ and $CH_3$ groups ($^2H$ NMR). However, isotopomers, e.g., $PhCD_2CH_3$, may well have been present. The $^{13}C$ NMR of $d^2$-**2** did

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not give sufficiently intense $CH_2$ or $CH_3$ resonances for interpretation even after 5000 scans even in the presence of Cr(acac)$_3$.

**NMR Studies.** Reactions with allylbenzene and 1-phenyl-3-butene were run in an NMR tube (1, 30 mg; 180 K; olefin 10 mol equiv/Ir; $CD_2Cl_2$ 0.5 mL). The changes described in the text were observed on warming the solution to room temperature for allylbenzene. 1-Phenyl-3-butene isomerized to the corresponding 2- and then 1-butenes below 250 K. Only at 290 K did the resonances of [Ir(BuPh)(PPh$_3$)$_2$]BF$_4$ (see Table I) appear. Allyl phenyl ether isomerized to allyl propenyl ether below 215 K, the lowest temperature studied. The rhodium complex [Rh(PhEt) (PPh$_3$)$_2$]BF$_4$ was observed at 290 K in the reaction of styrene with [RhH$_2$(EtOH)$_2$(PPh$_3$)$_2$]BF$_4$ but was too unstable to be isolated in a pure state.

**Dihydrido($\eta^3$(Cl,C,C)-2,6-dichlorostyrene)bis(triphenylphosphine)iridium(III) Tetrafluoroborate.** The title complex was formed when 2,6-dichlorostyrene was used in the synthesis described above. Spectral and other data are given in Table I. Analogous species were obtained with 2-XC$_6$H$_5$CH=CH$_2$ (X = Cl, Br, and I), but these were only observed by $^1$H NMR. Their thermal instability precluded their isolation in the pure state.

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# Phase-Transfer Reactions Catalyzed by Lipophilic [2.2.2]Cryptands and Dicyclohexano-18-crown-6: Dehydrating Effect of Concentrated Aqueous Alkaline Solutions

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**Abstract:** A study of how the concentration of aqueous KOH affects the hydration and hence the reactivity of anions (Cl$^-$, Br$^-$, I$^-$, SCN$^-$, N$_3^-$) in aliphatic nucleophilic substitutions catalyzed by lipophilic [2.2.2,C$_{10}$]cryptand (**1a**) and dicyclohexano-18-crown-6 (DCH 18C6) (**2**) under phase-transfer conditions is reported. A comparison with the same reactions performed in classical liquid–liquid PTC and homogeneous anhydrous conditions is also included. Unlike quaternary onium salts, even at the highest KOH concentrations (53%; i.e., conditions in which $a_{H_2O} \sim 0$), water in the presence of **1a** is not completely removed. Residual hydration depends on the nature of the anion and is the highest for anions with localized and/or less polarizable charge, such as Cl$^-$, Br$^-$, and N$_3^-$. As a consequence, rate constants noticeably increase in comparison with those found under conventional PTC conditions but do not reach those of anhydrous solutions. The different behavior of cryptates and quaternary salts is discussed on the basis of the different topology of the two systems. Behavior of crown ethers is in between that of quaternary salts and cryptates, since residual hydration in the presence of 53% aqueous KOH is lower than that of cryptates, whereas anionic reactivity becomes practically identical with that found under anhydrous conditions.

The presence of a limited number of water molecules in the organic phase greatly influences reactions performed under liquid–liquid phase transfer catalysis (PTC) conditions.[1-3] In particular the specific hydration of the anions strongly decreases the reaction rates[4-8] and may also influence the outcome of reactions.[9]

Highly concentrated aqueous solutions of KOH or NaOH were found to be an effective system for ensuring an anhydrous organic phase under liquid–liquid PTC conditions in the presence of quaternary onium salts.[10,11] In this way, unhydrated anions are transferred from the aqueous to the organic phase by quaternary cation Q$^+$; hence, the anionic reactivity becomes identical with that found under anhydrous homogeneous conditions.[10] The main disadvantage of this system is that quaternary onium salts are easily decomposed by the strongly alkaline solution, in some cases even at room temperature.[10,12,13]

Lipophilic cryptands or crown ethers are effective phase-transfer agents;[1-3,7,8] moreover, they are chemically stable even in the presence of strongly alkaline aqueous solutions. Therefore, it was of interest to determine whether the dehydrating effect of these alkaline solutions also works for cryptands and crown ethers.

Here we report a study of how the concentration of aqueous KOH affects the hydration and hence the reactivity of anions (Cl$^-$, Br$^-$, I$^-$, SCN$^-$, N$_3^-$) in aliphatic nucleophilic substitutions, catalyzed by [2.2.2,C$_{10}$]cryptand (**1a**) or by dicyclohexano-18-crown-6

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