Hydrogen Transfer and C–H Activation in a Dihydroiridium Amido-alkene Complex

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Dihydrogen addition to the alkene complex (**5**) is regiospecific and stereoselective; the dihydride mixture is converted into alkyl hydrides and ultimately into a chelation-controlled C–H insertion product (**10**).

All attempts to characterise the putative dihydride formed in the rate-determining step of asymmetric homogenous hydrogenation have failed.[1] Special structural features in the enamide are thought to make hydride migration unusually easy so that the first observed transient is an alkylrhodium hydride.[2] We turned to modified alkene complexes in order to delineate this initial step.

Preliminary experiments showed that the unsaturated amides (**1**)[3] and (**2**)† reacted with the dipamp–rhodium methanol solvate[4] to give stable spectroscopically characterised 1 : 1 complexes, homologous with rhodium enamides. Slow hydrogenation with catalytic turnover was observed at 25 °C. This encouraged a diversion of effort to iridium chemistry, and complexes (**3**) and (**4**) were prepared according to previously defined procedures.[5] The former, but not the latter, reacted with dipamp ($-70\,°C \rightarrow -10\,°C$, 30 min) by specific displacement of one mole of amide (**1**). Complex (**5**) which resulted was treated with H_2 to discharge the red colour ($-70\,°C$, $\leqslant 1$ min) and ^1H or ^{31}P n.m.r. spectra were recorded immediately. These revealed two dihydrides (**6a**) and (**6b**) in the ratio 4 : 1, with Ir–H chemical shifts in the range of -8 to -10 p.p.m. (Table 1). Their structural assignment, with one hydride *trans* to P and one *trans* to CH=CH, was confirmed by preparation of the related mixture (**7a**) + (**7b**), for which close precedents exist.[6] The addition of H_2 is completely regiospecific, and finds parallels in the work of Johnson and Eisenberg.[7] Following their interpretation, the regiochemical preference is ordained by overlap of $\sigma^*(H_2)$ with π^*(CH=CH) as it interacts with the metal d_π-orbital. This in turn raises an interesting analogy with the H_2 addition step in asymmetric hydrogenation, since previous work had considered only the dihydride formed by H_2 addition along the P–Rh–O vector.[1,8] We shall return to a more detailed discussion of this point elsewhere.

On warming the sample of (**6**) to *ca.* $-45\,°C$, partial rearrangement to the isomeric dihydrides (**8a**) and (**8b**) occurred, one of the pair (configuration unspecified) being very strongly predominant ($\geqslant 95\%$). This may be the thermodynamically preferred geometry, as $>50\%$ isomerisation occurs, but the point is not conclusively established since a further rearrangement occurs in competition, giving rise to alkyl hydrides (**9a**) and (**9b**) by hydride migration. They become the dominant components on warming to $-10\,°C$. The observation constitutes the first transformation of a metal–alkene dihydride into an alkylmetal hydride, although both types of intermediates had been observed separately; the related monohydride to alkyl transformation is well precedented.[9]

Around 0 °C a further rearrangement occurs indicated *inter alia* by loss of one N–Me group in the ^1H n.m.r. spectrum and replacement by a diastereotopic N–CH_2. At 25 °C this is the major component ($>90\%$) and its structure (**10**) was determined by n.m.r. spectroscopy, using 2-D COSY and nuclear Overhauser effect (n.O.e) techniques as previously described.[10] The results are delineated in Figure 1, and indicate several features in common with alkyl hydrides derived from iridium enamides.[10] Reductive elimination in (**9**) creates a

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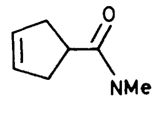
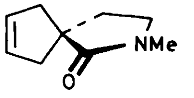
† Compound (**2**) was prepared in a similar manner by successive treatment of *N*-methylpyrrolidone with $LiNPr^i_2$ (-70 to 0 °C), *cis*-1,4-dichlorobut-2-ene (-70 to 0 °C), and $LiNPr^i_2$ (-70 to 25 °C, 16 h). Compounds (**2**), (**3**), and (**4**) were obtained analytically pure and were spectroscopically characterised.

Table 1. N.m.r. spectroscopic parameters of hydride complexes

Complex	^{1}H N.m.r. (Ir–H) δ; J(HP)/Hz; T/°C	^{31}P N.m.r. δ/p.p.m.; J(PP)/Hz	Temp. range observed/°C
(6a) H_a	−9.20; 117, 15.7; −70	Br.	−70 to −25
H_b	−8.73(br.)		
(6b) H_a	−9.48; 120, 15; −43	Br.	−70 to −25
H_b	−8.63; 21, 21		
(7a) H_a	−10.1; 93, 16; −10	Br.	
H_b	−13.7; 18, 18	Br.	
(7b) H_a	−9.8; 90, 17, −10	Br.	
H^b	−13.3; 17, 17		
(8a) H_a	−29.95; 15, 21; −28	33.2, 45.6, br.	−45 to −10
H_b	−7.88; 100, 18		
(8b) H_a	−29.78; br.; −10		−10
H_b	−7.88; 100, 18		
(9a)	−28.66; 19, 10; −25	29.5, 37.5; 17	−45 to −10
(9b)	−28.35; 19, 11; −25	28.3, 35.5; 17.5	−45 to −10
(10)	−28.45; 19, 13; 25	27.4, 35.3; 12	≥0



(1)



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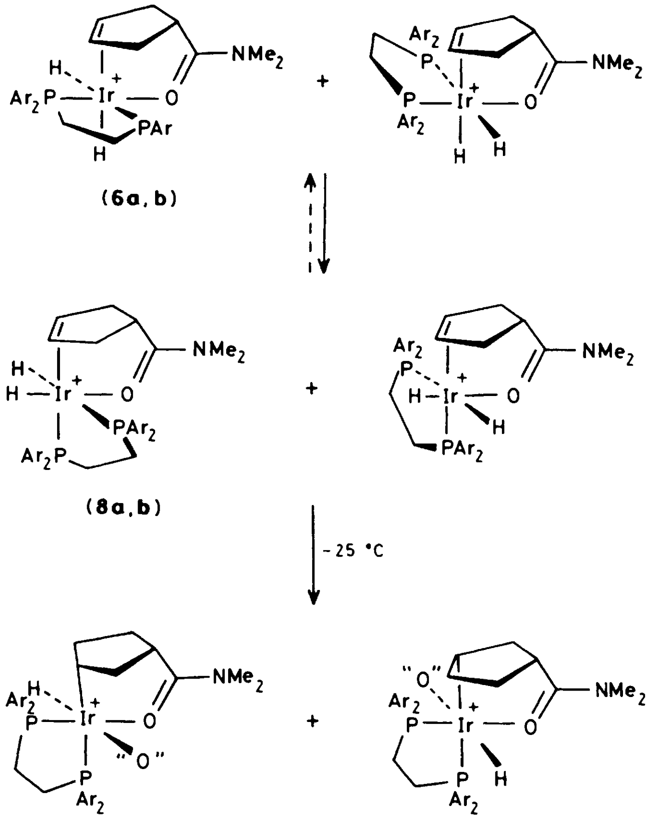
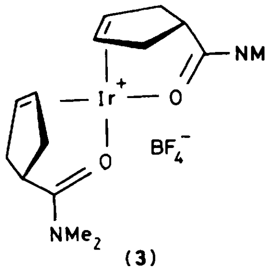


(6a, b)

(8a, b)

(9a, b)



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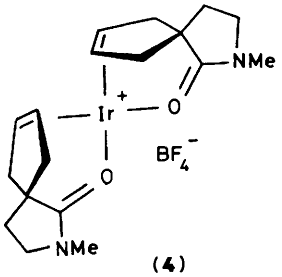

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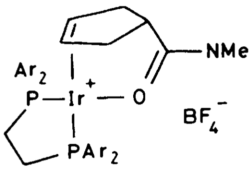

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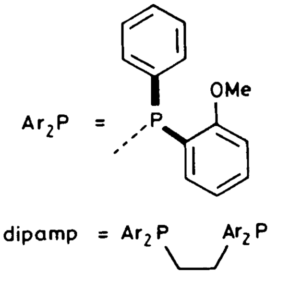
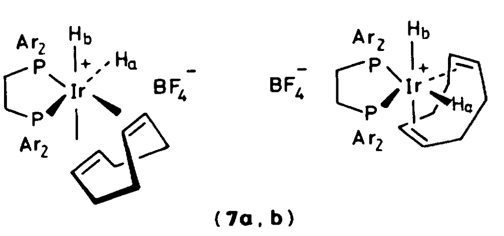
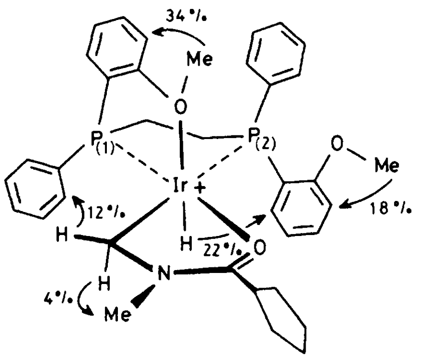




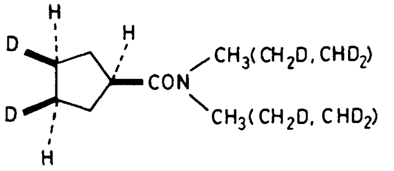
(7a, b)

vacant co-ordination site, leading to intramolecular C–H activation facilitated by the carbonyl group. When D_2 addition to complex **(5)** is effected at ambient temperature, the initial product is ≥80% an iridium hydride deuteriated in the cyclopentane ring. Shaking under D_2 at 20 °C causes immediate H–D exchange, revealed both by the halving of Ir–H intensity and splitting of the O–CH_3 signal at 3.16 p.p.m.[10] When the solution was kept under D_2 for 24 h followed by chromatographic isolation, the recovered cyclopentane **(11)** had the indicated isotope distribution. Exchange occurs

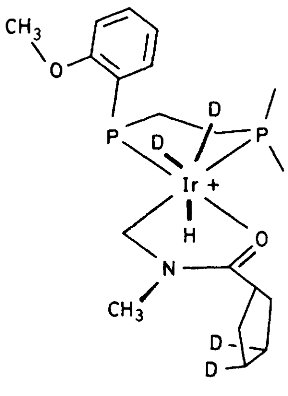


(10)

Figure 1. N.O.e.s for (**10**).



(11)



(12)

through ligand dissociation of OCH_3, D_2 addition to the metal, and internal rearrangement in the putative intermediate (**12**) before loss of HD.[11]

Selective activation of C–H α to an amide nitrogen is novel and indicates participation of the carbonyl oxygen which remains bound to the iridium. It is reminiscent of the directed α-lithiation of amides,[12] such that we expect further parallels between C–H activation by low-valent transition metals, and by organolithium reagents.

Future work will consider chiral analogues of amide (**1**), further to elucidate the origins of enantioselection in the H_2 addition step.

We thank S.E.R.C. for a studentship (to P. J. M.) and Johnson-Matthey for a loan of previous metal salts.

Received, 9th April 1987; Com. 466

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