

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 solvate⁴ 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 → –10 °C, 30 min) by specific displacement of one mole of amide (**1**). Complex (**5**) which resulted was treated with H₂ to discharge the red colour (–70 °C, ≤ 1 min) and ¹H or ³¹P 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 H₂ is completely regio-

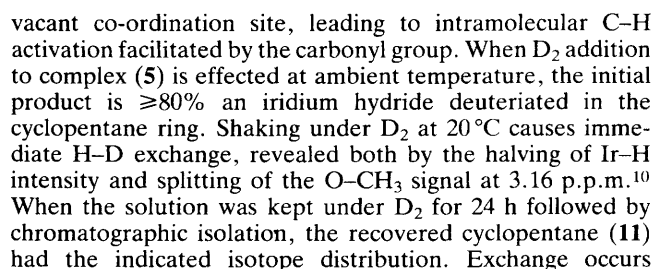
specific, and finds parallels in the work of Johnson and Eisenberg.⁷ Following their interpretation, the regiochemical preference is ordained by overlap of σ*(H₂) with π*(CH=CH) as it interacts with the metal d_π-orbital. This in turn raises an interesting analogy with the H₂ addition step in asymmetric hydrogenation, since previous work had considered only the dihydride formed by H₂ 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 (≥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–CH₂. 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

† Compound (**2**) was prepared in a similar manner by successive treatment of *N*-methylpyrrolidone with LiNPr₂ (–70 to 0 °C), *cis*-1,4-dichlorobut-2-ene (–70 to 0 °C), and LiNPr₂ (–70 to 25 °C, 16 h). Compounds (**2**), (**3**), and (**4**) were obtained analytically pure and were spectroscopically characterised.

Complex	¹ H N.m.r. (Ir–H) δ; <i>J</i> (HP)/Hz; <i>T</i> /°C	³¹ P N.m.r. δ/p.p.m.; <i>J</i> (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



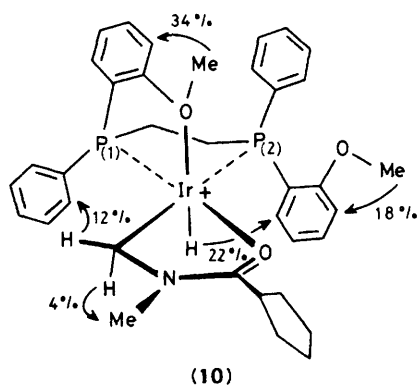
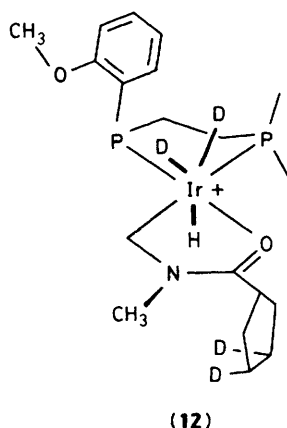
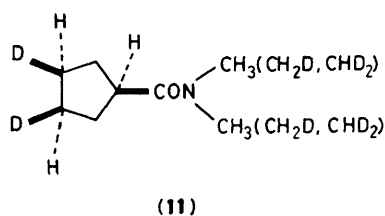


Figure 1. N.O.e.s for (10).



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.

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