Solution Structures of Iridium Alkyl Hydrides pertaining to Asymmetric Hydrogenation

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Alkyliridium hydrides (**3a**) and (**5**) derived from diastereoisomerically pure enamide complexes, have the opposite configuration at C_α, but the same configuration at Ir.

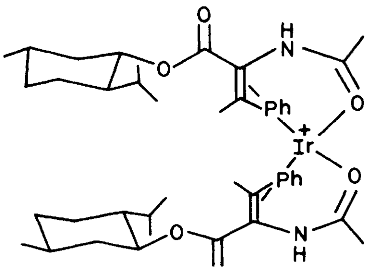
Previous studies on asymmetric hydrogenation have demonstrated the formation of a transient alkylrhodium hydride as the first observable intermediate subsequent to rate-determining H_2 addition.[1,2] The corresponding iridium complexes are stable at ambient temperature.[3] It recently became possible to prepare iridium enamide complexes where the configuration of the bound alkene is defined, *via* the resolved *S*-menthyl ester (**1**) or its enantiomer, and hence access to alkyliridium hydrides in both stereoisomeric series is feasible.[4] Their availability provides new structural insights, which are described below.

Reaction of complex (**1**) with one equivalent of the ligand dipamp in CH_2Cl_2 or CD_2Cl_2 at −80 °C gave complex (**2**), the more stable C_α-*si* diastereoisomer. When the resulting red solution was exposed to H_2 at 0 °C slow conversion into an alkyliridium hydride occurred, without observable intermediates (monitoring by ^1H n.m.r.). The product (**3a**) (~95%) has a well-dispersed aromatic region in the ^1H n.m.r. spectrum at 500 MHz, and the connectivity was fully established by a 2-D COSY experiment. Individual phenyl or *o*-anisyl protons were related to P(1) (28.4 p.p.m.) or P(2) (34.5 p.p.m.) by selective ^{31}P decoupling. Examination of the $^{13}C_\alpha$-labelled methyl ester complex (**3b**) completed the assignment, since C_α had a 72 Hz *trans*-coupling to P(2).

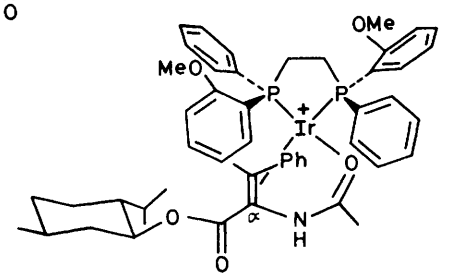
The absolute configuration was then determined by intracomplex ^1H nuclear Overhauser effect (n.O.e.) experiments[3,5] (Figure 1). Notable features include the spatial proximity of Ir–H to an assigned *ortho*-proton, and the strong n.O.e.s between $-OCH_3$ groups and adjacent C–H indicating coplanarity of $-OCH_3$ and its arene ring.[6] The OCH_3 related to P(1) (δ 3.25 p.p.m.) shows n.O.e.s both to the phenyl group on P(2) and the *ortho*-aryl protons of the benzyl group. This indicates that Ir–H and CH_2Ph are on *opposite* sides of the iridium–biphosphine plane.

A similar procedure was employed to prepare the alternative enamide (**4**) from the enantiomer of complex (**1**) and dipamp, and this was quickly hydrogenated at −70 °C before C_α-*re* $\rightleftharpoons$ C_α-*si* equilibration could occur. Rapid H_2 addition was observed at this temperature, and two transient alkyl hydride species were observed (δ −26.9 and −27.7 p.p.m., 6 : 1, amide-bound *trans* to H, *vide infra*) which had disappeared on warming to −40 °C, being completely replaced by a third hydridic species which was a minor component (30%) at −70 °C. This new alkyl hydride (**5**) persisted at ambient temperature. Its ^1H n.m.r. spectrum was fully assigned as before, and an extensive series of n.O.e. experiments conducted (Figure 2). The overall pattern was similar to that established for (**3a**), with one significant difference. Irradiation of the iridium hydride caused an n.O.e. at C–H (*pro S*) of the benzyl group, indicating that they are on the *same* side of the P–Ir–P plane. One of the diastereotopic CH_3 groups of the menthyl Pr^i residue caused an n.O.e. to *ortho*- and *meta*-protons of the benzyl group and the other to *ortho*- and *meta*-protons of the anisyl group on P(1), indicating that the menthyl residue possesses substantial conformational freedom, since these arene residues are well separated in space.

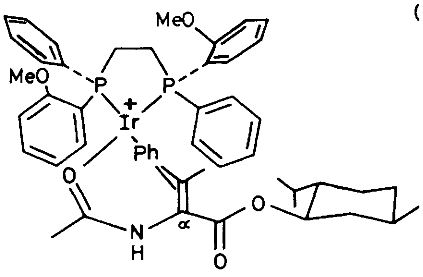
The nature of the ligand *trans* to hydride was discovered adventitiously. When D_2 was added to (**2**), an iridium



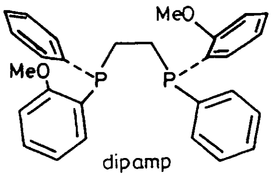
(1)



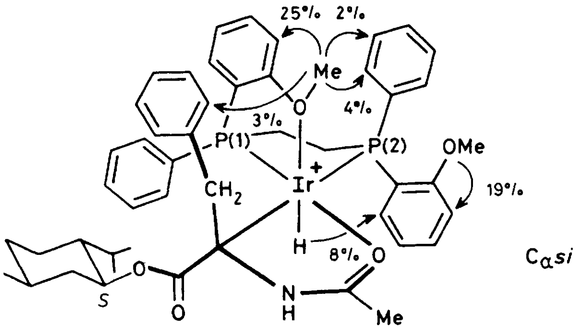
(2)



(4)

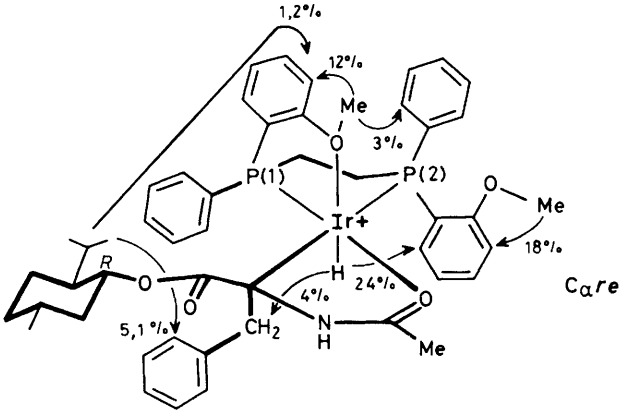


dipamp



(3a) (3b) = Me ester

Figure 1. The structure of (**3a**) derived from the C_α-*si* diastereoisomer of the enamide complex. Observed n.O.e. values are indicated.

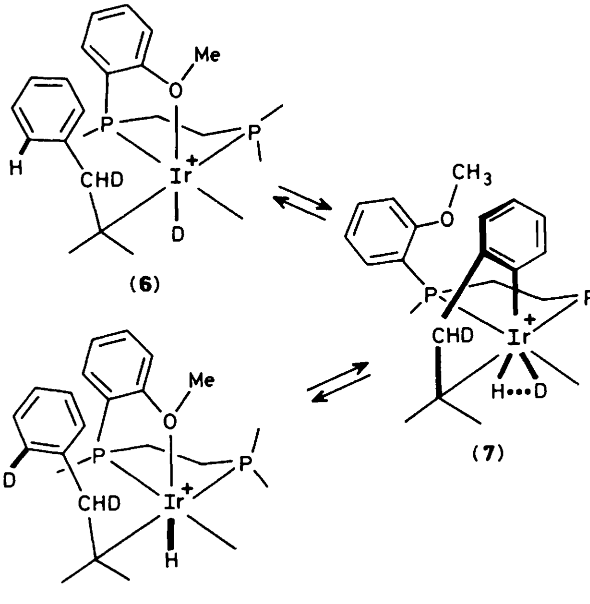


(5)

Figure 2. The structure of (**5**), derived from the C_α-*re* diastereoisomer of the enamide complex. Observed n.O.e. values are indicated.

deuteride formed in which in which the *pro R* benzylic hydrogen at δ 2.45 p.p.m. had been specifically replaced by deuterium. When the solution was kept at 20 °C, intramolecular exchange occurred with deuterium incorporation at the *ortho*-benzyl site,[7] and concomitant growth of Ir–H was revealed by difference spectroscopy. At the same time the OCH_3 group related to P(1) became split, with the signal in the Ir–D complex 0.005 p.p.m. downfield from that in the Ir–H complex;[8] the latter grows to an equilibrium value of about 60% of the total over 24 h. Similar effects are observed with (**3b**), here confirmed by ^2H n.m.r. studies, and with (**5**). In this last case the exchange process involved more than one site in the aromatic region, and was not delineated in detail. Taken together, these observations demonstrate that the $-OCH_3$ of P(1) is bound to iridium, although it dissociates readily in (**3a**), thereby permitting exchange of Ir–D with the *ortho*-H through intermediates (**6**) and (**7**) (Scheme 1).

The structure of iridium alkyl hydrides, related to both major and minor diastereoisomers in asymmetric hydrogenation has thus been defined. The ligand promotes a strong preference for *S*-configuration at iridium[9] irrespective of the alkyl configuration, and one methoxy group occupies the



Scheme 1. Mechanism for intracomplex H–D exchange in (**3a**) indicated by the observed site specificity.

trans-Ir–H site. In the rhodium catalytic cycle at ambient temperature the alkyl hydride has a lifetime of about 30 ms,[1,2] sufficient for reorganisation of the co-ordination sphere so that it should be isostructural with its iridium analogue. This would explain the observed inertness of the dipamp complex towards MeCN at −50 °C,[1] in contrast to the reactivity of the related diphos-Rh (diphos = $Ph_2PCH_2CH_2PPh_2$) complex[2] which lacks the possibility for internal solvation.

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