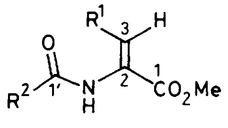
Iridium Analogues of Catalytic Intermediates in Asymmetric Hydrogenation

Nathaniel W. Alcock,[a] John M. Brown,[b] Andrew E. Derome,[b] and Andrew R. Lucy[b]

[a] *Department of Chemistry and Molecular Sciences, University of Warwick, Coventry CV4 7AL, U.K.*
[b] *Dyson Perrins Laboratory, South Parks Road, Oxford OX1 3QY, U.K.*

Stable enamide and hydridoalkyl complexes of iridium have been observed and compared with rhodium counterparts; in one case, the absolute configuration was determined by n.m.r. spectroscopy.



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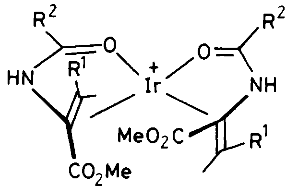

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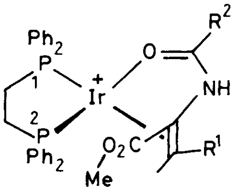

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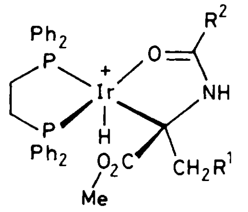

(4)

a; R^1 = Ph, R^2 = Me
b; R^1 = R^2 = Ph
c; R^1 = C_6D_5, R^2 = Me

Following earlier studies on the mechanism of asymmetric hydrogenation,[1] we have now prepared enamide complexes of iridium and studied their reactivity towards H_2, hoping to gain further information from the anticipated increase in stability of alkyl intermediates.[2] Complexes of the type (**6**) (Rh replacing Ir) are directly involved in the catalytic cycle but they have not been isolated. The present work on the iridium analogues provides further evidence.

Established procedures did not lead to the desired enamide diphosphine complexes.[1,3] Instead, stable crystalline iridium di-enamide cations were synthesised as precursors [*e.g.* $(C_2H_4)_4IrCl$ + 2-(*Z*)-PhCH=CH(NHAc)CO_2Me (**1a**) (20 °C) then $AgBF_4$, *ex.* CH_2Cl_2–Me_2CO]. The *X*-ray structure of complex (**2a**) is shown in Figure 1.† Each cation is homochiral and possesses a C_2 symmetry axis. Co-ordination of the olefinic double bond is unsymmetrical, with C(11) 1.16 Å out of the O–Ir–O plane and C(8), N(1), and C(1) essentially in that plane. The di-enamide complexes react with $Ph_2PCH_2CH_2PPh_2$ (diphos) in CH_2Cl_2 or MeOH by clean displacement of one molecule of enamide giving complexes (**3**). N.m.r. experiments employing ^{13}C labelled analogues of (**1b**) in the preparation demonstrated that (**3b**) is isostructural with its rhodium counterpart (Table 1).[4] Rapid conversion of (**3**) into an alkyliridium hydride (**4**) was demonstrated to occur

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† *Crystal data for* (**2a**): $C_{34}H_{30}IrN_2O_6(BF_4)$, M = 841.6, a = 11.386(2), b = 10.257(2), c = 14.685(2) Å, β = 108.66°, U = 1625.9(5) Å^3, monoclinic, space group $P2/n$, Z = 2 with twofold molecular symmetry, D_c = 1.72, λ = 0.71069 (Mo-K_α), μ = 41.6 cm^{-1}. Crystals were deep red blocks with well-defined faces, 0.35 × 0.16 × 0.25 mm. Data were collected on a Syntex 4-circle diffractometer. An absorption correction was applied by the analytical method; maximum and minimum transmission factors were 0.65 and 0.55. From a total of 3033 unique measured reflections, 2368 [$I > 3\sigma(I)$] were considered observed. Systematic absences $h\,0\,l$, $h + l \neq 2n$ indicated space group Pn or $P2/n$ (non-standard setting of $P2/c$). Pn was initially assumed but location of light atoms indicated $P2/n$ to be correct. Refinement was carried out by cascaded least-squares applying anisotropic thermal parameters to all atoms other than H (located at calculated positions and not refined) employing the SHELXTL program package, R = 0.035.

The atomic co-ordinates for this work are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW.

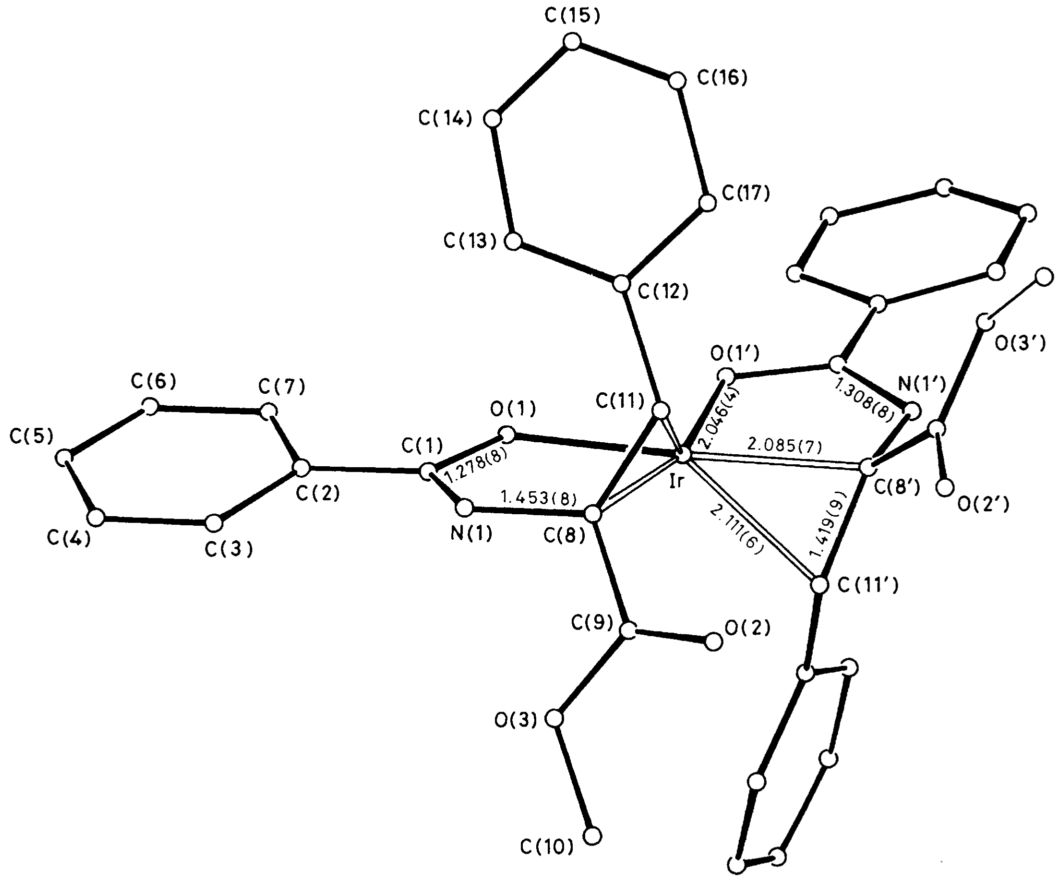

Figure 1. The X-ray structure of complex (**2a**) showing principal bond lengths; BF_4^- counter-ions omitted. Main bond angles: O(1)–Ir–C(8), 79.3(2); O(1)–Ir–O(1'), 86.2(3); O(1)–Ir–C(8'), 164.9(2); C(8)–Ir–C(8'), 115.4(3); N(1)–C(8)–C(11), 122.3(5); C(8)–C(11)–C(12), 129.9(6); N(1)–C(8)–C(9), 112.9(6); Ir–O(1)–C(1), 116.1(4)°.

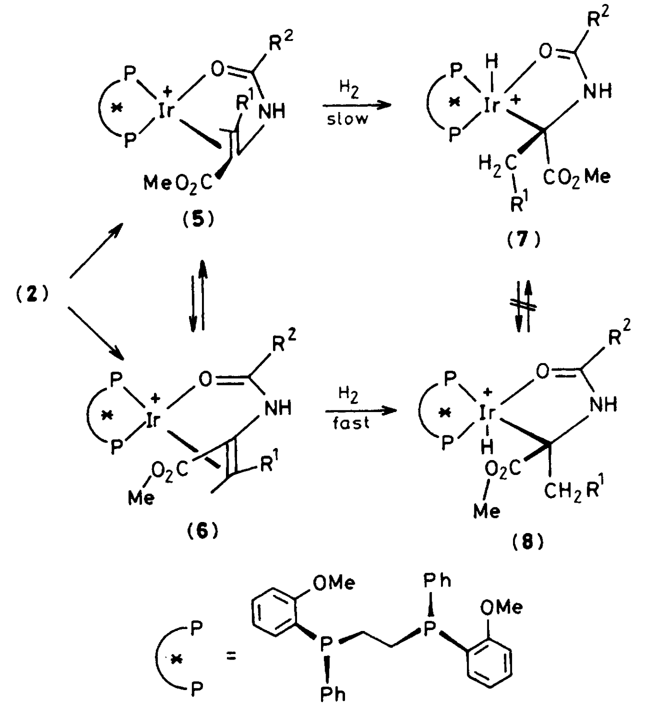

Table 1. N.m.r. parameters for labelled enamides and alkyliridium hydrides prepared from ^{13}C-labelled analogues of (**1b**) and $Ph_2PCH_2CH_2PPh_2$. ^{13}C Chemical shifts are recorded as δ(bound) −δ(free). Coupling constants (Hz) betwen the labelled carbon and P(1) are recorded in square brackets.

	δ P(1)[a]	δ P(2)[a]	δ C(1)[a]	δ C(2)[a]	δ C(1')[b]
Enamide (**3b**)	53.3	30.6	2.5[3.4]	47.3[20.5]	18.7[small]
Alkyl hydride (**4b**)	30.9	18.3	14.2[4.2]	60.4[67]	14.4[7.4]

[a] −30 °C. [b] −5 °C.

at −70 °C on exposure to H_2, with no perceptible formation of intermediates. In a similar manner it was shown that (**4b**) (δ_H −27.1) is isostructural with the rhodium alkylhydride complexes by ^{13}C labelling (Table 1). The thermal stability of the iridium complexes is considerably greater. In the presence of an excess of substrate (**1a**) (50 : 1) slow catalytic turnover of (**4a**) occurs at room temperature with presumed rate-determining breakdown of the alkyliridium hydride.[5]

Reaction of (*R*,*R*)-1,2-bis[(2-methoxyphenyl)phenylphosphino]ethane (dipamp) with complex (**2a**) led to a mixture of two diastereoisomers (**5a**) and (**6a**) in comparable

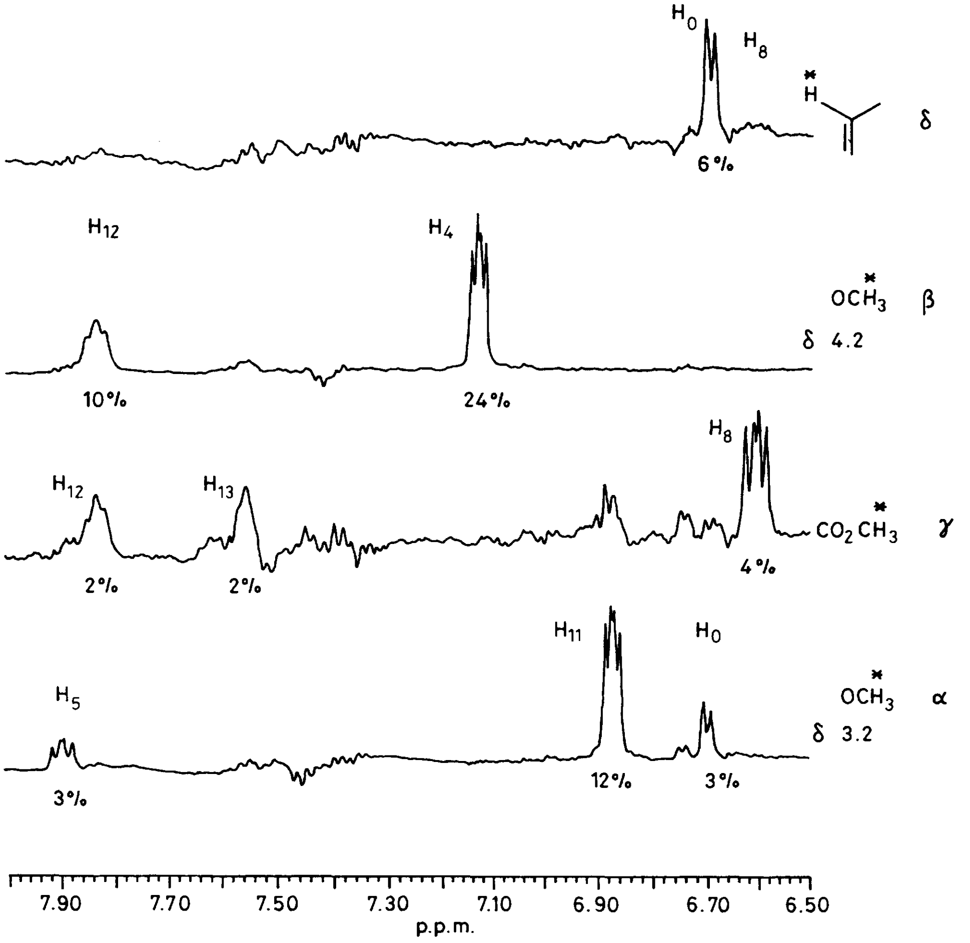

Figure 2. Results of n.O.e. difference experiments on complex (**5a**); sites of irradiation as indicated for each trace.

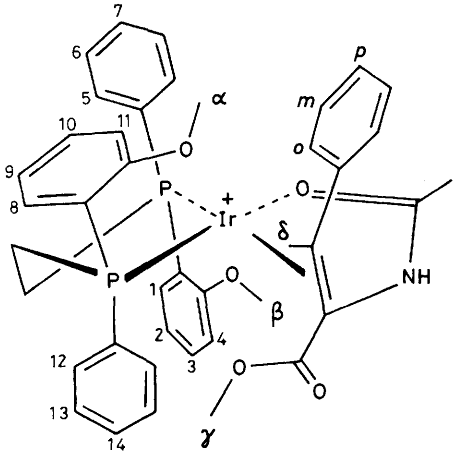

Figure 3. Configuration and solution conformation of complex (**5a**) revealed by difference n.O.e. experiments.

proportions. In CD_3OD they equilibrate over 2 h to a 98:2 mixture with the former predominating. A similar but slower reaction occurs in CD_2Cl_2. It proved possible to determine the absolute configuration and solution conformation of complex (**5a**) by n.m.r. spectroscopy. At 500 MHz, the aromatic region is well-dispersed and a 2D-COSY experiment employing the deuteriated substrate (**1c**) revealed the connectivities of individual rings. A further $^{31}P/^{1}H$ heteronuclear correlation spectrum[6] identified all ligand *ortho*-protons and specifies their neighbouring phosphorus nuclei. With the assignment of aryl protons completed, a series of nuclear Overhauser effect (n.O.e.) difference spectra were recorded (Figure 2). The 3% enhancement of H_O on irradiation of α-OCH_3 requires that the absolute configuration of bound olefin is *si*. Irradiation of γ-OCH_3 produces enhancements of *ortho*-protons H_8 and H_{12} (and a significant effect on *meta*-proton H_{13}). Irradiation of either α-OCH_3 or β-OCH_3 causes enhancement of the *ortho*-phenyl protons of the remote phosphine. Assembling a molecular model with the appropriate inter-proton contacts demonstrates that the preferred λ conformation[7] of the chelate backbone and absolute configuration are as illustrated in Figure 3.

With an excess of H_2, the first-formed mixture of enamide complexes (**5a**) and (**6a**) reacts to form a mixture of alkylhydrides (**7a**) and (**8a**), which is stable at room temperature in solution and does not change in composition on standing. This is in contrast to the rhodium analogues, where the thermodynamically preferred diastereoisomer isomerises faster than it reacts with H_2, so that only one alkylhydride is observed.[1,8] With a deficiency of H_2 the labile isomer (**6a**) reacts more than 20 times faster than the stable isomer (**5a**), and complex (**8a**) is the near-exclusive product. Taken together, these observations demonstrate some close parallels between rhodium and iridium enamide chemistry, but in the latter case the higher kinetic stability in solution makes structural information much more accessible.

We thank Professor J. Halpern, whose results on iridium enamide complexes (prepared by a different route) will be published independently, for a full exchange of information. Dr. P. A. Chaloner provided samples of labelled enamides, and Johnson-Matthey PLC kindly loaned iridium salts. We thank the S.E.R.C. for postdoctoral support (to A. R. L.) and for a grant (to N. W. A.) towards the purchase of a Syntex 4-circle diffractometer.

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