Asymmetric Homogeneous Hydrogenation Catalysed by Rhodium Complexes; the Binding Modes of Enamides Defined by ^{13}C N.M.R. Spectroscopy

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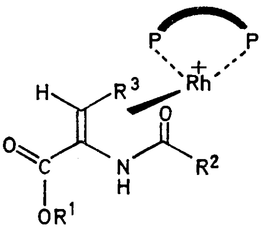
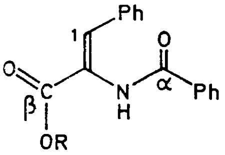
Summary The mode of enamide binding in their rhodium diphosphine complexes has been defined by ^{13}C n.m.r. spectroscopy.

ASYMMETRIC hydrogenation of *Z*-dehydroamino acids by rhodium complexes of chelating diphosphines may proceed with high optical efficiency. Reaction involves a non-hydridic, complexed enamide, suggested to have structure

(**1**).[1] We now report n.m.r. experiments employing the singly labelled *Z*-enamides (**2a**—**f**), prepared[2] from ^{13}C-enriched benzoic acid or glycine (^{13}C=O, 90%) which confirm and extend this proposal.



(1)

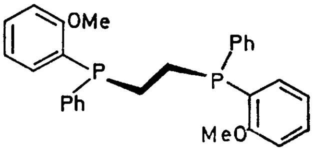


(2)

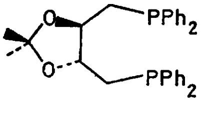
R	Label
a ;H	1
b ;H	α
c ;H	β
d ;Me	1
e ; Me	α
f ; Me	β

$Ph_2P[CH_2]_nPPh_2$

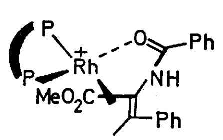
(3) ; *n* = 2
(4) : *n* = 3
(5) ; *n* = 4



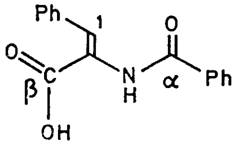
(*RR*)-(6)



(7)



(8)



(9)

	Label
a ;	1
b ;	α
c ;	β

The rhodium enamide complexes of the phosphines (**3**)—(**7**) were prepared from methanol complexes generated *in situ*[1,3] as previously described using each labelled substrate in turn, and their carbon and phosphorus n.m.r. spectra were recorded.^{13}C N.m.r. chemical shifts (Figure 1) unequivocally demonstrate that the olefin and amide groups are co-ordinated to the metal but that the carboxy group is not. Olefinic carbon C-1 is shifted 43—54 p.p.m. to higher field and is coupled to rhodium [*J*(Rh–C) 11–15 Hz], these values being in the normal range for π-complexes of rhodium.[4] Amide carbon C_α is shifted to low field by 10·5—13 p.p.m. and is normally coupled to both phosphorus atoms, but not to rhodium.[5] The larger coupling is to the higher field phosphorus nucleus [typically *J*(C–P-1) 7 and *J*(C–P-2) 2 Hz, *J*(*cis*) > *J*(*trans*)?]. Carboxy carbon C_β is shifted to a much lesser extent but shows coupling to P-1 [J(C–P-1) 3—5 Hz].

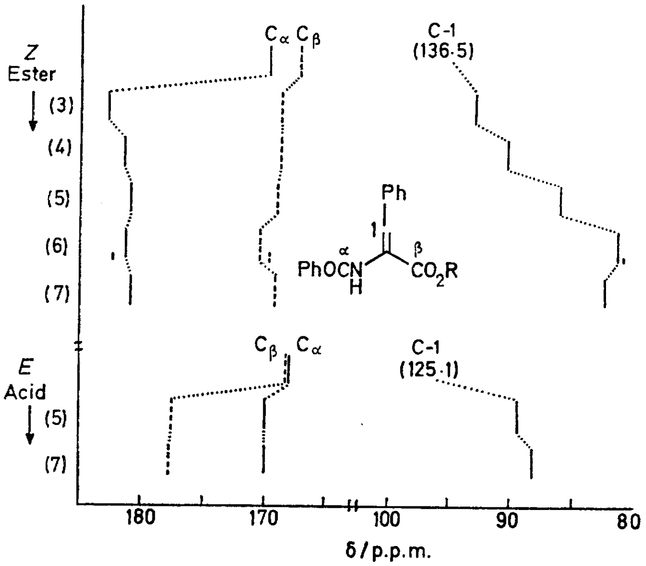
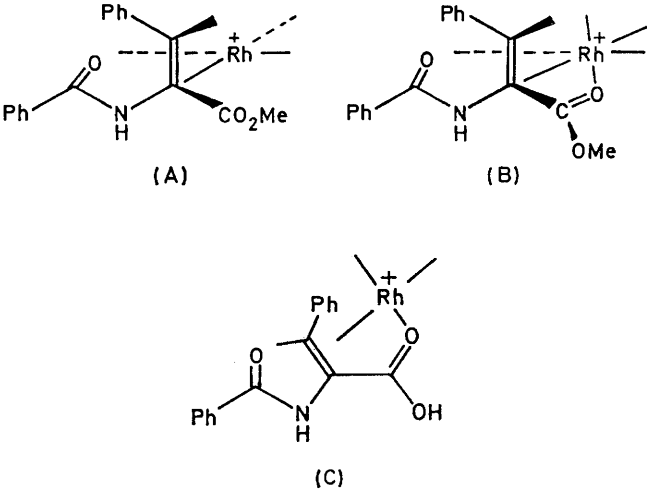


FIGURE 1. ^{13}C Chemical shifts of rhodium enamide complexes in [$^2H_4$]methanol relative to external Me_4Si.



(A) (B)

(C)

Modes of ligand binding in rhodium enamide complexes.

The complexes of dehydroamino acids and their esters have very similar spectra with no systematic trends. The asymmetric phosphines (**6**) and (**7**) show comparable behaviour to their achiral analogues. In the case of (**6**), however, two signals in the ratio 9:1 are observed, corresponding to the major and minor diastereoisomeric complexes. Their ^{13}C n.m.r. signals are resolved in the spectra of all three labelled complexes of acid and ester. The chemical shift difference between major and minor diastereoisomers is invariably small (< 1 p.p.m.) and thus the enamide binds to rhodium in the same manner. These results suggest that the enamide intermediates have structure (A) in which the olefin group is orthogonal to the co-ordination plane[6] but the amide is more nearly in-plane with a strong σ-bonding component and little back-donation into π^*(C=O), consistent with its downfield chemical shift.

The complexes show disparate spectral behaviour at low temperature. The 5-ring chelates derived from (**3**) and (**6**) are affected only to a minor degree, but 6- and 7-ring chelates derived from (**4**), (**5**), and (**7**) exhibit marked changes. As the temperature is lowered, C-1 shifts to higher field (up to 20 p.p.m., 300 $\rightarrow$ 200 K) whereas C_β shifts to lower field, the chemical shift change on complexation approximately doubling between 300 and 180 K.

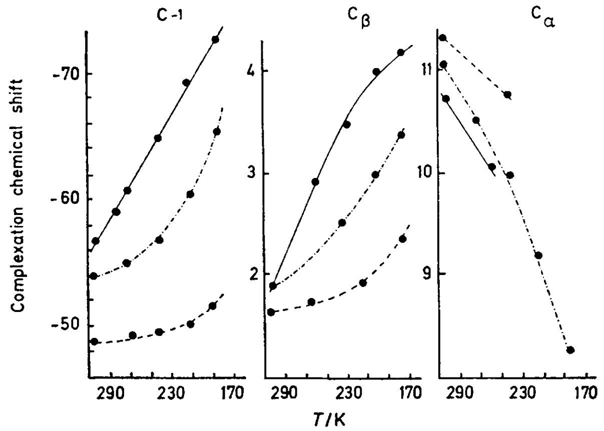


FIGURE 2. Temperature dependence of the ^{13}C n.m.r. chemical shifts of (**8**) in [$^2H_4$]methanol. Phosphine ligands are: (**7**), ——; (**5**), —·—·—; and (**3**) or (**6**), — — —.

Amide carbon C_α moves to somewhat higher field over the same temperature range. Typical behaviour is recorded in Figure 2, suggesting that the 5-ring chelate complexes are structure invariant over the temperature range, but that 6- and 7-ring chelates have an increased contribution from structure (B)[7] as the temperature decreases, resulting in enhanced back-donation into π^*(C=C) and shift of the C-1 resonance to higher field.

Z-Enamides are hydrogenated in methanol solution with high optical efficiency by a range of asymmetric complexes, but the corresponding *E*-enamides such as (**9**) are not.[8] The complexes derived from (**9a**—**c**) and ligands (**5**)† or (**7**) show a marked upfield shift of C-1 in the ^{13}C n.m.r. spectrum and C_β is now shifted 8—10 p.p.m. to lower field; C_α, however, is <2 p.p.m. downfield from its position in (**9**). No strong ^{13}C–P couplings are observed and, although the *trans*-4,5-bis(diphenylphosphinomethyl)-2,2-dimethyldioxolan complexes of (**9a**) and (**9c**) have broadened ^{13}C signals, diastereoisomer separation is not observed. This clearly demonstrates that *E*-dehydroamino acids form bidentate complexes (C) in which olefin and carboxy groups are bound to the metal, but the amide is not.‡ The alternative bidentate form analogous to (A) possesses a severe P–Ph/C–Ph repulsive interaction.

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† With low enamide:rhodium/phosphine ratios, a 1:2 complex of unknown structure is formed concomitantly and its relative proportion (^{31}P n.m.r.) increases with decreasing temperature.

‡ Here, and in other examples, *E*-acid rhodium enamide complexes exhibit much higher *J*(Rh–P) values (*ca.* 180 Hz).

[1] J. M. Brown and P. A. Chaloner, *J.C.S. Chem. Comm.*, 1978, 321; *Tetrahedron Letters*, 1978, 1877; *cf.* H. B. Kagan, N. Langlois, and T. P. Dang, *J. Organometallic Chem.*, 1975, **90**, 353.

[2] Benzoic acid: H. J. Dauben, C. Reid, and P. E. Yankwich, *Analyt. Chem.*, 1947, **19**, 828; benzaldehyde: G. W. J. Fleet, C. J. Fuller, and P. J. C. Harding, *Tetrahedron Letters*, 1978, 1437; enamides: B. D. Vineyard, W. S. Knowles, M. J. Sabacky, G. L. Bachman, and D. J. Weinkauff, *J. Amer. Chem. Soc.*, 1977, **99**, 5946.

[3] J. Halpern, D. P. Riley, A. S. C. Chan, and J. J. Pluth, *J. Amer. Chem. Soc.*, 1977, **99**, 8055.

[4] A. C. Jesse, M. A. M. Meester, D. J. Stufkens, and K. Vrieze, *Inorg. Chim. Acta*, 1978, **26**, 129, and references therein.

[5] We cannot distinguish between through-bond and through-space coupling; examples of the latter are well recognised in organometallic complexes, *e.g.* K. Tani, L. D. Brown, J. Ahmed, J. A. Ibers, M. Yokote, A. Nakamura, and S. Otsuku, *J. Amer. Chem. Soc.*, 1977, **99**, 7876.

[6] R. G. Bell and N. C. Payne, *Inorg. Chem.*, 1977, **16**, 1187; R. R. Ryan, P. G. Eller, and G. Kubas, *ibid.*, 1976, **15**, 797, and references therein.

[7] Further examples of tridentate enamide complexes, which have characteristic ^{31}P n.m.r. spectra with lower P-1–Rh coupling constants (*ca.* 120 Hz), have been identified: P. A. Chaloner and R. Glaser, unpublished results.

[8] G. Gelbard, H. B. Kagan, and R. Stern, *Tetrahedron*, 1976, **32**, 233; C. Detellier, G. Gelbard, and H. Kagan, *J. Amer. Chem. Soc.*, 1978, **100**, 7556; *cf.* K. E. Koenig and W. S. Knowles, *ibid.*, 1978, **100**, 7561 for the first example of a high optical yield in an *E*-enamide hydrogenation (in benzene).