Asymmetric Hydrogenation Catalysed by Rhodium Complexes of (2*R*,4*R*)-Bis(diphenylphosphinomethyl)dioxolan. A Stable Rhodium Dihydride Derived from a Chelating Diphosphine Complex

By JOHN M. BROWN,[a]* PENNY A. CHALONER,[a] GÉRARD DESCOTES,[b] ROBERT GLASER,[c] DOMINIQUE LAFONT,[b] and DENIS SINOU[b]

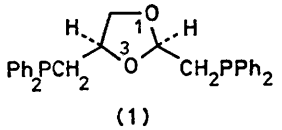
([a]*Dyson Perrins Laboratory, South Parks Road, Oxford* OX1 3QY, [b]*Laboratoire de Chimie Organique II, C.N.R.S.* 689, *Université Lyon I, Villeurbane, France, and* [c] *Chemistry Department, Ben Gurion University of Negev, Be'ersheva, Israel*)

Summary The mechanism of hydrogenation by rhodium complexes of the diphosphine, (2*R*,4*R*)-bis(diphenylphosphinomethyl)dioxolan, is deduced from phosphorus-31 n.m.r. studies.

THE asymmetric ligand (2*R*,4*R*)-bis(diphenylphosphinomethyl)dioxolan (dioxop) (**1**) is readily derived from D-glucose[1] and is the precursor of the hydrogenation catalyst (**2**). This is interesting in a number of respects since it effects asymmetric reduction of $\alpha\beta$-unsaturated acids and of dehydroamino acids, but triethylamine is essential for a high optical yield, and dehydroamino acid esters are reduced with low stereoselectivity. The studies reported herein define the sequence of events in hydrogenation by

complexes of this ligand and clarify the role of triethylamine.

Complex (**2**) has nonequivalent phosphorus nuclei and exhibits temperature-independent ^{31}P n.m.r. spectrum in methanol solution which is a rhodium-coupled AB quartet [δ_A 11·9 and δ_B 9·0 p.p.m., $J(P_A–Rh)$ 147 $J(P_B–Rh)$ 144, and $J(P_A–P_B)$ 31 Hz]. Hydrogenation in methanol is rapid (0·05 M, 1 ml, 1 atm, 4 min) and gives rise to a single species (**3**) [^{31}P n.m.r. δ 44·6 p.p.m., J(P–Rh) 119 Hz; ^1H n.m.r. δ −19·1 and −21·3 (br m)] which is the first example of a cationic rhodium dihydride derived from a chelating diphosphine.[2] Inspection of molecular models demonstrates that O-3 co-ordinates with little angle strain when the phosphines are mutually *trans*, and the ligand structure then closely resembles that found in known cationic rhodium phosphino-ether complexes such as (**4**).[3] On standing the solution of (**3**) at room temperature under argon hydrogen is slowly lost ($t_{\frac{1}{2}}$ *ca.* 4 h) and the solution changes in colour from pale to deep yellow, to form the *cis*-chelated methanol complex[2] (**5**) [δ_P 40·0 p.p.m., J(Rh–P) 212 Hz] again with isochronous phosphorus nuclei. The rate of formation of (**5**) is unaffected by the presence of triethylamine. Excess cyclo-octa-1,5-diene effects quantitative reformation of (**2**) from (**3**).



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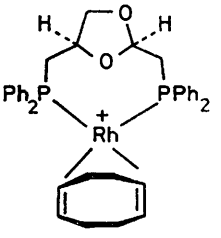

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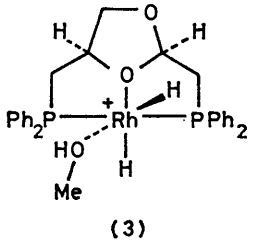

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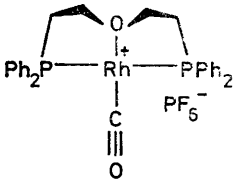


(4)

The addition of an excess of α-benzamidocinnamic acid (**6a**) to a solution of (**3**) in methanol under argon leads to the formation of a yellow enamide complex[4] although the reaction is not particularly rapid at 245 K. From the sharp eight-line ^{31}P n.m.r. spectrum (Table) it is apparent that only one of the four possible diastereoisomeric species is formed. Both the light yellow colour and small Rh–P coupling constant to P-2 suggest a five co-ordinate species. The complexes derived from acetamide, (**6c**), and the methyl ester, (**6b**), exhibit phosphorus-31 n.m.r. spectra with similar characteristics.

Formation of complex (**7a**) from (**3**) is markedly catalysed by triethylamine, which is not true for the related species derived from the ester (**6b**). The catalysed reaction of (**6a**) may be followed by phosphorus-31 n.m.r. spectroscopy at 245 K, and occurs at the same rate for molar ratios of NEt_3:(**6a**):(**3**) of 4·5:4·5:1·0 and 9·0:4·5:1·0. During the course of the reaction one or more intermediate species [δ 31·1 p.p.m., J (Rh–P) 128 Hz; δ 28·5, J (Rh–P) 126·5] build up to a steady state concentration of $\leqslant$ 20% of the total complex and then decay. No such behaviour is seen when acetic acid is substituted for (**6a**), and the acetamide (**6c**) gives rise to an intermediate with a similar but distinct n.m.r. spectrum. The evidence therefore suggests reversible formation of a hydridocarboxylate complex [*e.g.*, (**8**)] closely related to the known species (**9**),[5] the phosphorus–rhodium coupling constants being consistent with a *trans*-phosphine *cis*-hydride arrangement, there being two diastereoisomers with similar chemical shifts and coupling constants.† The methyl ester (**6b**) behaves quite

TABLE. ^{31}P N.m.r. spectra of dioxop enamide complexes at 245 K.[a,b]

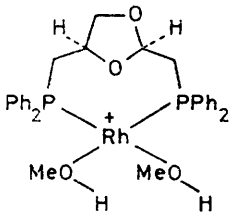
Substrate	δ/p.p.m. P-1	δ/p.p.m. P-2	J(Rh–P-1)	J(Rh–P-2)	J(P-1–P-2)
(**6a**)	49·3	13·2	163	116	28
(**6b**)	54·1	15·2	156	113	28
(**6c**)	53·1	15·2	156	112	28
cf. the complex of (**6a**) with diop[c]	35·0	10·5	151	151	51

^{13}C N.m.r. spectra of rhodium complexes of α-benzamidocinnamic acid.[b]

Ligand	Temperature/K	Labelling site	δ/p.p.m. Free ligand	δ/p.p.m. Bound ligand	J(C–P-1)	J–CP-2)
dioxop	245	Carboxy	168·4	177·8[d]	—	5·0
"	"	Amide	169·8	175·1	3·5	—
$Ph_2PCH_2CH_2PPh_2$	264	Carboxy	168·4	170·1	—	3·5
"	303	Amide	169·8	182·7	1·5	6·0
diop[c]	260	Carboxy	168·4	171·5	—	3·5
"	260	Amide	169·8	180·0	2·5	8·5

[a] ^{31}P N.m.r. chemical shifts are quoted in p.p.m. downfield from external 85% H_3PO_4. [b] Coupling constants are in Hz. [c] diop = *trans*-4,5-Bis(diphenylphosphinomethyl)-2,2-dimethyldioxolan. [d] There is also a coupling of 2·5 Hz to rhodium.

† *Added in proof*: The transient intermediate (**8**) is a rhodium hydride with two broad ^1H n.m.r. signals at δ −19·8 and −18·1.



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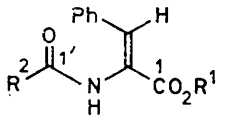
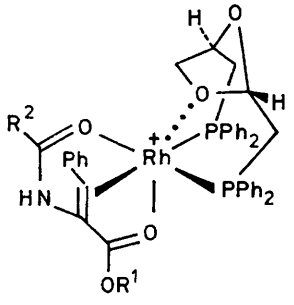


(6)

a; R^1 = H, R^2 = Ph
b; R^1 = Me, R^2 = Ph
c; R^1 = H, R^2 = Me
d; as a, C-1 = ^{13}C (90%)
e; as a, C-1′ = ^{13}C (90%)



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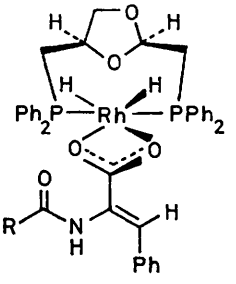
R^1 and R^2 as in (6)



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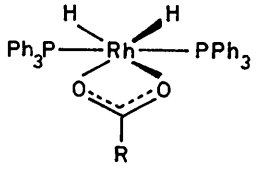

(9)

differently, and no catalysis of enamide complex formation is observed in the presence of triethylamine. This corroborates the lack of sensitivity of optical yields in dehydroamino acid ester hydrogenation to added triethylamine.

Experiments conducted with carbon-13 labelled enamides (**6d**) and (**6e**) demonstrate appreciable carbon–phosphorus couplings in the product (**7**), but not in the intermediate (**8**). The results are, however, quite unlike those obtained with *Z*-enamide complexes of other chiral chelating phosphines (Table).[6] In the case of dioxop, the carboxylate carbon participates to an unusual degree, and the extent of amide binding appears to be much lower. We suggest that in complexes (**7a**) and (**7b**), the ligand is bound in a tridentate fashion; because of the similarities in the phosphorus-31 spectrum of (**7c**) it seems probable that its structure is similar.

These experiments demonstrate that the role of triethylamine in enamide hydrogenations catalysed by complexes of (**1**) is to promote the formation of an enamide complex (**7**), causing hydrogenation to occur by a route which is optically efficient. In the absence of base the pathway involves co-ordination of the enamide to give a dihydride (**3**), possibly in a non-chelate manner. This mechanism results in a considerably lower optical yield.

Other aspects of triethylamine-promoted asymmetric hydrogenations[7] will be reported separately.

We thank I.B.M. and the E. P. Abraham Research Fund for Fellowships (to P. A. C.) and Johnson-Matthey Ltd. for the loan of rhodium salts.

(*Received, 2nd February* 1979; *Com.* 097.)

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