Diversity of Behaviour of Bicyclo[2.2.1]heptadiene–Bis-phosphine–Rhodium Complexes on Hydrogenation in Methanol

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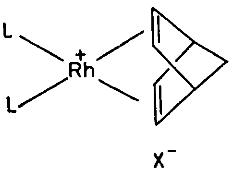
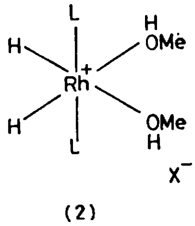
Summary Hydrogenation of the title complexes may form either a methanol complex or a dihydride, depending on the nature of the phosphine.

Homogeneous hydrogenation of olefins by neutral rhodium(I) complexes mainly follows a pathway in which the initial step is addition of hydrogen to the metal.[1] Cationic complexes containing monophosphine ligands are thought to catalyse hydrogenation by a similar mechanism,[2] and this is corroborated by recent observations of Halpern and his co-workers.[3] Bis(triphenylphosphine)bicyclo[2.2.1]-heptadienerhodium(I) tetrafluoroborate (**1a**) in methanol solution absorbs 3 mol of hydrogen to form norbornane and the dihydride (**2**). This is in contrast with the behaviour of the corresponding diene bis(diphenylphosphino)ethane complex which on hydrogenation under identical conditions absorbs only 2 mol to form the methanol complex (**3b**). The chelating phosphine cannot form a *trans*-bisphosphine dihydride and it was suggested that this factor is responsible for the change in reaction course. We report that the equilibrium between (**2**) and (**3**), and their relative ease of formation, is highly sensitive to the nature of the phosphine.



(1)



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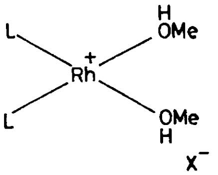


(3)

a; L = PPh_3, X = BF_4
b; L,L = $Ph_2P[CH_2]_2PPh_2$, X = ClO_4
c; L = Ph_2PMe, X = BF_4
d; L = o-MeC_6H_4PPhMe, X = BF_4
e; L = o-$MeOC_6H_4PPhMe$, X = BF_4

Complex (**1a**) reacts with hydrogen in methanol solution, and the resulting ^{31}P n.m.r. spectrum (Table) is characteristic[4] of a *trans*-bisphosphine complex with *cis*-hydrides. Extensive pumping (195 → 300 K, 10 min, 0·1 mmHg) produces only a trace of a second species thought to be the methanol complex (**3a**).

The corresponding diphenylmethylphosphine complex (**1c**) takes up hydrogen much more slowly. Only the dihydride complex (**2c**) is initially observed although (**3c**) may be formed, either by brief evacuation or sealing the solution under argon at room temperature and leaving it for 20 min before recording the spectrum.

Table. ^{31}P N.m.r. data for complexes (**1**)—(**3**).[a]

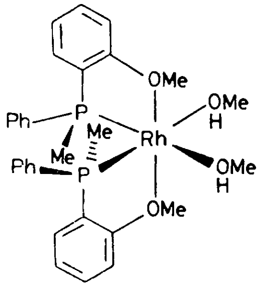
Ligand L	(**1a**—**e**) δ	*J*	$t_{\frac{1}{2}}$ for hydrogen uptake/s	(**2a**—**e**) δ	*J*	(**3a**—**e**) δ	*J*
PPh_3	27·6	156	<120	41·4	121	56·7	206
PPh_2Me	3·5	140	>300	23·8	118	40·1	203
o-MeC_6H_4PPhMe	9·3	153		22·1	118	35·8	202
	8·4	153	<10	21·6	116	34·4	202
(R)-o-$MeOC_6H_4$ PPhMe	9·8	156	<60			38·5	206
(R)+(S)-o-$MeOC_6H_4PPhMe$	12·0	157		19·6	118		
				19·3	119		

[a] Chemical shifts (δ) are recorded in p.p.m. downfield from 85% H_3PO_4; coupling constants (*J*) are in Hz.

Complex (**1d**), derived from methylphenyl-*o*-tolylphosphine exists as an approximately equal mixture of (R^*R^*) and (RS)-diastereoisomers in solution. Hydrogenation occurs very rapidly and cleanly, giving (**3d**) as the only initial product although uptake is strongly inhibited by traces of excess of phosphine. When the solution of (**3d**) is set aside the diastereoisomer resonating at lower field becomes predominant (*ca.* 70:30). On further hydrogenation, a mixture of (**2d**) and (**3d**) is observed and eventually only the former, which is stable under a hydrogen atmosphere, remains.

Complex (**1e**), derived from *rac*-*o*-methoxyphenyl methylphenylphosphine likewise exists as an approximately equal mixture of (R^*R^*)- and (RS)-diastereoisomers. On hydrogenation, however, only one methanol complex (**3e**) is formed (>97%) and this was shown to be the (R^*R^*)-diastereoisomer by comparison with an authentic sample of the (RR)-complex derived from (R)-(*o*-methoxyphenyl)-methylphenylphosphine.[5] The initial product (**3e**) is very resistant to further uptake of hydrogen although *ca.* 15% of the dihydride (**2e**) was produced after bubbling hydrogen through the solution for several minutes, two diastereoisomers being formed in approximately equal amounts when the racemic complex was employed.

We suggest that the unusual stability of the methanol complex (**3e**) towards hydrogenation and the stereoselectivity observed in its formation are due to weak bonding of the methoxy oxygen atoms to the metal.[6] Replacement of the π-acceptor ligand norbornadiene by two methanol molecules will increase the basicity of the metal and consequently enhance the tendency for ligand association by destabilising the square-planar state.[7] Ether bonding in cationic rhodium complexes is well established.[8] The (*RR*)-diastereoisomer constrained by methoxy–metal bonding has a methyl–methyl non-bonded interaction, shown in (**4**), whilst the (*RS*) diastereoisomer would suffer a much more unfavourable methyl–phenyl interaction. Supportive evidence from crystal structures is sparse,[9] although complex (**5**) adopts a conformation in the solid-state whereby the two ethyl groups are proximal and staggered.



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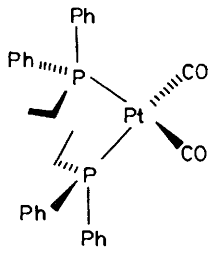
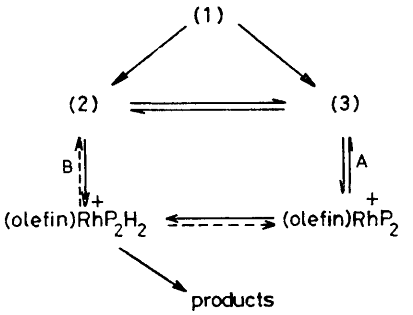


(5)

The mechanism of homogeneous hydrogenation by cationic rhodium complexes is not completely clarified. With chelating phosphine ligands, route A (Scheme) is thought to be followed[3,10] although monophosphine complexes have been considered to react predominantly by route B. The present studies emphasise that the major intermediate present under hydrogenation conditions in the latter case is critically dependent on the structure of the phosphine, and this will almost certainly determine the precise reaction pathway.



Scheme

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