

**Stereochemistry of Hydrogenation of Cyclonona-1,2-diene with Supported
Platinum Metals and Soluble Rhodium Complexes as Evidence for
Allylic Intermediates**

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Summary The formation of *trans*-cyclononene upon hydrogenating cyclonona-1,2-diene with supported platinum metals or the soluble complexes $\text{ClRh}(\text{PPh}_3)_3$ and $\text{HRh}(\text{PPh}_3)_4$ as catalysts furnishes evidence that π -allylic structures are intermediates in these reactions.

WHETHER or not π -allylic structures are formed in the platinum metal-catalysed hydrogenation of allenes is an unsettled question.¹ Crombie *et al.* found no reason for invoking π -allylic species to explain the results of their extensive study of the stereochemistry of hydrogenation of acyclic allenes.² Earlier, Moore³ had argued that the

formation of *trans*-cyclononene as an initial product (17%) of the hydrogenation of cyclonona-1,2-diene (Pd/C) is evidence that a π -allylic structure, which exists mainly in the *cis-trans* (*Z-E*)⁴ configuration, is an important intermediate. The transfer of a hydrogen atom to C(1) from the direction of the catalytic site would give *trans*-cyclononene, while the like transfer of hydrogen to C(3) would yield *cis*-cyclononene. Moore's argument that the *trans*-isomer, the thermodynamically less stable isomer, could not have been formed by the direct addition of hydrogen to the sterically hindered face of the allene, is supported by the observation that a reagent as small as di-imide reacts with the allene to give only *cis*-cyclononene.⁵ Although π -allylic complexes of rhodium are known,⁶ the hydrogenation of cyclonona-1,2-diene with ClRh(PPh₃)₃ as catalyst has been reported to yield none of the *trans*-cyclononene,⁷ a result which appears to weaken Moore's argument.

We have hydrogenated cyclonona-1,2-diene using as catalysts supported Pd, Rh, Pt, and Ir and two soluble complexes of rhodium: ClRh(PPh₃)₃⁸ and HRh(PPh₃)₄.⁹

TABLE. Initial composition (mole %) of the product of hydrogenation of cyclonona-1,2-diene

Catalyst	Conditions ^a	Cyclononene		Cyclononadiene isomers	Cyclononane
		<i>cis</i>	<i>trans</i>		
5% Rh/Al ₂ O ₃	(A)	90.3	7.2	0	2.5
5% Pd/C	(A)	85.0	15.0	Traces	0
1% Pd/Al ₂ O ₃	(A)	85.0	15.0	Traces	Traces
5% Ir/C	(A)	84.0	2.0	0	14.0
5% Pt/Al ₂ O ₃	(A)	82.5	14.0	0	3.5
ClRh(PPh ₃) ₃ ^b	(B)	91.8	6.0	2.2	Traces
HRh(PPh ₃) ₄ ^c	(B)	63.0	19.0	18.0	0

^a (A): cyclohexane solvent; 29.3 °C; 1 atm H₂; (B): benzene-cyclohexane (1:1) solvent; 60 °C; 1.25 atm H₂. ^b 7.2 × 10⁻³ mol⁻¹; cyclonona-1,2-diene: 9.7 × 10⁻² mol⁻¹. ^c 8.7 × 10⁻³ mol⁻¹; cyclonona-1,2-diene: 14.6 × 10⁻² mol⁻¹.

Palladium, whether supported on carbon or alumina, gave results in close agreement with the report of Moore.³ The selectivity for the formation of *trans*-cyclononene remained virtually constant until about 90% of the allene was consumed, at which point the isomerization of *trans*- to *cis*-cyclononene became important and cyclononane was formed. Traces of *cis,cis*-cyclonona-1,3-diene also appeared in the initial product.

The other platinum metals (Table) gave less *trans*-cyclononene, whose initial proportion decreased in the order Pt > Rh > Ir, and it was accompanied by the saturated product, cyclononane, whose initial fraction increased in the order Rh < Pt < Ir. Thus the relationship between the metal and its selectivity for the formation of these products resembles the relationship of their selectivities for the hydrogenation of alkynes to alkenes and alkanes.¹⁰ No products of the isomerization of the allenes were found with these metals.

Both soluble rhodium complexes cause the formation of *trans*-cyclononene as an initial product but it is accompanied by products of the isomerization of the allene. Not surprisingly, HRh(PPh₃)₄ was the more active in this regard.¹¹

With the catalyst HRh(PPh₃)₄, in addition to *cis,cis*-cyclonona-1,3-diene, a second isomer is formed which is neither *cis,cis*-cyclonona-1,4-diene nor *cis,cis*-cyclonona-1,5-diene; most probably it is *cis,trans*-cyclonona-1,3-diene.¹² The isomerization of cyclonona-1,2-diene, carried out at 60 °C under nitrogen gave in 1.5 h 5.2% conversion of the allene, mainly into *cis,cis*-cyclonona-1,3-diene; 0.3% of the second isomer was also formed. We have not attempted, as yet, the isolation and characterization of the π -allylic complex which undoubtedly is formed.⁸

The results obtained using the soluble complexes, particularly HRh(PPh₃)₄ which has been shown to add to acyclic allenes to form π -allylic complexes, support Moore's interpretation of the significance of the formation of *trans*-cyclononene from cyclonona-1,2-diene, *i.e.*, that a π -allylic

complex must be an intermediate. This does not rule out the possibility that a portion of the *cis*-isomer is formed by a more direct addition mechanism like that described by Crombie and his associates. The relative importance of these competing mechanisms would appear to be a function of the catalyst as illustrated by the strikingly different product distribution obtained with the two soluble complexes as well as the differences observed with the supported platinum metals. The conclusion that π -allylic intermediates are formed with all the platinum metal catalysts we have examined to date may not be too surprising with the knowledge that stable π -allylic complexes of these platinum-metals have been identified.¹³

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