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Carbonium *vs.* carbenium ion-like transition state geometries for carbocation cyclization – how strain associated with bridging affects 5-*exo vs.* 6-*endo* selectivity†

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Abstract

Quantum chemical calculations are used to explore the origins of regioselectivity for proton-, Pt(II)- and Pd(II)-promoted cyclizations of 1,5-hexadienes, 5-aminoalkenes, and allylic acetimidates. The strain associated with achieving carbonium ion-like transition state geometries is shown to be a key factor in controlling 5-*exo vs.* 6-*endo* selectivity.

Introduction

The cyclization of carbocations derived from 1,5-hexadienes is a reaction that is broadly applied to the synthesis of complex carbocyclic structures. Transition metal promoted cyclization of 1,5-hexadienes generally leads to products containing or derived from 6-membered rings, *i.e.*, 6-*endo* cyclization. For example, after activation of the less substituted alkene by the transition metal and generation of a carbocyclic intermediate, ring-opening to form Cope products (Fig. 1a),[1,2] attack by appended nucleophiles (Fig. 1b)[3] or H-abstraction (to form cyclic alkenes)[3,4] can occur. Similar reactivity has been observed for related allylic trichloroacetimidates.[1g] However, for 5-ami-nopentenes, only 5-*exo* cyclization has been described (6-*endo* products are thought to arise from rearrangements of species formed by initial 5-*exo* cyclization).[5] Although empirical guidelines exist, no mechanistic model rationalizes and/or predicts the regio-direction of such electrophilic cyclization reactions. A hypothesis invoking a stereocontrolling role for nonclassical (*i.e.*, bridged/carbonium) ion intermediates stimulated the following computational investigation. As will be discussed, a predictive model has emerged.

Nature initiates such cyclizations *via* alkene protonation (Fig. 1c) or alkylation (*i.e.*, *via* a prior cyclization event; Fig. 1d), generally to form the most substituted carbocation, and then generates the product (5- or 6-membered ring) with the most substituted carbocation center.[6] The issue of 5-*exo vs.* 6-*endo* selectivity was debated for many years in the context of sterol biosynthesis, but it now seems clear that apparent 6-*endo* cyclizations to form

†Electronic supplementary information (ESI) available: Computational details and additional references.

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secondary carbocations are less favorable than 5-*exo* cyclizations to form tertiary carbocations followed by rearrangements that avoid secondary carbocations as minima (*e.g.*, Fig. 1d).[6] Biosynthetic cyclizations have, not surprisingly, been mimicked in the laboratory in attempts to synthesize complex hydrocarbons.[7]

Herein, we report the results of quantum chemical calculations[8] that unveil the factors controlling 5-*exo vs.* 6-*endo* selectivity for Pt(II)- and Pd(II)-promoted cyclization of 1,5-hexadienes.[9] This investigation focused on the viability of cyclic 3-center 2-electron bonding arrays (*i.e.*, nonclassical or carbonium ions) as intermediates, transition state structures, or species found elsewhere along reaction coordinates (Scheme 1).[10] The presence of nonclassical delocalization causes the strain associated with bicyclic structures to be expressed in a fashion that affects competing 5-*exo* and 6-*endo* reaction pathways. We contrast the role of this selectivity control element for cyclizations of hydrocarbon substrates (π-nucleophiles) and those of allylic acetimidates and aminoalkenes (lone pair nucleophiles).

Results and discussion

First we focused on the structures and relative energies of the cationic intermediates produced *via* 6-*endo* and 5-*exo* cyclizations promoted by Pt(II) (modeled using $[Pt(PH_3)_3]^{2+}$) and protonation (Scheme 1). No evidence of cyclic 3-center 2-electron bonding[10] was found for any of the computed minima for Pt-containing systems (*e.g.*, Fig. 2, top, resembling **A** and **B**), though nonclassical minima (**C** and **D**) were found for some protonated systems ($R^1 = H/R^2 = CH_3/R^3 = H$ [Fig. 2, bottom], $R^1 = H/R^2 = H/R^3 = CH_3$, $R^1 = H/R^2 = CH_3/R^3 = CH_3$).**11** When $R^1 = CH_3$, **A** and **B** are tertiary carbocations (classical/carbenium ions), not in need of nonclassical delocalization, and when $R^1 = R^2 = R^3 = H$, nonclassical delocalization leads to primary carbocation character at the R^2/R^3-bearing carbon (obviously, to be avoided).

As shown in Table 1, for all protonated systems except that with a tetrasubstituted C=C double bond (entry 8), the intermediate derived from 6-*endo* cyclization is lower in energy than that from 5-*exo* cyclization. This preference is largest for systems where nonclassical intermediates are found (entries 3, 4 and 7). Considering these intermediates as distorted bicyclo-[3.1.0]- and bicyclo[2.1.0]-alkanes suggests that the large energy difference between the 5-*exo* and 6-*endo* intermediates is related to ring strain. The computed ring strain of bicyclo[2.1.0]pentane is ~24 kcal mol^{-1} higher than bicyclo[3.1.0]hexane, some residue of which must be present in the delocalized intermediate.[12,13] Relative stabilities of nonclassical 6-*endo* and 5-*exo* carbonium geometries can therefore be rationalized by inherent bicyclo-strain energies. Differences in hyperconjugation, steric repulsion between the two exocyclic methyl groups (see Fig. 2, D'_{H-Me-H}) and torsional strain (apparent from $R_1–C_5–C_6–R_2$ dihedral angles) also play a role, but the nature of the bicyclic architecture is most useful in predicting reaction outcome.

For the Pt-containing systems, each minimum is classical (*i.e.*, is a carbenium ion) and the 5-*exo* cyclization isomers are preferred (entries 2, 4, 6 and 8), likely a result of steric interactions between the hydrocarbon backbone and the $[Pt(PH_3)_3]^+$ group (this group is directly attached to the ring in **A**, but separated from it by a methylene in **B**).[14]

Transition state structures were also calculated for systems with tri- and tetrasubstituted C=C double bonds (Fig. 2 and 3), models of 1,5-hexadienes commonly used in Pt(II)- and Pd(II)-promoted cyclizations (*e.g.*, Fig. 1a/b).[1,3,4] As shown in Fig. 3, all predicted barriers for Pt(II)-promoted cyclization are small and all reactions are predicted to be downhill, while Pd(II)-promoted cyclizations are predicted to have higher barriers and to be uphill. Nonetheless, in all cases shown, there is a predicted *kinetic preference* for 6-*endo*

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cyclization, even when there is a thermodynamic preference for the 5-*exo* product (*i.e.*, Pt^{2+} with $R^1 = R^2 = R^3 = CH_3$). A rationale for this observation is outlined below.

All reactions are predicted to be reversible, but experimentally the intermediates are, in general, rapidly trapped through subsequent downhill reactions. If this trapping occurs faster than equilibration of the intermediates and is essentially irreversible, the kinetic preference should be manifested. For example, systems with appended OH nucleophiles (related to those in Fig. 1b) were examined computationally (see ESI†). For these systems, trapping of the cation formed in the initial cyclization event by C–O bond formation is predicted to be very exergonic and barrierless if the OH group is in the vicinity of the carbocation center. Thus, although thermodynamic preferences for ether products arising from initial 5-*exo* cyclization were predicted for some systems, the product distributions for these reactions are expected to reflect the kinetic preference for initial 6-*endo* cyclization, consistent with the fact that only products of 6-*endo* cyclization have been observed for Pt-promoted cyclizations of this type.[3,9,15]

The predicted 6-*endo* preference may result from the fact that the transition state structures for Pt(II)-promoted 1,5-diene cyclization (*e.g.*, Fig. 2, right) resemble nonclassical cations with bridging alkyl groups (although the partial C–C bonds in these structures are longer than expected for nonclassical minima, *e.g.*, Fig. 2, bottom). Thus, although bridged carbocations are not intermediates in Pt(II)- and Pd(II)-promoted cyclizations, they do appear along reaction coordinates for cyclization.[16]

Pd(II) catalysts also have been shown to promote exclusive 6-*endo* cyclizations en route to Cope products (Fig. 1a).[1,3,4] Previous computational studies showed the 6-*endo* cyclization to be feasible,[1f,g] but barriers were not compared with those for competing 5-*exo* pathways. As shown in Fig. 3, the 6-*endo* cyclization is kinetically and thermodynamically favored over the 5-*exo*, consistent with experimental observations, and again nonclassical transition state structures were generally observed (see ESI†).[1,3,4]

The possibility of a correlation between nonclassical transition state geometries and high 6-*endo* selectivity for 1,5-diene cyclization prompted the examination of two alternative types of systems (Fig. 4, top). Enamine-containing systems were examined to mitigate the issues of strain associated with nonclassical transition structure geometries (*vide supra*) for 5-*exo* cyclization, while maintaining sp^2 hybridization for the carbon next to the attacking atom. In contrast to the consistent 6-*endo* preferences shown in Fig. 3, kinetic preferences for both 5-*exo* and 6-*endo* cyclization are predicted for enamine nucleophiles, depending on the substitution of the metal-complexed π-bond. When the sp^2 carbon is replaced by an sp^3 carbon (*e.g.*, aminoalkenes **2a** and **2b**), kinetic preferences for both 5-*exo* and 6-*endo* cyclization are again predicted, and are again associated with the substitution of the metal-complexed π-bond. The use of Pd(II) instead of Pt(II) in these systems had a small effect on the energetics and did not change the predicted selectivities. To our knowledge, Pd(II) and Pt(II) promoted cyclizations of amines onto connected internal alkenes have not yet been reported in the literature.[5]

Allyl acetimidates were also examined (Fig. 4, bottom), since these have been utilized extensively in synthetic contexts.[1g] The key difference between these systems and those with C–C π-bonds is that the acetimidate reacts *via* its nitrogen lone pair rather than its π-bond. Similar barriers and exergonicities to those reported previously for 6-*endo* cyclizations in a study of Pd-promoted Cope-like rearrangements[1g] were found for our model systems. Again, kinetic preferences are predicted to depend on the presence or

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absence of an alkyl substituent on the metal-complexed π-bond, *i.e.*, a 5-*exo* preference is possible.[17]

Conclusions

These data together indicate that π and lone pair nucleophiles react differently! Since π-nucleophiles transition through bicyclo-structures, the ring strains of bicyclo[3.1.0] *versus* bicyclo [2.1.0] carbonium structures lead to a 6-*endo* preference for cyclizations onto metal-complexed π-bonds. In contrast, the less delocalized nature of transition state structures for attack by nucleophilic lone pairs releases the constraints of a bicyclic transition structure and enables 5-*exo*/6-*endo* selectivities to be controlled by substitution patterns on the metal-bound alkene.[18] Thus, we arrive at the following guidelines for predicting the kinetic selectivity of cyclization onto C=C π-bonds:

1. If the electrophilic π-bond is strongly activated such that a discrete carbocation is formed (*e.g.*, by protonation), then the most stable carbocation formed through cyclization onto the carbocation center is expected to predominate.
2. If the electrophilic π-bond is activated by complexation to an electron deficient metal, then…

a. 6-*endo* products are expected if the nucleophile is a π-bond.

b. Both 5-*exo* and 6-*endo* products are possible if the nucleophile is a lone pair, but the major product usually will be that from attack on the least electron-rich end of the electrophilic π-bond.

We look forward to the application of the concepts described herein to other systems and are eager to see if these simple selectivity guidelines prove to be truly general.

Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

Acknowledgments

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carbonium ion-like transition states would be strained bicyclo[2.1.0]- and bicyclo[1.1.0]-like species. The latter substrates instead react via an oxygen lone pair.

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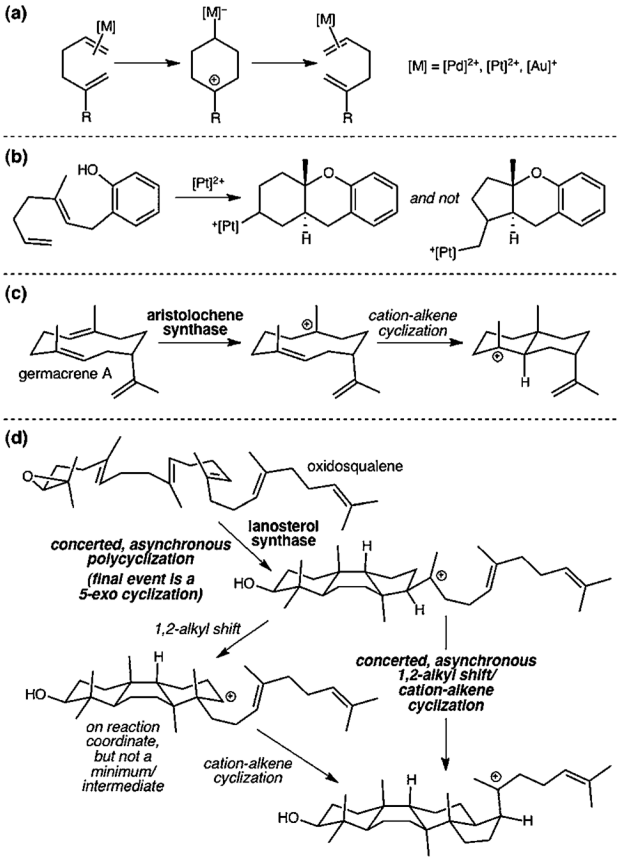

Fig. 1.
Selected reactions involving cationic cyclizations of 1,5-hexadienes.

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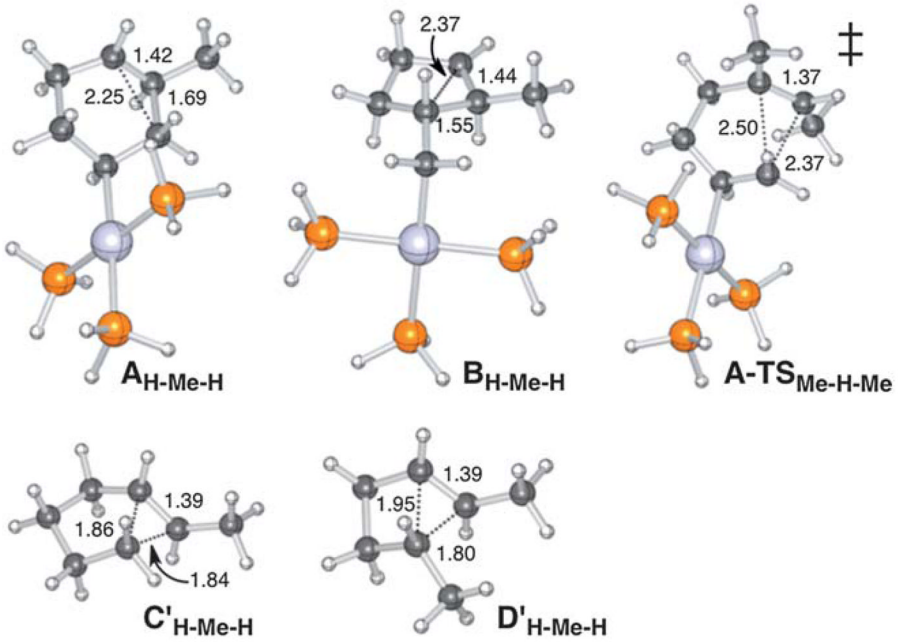

Fig. 2.
Representative structures of computed minima and a transition state structure.

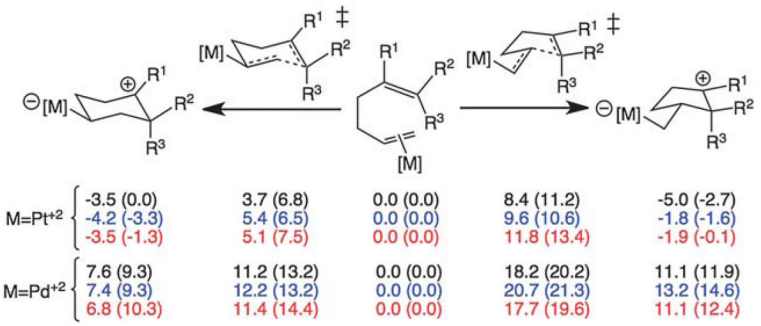

Fig. 3.

Computed reaction enthalpies (free energies in parentheses; kcal mol^{-1}; in DCE) and barriers for $[Pt(PH_3)_3]^{2+}$ and $[PdCl_2(NCMe)]$ promoted 6-*endo* and 5- *exo* cyclizations. Black are for $R^1 = R^2 = R^3 = CH_3$; blue are for R1 = R3 = CH_3/R2 = H; red are for $R^1 = R^2 = CH_3/R^3$ = H. Preferences for 6-*endo* cyclization with $[Pt(PH_3)_3]^{2+}$ are also predicted for systems with a methyl group added to the terminal carbon of the Pt-complexed C=C π-bond (and $R^1 = R^2 = R^3$ = H or $R^1 = R^2 = R^3 = CH_3$); see ESI† for details.

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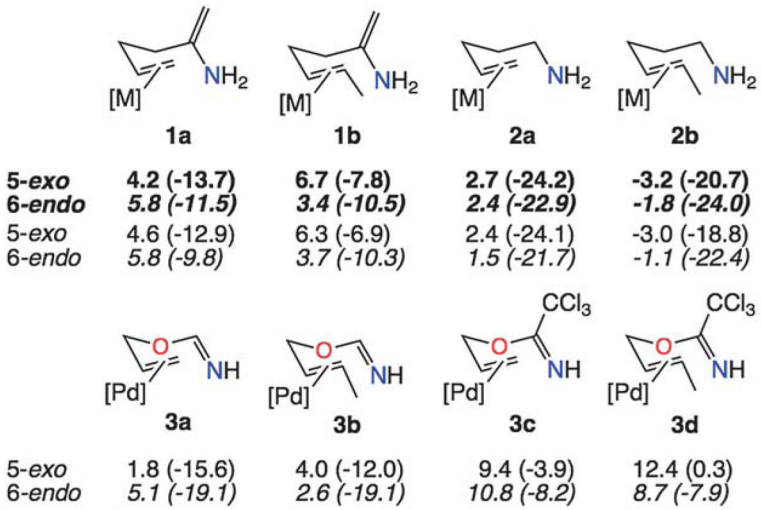

Fig. 4.

Free energy barriers and ender/exergonicities (kcal mol^{-1}; in DCE; exergonicities in parentheses) for systems with nitrogen nucleophiles. For **1a/b** and **2a/b**, bold values are for [M] = $[Pt(PH_3)_3]^{2+}$ and plain text values are for [M] = $[Pd(PH_3)_3]^{2+}$. For **3a**–**d**, [M] = $[PdCl_2(NCMe)]$. Barriers for **2b** are negative because they are based on an extended rather than productive conformation of the reactant.

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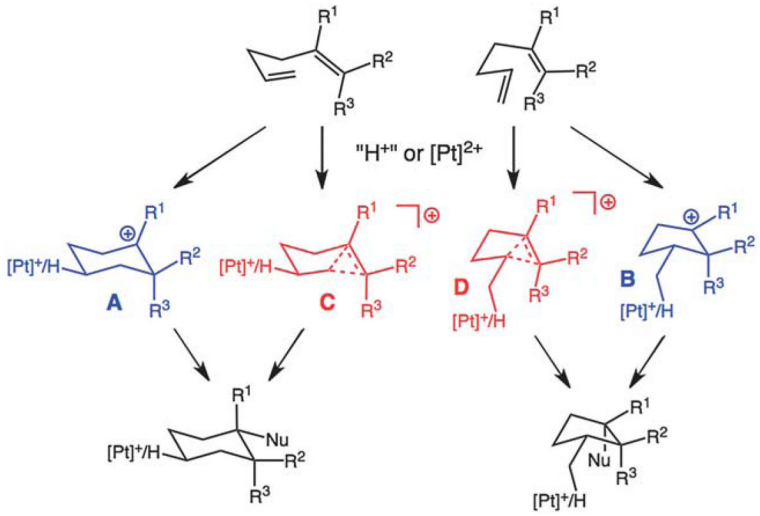

Scheme 1.
Cyclization pathways. Classical (carbenium) structures in blue; nonclassical (carbonium) structures in red.

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Table 1

Free energies (kcal mol^{-1}; gas phase) of intermediates formed *via* activation with $[Pt(PH_3)_3]^{2+}$ or H^+ relative to lowest energy intermediate for each system. R^1, R^2 and R^3 correspond to labels in Scheme 1

					6-*endo*		**5-*exo***	
Entry	**X**	**R^1**	**R^2**	**R^3**	**A**	**C**	**D**	**B**
1	H	H	H	H	0.0			3.8
	Pt				0.0			5.3
2	H	Me	H	H	0.0			2.0
	Pt				1.3			0.0
3	H	H	Me	H		0.0	12.6	
	Pt				0.0			5.5
4	H	H	H	Me		0.0	14.0	
	Pt				0.4			0.0
5	H	Me	Me	H	0.0			1.4
	Pt				0.0			2.4
6	H	Me	H	Me	0.0			1.6
	Pt				2.0			0.0
7	H	H	Me	Me		0.0	14.4	
	Pt				0.0[a]			12.2[a]
8	H	Me	Me	Me	0.8			0.0
	Pt				5.5			0.0

[a] These structures resemble 4- and 5-membered carbocycles with exocyclic 3° carbocation groups; structural data is available in the ESI.