CHEMISTRY
A EUROPEAN JOURNAL

DOI: 10.1002/chem.200800704

Is the Hoveyda–Grubbs Complex a Vinylogous Fischer-Type Carbene? Aromaticity-Controlled Activity of Ruthenium Metathesis Catalysts

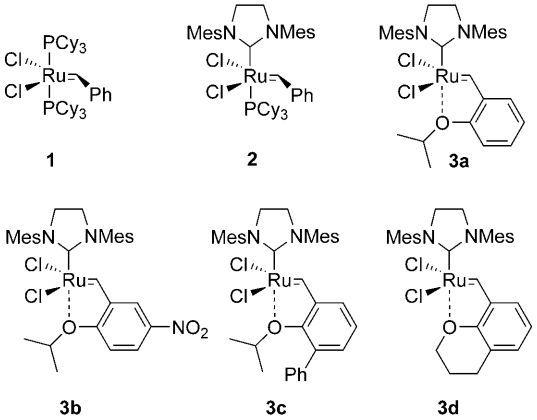
Michał Barbasiewicz,*[a, c] Anna Szadkowska,[a] Anna Makal,[b] Katarzyna Jarzembska,[b] Krzysztof Woźniak,[b] and Karol Grela*[a]

Abstract: Three naphthalene-based analogues (**4a**–**c**) of the Hoveyda–Grubbs metathesis catalyst exhibited immense differences in reactivity. Systematic structural and spectroscopic studies revealed that the ruthenafurane ring present in all 2-isopropoxyarylidene chelates possesses some aromatic character, which inhibits catalyst activity. This aromatic stabilization within the chelate ring may be controlled by variation of the polycyclic core topology as was demonstrated for tetraline and phenanthrene derivatives (**4d**,**e**). General conclusions about a new mode of ligand-structure tuning in catalytic systems are presented.

Keywords: aromaticity · catalysis · ligand design · metallacycles · metathesis

Introduction

With the recognition of the major impact of olefin metathesis in modern organic synthesis,[1] a surge of productive research efforts in ruthenium-complex design has been witnessed in recent years, which is driven by the challenge to enhance the industrial potential of Grubbs catalysts (**1** and **2** Scheme 1).[2] Since the initial observation by Hoveyda[3a] and Blechert[3b] of improved catalytic properties of 2-alkoxybenzylidene complex (**3a**), continuous efforts were spent toward development of new catalytic systems balanced between stability and activity.[4] In this field we demonstrated that reducing the electron-density on the chelating oxygen atom by adding acceptor groups at the aromatic benzylidene ring (e.g. NO_2 in **3b**)[4a,b] and in the alkyl ether chain[4c] facilitated the initiation step, thus improving the rate of the metathesis reaction. The second strategy was based on the out-of-plane distortion of the alkoxy substituent, which weakens Ru–O coordination and is induced by steric congestion with a phenyl group (**3c**)[4d,e] or by incorporation of the chelating oxygen atom into the folded six-membered cyclic structure **3d**.[4f] On the other side the broad applica-



Scheme 1. Selected metathesis catalysts.

---

[a] Dr. M. Barbasiewicz, A. Szadkowska, Prof. K. Grela
Institute of Organic Chemistry
Polish Academy of Sciences
Kasprzaka 44/52, 01224 Warsaw (Poland)
Fax: (+48) 22 632 66 81
Homepage: http://zinc.icho.edu.pl/
E-mail: michal.barbasiewicz@chemie.uni-erlangen.de
grela@icho.edu.pl

[b] A. Makal, K. Jarzembska, Prof. K. Woźniak
Department of Chemistry
Warsaw University, Pasteura 1
02093 Warsaw (Poland)

[c] Dr. M. Barbasiewicz
Current address: Institut für Organische Chemie
Friedrich-Alexander Universität Erlangen-Nürnberg
Henkestraße 42, 91054 Erlangen (Germany)
Fax: (+49) 9131 85 26865

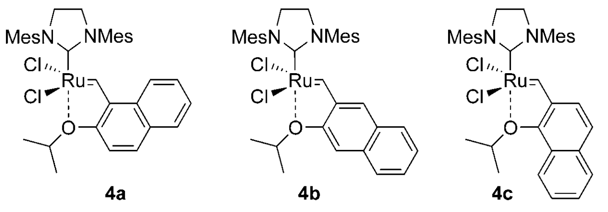
Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/chem.200800704. It contains details of complete ligand and catalyst syntheses, their characterization data and spectral reproductions, numerical data of kinetic experiments and details of X-ray structures (for compounds **3b**, **4a**, **4b**, **4d**, and **4e**).

tion profile of the metathesis reaction demands not only the most efficient catalytic systems, for example, in polymer chemistry slowly initiating so-called "latent catalysts" are sought after. Accordingly substitution of an alkoxystyrene ligand into strongly chelating nitrogen[5] and sulfur[6] congeners led to complexes of diminished activity, which allow longer handling of a monomer/catalyst mixture before the polymerization process.

In spite of these elucidations most new useful complexes were discovered by trial and error, as many opposing effects superimpose in the final catalytic output. Thus further formulation of the theoretical background to systematize results and promote further developments was required. In this report we present a new structure-reactivity concept, based on evaluation of the aromatic character of the chelate ring, which may serve as a tool to probe subtle electronic effects in catalytic systems and shed light on the aromaticity phenomena.

Results and Discussion

In one of our investigations of the structure-activity relationships of metathesis catalysts we synthesized a simple derivative of the parent Hoveyda catalyst, the stable naphthalene-based complex (**4a**, Scheme 2 and Figure 1 a).



Scheme 2. New complexes **4a–c** synthesized by a ligand exchange reaction with **2**.

Unexpectedly, the structural modification led to complete loss of activity toward common substrates in the initial screening of model RCM and CM reactions. This result seemed to be surprising as the close structural similarity with the parent Hoveyda complex **3a** could not justify this behavior. First we assumed that some specific detail of the structure must inhibit the ligand dissociation step. The interaction of the flagpole hydrogen atom of the second aromatic ring (position 8 at naphthalene core) with the carbene moiety or the NHC structure were considered among others.

To solve this riddle we synthesized the remaining isomers of the naphthalene-based catalysts for a systematic comparison of the effect of the aromatic ring annelated on the parent complex **3a**. Surprisingly, we observed in a preliminary screening that only one complex (**4b**, Figure 1 b) exhibited catalytic activity comparable to the parent Hoveyda catalyst, whereas two others (**4a** and **4c**) were completely ineffective toward a set of model RCM substrates.

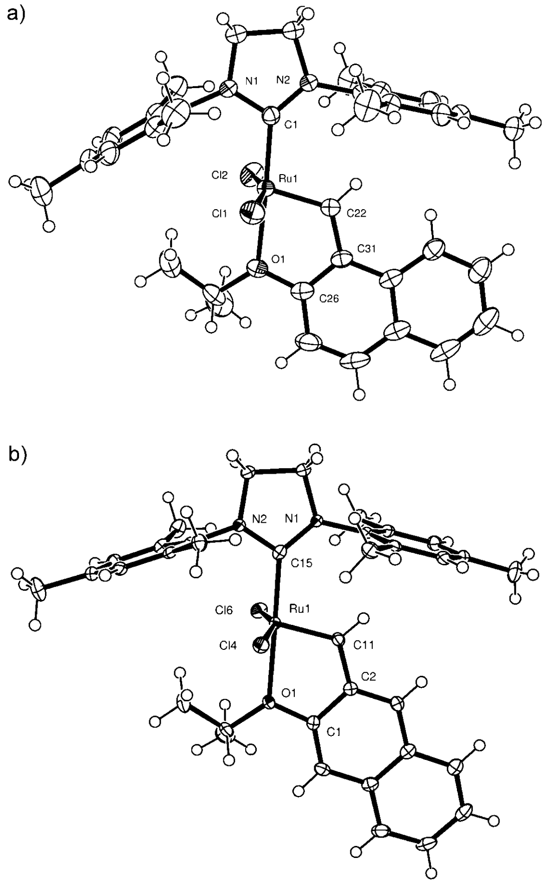
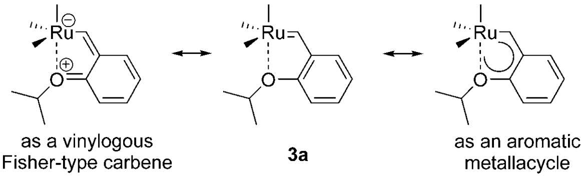


Figure 1. X-ray crystallographic structures[7] of complexes **4a** (a) and **4b** (b) represented by thermal ellipsoids drawn at the 50% probability level.

Especially unusual was the magnitude of this ligand effect. Simple modifications of the Hoveyda complex lead usually to changes in the catalytic activity, but none of them could so dramatically influence this system, especially toward deprivation of catalytic activity (usually steric congestions result in diminished stability and improved catalytic output). For a deeper understanding of these differences, structural crystallographic studies of the presented complexes were carried out. Casual analysis of structures of the synthesized compounds confirmed general structural similarities with complex **3a** in ligand orientation and the characteristic Ru−O bond length varied to a minor extent, in the range of 0.05 Å. This suggested that none of the known concepts of the structure-activity relationship of the Grubbs–Hoveyda type complexes could unambiguously explain the experimental results. Consideration of simple electron-density effects acting on the stability of the chelate predicts similar properties for catalysts **4a** and **4b** because both of them are based on a 2-naphthol core. On the other hand, the proximity of the flagpole hydrogen atom of the second-closest aromatic ring to the Ru=CH group and the mesitylene ring of the NHC ligand exerts an effect present in complex **4a** only.

Benzylidene ruthenium complexes belong to the class of the carbene complexes of moderate electron density. Reaction with ethyl vinyl ether may transform them into electron-rich Fischer-type carbene complexes of substantially diminished activity (the property used sometimes for quenching metathesis reactions).[8] In fact the parent Hoveyda–Grubbs catalyst, on the basis of the so-called vinylology concept,[9] can be classified as a Fischer-type complex, in which the isopropoxy group functions as a mesomeric donor for a through-bond π-conjugation with the carbene moiety. One of the arguments toward this interpretation is the planar configuration of the chelating oxygen atom, which ensures sp^2 hybridization and conjugation with the aromatic ring (Scheme 3, left).



Scheme 3. Electronic character of the ruthenium complex **3a**.[10]

The structure of naphthalene exhibits substantial bond alternation,[11] which is generally attributed to differences in bond orders and manifestly lower aromatic stabilization (calculated per one ring) as compared with the ideal hexagonal aromatic prototype, benzene. Partial double-bond character of C1−C2 and single-bond character of C2−C3 (numbered for the naphthalene core) led us to assume that only structures built on the C1−C2 side of naphthalene (**4a**, **4c**) are able to establish efficient conjugation within the chelate ring. On the other side, **4b** resembles the parent Hoveyda complex **3a**, in which the aromatic stabilization (ring current) of the substituted benzene reduces this conjugation.[12] We supposed that except for some minor random effects displayed in these structures, the main structural difference between naphthalene isomers is the propensity to conduct electronic π density, which affects the conjugation between −OR and Ru=CH groups. This conjugation of the substituents increases the electron density at the ruthenium center and reduces the rate of the reaction with olefinic substrates.

In subsequent studies we compared the spectral data (^{1}H and ^{13}C NMR spectra) of compounds **4a–c** as a probe of their electronic properties. Taking the NMR data of **3a** as a point of reference we observed that both inactive catalysts (**4a**, **4c**) exhibited a substantial deshielding effect (ca. +1.6 ppm) at the alkylidene hydrogen atom and a slight shielding effect for the alkylidene carbon nucleus (ca. −6.5 ppm). In fact *p*-donor heteroatoms of Fischer-type carbenes cause a shielding effect on the alkylidene proton[13] compared with unsubstituted complexes and cannot justify the opposite trend observed for complexes **4a** and **4c**. The magnitude of the differences in the NMR chemical shifts for the proton located at the conjugated chelate ring seemed to not be accidental and pointed our attention towards subtle effects arising from the topology of electron distribution at the naphthalene core.

The electronic properties of polyaromatic hydrocarbons (PAHs) are the matter of continuous theoretical and synthetic studies.[14] In this area a simple graph-topology driven concept (the Clar rule)[15,16c] allows a qualitative evaluation of their stability. The more aromatic (Clar) sextets that can be written for an investigated structure, the greater the predicted stability. On the basis of this theory, angular PAHs (phenanthrene, chrysene, picene, etc.) differ from linear ones (anthracene, naphthacene, pentacene, etc.) in a way that is related to the number of aromatic sextets per total number of rings.[15,17] Not only simple aromatic benzene rings can be regarded as building blocks for these systems. The resonance-assisted hydrogen-bonding concept, introduced by Gilli,[18] extended this methodology to other cyclic structures, such as, benzoannelated β-ketoenolates, in which hydrogen bonding between hydroxy and carbonyl groups constitutes a novel pseudoaromatic ring within the polycyclic structure. Recently, such a conjugation effect for systems of various topologies was investigated theoretically.[16] Accordingly, both hydrogen and lithium bonds in chelate rings fill the criteria for resonance stabilization, the latter even more efficiently, probably due to better orbital overlap.[16c] These studies also confirmed the substantial differences between linear and bent polyarenes and qualitatively supported our presumptions.

In fact, the conjugation effect in the investigated ruthenium chelates may be generalized as a cyclic ring current with some aromatic character. Namely, the electronic properties of naphthalene-based catalysts **4a–c** *may resemble structures of higher (tricyclic) all-carbon analogues, phenanthrene and anthracene (considering extension of the structure by a chelate ring) and inherit the differences of their aromatic properties.* In this respect the concept of metalloaromaticity[19] introduced by Calvin and Wilson in 1945[20] is richly evoked to explain the properties of organometallic compounds in terms of their stability, reactivity and structure. Numerous studies were conducted in this field for example, synthesis of classes of iridacycles,[19b,c] ferrabenzenes,[21] ruthenabenzenes,[22] molybdafuranes,[23] as well as simple acac[24] and diimine complexes.[19d] At this moment we realized that aromatic stabilization of the chelate may be responsible for the unexpected lack of reactivity of complexes **4a** and **4c**, which operate at the initiation step (stabilizes the chelate for the dissociation[20,25] or retards the reaction with the olefin in an associative[26] mechanism) and may justify the pronounced "on/off" effect in the catalytic activity as amplifying small energetic differences by the kinetic pattern of the precatalyst activation process.

To prove this concept we evaluated the general criteria of aromaticity present in the literature:[27,28] structural (bond equalization) and magnetic (diamagnetic ring current investigated by NMR), and compared them with the energetic one (based on resonance stabilization), which was attributed to the activity pattern. The results are presented in Table 1.

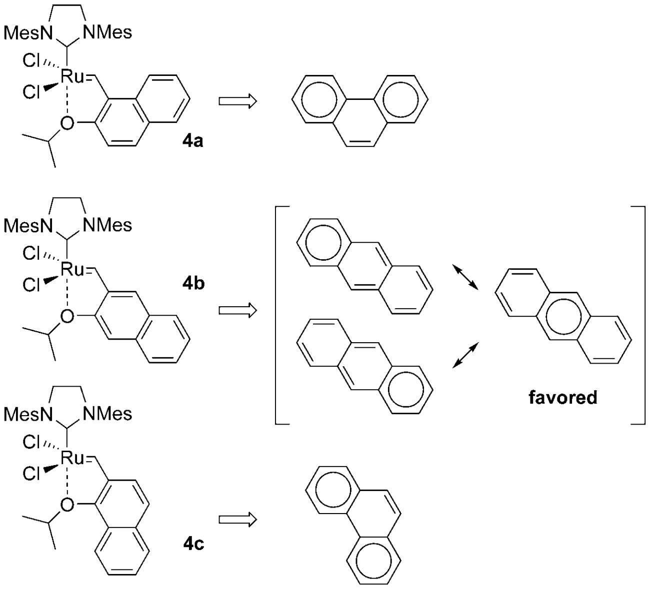
Table 1. Selected parameters of complexes **3a**,**b** and **4a**–**e** applied for evaluation of the aromatic character of a chelate ring.

Complex	Activity at 0 °C[a]	$\delta(^1H)$ [ppm][b]	HOMA[c]	Clar prediction[d]
3a	active	16.56	0.983	nonconjugated
4a[e]	inactive[f]	18.15	0.877	conjugated
4b	active	16.75	0.952	nonconjugated
4c[e]	inactive[f]	18.19	n. d.[g]	conjugated
4d	active	16.39	0.985	nonconjugated
4e[e]	inactive[h]	18.36	0.910	partially conjugated
3b	active	16.47	0.968/0.983[i]	nonconjugated

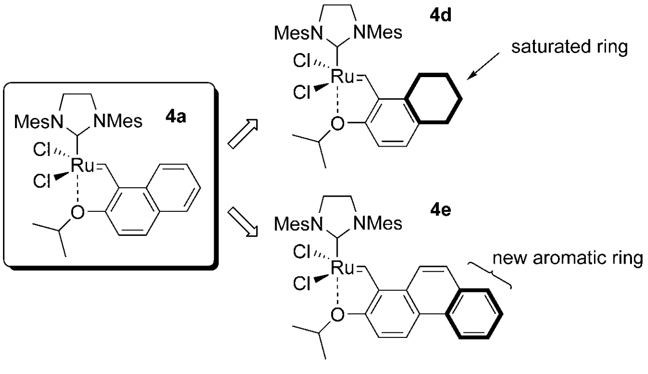
[a] Precise data are presented in Figure 3. [b] Signal of benzylidene proton measured in $CDCl_3$. [c] Calculated for the homocarbon aromatic ring adjacent to the chelate according to the ref. [29]. [d] The character of the chelate is based on analogy with polyaromatic hydrocarbons (see the text below). [e] System with strongly conjugated chelate. [f] Active at 110 °C. [g] We failed to obtain good quality crystals suitable for X-ray measurements. [h] Active at 80 °C. [i] Two molecules present in the crystal structure.

In spectroscopic studies, the strong deshielding effect present in complexes **4a** and **4c** was perfectly consistent with the diamagnetic ring current observed in all aromatic systems, giving reliable proof for the formulated concept. Next, the harmonic oscillator model of aromaticity (HOMA)[29] was applied for the analysis of X-ray structures. This evaluation technique is based on parametrization of the degree of bond-length alternation giving numerical values close to 1 (for highly aromatic symmetrical structures with equal C–C distances) and 0 (for hypothetical cyclic polyenes with alternating single and double bonds). Our analysis was limited to evaluation of local aromaticity of adjacent all-carbon rings as no parametrization was accessible for Ru=CH and O–Ru bonds.[30] The obtained results were consistent with expectations based on simple analysis of aromatic ring distribution based on Clar rule considerations[15,17a] with chelate ring-expanding polycyclic character of the ligand core (middle ring of reduced aromaticity for structure **4a** and highly aromatic for complex **4b**, see Scheme 4). However, these changes were minor, probably due to the generally low magnitude of aromatic stabilization of a ruthenacycle, as compared to other aromatic systems.[31]

For the purpose of a decisive proof of a topology-based reactivity profile of complexes **4a**–**c** we decided to apply the very subtle effects that govern the electronic structure of polyaromatic systems in order to restore the catalytic activity of inactive complex **4a**. A partially saturated analogue of **4a**, based on the tetraline core (**4d**), and phenanthrene derivative **4e** were synthesized. We expected that both modifications would reduce the conjugation of the metallocycle and restore the catalytic activity of the complexes (Scheme 5).



Scheme 4. Structural analogies[32] of complexes **4a**–**c**. Metallacycles (left) mimic electron distribution of polycyclic hydrocarbons—phenanthrene and anthracene (right). According to the Clar rule substantial aromatic character of the chelate is predicted for complexes **4a** and **4c**. For **4b** three possible structures contribute and the symmetrical one is slightly favored.[15,17a]



Scheme 5. Structural changes were applied to restore catalytic activity similar to that of complex **4a**. A saturated ring was introduced to give tetraline derivative **4d** (top) and the extended polyaromatic system of phenanthrene derivative **4e** was employed (bottom, see text for details).

Saturation of the distal aromatic ring gave complex **4d**, which was designed to have similar electronic properties to the parent Hoveyda complex **3a**, with a single aromatic ring. At the same time the change of geometry was only minor, leaving possible steric hindrance between the alkylidene group and the mesitylene ring of the NHC ligand relatively intact. In the second investigated structure we chose a modification far from the coordination sphere of the ruthenium ion (Scheme 5 and Figure 2), as presumably meaningless in the sense of current mechanistic concepts of reactivity.

By analogy between the investigated naphthalene-based catalysts with the corresponding polyaromatics of similar topological structure (anthracene and phenanthrene, Scheme 4) the ligand of **4a** was expanded by the next aromatic ring, leading to the metalla-analogue of chrysene **4e**. Once again, simple considerations suggested that this modification should, at least partially, restore the catalytic activity[16c] due to possible inversion of the aromatic sextet distri-

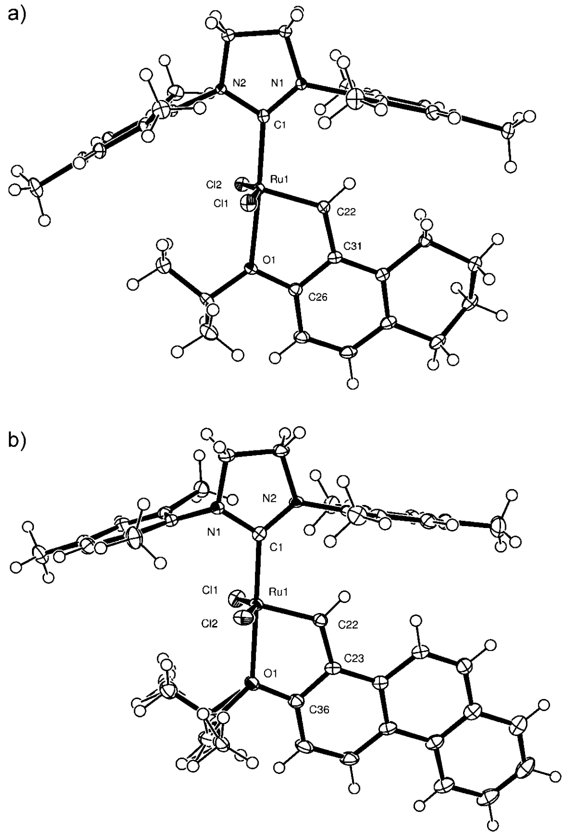
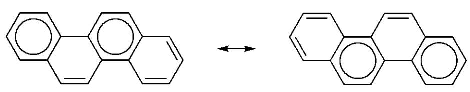


Figure 2. X-ray crystallographic structure[7] of complexes **4d** (a) and **4e** (b) represented by thermal ellipsoids drawn at the 50 % probability level. The isopropoxy group in **4e** exhibits disorder in the crystal lattice.

bution within the polyaromatic core according to the Clar rule.[15]



The results of systematic activity studies performed on a model RCM reaction of *N,N*-diallyltosylamine with 1 mol % of the catalyst are presented in Figure 3.

Initial screening at 0 °C (Figure 3, top) demonstrated similar catalytic performance for complexes **3a** and **4b** as intermediate between highly-active nitro catalyst **3b** and tetraline derivative **4d** of slightly diminished output. Under these conditions complexes **4a**, **4c**, and **4e** were completely inert and the product of an RCM reaction was not detected in reaction mixtures. For more precise differentiation, analogous reactions were performed at 80 °C in dichloroethane (Figure 3, bottom). Under these conditions the activity of complexes **4a** and **4c** was still negligible (<5 % conversion), whereas the "restored activity" complex **4e** reacted much more efficiently, consistent with our expectations.

Finally, we set out to initiate inert complexes **4a** and **4c** under more vigorous conditions to demonstrate the scope of

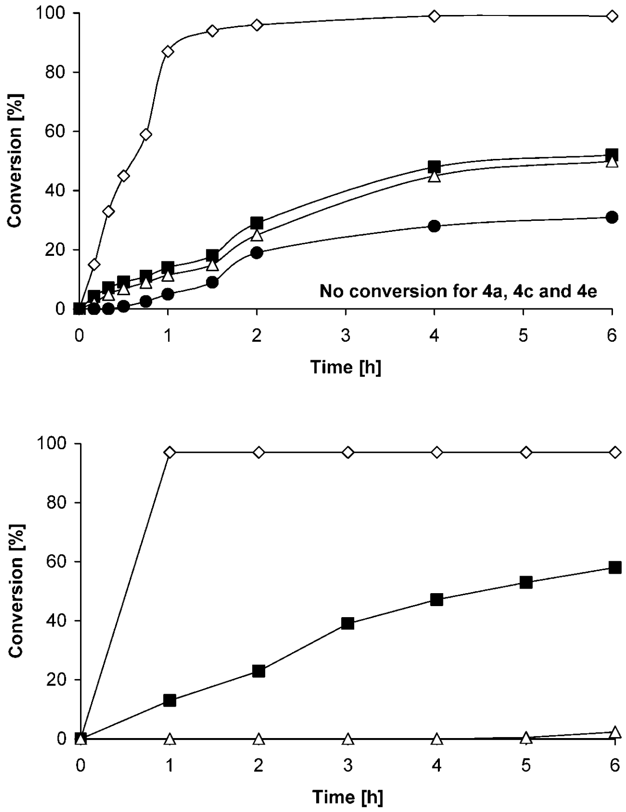


Figure 3. Activity profiles of complexes **3b** (◇), **4b** (■), **3a** (△), **4d** (●) in RCM reactions of *N,N*-diallyltosylamine at 0 °C (top) and **3a** (◇), **4e** (■), and **4a** and **4c** (△) at 80 °C (bottom).

their application as latent systems and to evaluate the strength of the ligand effect, which controls precatalyst activation and release of active catalytic species. In refluxed toluene (110 °C) both complexes showed similar activity, leading to the RCM product of diethyl diallylmalonate in approximately 45 % conversion (ca. 60 % for 2.5 mol % of catalyst, Figure 4). After the fast initiation step, reaction progress was stopped within 4–6 h, which can be attributed to catalyst decomposition at elevated temperature.

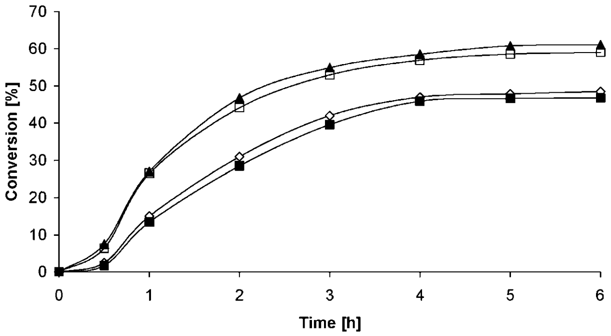


Figure 4. Activity profiles of complexes **4a** (▲) and **4c** (□) at 2.5 mol% catalyst loading, and **4a** (◇) and **4c** (■) at 1 mol% catalyst loading in RCM reactions of diethyl diallylmalonate at 110 °C.

According to the presented concept and the expected inductive[4a–c] and steric[4d–f] modes of catalyst activation, a third novel mode, aromatic conjugation of a chelate, can be varied in a continuous way, as the aromatic stabilization may differ for aromatic systems of diverse topologies.

Conclusion

The presented results demonstrate that simple qualitative analysis of conjugated cyclic structures with Clar's rule may help explain and serve as a tool for fine-tuning the ligand effects in the design of novel catalytic systems. As many conjugated ligands, such as, ketoenolates,[22] Schiff bases,[10,33] salens,[34] and diiminopyridines[35] have numerous practical applications, the precise mechanism of their action is still a matter of discussion. In the presented model, bond order alternation in the naphthalene moiety enables the manipulation of conjugation within the chelate ring,[20,25] whereas other structural parameters remain almost intact. In the design of Hoveyda–Grubbs type metathesis catalysts this idea reveals that the isopropoxy group functions not only as a simple chelating arm, but is an inherent part of the conjugated ring influenced by the π-electrons of the ligand. Depending on the topology of the ligand core this effect may be controlled in a broad range from minor to substantial, in which the aromatic character of the chelate inhibits the initiation step and decreases the catalytic activity of the carbene complex. Application of metathesis technology justifies development of systems of any type, the pharmaceutical and fine-chemical industries ideally require highly active catalysts in ppm amounts and at low temperatures,[1e] whereas dormant catalysts with retarded initiation are useful in metathesis polymerization processes.[5] As both types of metathesis catalysts find important practical applications, the concept formulated herein can be of practical importance since it delivers a better understanding of the mode of action of the complexes[36] and can lead to new ruthenium chelates of tailored activity.

Experimental Section

General methods: For a detailed description of the experimental methods and instruments used, see Supporting Information. CCDC-698596 (**3b**), CCDC-698342 (**4a**), CCDC-698343 (**4b**), CCDC-698344 (**4d**), and CCDC-698345 (**4e**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Representative procedure for the synthesis of catalysts 4a–e: (Unoptimized for specific cases with polycyclic ligands). 2-Isopropoxy-1-vinylnaphthalene (0.051 g; 0.24 mmol), CuCl (0.024 g; 0.24 mmol), and CH_2Cl_2 (15 mL) were placed in a Schlenk flask. Afterwards, Grubbs second-generation carbene complex (0.170 g; 0.20 mmol) was added and the resulting solution was stirred under argon at 40 °C for 30 min. From this point on, all manipulations were carried out in air with reagent-grade solvents. The reaction mixture was concentrated under vacuum and the resulting material was dissolved in ethyl acetate (ca. 10 mL), a white solid was filtered off and the filtrate was concentrated under vacuum. The product was purified by column chromatography. Elution with cyclohexane, then cyclohexane/ethyl acetate (1:1) removed **4a** as a light green band. The solvent was evaporated and the product was dissolved in a small amount of CH_2Cl_2, then methanol was added until green crystals precipitated. The precipitate was filtered off, washed with methanol and dried in vacuo to afford complex **4a** (0.030 g, 22 %) as a light green solid.

Kinetic studies of complexes 4a–e

At 0 °C: Two sets of RCM reactions were used as a test to compare the activity of the catalysts: cyclization of *N,N*-diallyltosylamine and *N,N*-di(3-buten-1-yl)tosylamine in CH_2Cl_2 at 0 °C. Typically 1 mol % of the catalyst (0.004 mmol) was added to a solution of substrate (0.350 mmol) and an internal standard in CH_2Cl_2 (17.5 mL) at 0 °C. The reaction was run at 0 °C under argon and samples were taken after 5, 10, 20, 30, 45, and 60 min and 2, 4, and 6 h, and were analyzed by GC.

At 80 °C: Two sets of RCM reactions were used as a test to compare the activity of catalysts: cyclization of *N,N*-diallyltosylamine in $C_2H_4Cl_2$ and in toluene at 80 °C. Typically 1 mol % of the catalyst (0.004 mmol) was added to a solution of substrate (0.350 mmol) and an internal standard in 17.5 mL of solvent at 80 °C. The reaction was run at 80 °C under argon and samples were taken after 1, 2, 3, 4, 5, and 6 h, and were analyzed by GC.

At 110 °C: Typically 1 mol % of the catalyst (0.004 mmol, 2.4 mg) was added to the solution of substrate (diethyl diallylmalonate) (0.350 mmol) and an internal standard in toluene (17.5 mL) at room temperature. The reaction was run at 110 °C under an argon atmosphere for 6 h and samples were taken for GC after: 15 and 30 min and 1, 2, 3, 4, 5, and 6 h. The same procedure was applied for 2.5 mol % of the catalysts (0.180 mmol substrate scale).

Acknowledgements

The authors thank Professor J. Lewiński (Faculty of Chemistry, Warsaw University of Technology) for his commitment to science and the education of young co-workers, which was always stimulating and grounded a fundamental knowledge helpful in formulation of this concept. We thank Dr S. Harutyunyan for some early experiments (preparation of **4a**) made during her sabbatical stay in 2002. X-ray single crystal measurements were accomplished at the Structural Research Lab. of the Chemistry Department, Warsaw University, Poland. SRL has been established with financial support from the European Regional Development Fund in the Sectoral Operational Programme "Improvement of the Competitiveness of Enterprises, years 2004–2006" project no: WKP 1/1.4.3/1/2004/72/72/165/2005/U. Support from the Foundation for Polish Science for K. G. (professorship Mistrz), A. M. (program START) and program NOVUM is greatly acknowledged. Part of this work was supported by grant N N204 0302 33 from the Ministry of Science and Higher Education (K. W.).

---

[1] For selected reviews on olefin metathesis, see: a) T. M. Trnka, R. H. Grubbs, *Acc. Chem. Res.* **2001**, *34*, 18–29; b) R. H. Grubbs, *Handbook of Metathesis*, Wiley, Weinheim, (Germany), **2003**; c) S. J. Connon, S. Blechert, *Angew. Chem.* **2003**, *115*, 1944–1968; *Angew. Chem. Int. Ed.* **2003**, *42*, 1900–1923; d) D. Astruc, *New J. Chem.* **2005**, *29*, 42–56; e) H. Clavier, K. Grela, A. Kirschning, M. Mauduit, S. P. Nolan, *Angew. Chem.* **2007**, *119*, 6906–6922; *Angew. Chem. Int. Ed.* **2007**, *46*, 6786–6801.

[2] For an industrial perspective, see: A. M. Thayer, *Chem. Eng. News* **2007**, *85*, 37–47.

[3] a) S. B. Garber, J. S. Kingsbury, B. L. Gray, A. H. Hoveyda, *J. Am. Chem. Soc.* **2000**, *122*, 8168–8179; b) S. Gessler, S. Randl, S. Blechert, *Tetrahedron Lett.* **2000**, *41*, 9973–9976.

[4] a) K. Grela, S. Harutyunyan, A. Michrowska, *Angew. Chem.* **2002**, *114*, 4210–4212; *Angew. Chem. Int. Ed.* **2002**, *41*, 4038–4040; b) A. Michrowska, R. Bujok, S. Harutyunyan, V. Sashuk, G. Dolgonos, K.

Grela, *J. Am. Chem. Soc.* **2004**, *126*, 9318–9325; c) M. Bieniek, R. Bujok, M. Cabaj, N. Lugan, G. Lavigne, D. Arlt, K. Grela, *J. Am. Chem. Soc.* **2006**, *128*, 13652–13653; d) H. Wakamatsu, S. Blechert, *Angew. Chem.* **2002**, *114*, 2509–2511; *Angew. Chem. Int. Ed.* **2002**, *41*, 2403–2405; e) M. Zaja, S. J. Connon, A. M. Dunne, M. Rivard, N. Buschmann, J. Jiricek, S. Blechert, *Tetrahedron* **2003**, *59*, 6545; f) M. Barbasiewicz, M. Bieniek, A. Michrowska, A. Szadkowska, A. Makal, K. Woźniak, K. Grela, *Adv. Synth. Catal.* **2007**, *349*, 193–203.

[5] For a recent example from our laboratory, see: a) M. Barbasiewicz, A. Szadkowska, R. Bujok, K. Grela, *Organometallics* **2006**, *25*, 3599–3604; b) X. Gstrein, D. Burtscher, A. Szadkowska, M. Barbasiewicz, F. Stelzer, K. Grela, C. Slugovc, *J. Polym Sci. Part A: Polym. Chem.* **2007**, *45*, 3494–3500.

[6] a) K. Grela, A. Szadkowska, M. Barbasiewicz, R. Kadyrov, (Degussa AG), DE Patent Application 102007020694.3, **2007**; b) R. Kadyrow, A. Rosiak, J. Tarabocchia, A. Szadkowska, K. Grela, in *Catalysis of Organic Reactions*, Chemistry Industries Series, (Ed.: M. G. White), Taylor & Francis, London, in press ; c) A. Ben-Asuly, E. Tzur, C. E. Diesendruck, M. Sigalov, I. Goldberg, N. G. Lemcoff, *Organometallics* **2008**, *27*, 811–813; d) For a review on latent catalysts, see: A. Szadkowska, K. Grela, *Curr. Org. Chem.* **2008**, in press.

[7] L. J. Farrugia, *J. Appl. Crystallogr.* **1997**, *30*, 565–565.

[8] a) J. Louie, R. H. Grubbs, *Organometallics* **2002**, *21*, 2153–2164; b) M. L. Macnaughtan, M. J. A. Johnson, J. W. Kampf, *Organometallics* **2007**, *26*, 780–782; c) S. L. Bolton, J. E. Williams, M. B. Sponsler, *Organometallics* **2007**, *26*, 2485–2487; d) J. E. Williams, M. J. Harner, M. B. Sponsler, *Organometallics* **2005**, *24*, 2013–2015.

[9] For example: H. Zipse, *J. Chem. Soc. Perkin Trans. 2* **1997**, 2691–2697.

[10] The ruthenium and oxygen charges illustrated in the first scheme do not denote the formal or absolute charges of these atoms but tiny relocations of electron density due to assumed conjugation of the electron density of these atoms with the aromatic ring. For a similar presentation of a conjugation effect with an NHC ligand, see: K. Vehlow, S. Gessler, S. Blechert, *Angew. Chem.* **2007**, *119*, 8228–8231; *Angew. Chem. Int. Ed.* **2007**, *46*, 8082–8085.

[11] T. Uto, T. Nishinaga, A. Matsuura, R. Inoue, K. Komatsu, *J. Am. Chem. Soc.* **2005**, *127*, 10162–10163, and references therein.

[12] Compare: a) J. Lewiński, J. Zachara, K. B. Starowieyski, Z. Ochal, I. Justyniak, T. Kopeć, P. Stolarzewicz, M. Dranka, *Organometallics* **2003**, *22*, 3773–3780; b) J. Lewiński, J. Zachara, P. Stolarzewicz, M. Dranka, E. Kolodziejczyk, I. Justyniak, J. Lipkowski, *New J. Chem.* **2004**, *28*, 1320–1325.

[13] For example, for the vinylic proton in the ethoxymethylene ruthenium complex $\delta = 13.63$ ppm, ref. [8a]. However, this value can not be directly compared, due to the planar orientation of the =CH(OMe) group.

[14] a) Thematic issue of *Chem. Rev.* **2005**, *105*, 3433–3947; b) R. G. Harvey, *Polycyclic Aromatic Hydrocarbons*, Wiley, New York, **1997**; for a discussion of the use of the topology of an aromatic core to design properties of NHC ligands, see: c) M. Nonnenmacher, D. Kunz, F. Rominger, T. Oeser, *J. Organomet. Chem.* **2005**, *690*, 5647–5653; compare also: d) Q. Yao, M. Zabawa, J. Woo, C. Zheng, *J. Am. Chem. Soc.* **2007**, *129*, 3088–3089; for η^2-coordination of polyaromatic systems, see: e) B. C. Brooks, T. B. Gunnoe, W. D. Harman, *Coord. Chem. Rev.* **2000**, *206–207*, 3–61; f) R. M. Chin, L. Dong, S. B. Duckett, M. G. Partridge, W. D. Jones, R. N. Perutz, *J. Am. Chem. Soc.* **1993**, *115*, 7685–7695; g) Z. Xu, *Coord. Chem. Rev.* **2006**, *250*, 2745–2757; h) M. A. Petrukhina, *Coord. Chem. Rev.* **2007**, *251*, 1690–1698; for a discussion of the interplay between electronic delocalization and localization, see: i) S. Shaik, *New J. Chem.* **2007**, *31*, 2015–2028; for a recent theoretical treatment, see: j) J.-I. Aihara, M. Makino, *Chem. Asian J.* **2008**, *3*, 585–591; k) S. Fias, P. W. Fowler, J. L. Delgado, U. Hahn, P. Bultinck, *Chem. Eur. J.* **2008**, *14*, 3093–3099.

[15] G. Portella, J. Poater, M. Solà, *J. Phys. Org. Chem.* **2005**, *18*, 785–791.

[16] a) A. Filarowski, A. Kochel, K. Cieslik, A. Koll, *J. Phys. Org. Chem.* **2005**, *18*, 986–993; b) M. Palusiak, S. Simon, M. Solà, *J. Org. Chem.* **2006**, *71*, 5241–5248; c) T. M. Krygowski, J. E. Zachara, B. Ośmialowski, R. Gawinecki, *J. Org. Chem.* **2006**, *71*, 7678–7682; d) R. I. Zubatyuk, Y. M. Volovenko, O. V. Shishkin, L. Gorb, J. Leszczynski, *J. Org. Chem.* **2007**, *72*, 725–735; e) M. Palusiak, T. M. Krygowski, *Chem. Eur. J.* **2007**, *13*, 7996–8006; f) T. M. Krygowski, J. Zachara-Horeglad, *J. Phys. Org. Chem.* **2007**, *20*, 594–599; g) P. Sanz, O. Mó, M. Yáñez, J. Elguero, *Chem. Eur. J.* **2008**, *14*, 4225–4232.

[17] a) M. K. Cyrański, B. T. Stępień, T. M. Krygowski, *Tetrahedron* **2000**, *56*, 9663–9667; for more sophisticated analysis, see: b) J. Poater, R. Visser, M. Solà, F. M. Bickelhaupt, *J. Org. Chem.* **2007**, *72*, 1134–1142, and references therein.

[18] G. Gilli, F. Bellucci, V. Ferretti, V. Bertolasi, *J. Am. Chem. Soc.* **1989**, *111*, 1023–1028.

[19] For reviews, see: a) H. Masui, *Coord. Chem. Rev.* **2001**, *219–221*, 957–992; b) J. R. Bleeke, *Chem. Rev.* **2001**, *101*, 1205–1227; c) J. R. Bleeke, *Acc. Chem. Res.* **2007**, *40*, 1035–1047; d) U. Rosenthal, V. V. Burlakov, M. A. Bach, T. Beweries, *Chem. Soc. Rev.* **2007**, *36*, 719–728; e) Y.-Z. Huang, S.-Y. Yang, X.-Y. Li, *J. Organomet. Chem.* **2004**, *689*, 1050–1056; f) M. Ghedini, I. Aiello, A. Crispini, A. Golemme, M. La Deda, D. Pucci, *Coord. Chem. Rev.* **2006**, *250*, 1373–1390; for some theoretical treatment, see: g) M. K. Milčić, B. D. Ostojić, S. D. Zarić, *Inorg. Chem.* **2007**, *46*, 7109–7114; h) Y.-Z. Huang, S.-Y. Yang, X.-Y. Li, *Coord. Chem. Rev.* **2004**, *689*, 1050–1056; i) I. Fernández, G. Frenking, *Chem. Eur. J.* **2007**, *13*, 5873–5884; j) Z. Li, C. Zhao, L. Chen, *J. Mol. Structure, THEOCHEM* **2007**, *807*, 17–23; k) for group 14 organometallics, see: V. Y. Lee, A. Sekiguchi, *Angew. Chem.* **2007**, *119*, 6716–6740; *Angew. Chem. Int. Ed.* **2007**, *46*, 6596–6620; l) for all metal systems, see: Y. Wang, G. H. Robinson, *Organometallics* **2007**, *26*, 2–11; m) A. I. Boldyrev, L.-S. Wang, *Chem. Rev.* **2005**, *105*, 3716–3751; for other manifestations of metalloaromaticity phenomena, see: n) A. Castiòeiras, A. G. Sicilia-Zafra, J. M. González-Pérez, D. Choquesillo-Lazarte, J. Niclós-Gutiérrez, *Inorg. Chem.* **2002**, *41*, 6956–6958; o) Z. D. Tomić, V. M. Leovac, Ž. K. Jaćimović, G. Giester, S. D. Zarić, *Inorg. Chem. Commun.* **2006**, *9*, 833–835; p) Y.-F. Jiang, C.-J. Xi, Y.-Z. Liu, J. Niclós-Gutiérrez, D. Choquesillo-Lazarte, *Eur. J. Inorg. Chem.* **2005**, 1585–1588; q) E. Craven, C. Zhang, C. Janiak, G. Rheinwald, H. Lang, *Z. Anorg. Allg. Chem.* **2003**, *629*, 2282–2290; r) B. E. Bursten, R. F. Fenske, *Inorg. Chem.* **1979**, *18*, 1760–1765.

[20] M. Calvin, K. W. Wilson, *J. Am. Chem. Soc.* **1945**, *67*, 2003–2007.

[21] R. Ferede, N. T. Allison, *Organometallics* **1983**, *2*, 463–465.

[22] a) U. Englert, F. Podewils, I. Schiffers, A. Salzer, *Angew. Chem.* **1998**, *110*, 2196–2197; *Angew. Chem. Int. Ed.* **1998**, *37*, 2134–2136; b) S. H. Liu, W. S. Ng, H. S. Chu, T. B. Wen, H. Xia, Z. Y. Zhou, C. P. Lau, G. Jia, *Angew. Chem.* **2002**, *114*, 1659–1661; *Angew. Chem. Int. Ed.* **2002**, *41*, 1589–1591.

[23] J. D. Carter, T. K. Schoch, L. McElwee–White, *Organometallics*, **1992**, *11*, 3571–3578.

[24] For example: J. Vicente, M. T. Chicote, *Coord. Chem. Rev.* **1999**, *193–195*, 1143–1161.

[25] For systematic studies of naphthalene-based copper, nickel and iron complexes, see: J. Costamagna, J. Vargas, R. Latorre, A. Alvarado, G. Mena, *Coord. Chem. Rev.* **1992**, *119*, 67–88.

[26] Compare: A. J. Giessert, N. J. Brazis, S. T. Diver, *Org. Lett.* **2003**, *5*, 3819–3822.

[27] There is no single indicator of aromaticity: F. Feixas, E. Matito, J. Poater, M. Solà, *J. Chem. Phys. A* **2007**, *111*, 4513–4521, and references therein.

[28] M. K. Cyrański, *Chem. Rev.* **2005**, *105*, 3773–3811.

[29] a) T. M. Krygowski, *J. Chem. Inf. Comput. Sci.* **1993**, *33*, 70–78; b) L. Sobczyk, J. S. Grabowski, T. M. Krygowski, *Chem. Rev.* **2005**, *105*, 3513–3560.

[30] We expected that a fully conjugated (aromatic) ruthenium chelate may be synthesized by a ligand exchange reaction of Grubbs second-generation catalyst with 1-methoxybutadiene. Surprisingly NMR characterization of product showed that the reaction proceeds at the methoxy substituted double bond, leading to the complex typ-

ical for reaction with ethyl vinyl ether $(NHC)(Cl)_2(PCy_3)Ru{=}CH{-}OMe$.

[31] For systems more aromatic than benzene, see: M. Laskoski, W. Steffen, M. D. Smith, U. H. F. Bunz, *Chem. Commun.* **2001**, 691–692.

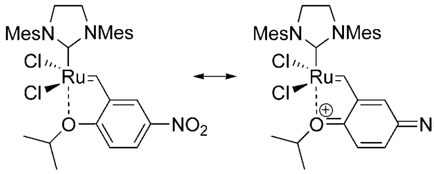
[32] For the concept of isolobal analogies, based on features of interacting orbitals, see: R. Hoffmann, *Angew. Chem.* **1982**, *94*, 725–739; *Angew. Chem. Int. Ed. Engl.* **1982**, *21*, 711–724.

[33] For example: a) R. Drozdzak, B. Allaert, N. Ledoux, I. Dragutan, V. Dragutan, F. Verpoort, *Adv. Synth. Catal.* **2005**, *347*, 1721–1743; b) J. B. Binder, I. A. Guzei, R. T. Reines, *Adv. Synth. Catal.* **2007**, *349*, 395–404.

[34] M. Bandini, P. G. Cozzi, A. Umani-Ronchi, *Chem. Commun.* **2002**, 919–927.

[35] V. C. Gibson, C. Redshaw, G. A. Solan, *Chem. Rev.* **2007**, *107*, 1745–1776.

[36] On the basis of this concept we analyzed the structure of the highly active nitro-substituted Hoveyda–Grubbs catalyst **3b** and considered the contribution of a quinonoid-type structure, which precluded effective conjugation within the chelate ring, compare: a) T. M. Krygowski, K. Woźniak, R. Anulewicz, D. Pawlak, W. Kolodziejski, E. Grech, A. Szady, *J. Phys. Chem. A* **1997**, *101*, 9399–9404; b) T. M. Krygowski, B. T. Stępień, *Chem. Rev.* **2005**, *105*, 3482–3512. Out-of-plane distortion of the alkoxy group in complexes **3c,d** may ultimately result in a similar effect.



Received: April 4, 2008