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Ruthenium(II) Arene Complexes with Asymmetrical Guanidinate Ligands: Synthesis, Characterization, and Application in the Base-Free Catalytic Isomerization of Allylic Alcohols

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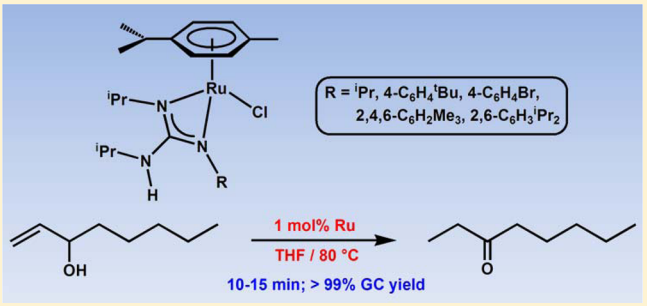
Supporting Information

ABSTRACT: The ruthenium(II) arene dimer $[\{RuCl(\mu\text{-}Cl)(\eta^6\text{-}p\text{-cymene})\}_2]$ readily reacted with 4 equiv of guanidines $(^iPrHN)_2C{=}NR$ (R = ^{i}Pr (**1a**), 4-$C_6H_4{}^t$Bu (**1b**), 4-C_6H_4Br (**1c**), 2,4,6-$C_6H_2Me_3$ (**1d**), 2,6-$C_6H_3{}^iPr_2$ (**1e**)) in toluene at room temperature to generate the mononuclear complexes $[RuCl\{\kappa^2N,N'\text{-}C(NR)(N^iPr)NH^iPr\}(\eta^6\text{-}p\text{-cymene})]$ (**2a**–**e**) and the easily separable guanidinium chloride salts $[(^iPrHN)_2C(NHR)][Cl]$ (**3a**–**e**). Compounds **2a**–**e** and **3a**–**e** were fully characterized by elemental analysis and IR and NMR spectroscopy. The structures of $[RuCl\{\kappa^2N,N'\text{-}C(N^iPr)_2NH^iPr\}(\eta^6\text{-}p\text{-cymene})]$ (**2a**) and $[RuCl\{\kappa^2N,N'\text{-}C(N\text{-}4\text{-}C_6H_4{}^t\text{Bu})(N^iPr)NH^iPr\}(\eta^6\text{-}p\text{-cymene})]$ (**2b**) were also determined by X-ray diffraction analysis. Regardless of the steric requirements of the aromatic substituents, a nonsymmetric coordination of the guanidinate anions in **2b**–**e** was observed, in complete accord with theoretical calculations (DFT) on the corresponding $[RuCl\{\kappa^2N,N'\text{-}C(NR)(N^iPr)\text{-}NH^iPr\}(\eta^6\text{-}p\text{-cymene})]$ and $[RuCl\{\kappa^2N,N'\text{-}C(N^iPr)_2NHR\}(\eta^6\text{-}p\text{-cymene})]$ models. Remarkably, complexes **2a**–**e** were active catalysts for the redox isomerization of allylic alcohols in the absence of base, which represents the first catalytic application known for ruthenium guanidinate species.



INTRODUCTION

Guanidinate monoanions of the general formula $[(RN)_2CNR_2]^-$ are closely related to the well-known amidinates, differing only in that they contain an amino (R_2N) substituent on the ligand's central carbon which results in a higher steric and electronic tunability. Since the preparation of the first transition-metal guanidinate complex by Lappert and co-workers in 1970,[1] a huge number of coordination complexes involving metals from across the periodic table have been described.[2,3] In these, the guanidinate anions have exhibited many coordination modes, but by far the two most common are when they act as delocalized N,N′-chelating or bridging ligands (Figure 1).

Remarkably, despite the great variety of transition-metal guanidinates reported to date in the literature, ruthenium derivatives remain surprisingly rare. Thus, in addition to a series of diruthenium complexes bridged by the *N,N′,N″*-triphenylguanidinate monoanion described by Berry and co-workers,[4] at the beginning of our work in the field, only the following mononuclear derivatives were known: (i) the octahedral species $[Ru\{\kappa^2N,N'\text{-}C(NPh)_2NHPh\}_2(CO)(PPh_3)]$,[5] $[RuH\{\kappa^2N,N'\text{-}C(NPh)_2NHPh\}(CO)(PPh_3)_2]$,[6] and $[Ru\{\kappa^2N,N'\text{-}C(NPh)_2NHPh\}_3]$[7] and (ii) the half-sandwich ruthenium(II) arene complex $[RuCl\{\kappa^2N,N'\text{-}C(NPh)_2NHPh\}(\eta^6\text{-}p\text{-cymene})]$.[8,9] Very recently, with our work already in progress, a family of related chloride and azide $(\eta^6\text{-}p\text{-cymene})Ru^{II}$ derivatives bearing *N,N′,N″*-triarylguanidinates has been described by Thirupathi and co-workers, along with a thorough structural characterization in both solution and the solid state, and reactivity studies of the azido complexes with activated alkynes ([3 + 2] cycloaddition reactions).[10] As in the preceding cases, guanidinate monoanions generated from guanidines with the symmetric substitution pattern $(ArHN)_2C{=}NAr$ were employed by Thirupathi. It is also worthy of note that, despite the burgeoning role of ruthenium in catalytic organic synthesis,[11] none of the ruthenium guanidinate complexes reported so far have been explored in homogeneous catalysis. This fact contrasts with the chemistry of related ruthenium amidinate systems, which have found application in different catalytic transformations.[12]

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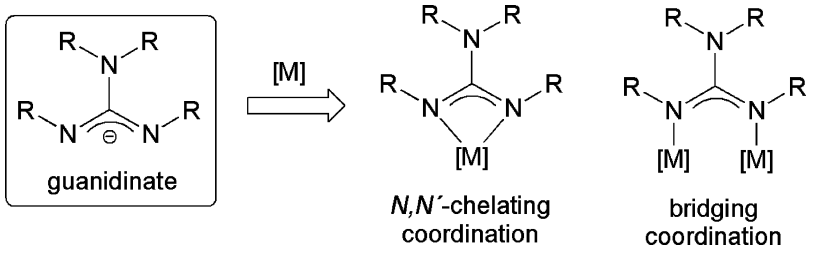


Figure 1. Guanidinate monoanions and their most common coordination modes.

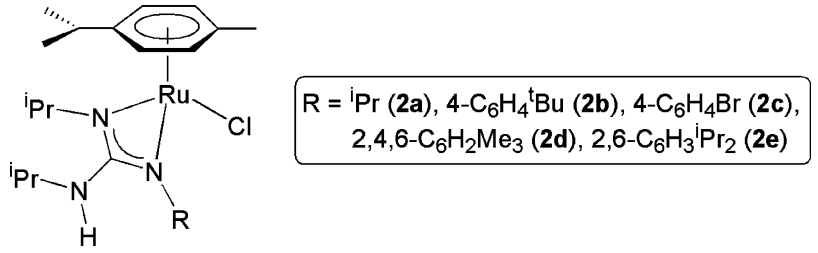
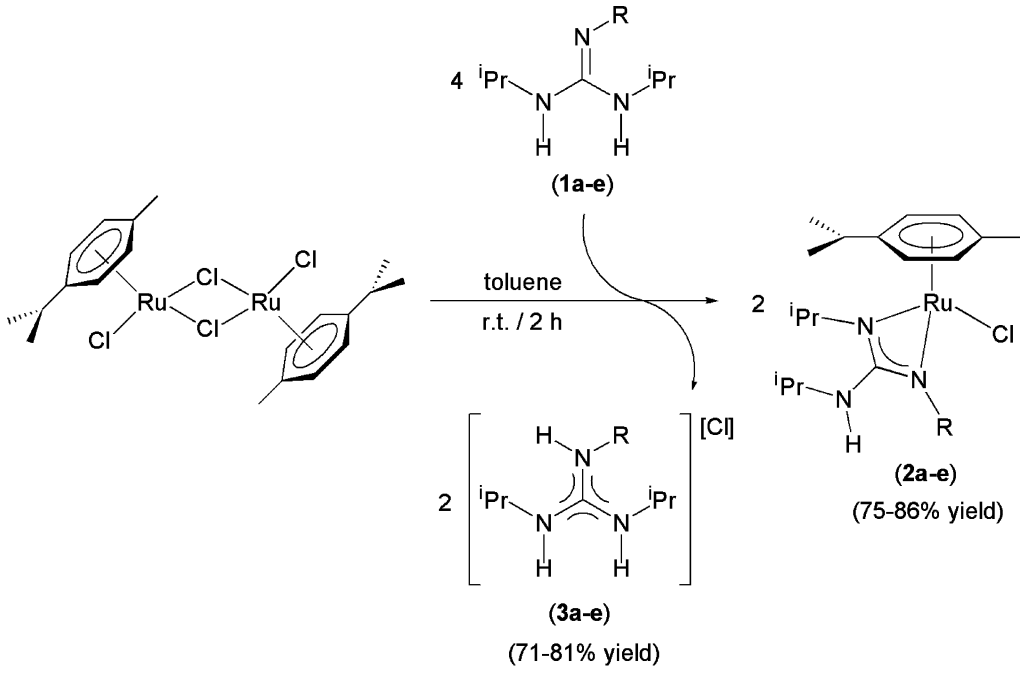


Figure 2. Structure of the ruthenium(II) arene complexes synthesized in this work.

Scheme 1. Synthesis of the Mononuclear Ru(II) Complexes [RuCl{κ^2*N,N′*-C(NR)(N^{i}Pr)NH^{i}Pr}(η^6-*p*-cymene)] (2a−e)



To bridge this gap, herein we describe the preparation of the novel ruthenium(II) arene complexes **2a−e** (Figure 2), generated from the reactions of the readily available guanidines (^{i}PrHN)$_2$C=NR (R = ^{i}Pr (**1a**), 4-C$_6$H$_4$^{t}Bu (**1b**), 4-C$_6$H$_4$Br (**1c**), 2,4,6-C$_6$H$_2$Me$_3$ (**1d**), 2,6-C$_6$H$_3$^{i}Pr$_2$ (**1e**))[13] with the dimeric precursor [{RuCl(μ-Cl)(η^6-*p*-cymene)}$_2$],[14] and their application in the catalytic isomerization of allylic alcohols to carbonyl compounds.[15] The present paper brings novelty since (i) compounds **2b−e** represent the first examples of ruthenium complexes containing asymmetrical monoanionic guanidinate ligands and (ii) unlike the majority of ruthenium catalysts previously described for redox isomerizations of allylic alcohols, complexes **2a−e** operate without the assistance of base.[15]

RESULTS AND DISCUSSION

Synthesis and Characterization of Complexes [RuCl{κ^2*N,N′*-C(NR)(N^{i}Pr)NH^{i}Pr}(η^6-*p*-cymene)] (2a−e). The novel ruthenium-guanidinate complexes [RuCl{κ^2*N,N′*-C(NR)-(N^{i}Pr)-NH^{i}Pr}(η^6-*p*-cymene)] (R = ^{i}Pr (**2a**), 4-C$_6$H$_4$^{t}Bu (**2b**), 4-C$_6$H$_4$Br (**2c**), 2,4,6-C$_6$H$_2$Me$_3$ (**2d**), 2,6-C$_6$H$_3$^{i}Pr$_2$ (**2e**)) were synthesized by following the same procedure reported by Bailey and Thirupathi for the preparation of related symmetrical [RuCl{κ^2*N,N′*-C(NAr)$_2$NHAr}(η^6-*p*-cymene)] species.[8,10] Thus, as shown in Scheme 1, treatment of [{RuCl(μ-Cl)(η^6-*p*-cymene)}$_2$] with 4 equiv of guanidines (^{i}PrHN)$_2$C=NR (**1a−e**), in toluene at room temperature, led to the precipitation of the corresponding guanidinium chloride salts [(^{i}PrHN)$_2$C(NHR)]-

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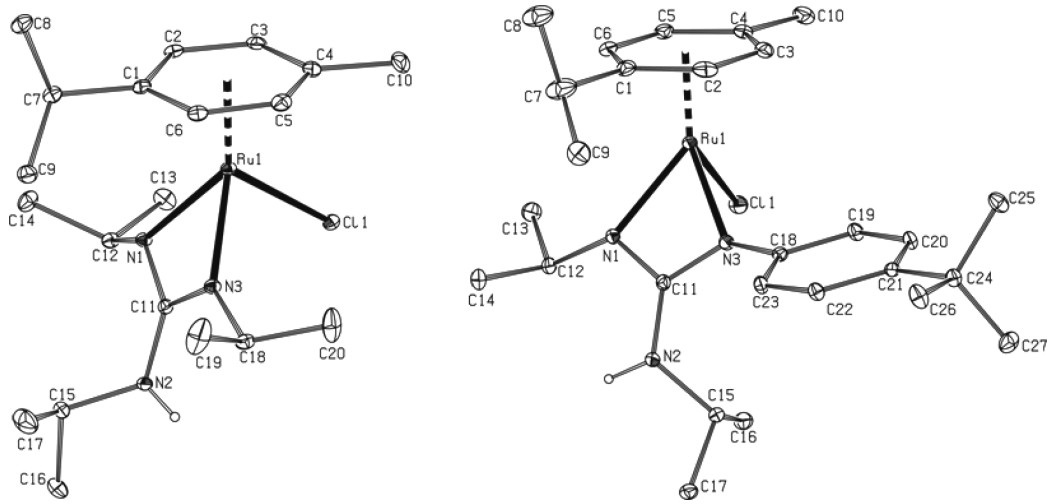

Figure 3. ORTEP-type views of the structures of the ruthenium complexes **2a** (left) and **2b** (right) with the crystallographic labeling schemes. Hydrogen atoms, except that on N(2), have been omitted for clarity in both structures. Thermal ellipsoids are drawn at the 10% probability level.

[Cl] (**3a**−**e**) and the clean formation of the mononuclear complexes **2a**−**e**, which were crystallized from the solution by concentration, filtration of **3a**−**e**, and cooling. Both complexes **2a**−**e** and the guanidinium salts **3a**−**e** were isolated as air-stable solids in high yields (75−86% and 71−81%, respectively) and characterized by elemental analysis and IR and NMR (^{1}H and ^{13}C{^{1}H}) spectroscopy (details are given in the Experimental Section). The asymmetric coordination of the guanidinate anions in complexes **2b**−**e** was clearly reflected in their ^{1}H and ^{13}C{^{1}H} NMR spectra by the appearance of four well-differentiated signals for the aromatic CH protons and carbons of the η^6-coordinated cymene ring, a typical situation in (η^6-*p*-cymene)ruthenium(II) complexes where the metal is a stereogenic center.[16] In the case of the symmetric complex **2a**, these CH units are two-by-two equivalent, leading only to two signals in the spectra. The expected resonances for the guanidinate ligands were also observed in the ^{1}H and ^{13}C{^{1}H} NMR spectra of **2a**−**e**, with a downfield singlet for the central CN_3 carbon at δ_C 160.8−165.4 ppm being their most characteristic hallmark (for the guanidinium salts **3a**−**e** this carbon resonates at slightly higher fields (δ_C 153.6−156.1 ppm)). It is also worthy of note that for complexes **2d**,**e**, containing the bulky aryl substituents mesityl and 2,6-diisopropylphenyl, restricted rotation around the N−Ar bond takes place in solution, as clearly evidenced in their ^{1}H and ^{13}C{^{1}H} NMR spectra by the chemical inequivalence of the Me and ^{i}Pr groups located in the ortho positions of the aromatic rings. This fact clearly reflects the high steric hindrance between these aryl groups and the *p*-cymene ligand.

The structures of the symmetrical complex [RuCl{κ^2*N*,*N*′-C(N^{i}Pr)$_2$NH^{i}Pr}(η^6-*p*-cymene)] (**2a**) and the unsymmetrical complex [RuCl{κ^2*N*,*N*′-C(N-4-C$_6$H$_4$^{t}Bu)(N^{i}Pr)NH^{i}Pr}(η^6-*p*-cymene)] (**2b**) were fully confirmed by means of X-ray diffraction methods. Single crystals suitable for X-ray analysis were obtained by slow diffusion of *n*-pentane into saturated solutions of these compounds in diethyl ether. ORTEP views of the molecules are shown in Figure 3, and selected structural parameters are collected in Table 1.

A typical three-legged piano-stool geometry, with the ruthenium atom surrounded by the η^6-bonded *p*-cymene ligand, a terminal chloride, and the corresponding chelating guanidinate anion, is observed in both cases. The Ru−N(1) and Ru−N(3) bond lengths, in the range 2.076(2)−2.1196(19) Å, are comparable to those previously found in the crystal structures of [RuCl{κ^2*N*,*N*′-C(NAr)$_2$-NHAr}(η^6-*p*-cymene)] (Ar = Ph,[8] 4-C$_6$H$_4$Me,[10] 2-C$_6$H$_4$Me,[10] 2-C$_6$H$_4$OMe,[10] 2,4-C$_6$H$_3$Me$_2$[10]) (2.086(3)−2.149(3) Å). As observed for these complexes, the CN_3 cores of the guanidinate skeletons in **2a**,**b** are perfectly planar, as indicated by the sum of angles around the central C(11) carbons of 359.9° (**2a**) and 360° (**2b**). Concerning the bonding of the guanidinate anions to ruthenium, it is best

Table 1. Selected Bond Distances (Å) and Bond Angles (deg) for 2a,b[a]

	2a	2b
Bond Distances		
Ru−C*	1.66433(17)	1.6655(2)
Ru−Cl(1)	2.4284(6)	2.4147(9)
Ru−N(1)	2.1196(19)	2.108(3)
Ru−N(3)	2.076(2)	2.085(3)
C(11)−N(1)	1.340(3)	1.319(4)
C(11)−N(2)	1.385(3)	1.375(4)
C(11)−N(3)	1.322(3)	1.338(4)
N(1)−C(12)	1.458(3)	1.469(4)
N(2)−C(15)	1.454(3)	1.477(4)
N(3)−C(18)	1.460(3)	1.396(4)
Bond Angles		
C*−Ru−Cl(1)	126.800(17)	129.42(2)
C*−Ru−N(1)	134.97(5)	135.12(8)
C*−Ru−N(3)	136.83(6)	135.68(8)
Cl(1)−Ru−N(1)	87.86(6)	85.33(8)
Cl(1)−Ru−N(3)	85.66(6)	84.92(9)
N(1)−Ru−N(3)	62.19(8)	62.3(1)
Ru−N(1)−C(11)	92.41(14)	93.7(2)
Ru−N(1)−C(12)	135.56(16)	136.4(2)
Ru−N(3)−C(11)	94.87(15)	94.2(2)
Ru−N(3)−C(18)	138.85(17)	132.0(2)
N(1)−C(11)−N(3)	109.0(2)	109.3(3)
N(1)−C(11)−N(2)	124.4(2)	125.0(3)
N(2)−C(11)−N(3)	126.5(2)	125.7(3)
C(11)−N(1)−C(12)	123.4(2)	122.3(3)
C(11)−N(2)−C(15)	121.8(2)	121.4(3)
C(11)−N(3)−C(18)	125.6(2)	129.7(3)

[a] C* denotes the centroid of the *p*-cymene ring (C(1), C(2), C(3), C(4), C(5), and C(6)).

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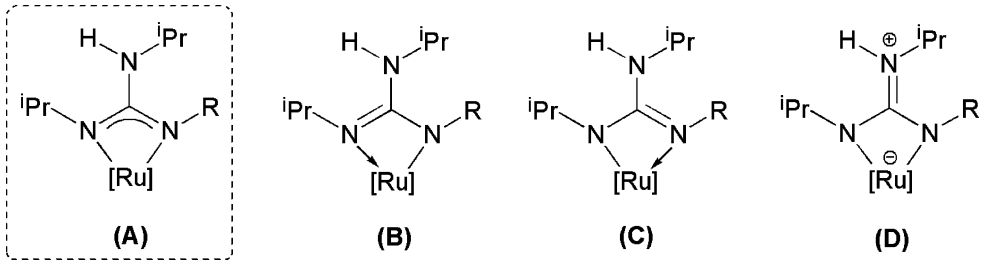

Figure 4. Resonance forms of the guanidinate ligands in complexes **2a–e**.

described through the diazaallyl resonance form **A** (Figure 4). The C–N bond distances between the metal-coordinated nitrogen atoms N(1) and N(3) and the central carbon C(11) of the ligand, very similar in both structures (1.319(4)-1.340(3) Å) and significantly shorter than that of the C(11)–N(2) bond (1.385(3) Å (**2a**) and 1.375(4) Å (**2b**)), are in complete accord with the higher contribution of the delocalized form **A** over the alternative resonance forms **B–D** to the bonding.

It is also worthy of note that the crystal packings of the two molecules are different. Thus, while in the case of [RuCl{κ^2*N*,*N*′-C(N-4-$C_6H_4{}^tBu$)(N^iPr)NH^iPr}(η^6-*p*-cymene)] (**2b**) no intermolecular interactions were found in the crystal lattice, the N(2)–H unit of [RuCl{κ^2*N*,*N*′-C(N^iPr)$_2NH^iPr$}(η^6-*p*-cymene)] (**2a**) is involved in a hydrogen bond with the chloride ligand of a neighboring molecule, thus leading to the formation of dimeric aggregates in the solid state (see Figure 5).[17] According

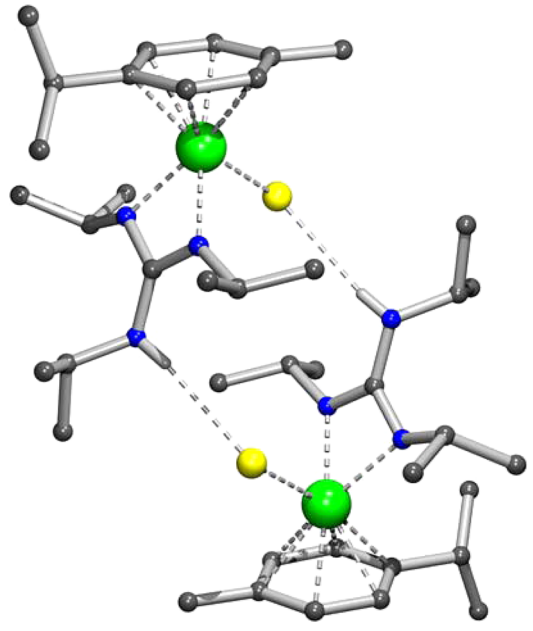

Figure 5. Hydrogen-bonding scheme for complex **2a**. Hydrogen atoms, except that on N(2), have been omitted for clarity. Distances (Å) and angle (deg) for the intermolecular N(2)-H···Cl(1) hydrogen bond are as follows: N(2)–H = 0.81; H–Cl(1) = 2.58; N(2)–Cl(1) = 3.354; N(2)–H–Cl(1) = 161.64.

to the classification of Jeffrey,[18] the distance and angle of the N–H···Cl contact of 2.58 Å and 161.64°, respectively, allow it to be classified as "weak" among the H bonds considered most common in chemical systems. The absence of this weak intermolecular interaction in the structure of **2b** is probably associated with the higher steric demand of the 4-$C_6H_4{}^tBu$ group in comparison to the ^{i}Pr group, which leads to a less compact crystal packing.

As noted above, restricted rotation of the N–aryl bond in complexes **2d,e** was observed by NMR spectroscopy as a result of the steric crowding in the metal environment. Despite this, guanidinate rearrangement from the asymmetrical (complexes **2b–e**) to the less congested symmetrical coordination (complexes **2′b–e**), via a formal 1,3-hydrogen shift, was not observed in solution (Scheme 2).[19] In order to account for the preferred asymmetric coordination of the guanidinate anions, the relative stability of complexes **2b–e** vs **2′b–e** was studied by means of DFT calculations at the B3LYP/6-31G(d)+LANL2DZ level of theory. For comparative purposes, the free anions **4b–e** and **4′b–e** were also investigated (Figure 6).

The optimized structures of **2b–e**, **2′b–e**, **4b–e**, and **4′b–e**, and their most relevant geometrical parameters, are given in the Supporting Information.[20] All of them were characterized as minima on the potential energy surface, and their absolute and relative energies are given in Table 2. According to our calculations, the unsymmetrical complexes **2b–e** are more stable than the symmetrical complexes **2′b–e** by 3.1–5.9 kcal/mol. The smallest energy difference was observed for the **2e**/**2′e** couple, in which the most sterically demanding 2,6-diisopropylphenyl group is present (3.1 kcal/mol). Concerning the free guanidinate anions **4b–e** and **4′b–e**, the former was much more stable than the latter, with energy differences ranging from 10.3 to 14.9 kcal/mol. In contrast to what is observed in the complexes, the presence of the bulkiest 2,6-diisopropylphenyl group results now in a marked preference for the nonsymmetric structure **4e**. All these theoretical predictions, which are in complete accord with the experimental results, suggest that electronic factors prevail over the steric factors to rationalize the observed structures. The stabilization associated with the electronic conjugation of the delocalized π electrons of the N–C–N linkages with the aromatic rings may be evoked to explain the higher thermodynamic stability of **2b–e** vs **2′b–e** and **4b–e** vs **4′b–e**.

Catalytic Isomerization of Allylic Alcohols. The redox isomerization of allylic alcohols represents an efficient, selective, and atom-economical approach for the preparation of saturated carbonyl compounds. The process involves the one-pot migration of the C=C bond of the allylic alcohol and subsequent tautomerization of the resulting enol (Scheme 3). This catalytic transformation has been extensively studied in academic laboratories during the last two decades, as it conveniently replaces the classical routes involving two-step sequential oxidation and reduction reactions,[15] and has found utility in the pharmaceutical industry for the transformation of the naturally occurring opiates morphine and codeine into the more commonly prescribed narcotic analgesics hydromorphone and hydrocodone.[21]

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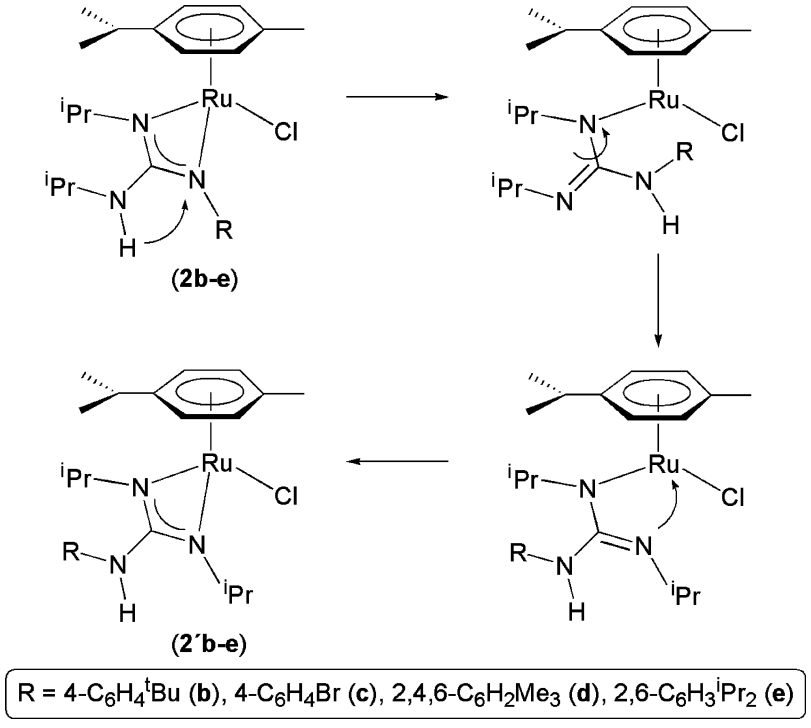
Scheme 2. Potential Isomerization of the Unsymmetrical Complexes 2b−e into the Symmetrical Complexes 2′b−e



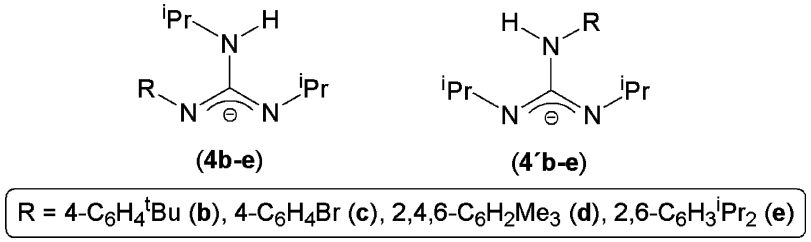


Figure 6. Structure of the guanidinate anions **4b−e** and **4′b−e**.

Table 2. Calculated Total (hartree) and Relative (kcal/mol) Energies for Ruthenium Complexes 2b−e and 2′b−e and Guanidinate Anions 4b−e and 4′b−e[a]

2b	−1 772.588 602 12 (0.0)	**4b**	−828.939 055 043 (0.0)
2′b	−1 772.579 963 55 (5.4)	**4′b**	−828.922 596 635 (10.3)
2c	−4 186.140 932 31 (0.0)	**4c**	−3 242.500 517 74 (0.0)
2′c	−4 186.131 577 88 (5.9)	**4′c**	−3 242.480 911 75 (12.3)
2d	−1 733.281 334 09 (0.0)	**4d**	−789.633 654 411 (0.0)
2′d	−1 733.272 761 79 (5.4)	**4′d**	−789.614 214 617 (12.2)
2e	−1 851.206 685 05 (0.0)	**4e**	−907.565 605 016 (0.0)
2′e	−1 851.201 805 35 (3.1)	**4′e**	−907.541 868 079 (14.9)

[a]B3LYP/6-31G(d)+LANL2DZ-optimized geometries.

The most effective catalysts presently available for the redox isomerization of allylic alcohols are based on ruthenium, rhodium, and iridium complexes,[15] with the first group being particularly attractive due to their lower cost. In this context, a huge number of ruthenium-based catalytic systems for this relevant transformation have been described in recent years.[22] Worthy of note, fast conversions are usually achieved in the presence of a base, since deprotonation of the hydroxyl group of the allylic alcohol is needed to enhance its coordinating ability.[23] In marked contrast to this common trend, we have found that the ruthenium guanidinate complexes [RuCl{κ^2*N*,*N*′-C(NR)-(N^{i}Pr)NH^{i}Pr}(η^6-*p*-cymene)] (R = ^{i}Pr (**2a**), 4-C$_6$H$_4$^{t}Bu (**2b**), 4-C$_6$H$_4$Br (**2c**), 2,4,6-C$_6$H$_2$Me$_3$ (**2d**), 2,6-C$_6$H$_3$^{i}Pr$_2$ (**2e**)) are able to promote the redox isomerization of allylic alcohols under base-free conditions. In this sense, all of them were able to convert selectively and almost quantitatively 1-octen-3-ol into octan-3-one, in remarkably short times (10−15 min), with the catalytic reactions being performed in THF (0.2 M solutions of the allylic

Scheme 3. Catalytic Redox Isomerization of Allylic Alcohols

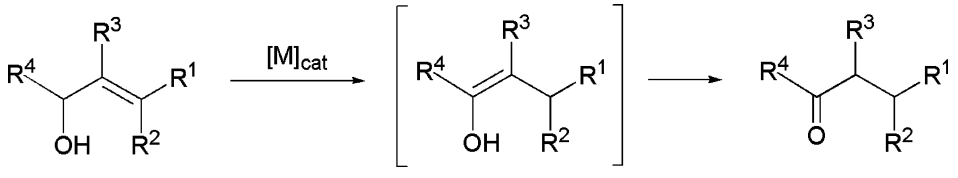


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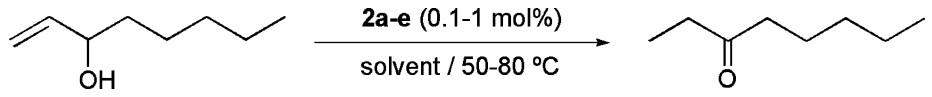
Table 3. Catalytic Isomerization of 1-Octen-3-ol into Octan-3-one using [RuCl{κ^2*N*,*N*′-C(NR)(N^{i}Pr)NH^{i}Pr}(η^6-*p*-cymene)] (**2a**−**e**) as Catalysts[a]



entry	cat.	amt of Ru, mol %	solvent	temp, °C	time	yield, %[b]
1	**2a**	1	THF	80	15 min	>99
2	**2b**	1	THF	80	15 min	>99
3	**2c**	1	THF	80	10 min	>99
4	**2d**	1	THF	80	10 min	>99
5	**2e**	1	THF	80	10 min	>99
6	**2c**	0.5	THF	80	20 min	>99
7	**2c**	0.1	THF	80	1 h	>99
8	**2c**	1	toluene	80	2 h	99
9	**2c**	1	1,2-dichloroethane	80	20 min	99
10	**2c**	1	MeOH	80	3 h	52
11	**2c**	1	H_2O	80	3 h	15
12	**2c**	1	THF	50	24 h	92
13[c]	**2c**	1	THF	80	2 h	>99

[a]Reactions performed under an N_2 atmosphere using 4 mmol of 1-octen-3-ol (0.2 M solutions). [b]Yields determined by GC. [c]Reaction performed in the presence of 20 equiv (per Ru) of free *p*-cymene.

alcohol) at 80 °C with a metal loading of 1 mol % (entries 1−5 in Table 3). Turnover frequencies of up to 540 h^{-1} were reached under these conditions (entries 3−5). As shown in entries 6 and 7, lower catalyst loadings were tolerated without a drastic increase in the reaction times. For example, using only 0.1 mol % of [RuCl{κ^2*N*,*N*′-C(N-4-C_6H_4Br)(N^{i}Pr)NH^{i}Pr}(η^6-*p*-cymene)] (**2c**), complete formation of octan-3-one took place in 1 h (TOF = 1000 h^{-1}; entry 7). The isomerization of 1-octen-3-ol into octan-3-one by means of complex **2c** (1 mol %) was also studied in other organic solvents (toluene, 1,2-dichloroethane, and methanol), as well as in water, but none of them allowed us to improve the result previously obtained in THF (entries 8−11 vs entry 3). The use of protic solvents (H_2O and MeOH) turned out to be particularly harmful due to the partial decomposition of **2c**, a process clearly appreciable to the naked eye by a color change of the solution from orange to black. Poorer results were also obtained on lowering the reaction temperature (e.g., at 50 °C in THF, 24 h of heating was needed to attain a 92% conversion; see entry 12). It is also important to note that, when the isomerization of 1-octen-3-ol with complex **2c** (1 mol %, THF, 80 °C) was performed in the presence of 20 equiv of free *p*-cymene, the performance shown by this catalyst was significantly reduced (entry 13 vs 3). This fact seems to indicate that the required vacant sites for coordination of the substrate may be generated by release of the arene ligand, possibly as a result of the steric hindrance between the bulky guanidinate substituents and the coordinated *p*-cymene unit.

To define the scope of this catalytic transformation, other allylic alcohols were subjected to the action of [RuCl{κ^2*N*,*N*′-C(N-4-C_6H_4Br)(N^{i}Pr)NH^{i}Pr}(η^6-*p*-cymene)] (**2c**) (Table 4). This complex was chosen because it could be easily crystallized on a large scale. Reactions were performed in all cases in THF (0.2 M solutions) at 80 °C using a Ru loading of 1 mol %. Thus, as observed for 1-octen-3-ol (entry 1), related aliphatic substrates AlkCH(OH)CH═CH_2 could also be efficiently converted into the corresponding ketones after only 10−30 min of heating (entries 2−5).

Complex **2c** proved also effective in the isomerization of aromatic allylic alcohols ArCH(OH)CH═CH_2, thus confirming the generality of this base-free catalytic transformation (entries 6−9). However, due probably to the steric congestion associated with the presence a bulky Ar group in an α position with respect to the alcohol unit, which disfavors their coordination to the metal, longer reaction times (3−24 h) were in these cases required to attain good conversions.[24] In addition, a marked influence of the electronic properties of the aryl rings on the reaction rates was observed, with those substrates bearing electron-withdrawing groups showing a remarkably lower reactivity (entries 7 and 8 vs 9). Finally, it is also worthy of note that the process is not restricted to allylic alcohols with a monosubstituted carbon−carbon double bond, since the isomerization of the disubstituted 3-penten-2-ol into pentan-2-one also took place efficiently after a short heating period (1 h; entry 10).

The effectiveness shown by [RuCl{κ^2*N*,*N*′-C(NR)(N^{i}Pr)-NH^{i}Pr}(η^6-*p*-cymene)] (**2a**−**e**) under base-free conditions raised the question of a possible cooperative effect of the pendant amino NH^{i}Pr group of the guanidinate ligands during catalysis. This group could facilitate the generation of the more coordinating oxo-allyl anion by deprotonation of the allylic alcohol. To answer this question, we decided to prepare the related amidinate complex [RuCl{κ^2*N*,*N*′-C(N^{i}Pr)$_2$Me}(η^6-*p*-cymene)] (**5**), by reacting [{RuCl(μ-Cl)(η^6-*p*-cymene)}$_2$] with the lithium amidinate salt Li[(^{i}PrN)$_2$CMe][25] (details are given in the Experimental Section), and explore its catalytic behavior (Scheme 4).[26] The remarkably lower catalytic activity shown by this complex in the redox isomerization of the model substrate 1-octen-3-ol seems to corroborate our hypothesis. More evidence supporting the direct participation of the pendant amino NH^{i}Pr group during the catalytic events is the fact that the activity of [RuCl{κ^2*N*,*N*′-C(N-4-C_6H_4Br)(N^{i}Pr)NH^{i}Pr}(η^6-*p*-cymene)] (**2c**) is drastically reduced in the presence of an acid. Thus, when the catalytic isomerization of 1-octen-3-ol into octan-3-one by means of **2c** (1 mol %) was performed with 1 equiv of HCl (Et_2O solution) per Ru in the medium, 6.5 h of heating was needed to achieve a quantitative conversion (13% after 1 h) of the substrate, instead of the 10 min required under acid-free conditions (entry 1 in Table 4).

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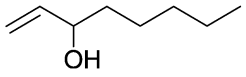
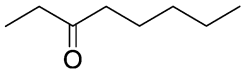
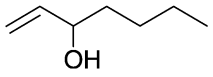
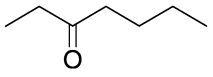
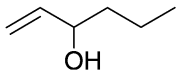
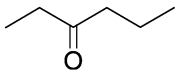
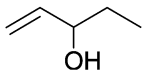
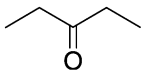
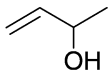
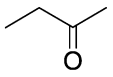
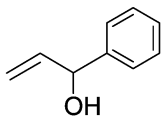
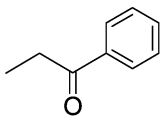
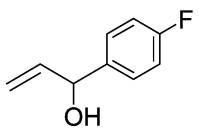
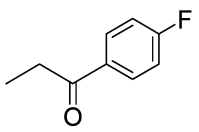
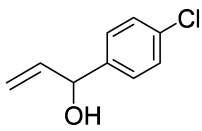
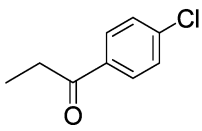
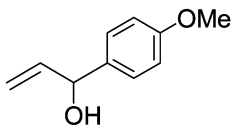
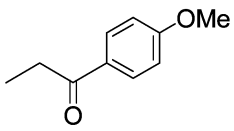
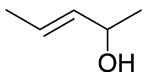
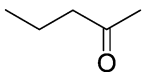
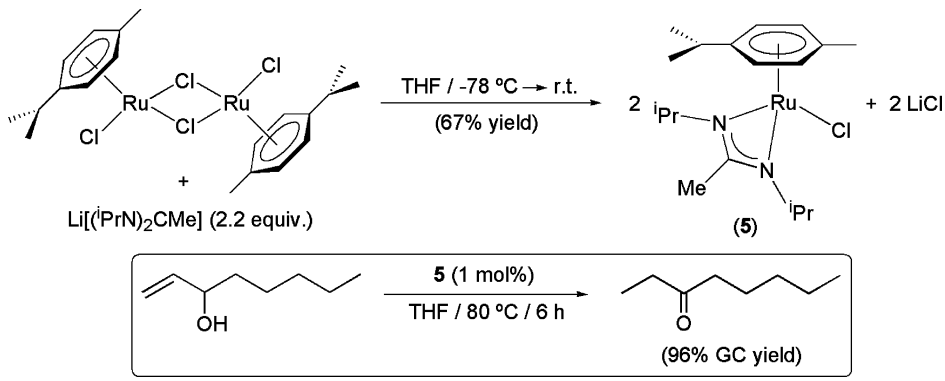
Table 4. Catalytic Isomerization of Allylic Alcohols Using [RuCl{κ^2*N,N′*-C(N-4-C_6H_4Br)(N^{i}Pr)NH^{i}Pr}(η^6-*p*-cymene)] (2c) as Catalyst[a]

Entry	Substrate	Product	Time	Yield[b]
1			10 min	> 99%
2			30 min	96%
3			30 min	97%
4			20 min	> 99%
5			10 min	> 99%
6			12 h	83%
7			24 h	88%
8			24 h	80%
9			3 h	99%
10			1 h	99%

[a]Reactions performed at 80 °C under N_2 atmosphere using 4 mmol of the corresponding allylic alcohol (0.2 M solutions in THF). [substrate]:[Ru] = 100:1. [b]Yields determined by GC.

Scheme 4. Synthesis and Catalytic Behavior of the Ruthenium(II) Amidinate Complex 5



CONCLUSION

In summary, the novel ruthenium(II) guanidinate complexes [RuCl{κ^2*N,N′*-C(NR)(N^{i}Pr)NH^{i}Pr}(η^6-*p*-cymene)] (R = ^{i}Pr (**2a**), 4-$C_6H_4{}^t$Bu (**2b**), 4-C_6H_4Br (**2c**), 2,4,6-$C_6H_2Me_3$ (**2d**), 2,6-$C_6H_3{}^i Pr_2$ (**2e**)) have been synthesized in high yields from the reaction of the dimer [{RuCl(μ-Cl)(η^6-*p*-cymene)}$_2$] with an excess of the corresponding guanidines (^{i}PrHN)$_2$C═NR, and two of them, namely [RuCl{κ^2*N,N′*-C(N^{i}Pr)$_2$NH^{i}Pr}(η^6-*p*-cymene)] (**2a**) and [RuCl{κ^2*N,N′*-C(N-4-$C_6H_4{}^t$Bu)(N^{i}Pr)-NH^{i}Pr}(η^6-*p*-cymene)] (**2b**), were structurally characterized by

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means of single-crystal X-ray diffraction techniques. Compounds **2b−e** represent the first examples of ruthenium complexes containing asymmetrical monoanionic guanidinate ligands reported to date in the literature. In addition, we have also demonstrated that complexes **2a−e** are efficient catalysts in the redox isomerization of allylic alcohols into the corresponding saturated ketones and that, unlike the majority of ruthenium catalysts previously described for this catalytic transformation, they are able to operate under base-free conditions. To the best of our knowledge, this is the first catalytic application known for ruthenium guanidinate species.

EXPERIMENTAL SECTION

Synthetic procedures were performed under an atmosphere of dry nitrogen using vacuum-line and standard Schlenk techniques. Solvents were dried by standard methods and distilled under nitrogen before use. All reagents were obtained from commercial suppliers and used without further purification, with the exception of the ruthenium(II) arene dimer $[\{RuCl(\mu\text{-}Cl)(\eta^6\text{-}p\text{-cymene})\}_2]$,[14] guanidines $(^iPrHN)_2C{=}NR$ (**1a−e**),[13] the lithium amidinate salt $Li[(^iPrN)_2CMe]$,[25] and the allylic alcohols 1-(4-fluorophenyl)-2-propen-1-ol,[27] 1-(4-chlorophenyl)-2-propen-1-ol,[28] and 1-(4-methoxyphenyl)-2-propen-1-ol,[29] which were prepared by following the methods reported in the literature. Infrared spectra were recorded on a Perkin-Elmer 1720-XFT spectrometer. The C, H, and N analyses were carried out with a Perkin-Elmer 2400 microanalyzer. NMR spectra were recorded on Bruker DPX300 and AV400 instruments. Chemical shifts are given in ppm, relative to internal tetramethylsilane. DEPT experiments have been carried out for all the compounds reported in this paper. GC and GC/MSD measurements were made on a Hewlett-Packard HP6890 apparatus (Supelco Beta-DexTM 120 column, 30 m length, 250 μm diameter) and an Agilent 6890N apparatus coupled to a 5973 mass detector (HP-1MS column, 30 m length, 250 μm diameter), respectively.

Reactions of the Dimer $[\{RuCl(\mu\text{-}Cl)(\eta^6\text{-}p\text{-cymene})\}_2]$ with Guanidines $(^iPrHN)_2C{=}NR$ (R = ^{i}Pr (1a), 4-$C_6H_4{}^t$Bu (1b), 4-C_6H_4Br (1c), 2,4,6-$C_6H_2Me_3$ (1d), 2,6-$C_6H_3{}^iPr_2$ (1e)). A solution of $[\{RuCl(\mu\text{-}Cl)(\eta^6\text{-}p\text{-cymene})\}_2]$ (0.306 g, 0.5 mmol) in 30 mL of toluene was treated with the appropriate guanidine **1a−e** (2 mmol) at room temperature for 2 h. The gradual appearance of a white solid precipitate of the guanidinium chloride salts $[(^iPrHN)_2C(NHR)][Cl]$ (**3a−e**) was observed. The resulting suspension was then concentrated to ca. 10 mL and filtered using a cannula. The white solid was washed with hexanes (2 × 10 mL) and diethyl ether (5 mL) to afford **3a−e** in pure form. The filtrate was stored in a freezer at −20 °C for 24−48 h, leading to complexes $[RuCl\{\kappa^2N,N'\text{-}C(NR)(N^iPr)NH^iPr\}(\eta^6\text{-}p\text{-cymene})]$ (**2a−e**) as yellow-orange crystals, which were separated, washed with hexanes (2 × 5 mL), and vacuum-dried. Characterization data for **2a−e** are as follows. **2a**: yield 0.364 g (80%); IR (KBr, cm^{-1}) ν 3289 (N−H); ^1H NMR (CD_2Cl_2) δ 5.42 and 5.18 (d, 2H each, $^3J_{HH}$ = 5.9 Hz, CH of cym), 3.50−3.32 (m, 3H, NC*H*Me$_2$), 2.87 (d, 1H, $^3J_{HH}$ = 10.8 Hz, NH), 2.80 (sept, 1H, $^3J_{HH}$ = 7.0 Hz, C*H*Me$_2$ of cym), 2.18 (s, 3H, Me of cym), 1.30, 1.20, and 1.11 (d, 6H each, $^3J_{HH}$ = 6.4 Hz, NCH*Me*$_2$), 1.27 (d, 6H, $^3J_{HH}$ = 7.0 Hz, CH*Me*$_2$ of cym) ppm; $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ 163.6 (s, CN_3), 97.9 and 96.7 (s, C of cym), 79.0 and 78.9 (s, CH of cym), 46.7 and 46.6 (s, NCHMe$_2$), 31.9 (s, CHMe$_2$ of cym), 26.0, 25.0, 23.8, and 22.3 (s, NCH*Me*$_2$ and CH*Me*$_2$ of cym), 15.1 (s, Me of cym) ppm. Anal. Calcd for $RuC_{20}H_{36}N_3Cl$: C, 52.79; H, 7.97; N, 9.23. Found: C, 52.66; H, 8.10; N, 9.17. **2b**: yield 0.409 g (75%); IR (KBr, cm^{-1}) ν 3338 (N−H); ^1H NMR (CD_2Cl_2) δ 7.24 and 7.09 (d, 2H each, $^3J_{HH}$ = 8.7 Hz, CH_{arom}), 5.33 and 5.04 (d, 1H each, $^3J_{HH}$ = 6.1 Hz, CH of cym), 5.21 and 5.09 (d, 1H each, $^3J_{HH}$ = 5.5 Hz, CH of cym), 3.34 (m, 2H, NC*H*Me$_2$ and NH), 3.21 (m, 1H, NC*H*Me$_2$), 2.71 (m, 1H, C*H*Me$_2$ of cym), 2.20 (s, 3H, Me of cym), 1.35 (s, 9H, C*Me*$_3$), 1.32 and 1.29 (d, 3H each, $^3J_{HH}$ = 6.3 Hz, NCH*Me*$_2$ or CH*Me*$_2$ of cym), 1.27 and 0.97 (d, 3H each, $^3J_{HH}$ = 6.9 Hz, NCH*Me*$_2$ or CH*Me*$_2$ of cym), 1.23 (d, 3H, $^3J_{HH}$ = 6.6 Hz, NCH*Me*$_2$ or CH*Me*$_2$ of cym), 0.96 (d, 3H, $^3J_{HH}$ = 6.0 Hz, NCH*Me*$_2$ or CH*Me*$_2$ of cym) ppm; $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ 161.1 (s, CN_3), 147.7 and 142.9 (s, C_{arom}), 125.0 and 121.9 (s, CH_{arom}), 98.3 and 96.8 (s, C of cym), 80.7, 79.3, 78.8, and 78.7 (s, CH of cym), 45.8 and 44.5 (s, NCHMe$_2$), 34.0 (s, CMe$_3$), 31.4 (s, CHMe$_2$ of cym), 31.3 (s, C*Me*$_3$), 25.5, 24.8, 23.7, 22.9, 22.4, and 22.1 (s, NCH*Me*$_2$ and CH*Me*$_2$ of cym), 18.8 (s, Me of cym) ppm. Anal. Calcd for $RuC_{27}H_{42}N_3Cl$: C, 59.48; H, 7.77; N, 7.71. Found: C, 59.60; H, 7.68; N, 7.83. **2c**: yield 0.488 g (86%); IR (KBr, cm^{-1}) ν 3355 (N−H); ^1H NMR ($CDCl_3$) δ 7.29 and 7.04 (d, 2H each, $^3J_{HH}$ = 8.5 Hz, CH_{arom}), 5.31 and 5.01 (d, 1H each, $^3J_{HH}$ = 5.5 Hz, CH of cym), 5.13 and 5.06 (d, 1H each, $^3J_{HH}$ = 5.7 Hz, CH of cym), 3.37−3.13 (m, 3H, NC*H*Me$_2$ and NH), 2.65 (m, 1H, C*H*Me$_2$ of cym), 2.19 (s, 3H, Me of cym), 1.31, 1.29, 0.97, and 0.94 (d, 3H each, $^3J_{HH}$ = 6.0 Hz, NCH*Me*$_2$ or CH*Me*$_2$ of cym), 1.24 and 1.20 (d, 3H each, $^3J_{HH}$ = 7.0 Hz, NCH*Me*$_2$ or CH*Me*$_2$ of cym) ppm; $^{13}C\{^1H\}$ NMR (CD_2Cl_2) δ 160.8 (s, CN_3), 149.9 and 111.6 (s, C_{arom}), 131.0 and 123.7 (s, CH_{arom}), 98.5 and 97.3 (s, C of cym), 80.6, 79.3, 79.0, and 78.6 (s, CH of cym), 45.7 and 44.8 (s, NCHMe$_2$), 31.4 (s, CHMe$_2$ of cym), 25.3, 24.7, 23.8, 22.7, 22.4, 22.0, and 18.8 (s, NCH*Me*$_2$, CH*Me*$_2$ of cym and Me of cym) ppm. Anal. Calcd for $RuC_{23}H_{33}N_3BrCl$: C, 48.64; H, 5.86; N, 7.40. Found: C, 48.82; H, 5.79; N, 7.29. **2d**: yield 0.435 g (82%); IR (KBr, cm^{-1}) ν 3343 (N−H); ^1H NMR (CD_2Cl_2) δ 6.89 and 6.82 (s, 1H each, CH_{arom}), 5.04, 5.03, 4.99, and 4.82 (d, 1H each, $^3J_{HH}$ = 5.5 Hz, CH of cym), 3.45 (d, 1H, $^3J_{HH}$ = 10.2 Hz, NH), 3.20 and 2.82 (m, 1H each, NC*H*Me$_2$), 2.72 (m, 1H, C*H*Me$_2$ of cym), 2.32, 2.28, and 2.27 (s, 3H each, Ar*Me*), 2.10 (s, 3H, Me of cym), 1.39, 1.26, and 0.91 (d, 3H each, $^3J_{HH}$ = 6.4 Hz, NCH*Me*$_2$ or CH*Me*$_2$ of cym), 1.31 (d, 3H, $^3J_{HH}$ = 6.8 Hz, NCH*Me*$_2$ or CH*Me*$_2$ of cym), 1.29 (d, 3H, $^3J_{HH}$ = 7.5 Hz, NCH*Me*$_2$ or CH*Me*$_2$ of cym), 0.74 (d, 3H, $^3J_{HH}$ = 5.3 Hz, NCH*Me*$_2$ or CH*Me*$_2$ of cym) ppm; $^{13}C\{^1H\}$ NMR (CD_2Cl_2) δ 163.0 (s, CN_3), 144.6, 133.4, 132.2, and 131.3 (s, C_{arom}), 121.9 and 128.6 (s, CH_{arom}), 101.5 and 92.4 (s, C of cym), 80.0, 79.4, 78.4, and 77.9 (s, CH of cym), 45.4 and 44.0 (s, NCHMe$_2$), 31.2 (s, CHMe$_2$ of cym), 26.0, 25.4, 24.4, 22.9, 22.7, 22.1, 20.5, 20.2, 18.7, and 18.6 (s, NCH*Me*$_2$, CH*Me*$_2$ of cym, Me of cym and Ar*Me*) ppm. Anal. Calcd for $RuC_{26}H_{40}N_3Cl$: C, 58.79; H, 7.59; N, 7.91. Found: C, 58.65; H, 7.62; N, 7.78. **2e**: yield 0.441 g (77%); IR (KBr, cm^{-1}) ν 3321 (N−H); ^1H NMR (CD_2Cl_2) δ 7.15−7.09 (m, 3H, CH_{arom}), 5.23 and 5.12 (d, 1H each, $^3J_{HH}$ = 5.6 Hz, CH of cym), 5.03 and 4.96 (d, 1H each, $^3J_{HH}$ = 6.2 Hz, CH of cym), 4.00, 2.84, and 2.69 (m, 1H each, NC*H*Me$_2$, C*H*Me$_2$ of cym or C*H*Me$_2$ of Ar), 3.25 (m, 2H, NC*H*Me$_2$, C*H*Me$_2$ of cym or C*H*Me$_2$ of Ar), 3.07 (d, 1H, $^3J_{HH}$ = 10.8 Hz, NH), 2.15 (s, 3H, Me of cym), 1.42 (d, 3H, $^3J_{HH}$ = 7.4 Hz, NCH*Me*$_2$, CH*Me*$_2$ of cym or CH*Me*$_2$ of Ar), 1.36, 1.34, and 1.33 (d, 3H, $^3J_{HH}$ = 6.7 Hz, NCH*Me*$_2$, CH*Me*$_2$ of cym or CH*Me*$_2$ of Ar), 1.31 (d, 3H, $^3J_{HH}$ = 7.0 Hz, NCH*Me*$_2$, CH*Me*$_2$ of cym or CH*Me*$_2$ of Ar), 1.26 (d, 6H, $^3J_{HH}$ = 6.4 Hz, NCH*Me*$_2$, CH*Me*$_2$ of cym or CH*Me*$_2$ of Ar), 1.05 (d, 3H, $^3J_{HH}$ = 7.1 Hz, NCH*Me*$_2$, CH*Me*$_2$ of cym or CH*Me*$_2$ of Ar), 0.95 (d, 3H, $^3J_{HH}$ = 6.0 Hz, NCH*Me*$_2$, CH*Me*$_2$ of cym or CH*Me*$_2$ of Ar), 0.60 (d, 3H, $^3J_{HH}$ = 5.8 Hz, NCH*Me*$_2$, CH*Me*$_2$ of cym or CH*Me*$_2$ of Ar) ppm; $^{13}C\{^1H\}$ NMR (CD_2Cl_2) δ 165.4 (s, CN_3), 147.3, 145.3, and 144.5 (s, C_{arom}), 123.9, 123.8, and 123.7 (s, CH_{arom}), 102.0 and 92.9 (s, C of cym), 80.2, 79.4, 78.2, and 76.1 (s, CH of cym), 45.7 and 44.3 (s, NCHMe$_2$), 31.4 (s, CHMe$_2$ of cym), 27.6 and 27.8 (s, CHMe$_2$ of Ar), 26.9, 26.7, 26.4, 25.5, 25.4, 25.0, 24.1, 22.9, 22.5, and 22.3 (s, NCH*Me*$_2$, CH*Me*$_2$ of cym and CH*Me*$_2$ of Ar), 18.2 (s, Me of cym). Anal. Calcd for $RuC_{29}H_{46}N_3Cl$: C, 60.76; H, 8.09; N, 7.33. Found: C, 60.69; H, 8.16; N, 7.21.

Characterization data for the guanidinium chloride salts **3a−e** are as follows. **3a**:[30] yield 0.175 g (79%); IR (KBr, cm^{-1}) ν 3312 (N−H); ^1H NMR ($CDCl_3$) δ 7.03 (broad s, 3H, NH), 3.97 (broad s, 3H, C*H*Me$_2$), 1.39 (broad s, 18H, CH*Me*$_2$) ppm; $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ 156.1 (s, CN_3), 46.9 (s, CHMe$_2$), 23.9 (s, CH*Me*$_2$) ppm. Anal. Calcd for $C_{10}H_{24}N_3Cl$: C, 54.16; H, 10.91; N, 18.95. Found: C, 54.01; H, 11.05; N, 18.85. **3b**: yield 0.252 g (81%); IR (KBr, cm^{-1}) ν 3411 (N−H), 3182 (N−H); ^1H NMR (CD_2Cl_2) δ 10.05 (broad s, 1H, NH), 7.65 (broad s, 2H, NH), 7.41 and 7.21 (broad d, 2H each, $^3J_{HH}$ = 7.5 Hz, CH_{arom}), 4.05 (broad s, 2H, C*H*Me$_2$), 1.34 (s, 9H, C*Me*$_3$), 1.20 (d, 12H, $^3J_{HH}$ = 6.0 Hz, CH*Me*$_2$) ppm; $^{13}C\{^1H\}$ NMR (CD_2Cl_2) δ 154.9 (s, CN_3), 149.0 and 134.5 (s, C_{arom}), 126.4 and 122.8 (s, CH_{arom}), 45.7 (s, CHMe$_2$), 34.4 (s, CMe$_3$), 31.0 (s, C*Me*$_3$), 22.4 (s, CH*Me*$_2$) ppm. Anal. Calcd for $C_{17}H_{30}N_3Cl$: C, 65.47; H, 9.70; N, 13.47. Found: C, 65.59; H, 9.87; N, 13.19. **3c**: yield 0.251 g (75%); IR (KBr, cm^{-1}) ν 3402 (N−H), 3221 (N−H); ^1H NMR (CD_2Cl_2) δ 10.04 (broad s, 1H, NH), 7.74 (broad, 2H, NH), 7.41 and 7.13 (broad d, 2H each, $^3J_{HH}$ = 7.7 Hz, CH_{arom}), 3.94

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(broad s, 2H, C*H*Me$_2$), 1.17 (broad s, 12H, CH*Me*$_2$) ppm; ^{13}C{^{1}H} NMR (CD_2Cl_2) δ 154.7 (s, CN_3), 136.1 and 119.0 (s, C_{arom}), 132.6 and 124.0 (s, CH_{arom}), 46.3 (s, CHMe$_2$), 22.6 (s, CH*Me*$_2$) ppm. Anal. Calcd for $C_{13}H_{21}N_3BrCl$: C, 46.65; H, 6.32; N, 12.55. Found: C, 46.54; H, 6.48; N, 12.69. **3d**: yield 0.229 g (77%); IR (KBr, cm^{-1}) ν 3393 (N−H), 3176 (N−H); ^{1}H NMR ($CDCl_3$) δ 9.37 (broad s, 1H, NH), 6.86 (s, 2H, CH_{arom}), 4.17 (broad s, 2H, C*H*Me$_2$), 2.26 (s, 3H, Ar*Me*), 2.17 (s, 6H, Ar*Me*), 1.15 (broad s, 12H, CH*Me*$_2$) ppm; N*H*^{i}Pr signals not observed; ^{13}C{^{1}H} NMR ($CDCl_3$) δ 153.6 (s, CN_3), 141.1, 138.1, and 136.0 (s, C_{arom}), 129.8 (s, CH_{arom}), 45.4 (s, CHMe$_2$), 23.0 (s, CH*Me*$_2$), 21.0 and 18.4 (s, Ar*Me*) ppm. Anal. Calcd for $C_{16}H_{28}N_3Cl$: C, 64.52; H, 9.47; N, 14.11. Found: C, 64.64; H, 9.38; N, 14.34. **3e**: yield 0.241 g (71%); IR (KBr, cm^{-1}) ν 3391 (N−H), 3227 (N−H); ^{1}H NMR ($CDCl_3$) δ 9.57 (broad s, 1H, NH), 7.89 (broad s, 2H, NH), 7.32 (t, 1H, $^3J_{HH}$ = 7.3 Hz, CH_{arom}), 7.17 (d, 2H, $^3J_{HH}$ = 7.3 Hz, CH_{arom}), 4.43 (broad s, 2H, NC*H*Me$_2$), 3.00 (broad s, 2H, C*H*Me$_2$), 1.16 (d, 12H, $^3J_{HH}$ = 6.0 Hz, CH*Me*$_2$), 1.14 (broad s, 12H, NCH*Me*$_2$) ppm; ^{13}C{^{1}H} NMR ($CDCl_3$) δ 155.8 (s, CN_3), 147.4 and 129.0 (s, C_{arom}), 129.6 and 124.6 (s, CH_{arom}), 45.1 (broad s, NCHMe$_2$), 28.3 (s, CHMe$_2$), 24.5 (broad s, NCH*Me*$_2$), 22.9 (s, CH*Me*$_2$) ppm. Anal. Calcd for $C_{19}H_{34}N_3Cl$: C, 67.13; H, 10.08; N, 12.36. Found: C, 67.24; H, 9.90; N, 12.43.

Preparation of the Amidinate Complex [RuCl{κ^2*N*,*N*′-C(N^{i}Pr)$_2$Me}(η^6-*p*-cymene)] (5).[26] The dimeric precursor [{RuCl(μ-Cl)(η^6-*p*-cymene)}$_2$] (0.122 g, 0.2 mmol) and the lithium amidinate salt Li[(^{i}PrN)$_2$CMe] (0.067 g, 0.45 mmol) were dissolved in 10 mL of dry tetrahydrofuran at −78 °C, and the resulting mixture was warmed to room temperature. The solvent was then removed under vacuum, the crude product extracted with hexanes (ca. 30 mL), and the extract filtered over Kieselguhr. Concentration of the resulting solution to ca. 5 mL resulted in the precipitation of a red solid, which was separated and vacuum-dried. Yield: 0.110 g (67%). ^{1}H NMR (C_6D_6): δ 5.08 and 4.81 (d, 2H each, $^3J_{HH}$ = 5.7 Hz, CH of cym), 3.41 (sept, 2H, $^3J_{HH}$ = 6.3 Hz, NC*H*Me$_2$), 2.74 (sept, 1H, $^3J_{HH}$ = 6.9 Hz, C*H*Me$_2$ of cym), 2.16 (s, 3H, Me of cym), 1.52 (s, 3H, N$_2$C*Me*), 1.25 (d, 12H, $^3J_{HH}$ = 6.3 Hz, NCH*Me*$_2$), 1.20 (d, 6H, $^3J_{HH}$ = 6.9 Hz, CH*Me*$_2$ of cym) ppm. ^{13}C{^{1}H} NMR (C_6D_6): δ 151.5 (s, NCN), 98.0 and 97.3 (s, C of cym), 78.9 and 78.3 (s, CH of cym), 47.8 (s, NCHMe$_2$), 32.1 (s, CHMe$_2$ of cym), 25.6 (s, NCH*Me*$_2$), 22.5 (s, CH*Me*$_2$ of cym), 19.0 (s, Me of cym), 13.1 (s, N$_2$C*Me*) ppm. Anal. Calcd for $RuC_{18}H_{31}N_2Cl$: C, 52.48; H, 7.58; N, 6.80. Found: C, 52.59; H, 7.52; N, 6.95.

General Procedure for the Catalytic Isomerization of Allylic Alcohols. In a sealed tube under a nitrogen atmosphere, the corresponding ruthenium complex **2a**−**e** (0.004−0.04 mmol; 0.1−1 mol % of Ru) was added to a solution of the corresponding allylic alcohol (4 mmol) in tetrahydrofuran (20 mL), and the resulting mixture was stirred at 80 °C for the indicated time (see Tables 3 and 4). The course of the reaction was monitored by regularly taking samples of ca. 10 μL, which after dilution with THF (3 mL) were analyzed by GC. The identity of the resulting carbonyl compounds was assessed by comparison with commercially available pure samples (Aldrich Chemical Co. or Acros Organics) and by their fragmentation in GC/MS.

Computational Details. All theoretical calculations were performed with the program package Gaussian03,[31] at the density functional theory (DFT) level by means of the hybrid B3LYP functional.[32] The molecular geometries were optimized, without any molecular symmetry constraint, using Pople's 6-31G(d) split valence basis set for C, H, N, Cl, and Br elements[33] and LANL2DZ for Ru, which combines quasi-relativistic effective core potentials with a valence double-basis set.[34] Frequency calculations were performed to determine whether the optimized geometries were minima on the potential energy surface. Optimized geometries and Cartesian coordinates for all the compounds studied can be found in the Supporting Information.

X-ray Crystal Structure Determination of Complexes 2a,b. Crystals suitable for X-ray diffraction analysis were in both cases obtained by slow diffusion of *n*-pentane into a saturated solution of the complex in diethyl ether. The most relevant crystal and refinement data are collected in Table S1 (Supporting Information). For both crystals, data collection was performed on a Oxford Diffraction Xcalibur Nova single-crystal diffractometer, using Cu Kα radiation (λ = 1.5418 Å). Images were collected at a 75 (**2a**) or 63 mm (**2b**) fixed crystal−detector distance, using the oscillation method, with 1° oscillation and variable exposure time per image (6−10 s for **2a** and 1.5−5 s for **2b**). Data collection strategy was calculated with the program CrysAlis^{Pro} CCD.[35] Data reduction and cell refinement was performed with the program CrysAlis^{Pro} RED.[35] An empirical absorption correction was applied using the SCALE3 ABSPACK algorithm as implemented in the program CrysAlis^{Pro} RED.[35] The software package WINGX[36] was used for space group determination, structure solution, and refinement. The structures were solved by Patterson interpretation and phase expansion using SIR92.[37]

Isotropic least-squares refinement on F^2 using SHELXL97[38] was performed. During the final stages of the refinements, all the positional parameters and the anisotropic temperature factors of all the non-H atoms were refined. The H atoms were geometrically located, and their coordinates were refined riding on their parent atoms (except that on N(2), which in both complexes was found from different Fourier maps and included in a refinement with isotropic parameters). The function minimized was $[\sum w(F_o^2 - F_c^2)/\sum w(F_o^2)]^{1/2}$, where $w = 1/[\sigma^2(F_o^2) + (aP)^2 + bP]$ (a and b values are given in Table S1) with $\sigma(F_o^2)$ from counting statistics and $P = (\mathrm{Max}(F_o^2,0) + 2F_c^2)/3$. The maximum residual electron density is in both cases located near heavier atoms. Atomic scattering factors were taken from ref 39. Geometrical calculations were made with PARST.[40] The crystallographic plots were made with PLATON.[41]

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

A CIF file and a table giving crystallographic data for compounds **2a**,**b** and figures and tables giving optimized geometries and Cartesian coordinates for **2b**−**e**, **2′b**−**e**, **4b**−**e**, and **4′b**−**e**. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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