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# Reactivity of the Dimer [{RuCl($\mu$-Cl)($\eta^3$:$\eta^3$-$C_{10}H_{16}$)}$_2$] ($C_{10}H_{16}$ = 2,7-Dimethylocta-2,6-diene-1,8-diyl) toward Guanidines: Access to Ruthenium(IV) and Ruthenium(II) Guanidinate Complexes

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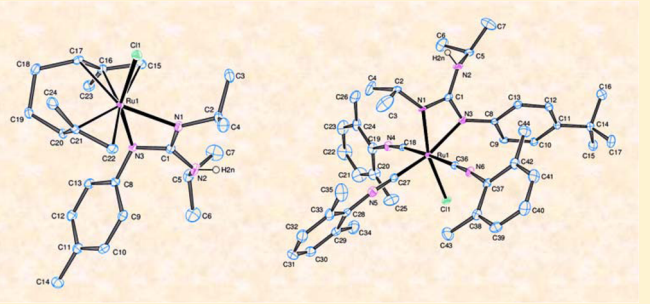
Supporting Information

**ABSTRACT:** The novel bis(allyl)ruthenium(IV) guanidinate complexes [RuCl{$\kappa^2$(*N*,*N*′)-C(NR)(N$^i$Pr)-NH$^i$Pr}($\eta^3$:$\eta^3$-$C_{10}H_{16}$)] ($C_{10}H_{16}$ = 2,7-dimethylocta-2,6-diene-1,8-diyl; R = Ph (**3a**), 4-$C_6H_4F$ (**3b**), 4-$C_6H_4Cl$ (**3c**), 4-$C_6H_4Me$ (**3d**), 3-$C_6H_4Me$ (**3e**) 4-$C_6H_4{}^t$Bu (**3f**)) have been synthesized by treatment of the dimeric precursor [{RuCl($\mu$-Cl)($\eta^3$:$\eta^3$-$C_{10}H_{16}$)}$_2$] (**1**) with 4 equiv of the corresponding guanidine ($^i$PrHN)$_2$C═NR (**2a**–**f**). The easily separable guanidinium chloride salts [($^i$PrHN)$_2$C(NHR)][Cl] (**4a**–**f**) are also formed in these reactions. Attempts to generate analogous Ru(IV) guanidinate complexes from ($^i$PrHN)$_2$C═NR (R = 2-$C_6H_4Me$ (**2g**), 2,4,6-$C_6H_2Me_3$ (**2h**), 2,6-$C_6H_3{}^i Pr_2$ (**2i**)) failed, due probably to the steric hindrance associated with the aryl group in these guanidines. On the other hand, the reaction of the dimer [{RuCl($\mu$-Cl)($\eta^3$:$\eta^3$-$C_{10}H_{16}$)}$_2$] (**1**) with ($^i$PrHN)$_2$C═N-4-$C_6H_4$C≡N (**2j**) led to the selective formation of the mononuclear derivative [$RuCl_2$($\eta^3$:$\eta^3$-$C_{10}H_{16}$){N≡C-4-$C_6H_4$-N═C(NH$^i Pr_2$)$_2$}] (**5**), in which the guanidine coordinates to ruthenium through the pendant nitrile unit. This result contrasts with that obtained by employing the related Ru(II) dimer [{RuCl($\mu$-Cl)($\eta^6$-*p*-cymene)}$_2$] (**6**), whose reaction with **2j** afforded the expected guanidinate complex [RuCl{$\kappa^2$(*N*,*N*′)-C(N-4-$C_6H_4$C≡N)(N$^i$Pr)-NH$^i$Pr}($\eta^6$-*p*-cymene)] (**7**). Treatment of **7** with dimer **1** yielded the dinuclear Ru(II)/Ru(IV) derivative **8**, via cleavage of the chloride bridges of **1** by the C≡N group of **7**. Reductive elimination of the 2,7-dimethylocta-2,6-diene-1,8-diyl chain in [RuCl{$\kappa^2$(*N*,*N*′)-C(NR)(N$^i$Pr)-NH$^i$Pr}($\eta^3$:$\eta^3$-$C_{10}H_{16}$)] (**3a**–**f**) readily took place in the presence of an excess of 2,6-dimethylphenyl isocyanide, thus allowing the high-yield preparation of the octahedral ruthenium(II) compounds *mer*-[RuCl{$\kappa^2$(*N*,*N*′)-C(NR)(N$^i$Pr)-NH$^i$Pr}(CN-2,6-$C_6H_3Me_2$)$_3$] (**9a**–**f**). The structures of [RuCl{$\kappa^2$(*N*,*N*′)-C(N-4-$C_6H_4$Me)(N$^i$Pr)-NH$^i$Pr}($\eta^3$:$\eta^3$-$C_{10}H_{16}$)] (**3d**), [RuCl{$\kappa^2$(*N*,*N*′)-C(N-4-$C_6H_4$C≡N)(N$^i$Pr)-NH$^i$Pr}($\eta^6$-*p*-cymene)] (**7**), and *mer*-[RuCl{$\kappa^2$(*N*,*N*′)-C(N-4-$C_6H_4{}^t$Bu)(N$^i$Pr)-NH$^i$Pr}(CN-2,6-$C_6H_3Me_2$)$_3$] (**9f**), as well as those of the guanidinium chloride salts **4a**–**c**, were unequivocally confirmed by X-ray diffraction methods. In addition, the catalytic behavior of the guanidinate complexes **3a**–**f** and **9a**–**f** in the redox isomerization of allylic alcohols was also explored.



## INTRODUCTION

Guanidinate monoanions have emerged in recent years as versatile and highly modular N,N′-donor ligands, mainly because of their easy access and the wide range of derivatives available through substitution at the terminal nitrogen atoms.[1,2] Although some examples of monodentate metal complexes **A** are known, the coordination chemistry of these heteroallyl ligands is largely dominated by the chelating and bridging binding modes **B** and **C**, respectively (Figure 1).[2]

A large number of metal guanidinate complexes of types **B** and **C** from across the periodic table have been described to date, and their utility in homogeneous catalysis and materials science has been demonstrated.[2] In this context, we have recently reported the preparation of a series of half-sandwich ($\eta^6$-arene)ruthenium(II) derivatives with symmetrically and asymmetrically substituted guanidinate ligands (**D** in Figure 2),

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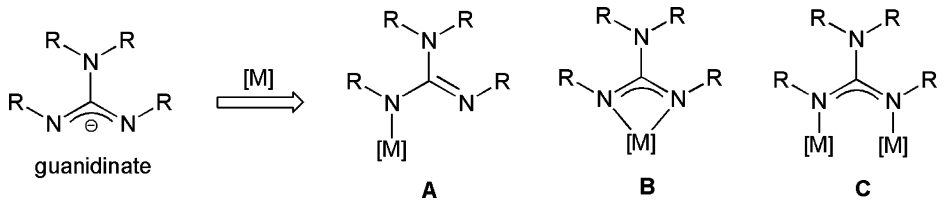


**Figure 1.** Guanidinate ligands and their coordination modes.

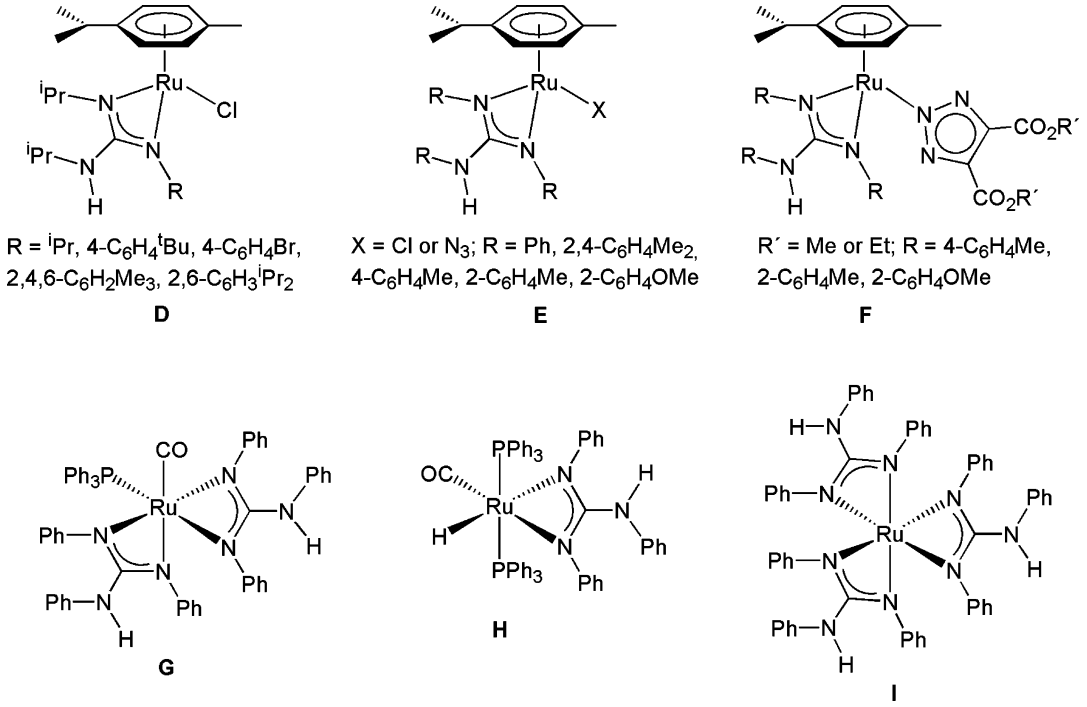


**Figure 2.** Structures of the mononuclear ruthenium complexes with monoanionic guanidinate ligands described in the literature.

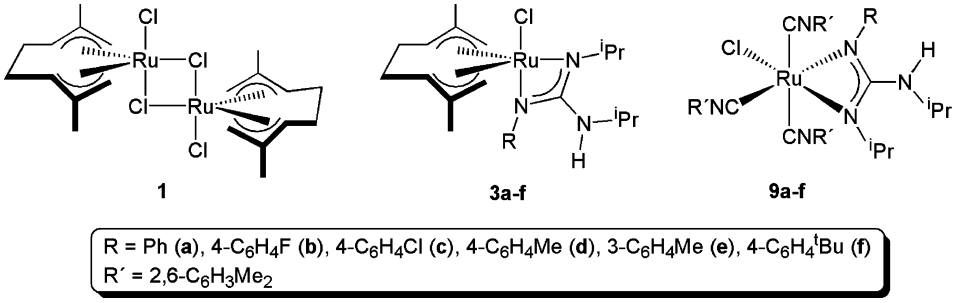


**Figure 3.** Structure of the ruthenium(IV) dimer **1** and the guanidinate complexes described in this work.

which proved to be catalytically active in the base-free redox isomerization of allylic alcohols.[3] Compounds **D** represent rare examples of mononuclear ruthenium guanidinate complexes since, in addition to the closely related species **E** and **F**,[4] only the octahedral ruthenium(II) (**G** and **H**[5]) and ruthenium(III) (**I**[6]) derivatives have been quoted so far in the literature. A mononuclear ruthenium(II) complex with a coordinated guanidinate dianion, namely [Ru{$\kappa^2$(*N*,*N*′)-C(NAc)$_2$=NAc}-($\eta^6$-*p*-cymene)(PPh$_3$)], was also described by Henderson and co-workers.[7] The rest of the ruthenium guanidinate compounds currently known are paddlewheel-type dinuclear species containing $Ru_2^{n+}$ ($n$ = 5, 6) cores, in which the nitrogenated monoanions adopt a bridging coordination (**C** in Figure 1).[8] It is worth noting that the catalytic potential of complexes **E**–**I** was not explored, a fact that contrasts with the chemistry of related mononuclear ruthenium amidinate systems, which have found several applications in homogeneous catalysis.[9]

Another significant difference between the ruthenium chemistry of amidinates [(RN)$_2$CR]$^-$ and guanidinates [(RN)$_2$CNR$_2$]$^-$ is that, to date, ruthenium(IV) representatives are only known for the former.[10] This fact, along with the continuous interest of our respective groups in the chemistry of the bis(allyl)ruthenium(IV) dimer [{RuCl($\mu$-Cl)($\eta^3$:$\eta^3$-C$_{10}$H$_{16}$)}$_2$] (C$_{10}$H$_{16}$ = 2,7-dimethylocta-2,6-diene-1,8-diyl; **1** in Figure 3)[11] and that of metal guanidinate complexes,[12] prompted us to explore the reactivity of [{RuCl($\mu$-Cl)($\eta^3$:$\eta^3$-C$_{10}$H$_{16}$)}$_2$] (**1**) toward guanidines. As a result of this study, we report herein the preparation of the first examples of


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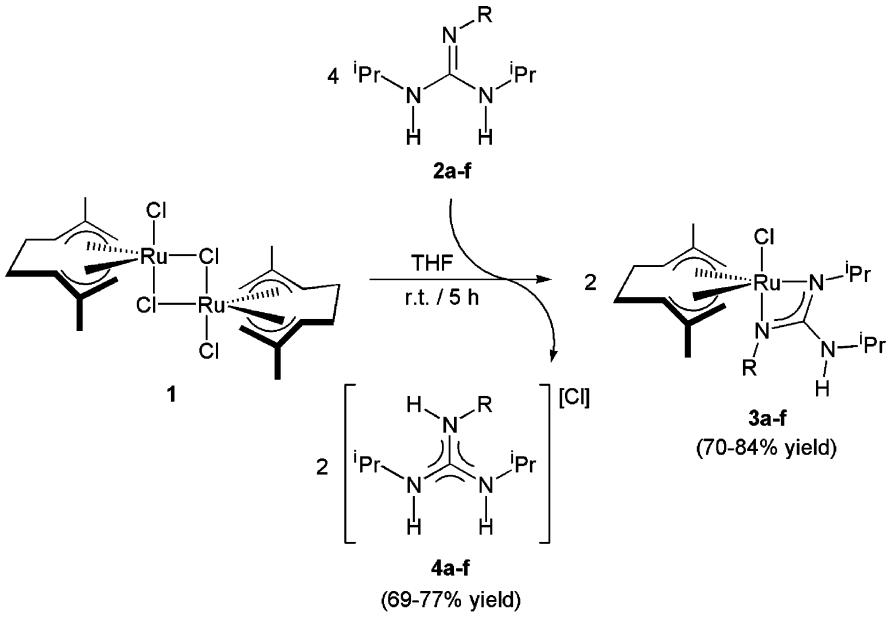
Scheme 1. Synthesis of the Bis(allyl)ruthenium(IV) Guanidinate Complexes [RuCl{$\kappa^2$(*N*,*N*′)-C(NR)(N$^i$Pr)-NH$^i$Pr}($\eta^3$:$\eta^3$-$C_{10}H_{16}$)] (**3a**−**f**)




R = Ph (**a**), 4-$C_6H_4F$ (**b**), 4-$C_6H_4Cl$ (**c**), 4-$C_6H_4Me$ (**d**), 3-$C_6H_4Me$ (**e**), 4-$C_6H_4{}^tBu$ (**f**)

ruthenium(IV) guanidinate complexes, namely [RuCl{$\kappa^2$(*N*,*N*′)-C(NR)(N$^i$Pr)-NH$^i$Pr}($\eta^3$:$\eta^3$-$C_{10}H_{16}$)] (**3a**−**f**), as well as a new family of octahedral ruthenium(II) derivatives with the formula *mer*-[RuCl{$\kappa^2$(*N*,*N*′)-C(NR)(N$^i$Pr)-NH$^i$Pr}-(CN-2,6-$C_6H_3Me_2$)$_3$] (**9a**−**f**) (see Figure 3). The latter were easily generated from **3a**−**f** through the reductive elimination of the 2,7-dimethylocta-2,6-diene-1,8-diyl chain, a process that takes place cleanly in the presence of an excess of 2,6-dimethylphenyl isocyanide. The catalytic behavior of complexes **3a**−**f** and **9a**−**f** in the redox isomerization of allylic alcohols is also briefly discussed.

## RESULTS AND DISCUSSION

Following a synthetic procedure similar to that used in the preparation of compounds **D** and **E** (Figure 2), the novel ruthenium(IV) guanidinate complexes [RuCl{$\kappa^2$(*N*,*N*′)-C(NR)(N$^i$Pr)-NH$^i$Pr}($\eta^3$:$\eta^3$-$C_{10}H_{16}$)] (**3a**−**f**) could be synthesized in high yield (70−84%) by the bridge-splitting reaction of the violet dimer [{RuCl($\mu$-Cl)($\eta^3$:$\eta^3$-$C_{10}H_{16}$)}$_2$] (**1**) with 4 equiv of the corresponding guanidine ($^i$PrHN)$_2$C═NR (R = Ph (**2a**), 4-$C_6H_4F$ (**2b**), 4-$C_6H_4Cl$ (**2c**), 4-$C_6H_4Me$ (**2d**), 3-$C_6H_4Me$ (**2e**) 4-$C_6H_4{}^tBu$ (**2f**)) (Scheme 1). These guanidines were obtained in high yields by a straightforward process of direct addition of anilines to diisopropylcarbodiimide, catalyzed by $ZnEt_2$.[12a] The reactions proceeded cleanly at room temperature in THF to give red solutions containing the desired complexes **3a**−**f**, along with the respective guanidinium chloride salts [($^i$PrHN)$_2$C(NHR)][Cl] (**4a**−**f**). The different solubility profiles of **3a**−**f** and **4a**−**f** in pentane allowed their easy separation at the end of the reactions (details are given in the Experimental Section). Although no intermediates could be detected, it is assumed that these reactions proceed through the initial cleavage of the chloride bridges of **1** and coordination of the guanidine to ruthenium through the more basic iminic nitrogen, followed by release of HCl (which is trapped by the excess guanidine present in the medium) and chelation of the resulting guanidinate anion.[4a]

Both the ruthenium complexes **3a**−**f** and the guanidinium salts **4a**−**f** were isolated as air-stable solids 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 data obtained being fully consistent with the proposed formulations. In particular, for complexes **3a**−**f**, the IR spectra showed a characteristic $\nu$(N−H) absorption band in the 3320−3341 cm$^{-1}$ region. For their part, the $^1$H NMR spectra of **3a**−**f** displayed a four-line pattern for the terminal allylic protons ($H_1$, $H_2$, $H_9$, and $H_{10}$) and two separated signals for the methyl substituents of the 2,7-dimethylocta-2,6-diene-1,8-diyl unit, indicative of inequivalent axial sites on the trigonal-bipyramidal ruthenium atom. The $^{13}$C{$^1$H} NMR spectra of these complexes also showed clearly that the halves of the bis(allyl) $C_{10}H_{16}$ ligand are in inequivalent environments, since 10 different signals were observed in all cases (see the Experimental Section). The expected resonances for the guanidinate ligands were also observed in the NMR spectra, the most significant features being (i) ($^1$H NMR) a doublet signal ($^3J_{HH}$ = 9.9−10.8 Hz) at $\delta_H$ 3.12−3.37 ppm, attributed to the NH proton, and (ii) ($^{13}$C{$^1$H} NMR) a downfield singlet for the central $CN_3$ carbon at ca. $\delta_C$ 161 ppm. The spectra also showed the chemical inequivalence of all the methyl and methynic units of the isopropyl substituents.

In order to confirm unequivocally the structure of complexes **3a**−**f**, a single-crystal X-ray diffraction study on [RuCl{$\kappa^2$(*N*,*N*′)-C(N-4-$C_6H_4Me$)(N$^i$Pr)-NH$^i$Pr}($\eta^3$:$\eta^3$-$C_{10}H_{16}$)] (**3d**) was undertaken. Diffraction-quality crystals were obtained by cooling at −10 °C a saturated solution of the complex in a hexane/$CH_2Cl_2$ mixture. The crystal structure determination revealed the existence of two independent molecules in the asymmetric unit (see Figure S1 in the Supporting Information). However, these molecules are structurally almost identical, and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*Organometallics* XXXX, XXX, XXX−XXX

for clarity only one will be discussed here. An ORTEP view, along with selected bonding parameters, is shown in Figure 4.

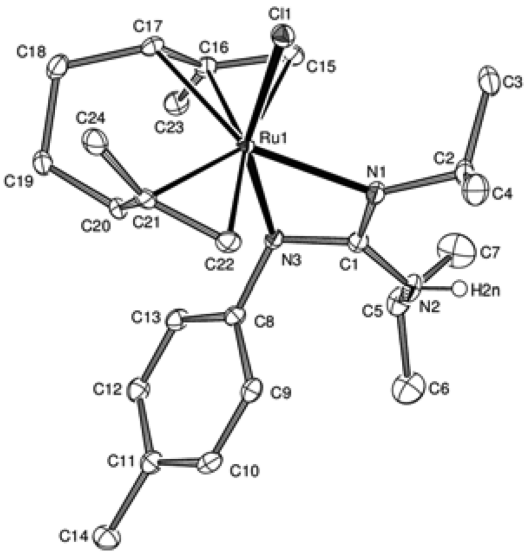


**Figure 4.** ORTEP type view of the structure of the ruthenium(IV) complex **3d** with the crystallographic labeling scheme. Hydrogen atoms, except that on N(2), have been omitted for clarity. Thermal ellipsoids are drawn at the 30% probability level. Selected bond distances (Å) and angles (deg): Ru−C* = 1.9664(2); Ru−C** = 1.9369(2); Ru−Cl(1) = 2.4534(8); Ru−N(1) = 2.146(2); Ru−N(3) = 2.141(2); Ru−C(15) = 2.219(3); Ru−C(16) = 2.226(3); Ru−C(17) = 2.222(3); Ru−C(20) = 2.191(3); Ru−C(21) = 2.196(3); Ru−C(22) = 2.195(3); C(1)−N(1) = 1.302(4); C(1)−N(2) = 1.352(4); C(1)−N(3) = 1.376(4); C(15)−C(16) = 1.409(4); C(16)−C(17) = 1.417(4); C(20)−C(21) = 1.418(4); C(21)−C(22) = 1.410(4); C*−Ru−Cl(1) = 90.76(2); C*−Ru−N(1) = 115.92(7); C*−Ru−N(3) = 97.34(6); C*−Ru−C** = 127.261(12); C**−Ru−Cl(1) = 97.543(19); C**−Ru−N(1) = 115.57(7); C**−Ru−N(3) = 96.68(7); Cl(1)−Ru−N(1) = 92.70(7); Cl(1)−Ru−N(3) = 154.46(7); N(1)−Ru−N(3) = 61.97(9); Ru−N(1)−C(1) = 94.45(18); Ru−N(3)−C(1) = 92.50(18); N(1)−C(1)−N(3) = 110.0(3); N(1)−C(1)−N(2) = 127.8(3); N(2)−C(1)−N(3) = 121.2(3); C(15)−C(16)−C(17) = 114.6(3); C(20)−C(21)−C(22) = 113.0(3). C* and C** denote the centroids of the allyl units (C(15), C(16), C(17), and C(20), C(21), C(22), respectively).

The geometry about the ruthenium atom is best described as a distorted trigonal bipyramid by considering the allyl groups as monodentate ligands bound to the metal through their respective centers of mass (C* and C**). The guanidinate ligand is coordinated edge-on to the ruthenium atom through one of the N$^i$Pr units, which resides in an equatorial position along with the allyl groups, and the N(*p*-tolyl) unit which is *trans* to the chloride ligand in an axial position. The Ru−N(1) and Ru−N(3) bond lengths observed (2.146(2) and 2.141(2) Å, respectively) fall within the upper limit found in the crystal structures of other mononuclear ruthenium guanidinate complexes previously described in the literature (2.076−2.149 Å).[3−6] Furthermore, as observed in other structures containing the "Ru($\eta^3$:$\eta^3$-$C_{10}H_{16}$)" unit,[11] the 2,7-dimethylocta-2,6-diene-1,8-diyl chain shows a local $C_2$ symmetry with no significant variation in the Ru−C distances (in the range 2.191(3)−2.226(3) Å). A striking feature of the structure is the small N(1)−Ru−N(3) bond angle of 61.97(9)°, which deviates significantly from the ideal 90°. This value reflects a high strain in the four-membered metallacycle as a consequence of the small "bite" of the guanidinate ligand. The sum of angles around the central carbon atom of the $CN_3$ skeleton (359°) indicates the planarity of the guanidinate anion, for which a significant contribution of the resonance form **K** (see Figure 5) to its bonding is observed. This bonding description, which is supported by the shorter C(1)−N(1) bond length (1.302(4) Å) in comparison with the C(1)−N(2) and C(1)−N(3) lengths (1.352(4) and 1.376(4) Å, respectively), contrasts with that previously found in the related ruthenium(II) complex [RuCl{$\kappa^2$(*N*,*N*′)-C(N-4-$C_6H_4$$^t$Bu)(N$^i$Pr)-NH$^i$Pr}($\eta^6$-*p*-cymene)] (**D** in Figure 2) previously described by us,[3] where the delocalized form **J** dominated over the alternative resonance forms **K**−**M**.[13]

On the other hand, we note at this point that, although the coordination of the guanidinate anions derived from **2a**−**f** to the [RuCl($\eta^3$:$\eta^3$-$C_{10}H_{16}$)] fragment could also lead to the formation of isomeric species of type **N** and **O** (Figure 6),[14]

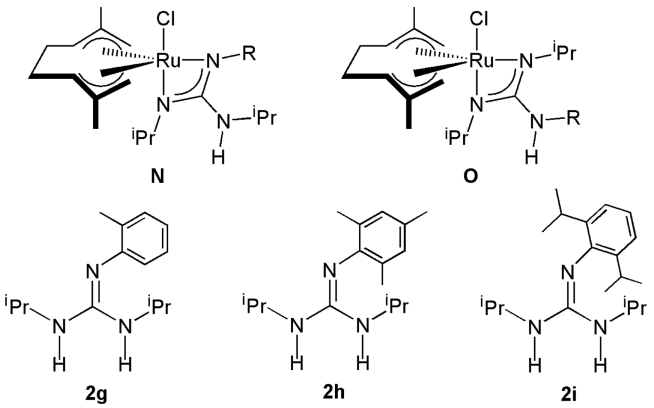


**Figure 6.** Structures of isomeric ruthenium(IV) complexes **N** and **O** and the guanidines **2g**−**i**.

complexes **3a**−**f** were the only ruthenium-containing products observed by NMR in the crude reaction mixtures. The higher steric repulsion between the bulkier N$^i$Pr unit located in an axial position and the octadienediyl chain in isomers **N** and **O** could explain the selective formation of complexes **3a**−**f**. In complete accord with this, dimer **1** was found to be completely

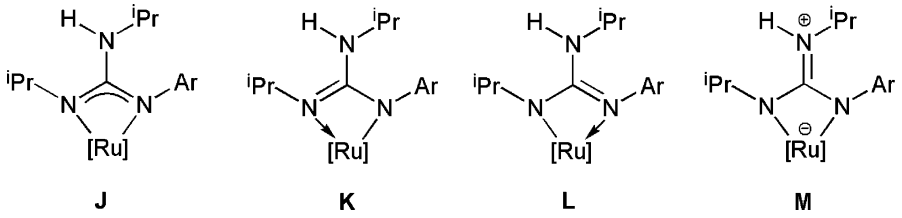


**Figure 5.** Resonance forms of the coordinated guanidinate ligands.



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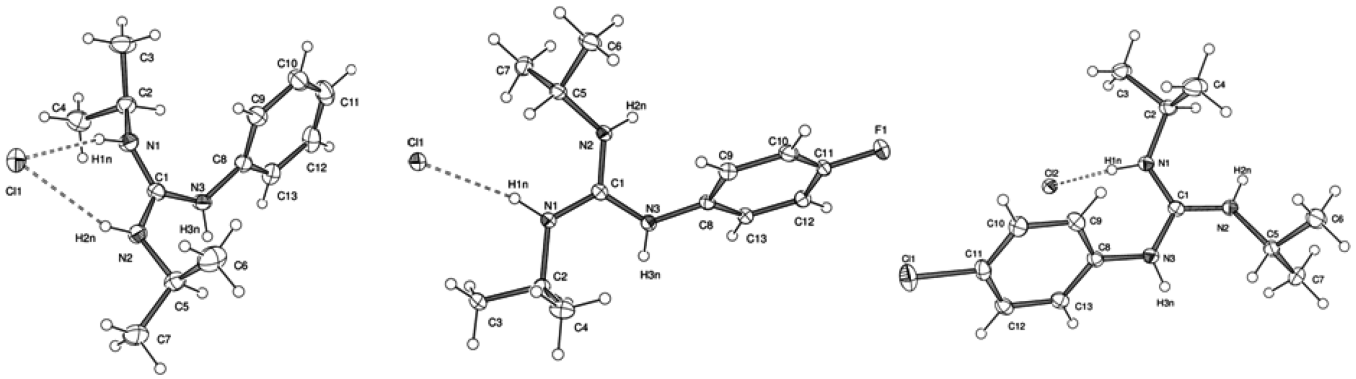
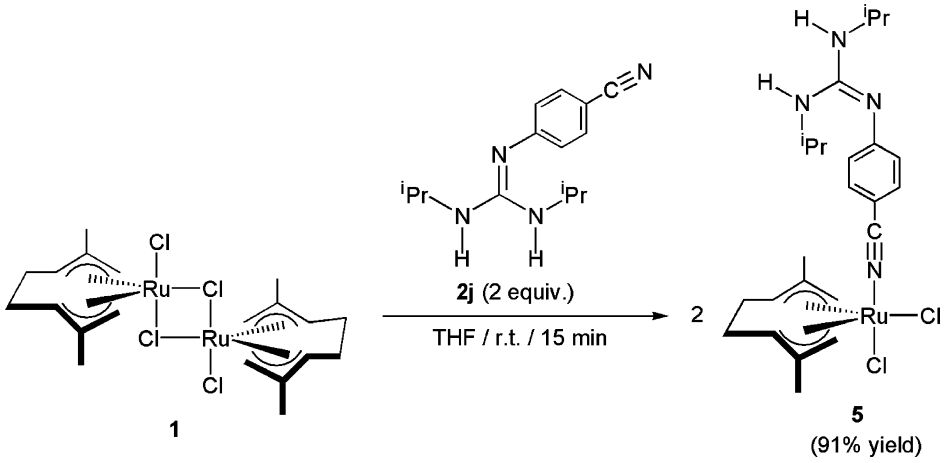


**Figure 7.** ORTEP type views of the structures of the guanidinium chloride salts **4a** (left), **4b** (middle), and **4c** (right) with the crystallographic labeling schemes. Thermal ellipsoids are drawn at the 30% probability level. Selected bond distances (Å) and angles (deg) for **4a**: C(1)−N(1) = 1.322(2); C(1)−N(2) = 1.337(2); C(1)−N(3) = 1.353(2); N(1)−C(1)−N(2) = 118.9(2); N(1)−C(1)−N(3) = 122.7(2); N(2)−C(1)−N(3) = 118.4(2); C(1)−N(1)−C(2) = 126.5(1); C(1)−N(2)−C(5) = 124.7(2); C(1)−N(3)−C(8) = 125.9(2). Selected bond distances (Å) and angles (deg) for **4b**: C(1)−N(1) = 1.328(2); C(1)−N(2) = 1.333(2); C(1)−N(3) = 1.357(2); N(1)−C(1)−N(2) = 121.7(2); N(1)−C(1)−N(3) = 119.8(2); N(2)−C(1)−N(3) = 118.6(1); C(1)−N(1)−C(2) = 124.5(2); C(1)−N(2)−C(5) = 126.5(2); C(1)−N(3)−C(8) = 124.8(1). Selected bond distances (Å) and angles (deg) for **4c**: C(1)−N(1) = 1.338(2); C(1)−N(2) = 1.323(2); C(1)−N(3) = 1.353(2); N(1)−C(1)−N(2) = 120.7(2); N(1)−C(1)−N(3) = 120.2(2); N(2)−C(1)−N(3) = 119.1(2); C(1)−N(1)−C(2) = 124.7(2); C(1)−N(2)−C(5) = 126.3(2); C(1)−N(3)−C(8) = 124.5(2).

**Scheme 2. Reactivity of the Ruthenium(IV) Dimer $[\{RuCl(\mu\text{-}Cl)(\eta^3{:}\eta^3\text{-}C_{10}H_{16})\}_2]$ (1) toward Guanidine 2j**




unreactive toward the $^{i}$Pr-trisubstituted guanidine $(^{i}PrHN)_2C{=}N^{i}Pr$. In this same line, the steric hindrance associated with the substitution in an ortho position of the aryl substituents in guanidines **2g−i** (see Figure 6) may also be behind the lack of reactivity found for the Ru(IV) dimer **1** with these guanidines. Attempts to synthesize the corresponding complexes $[RuCl\{\kappa^2(N,N')\text{-}C(NR)(N^{i}Pr)\text{-}NH^{i}Pr\}(\eta^3{:}\eta^3\text{-}C_{10}H_{16})]$ by reacting dimer **1** with a 2-fold excess of the lithium salts generated by deprotonation of **2g−i** with Li$^{n}$Bu also failed. A complex mixture of products was formed in this case.

Concerning the characterization of the novel guanidinium chloride salts **4a−e**,[15] their most relevant spectroscopic features are (i) (IR) the presence of two characteristic strong N−H absorption bands at 3159−3250 cm$^{-1}$, (ii) ($^1$H NMR) two broad singlets at $\delta_H$ 7.49−7.67 (2H) and 9.71−10.04 (1H) ppm, which were assigned to the N−H protons of the $^{i}$PrNH and ArNH groups, respectively, and (iii) ($^{13}C\{^1H\}$ NMR) a singlet resonance at ca. 154.5 ppm corresponding to the carbon atom of the central $CN_3$ core. Moreover, the molecular structures of compounds **4a−c** were determined by X-ray diffraction methods. Single crystals suitable for X-ray analysis were obtained in all cases by slow diffusion of pentane into a saturated solution of the salt in THF. ORTEP plots of the structures are shown in Figure 7; selected bonding parameters are given in the caption.[16] As observed in the structures of other guanidium salts previously described in the literature,[17] the central $CN_3$ fragment of the cations is perfectly planar (sum of NCN angles 360°) with very similar C−N distances (1.322(2)−1.357(2) Å). These values are intermediate between those of pure carbon−nitrogen single (1.41 Å) and double bonds (1.27 Å),[18] suggesting a large electronic delocalization within the $\pi$ system of the $CN_3$ core. Also of note is that, in the three structures, the chloride anions establish a series of strong, charge-assisted, hydrogen-bonding interactions with the NH groups of the guanidinium cations, which dominate the extended structures (details are given in the Supporting Information).

On the other hand, an interesting result was obtained when the dimer $[\{RuCl(\mu\text{-}Cl)(\eta^3{:}\eta^3\text{-}C_{10}H_{16})\}_2]$ (**1**) was reacted with the 4-cyanobenzene-substituted guanidine $(^{i}PrHN)_2C{=}N\text{-}4\text{-}C_6H_4C{\equiv}N$ (**2j**). Instead of the expected guanidinate complex, the reaction led to the selective formation of the mononuclear derivative $[RuCl_2(\eta^3{:}\eta^3\text{-}C_{10}H_{16})\{N{\equiv}C\text{-}4\text{-}C_6H_4\text{-}N{=}C\text{-}$



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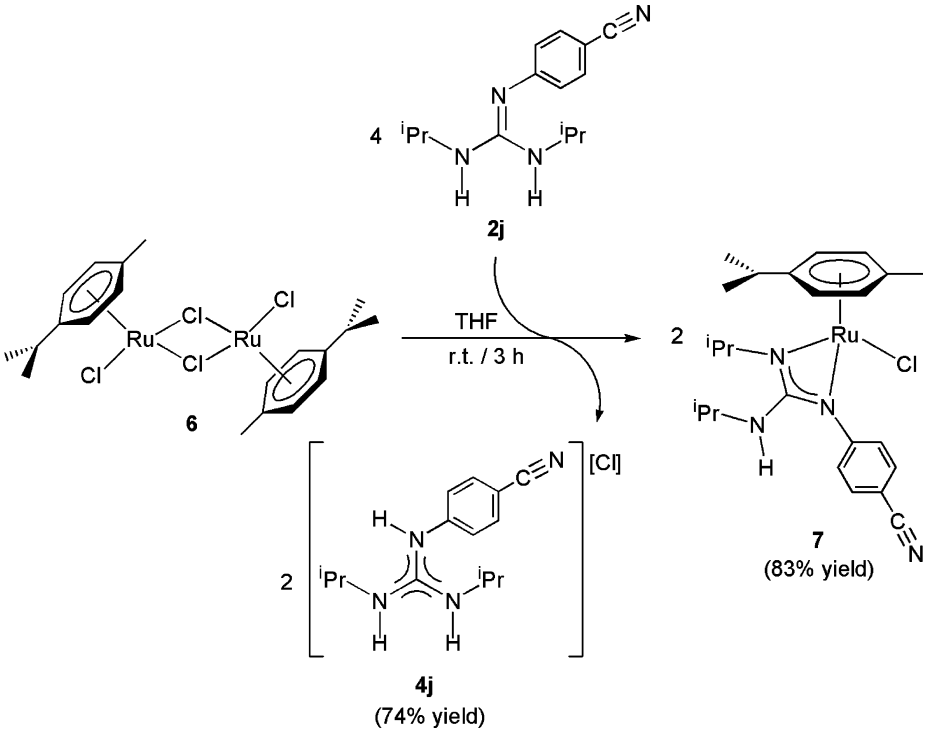
Scheme 3. Reactivity of the Ruthenium(II) Dimer $[\{RuCl(\mu\text{-}Cl)(\eta^6\text{-}p\text{-cymene})\}_2]$ (6) toward Guanidine 2j




$(NH^iPr_2)_2\}]$ (**5**), in which the guanidine **2j** coordinates to ruthenium through the pendant nitrile unit (Scheme 2). The reaction, which proceeded rapidly in THF at room temperature with only 2 equiv of **2j**, afforded **5** in an excellent 91% isolated yield. Coordination of the guanidine through the C≡N unit was supported by a downfield shift of the nitrile carbon resonance ($\delta_C$ 127.5 ppm) in comparison with that shown by the free guanidine **2j** ($\delta_C$ 120.2 ppm). The rest of the chemical shifts of the protons and carbons of the coordinated guanidine in complex **5** were almost identical with those found in the NMR spectra of the free ligand **2j**. Furthermore, the proposed axial coordination of the guanidine to the ruthenium center was fully supported by the appearance in the $^1H$ NMR spectrum of four terminal allyl and two methyl resonances for the 2,7-dimethylocta-2,6-diene-1,8-diyl chain, evidencing inequivalent environments for the halves of the bis(allyl) ligand (see the Experimental Section). This is also clearly reflected in the $^{13}C\{^1H\}$ NMR spectrum of **5**, which showed 10 separate signals for the $C_{10}H_{16}$ unit.[19]

Remarkably, the behavior of the Ru(IV) dimer $[\{RuCl(\mu\text{-}Cl)(\eta^3\text{:}\eta^3\text{-}C_{10}H_{16})\}_2]$ (**1**) toward guanidine **2j** differed significantly from that shown by the related (arene)ruthenium(II) dimer $[\{RuCl(\mu\text{-}Cl)(\eta^6\text{-}p\text{-cymene})\}_2]$ (**6**). Thus, as previously described with other guanidines,[3,4] the reaction of **6** with an excess of **2j** resulted in the high-yield formation of the expected guanidinate complex $[RuCl\{\kappa^2(N,N')\text{-}C(N\text{-}4\text{-}C_6H_4C{\equiv}N)(N^iPr)\text{-}NH^iPr\}(\eta^6\text{-}p\text{-cymene})]$ (**7**), along with the corresponding guanidinium chloride salt **4j** (Scheme 3). Analysis of the crude reaction mixture by $^1H$ NMR spectroscopy did not show the presence of any byproduct resulting from the coordination of the C≡N group of **2j** to the $[RuCl_2(\eta^6\text{-}p\text{-cymene})]$ fragment. It seems therefore that the coordination of this guanidine is governed by the electronic properties of the metal center, coordination of the nitrile vs imine unit being preferred in the case of the harder bis(allyl)$Ru^{IV}$ fragment.[20]

The novel compounds **7** and **4j** were characterized by elemental analysis and IR and NMR ($^1H$ and $^{13}C\{^1H\}$) spectroscopy, all data being fully consistent with the proposed formulations (details are given in the Experimental Section). In addition, the structure of complex **7** was unequivocally confirmed by means of an X-ray diffraction analysis. As in the case of **3d**, X-ray-quality crystals were obtained by cooling at −10 °C a saturated solution of the complex in a hexane/$CH_2Cl_2$ mixture. An ORTEP view of the molecule is shown in Figure 8; selected bonding parameters are given in the caption.

As is usual for this compound class, a pseudooctahedral three-legged piano-stool geometry around the metal center is observed. Similarly to the case of the Ru(IV) complex **3d**, the sum of angles around the central carbon atom C(1) of the guanidinate ligand (359.9°) indicates again the strict planarity of the $CN_3$ unit. In addition, a detailed inspection of the C−N bond lengths also suggests for **7** an important contribution of the resonance form **K** (see Figure 5) to the bonding. Thus, the C(1)−N(1) distance of 1.313(6) Å was found to be significantly shorter than the C(1)−N(2) and C(1)−N(3) distances (1.365(6) and 1.366(6) Å, respectively). The presence of the electron-withdrawing 4-cyanophenyl substituent on N(3), capable of stabilizing a negative charge on this nitrogen atom, appears to be responsible for these structural features since, in the analogous complex $[RuCl\{\kappa^2(N,N')\text{-}C(N\text{-}4\text{-}C_6H_4{}^tBu)(N^iPr)\text{-}NH^iPr\}(\eta^6\text{-}p\text{-cymene})]$ (**D** in Figure 2) previously described by us,[3] the bonding of the guanidinate ligand to ruthenium was best described through the delocalized resonance form **J** (see Figure 5).

Interestingly, the coordinative properties of the pendant cyano group remained intact in the ruthenium(II) complex **7**, since its treatment with 1/2 equiv of the dimer $[\{RuCl(\mu\text{-}Cl)(\eta^3\text{:}\eta^3\text{-}C_{10}H_{16})\}_2]$ (**1**) resulted in the high-yield formation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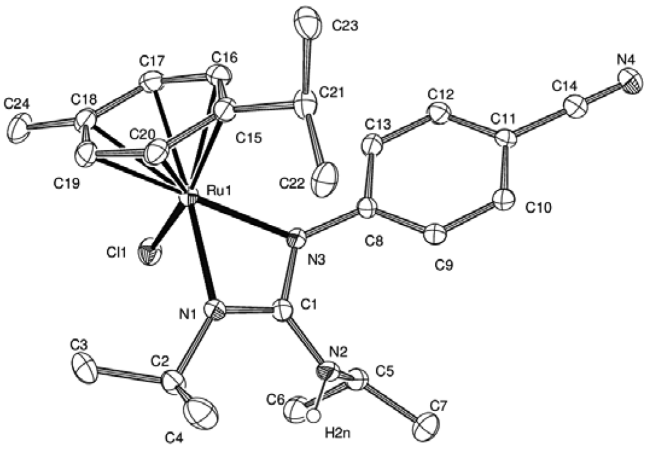


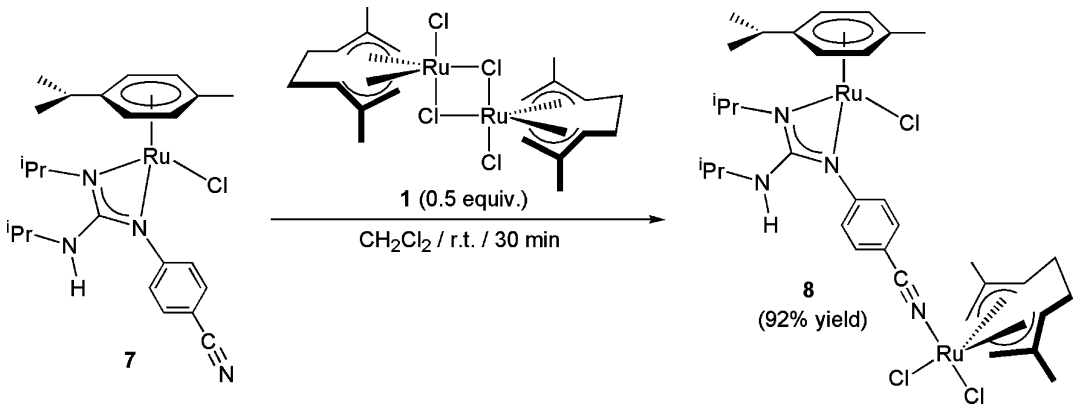

**Figure 8.** ORTEP type view of the structure of the ruthenium(II) complex **7** with the crystallographic labeling scheme. Hydrogen atoms, except that on N(2), have been omitted for clarity. Thermal ellipsoids are drawn at the 30% probability level. Selected bond distances (Å) and angles (deg): Ru−C* = 1.6566(4); Ru−Cl(1) = 2.424(2); Ru−N(1) = 2.114(4); Ru−N(3) = 2.100(4); C(1)−N(1) = 1.313(6); C(1)−N(2) = 1.365(6); C(1)−N(3) = 1.366(6); C(14)−N(4) = 1.136(6); C*−Ru−Cl(1) = 128.0(1); C*−Ru−N(1) = 135.8(1); C*−Ru−N(3) = 135.9(1); Cl(1)−Ru−N(1) = 85.8(1); Cl(1)−Ru−N(3) = 85.7(1); N(1)−Ru−N(3) = 62.2(1); Ru−N(1)−C(1) = 94.9(3); Ru−N(3)−C(1) = 93.9(3); N(1)−C(1)−N(2) = 127.9(4); N(1)−C(1)−N(3) = 108.5(4); N(2)−C(1)−N(3) = 123.5(4); C(11)−C(14)−N(4) = 179.6(6). C* denotes the centroid of the *p*-cymene ring (C(15), C(16), C(17), C(18), C(19), and C(20)).

of the dinuclear Ru(II)/Ru(IV) derivative **8** (Scheme 4). Although all attempts to crystallize this compound failed, the elemental analysis and IR and NMR data obtained were in full accord with the proposed formulation (see the Experimental Section). In particular, the coordination of the nitrile unit to the $[RuCl_2(\eta^3{:}\eta^3\text{-}C_{10}H_{16})]$ fragment was supported by (i) ($^{13}C\{^1H\}$ NMR) the appearance of a singlet resonance at $\delta_C$ 127.5 ppm for the C≡N carbon in the spectrum, a chemical shift identical with that found for complex **5** and slightly deshielded in comparison to that of **7** ($\delta_C$ 120.4 ppm), and (ii) (IR) a change in the C≡N absorption band (2239 $cm^{-1}$) with respect to that of **7** (2213 $cm^{-1}$). We stress the point that, to our knowledge, no previous examples of the use of guanidine **2j** to generate bimetallic complexes have been published in the literature.[21] The bimetallic compound **8**, along with $[\{RuCl(\mu\text{-}Cl)(\eta^3{:}\eta^3\text{-}C_{10}H_{16})\}_2]$ (**1**), $[(^iPrHN)_2C(NH\text{-}4\text{-}C_6H_4CN)][Cl]$ (**4j**), and a new complex that could correspond to $[RuCl_2(\eta^3{:}\eta^3\text{-}C_{10}H_{16})\{N{\equiv}C\text{-}4\text{-}C_6H_4\text{-}NH{=}C(NH^iPr_2)_2\}][Cl]$, was also formed when a THF solution of dimer **6** was treated with 4 equiv of **5**. However, all attempts to isolate **8** in pure form from this mixture failed.

In another vein, one of the most interesting aspects in the chemistry of (2,7-dimethylocta-2,6-diene-1,8-diyl)ruthenium(IV) complexes deals with its use as precursors of ruthenium(II) species, via reductive elimination of the bis(allyl) chain.[22] In this context, we have found that treatment of the complexes $[RuCl\{\kappa^2(N,N')\text{-}C(NR)(N^iPr)\text{-}NH^iPr\}(\eta^3{:}\eta^3\text{-}C_{10}H_{16})]$ (**3a−f**) with an excess of 2,6-dimethylphenyl isocyanide, in toluene at room temperature, results in the clean formation of the novel octahedral ruthenium(II) guanidinate derivatives *mer*-$[RuCl\{\kappa^2(N,N')\text{-}C(NR)(N^iPr)\text{-}NH^iPr\}(CN\text{-}2,6\text{-}C_6H_3Me_2)_3]$ (**9a−f**) (Scheme 5), which were isolated as air-stable yellow solids in 75−87% yield.[23] The reactions were completely stereoselective, no isomeric species being detected by NMR in the crude reaction mixtures.

The identity and stereochemistry of these compounds were unambiguously established by a single-crystal X-ray diffraction study on **9f**. An ORTEP type drawing of the molecular structure, along with selected bonding parameters, is depicted in Figure 9. The ruthenium atom is in a distorted-octahedral environment, being bonded to three 2,6-dimethylphenyl isocyanide molecules disposed in a *mer* fashion, two nitrogen atoms of the guanidinate monoanion, and one chloride ligand disposed *trans* with respect to the N$^i$Pr unit. As expected, all the isocyanide ligands are bound to ruthenium in a nearly linear fashion (Ru−C−N angles within the range 173.4(4)−176.9(4)°) with metal−carbon bond distances of 1.891(4)−1.993(4) Å. These bonding parameters fit well with those reported in the literature for other ruthenium(II) 2,6-dimethylphenyl isocyanide complexes.[24] As observed for **3d**, the small "bite" of the planar guanidinate ligand (sum of angles around C(1) of 359.9°) results in a relatively small value for the N(1)−Ru−N(3) angle (61.51°). However, in contrast to the case of **3d** and **7**, the C(1)−N(1) and C(1)−N(3) bond distances (1.323(5) and 1.343(5) Å) were now both shorter than the C(1)−N(2) distance (1.363(5) Å), suggesting in this case a major contribution of the delocalized resonance form **J** (see Figure 5) to the bonding. Significant differences between the Ru−N(1) and Ru−N(3) bond lengths were also observed (2.080(3) and 2.168(3) Å, respectively), probably as a result of the different *trans* influences of the chloride and isocyanide ligands.

**Scheme 4. Synthesis of the Dinuclear Ru(II)/Ru(IV) Complex 8**



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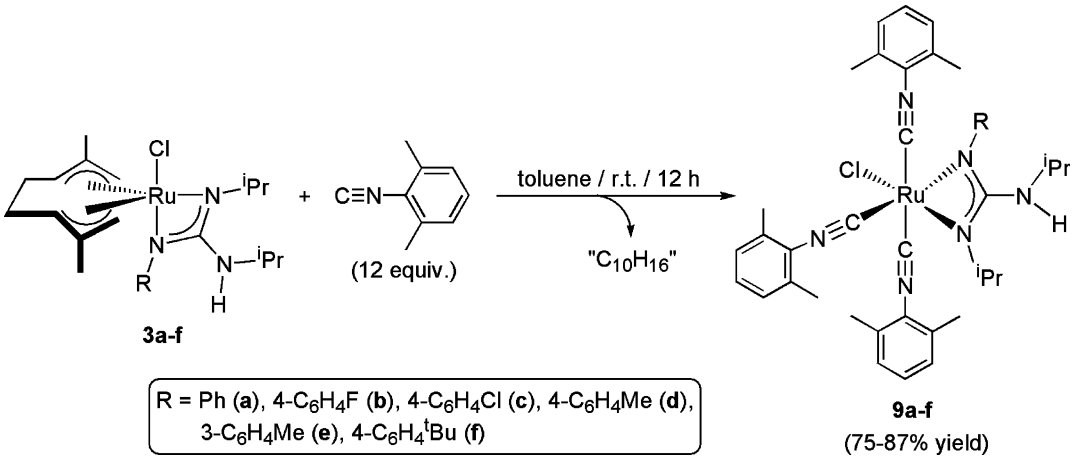
Scheme 5. Reactivity of the Ruthenium(IV) Guanidinate Complexes 3a−f toward 2,6-Dimethylphenyl Isocyanide



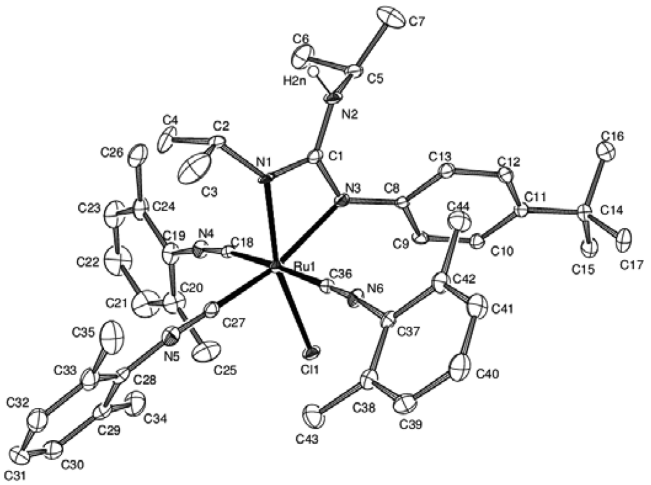
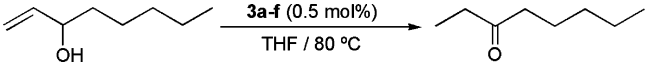



Figure 9. ORTEP type view of the structure of the ruthenium(II) complex **9f** with the crystallographic labeling scheme. Hydrogen atoms, except that on N(2), have been omitted for clarity. Thermal ellipsoids are drawn at the 30% probability level. Selected bond distances (Å) and angles (deg): Ru−Cl(1) = 2.439(1); Ru−N(1) = 2.080(3); Ru−N(3) = 2.168(3); Ru−C(18) = 1.993(4); Ru−C(27) = 1.891(4); Ru−C(36) = 1.982(4); C(1)−N(1) = 1.323(5); C(1)−N(2) = 1.363(5); C(1)−N(3) = 1.343(5); C(18)−N(4) = 1.158(5); C(27)−N(5) = 1.164(6); C(36)−N(6) = 1.147(5); Cl(1)−Ru−N(1) = 163.8(1); Cl(1)−Ru−N(3) = 102.34(9); Cl(1)−Ru−C(18) = 85.9(1); Cl(1)−Ru−C(27) = 92.1(1); Cl(1)−Ru−C(36) = 91.9(1); N(1)−Ru−N(3) = 61.5(1); N(3)−Ru−C(27) = 165.5(2); C(18)−Ru−C(36) = 177.1(2); Ru−N(1)-C(1) = 96.9(2); Ru−N(3)−C(1) = 92.3(3); N(1)−C(1)−N(3) = 109.2(3); N(1)−C(1)−N(2) = 125.4(4); N(2)−C(1)−N(3) = 125.3(4); Ru−C(18)−N(4) = 173.4(4); Ru−C(27)−N(5) = 176.7(4); Ru−C(36)−N(6) = 176.9(4); C(18)−N(4)−C(19) = 172.3(5); C(27)−N(5)−C(28) = 163.8(5); C(36)−N(6)−C(37) = 174.0(4).

The NMR data obtained for **9a−f** were in fully accord with the stereochemistry found in the solid-state structure of **9f** (details are given in the Experimental Section), the most noticeable spectroscopic features being those associated with the guanidinate $CN_3$ and isocyanide carbons, which resonate at ca. 159 ppm, and in the range 164.8−171.5 ppm (two singlet signals with intensity ratio 2:1), respectively. The IR spectra also showed the expected $\nu$(C≡N) absorptions for the isocyanide ligands (three independent bands in the ranges 2041−2068, 2104−2108, and 2156−2166 $cm^{-1}$).

As noted in the Introduction, the (arene)ruthenium(II) guanidinate complexes **D** (see Figure 2) had shown a remarkable activity in the redox isomerization of allylic alcohols (TOF up to 1000 $h^{-1}$ in THF at 80 °C).[3] It is worth noting that, in contrast to the vast majority of ruthenium catalysts known for this catalytic transformation,[25] these species were able to operate under base-free conditions.[26] This fact prompted us to explore the catalytic potential of the novel guanidinate complexes [RuCl{$\kappa^2$(*N,N′*)-C(NR)(N$^i$Pr)-NH$^i$Pr}($\eta^3$:$\eta^3$-$C_{10}H_{16}$)] (**3a−f**) and *mer*-[RuCl{$\kappa^2$(*N,N′*)-C(NR)(N$^i$Pr)-NH$^i$Pr}(CN-2,6-$C_6H_3Me_2$)$_3$] (**9a−f**) using 1-octen-3-ol as model substrate. For comparative purposes, the catalytic reactions were performed in THF at 80 °C without the addition of an external base. Thus, using a metal loading of 0.5 mol %, we found that the Ru(IV) complexes **3a−f** were all able to provide quantitatively the desired octan-3-one in a short amount of time (see Table 1).[27]

Table 1. Catalytic Isomerization of 1-Octen-3-ol into Octan-3-one using the Ru(IV) Complexes [RuCl{$\kappa^2$(*N,N′*)-C(NR)(N$^i$Pr)-NH$^i$Pr}($\eta^3$:$\eta^3$-$C_{10}H_{16}$)] (**3a−f**) as Catalysts[a]




| entry | catalyst | time | yield (%)[b] | TOF ($h^{-1}$)[c] |
|---|---|---|---|---|
| 1 | **3a** | 35 min | >99 | 343 |
| 2 | **3b** | 50 min | >99 | 240 |
| 3 | **3c** | 1.5 h | >99 | 133 |
| 4 | **3d** | 10 min | >99 | 1200 |
| 5 | **3e** | 15 min | >99 | 800 |
| 6 | **3f** | 10 min | >99 | 1200 |

[a]Reactions were performed at 80 °C, under an argon atmosphere, using 1 mmol of 1-octen-3-ol (0.2 M solutions in THF). [b]Yields determined by GC. [c]Turnover frequencies (((mol of product)/(mol of Ru))/time) were calculated at the time indicated in each case.

The best results in terms of activity were obtained with complexes **3d−f**, featuring an N-aryl unit substituted with an electron-releasing group, which were able to complete the reaction in only 10−15 min (entries 4−6). In general, the turnover frequencies (TOF) reached with **3e,f** (800−1200 $h^{-1}$) compare favorably with those previously obtained for the same reaction catalyzed by the (arene)ruthenium(II) guanidinate complexes **D** (TOF = 400−1000 $h^{-1}$).[28] On the other hand,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the higher reactivity of **3d−f** vs **3a−c** (entries 4−6 vs 1−3) can be rationalized in terms of the easier dissociation of the chloride ligand in the former. Such a dissociation process, which would generate the required vacant position for substrate binding, is expected to be favored with the greater electron density on the metal center.[29]

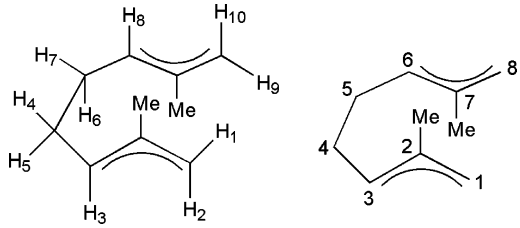
Finally, concerning the octahedral Ru(II) derivatives *mer*-[RuCl{$\kappa^2$(*N*,*N*′)-C(NR)(N$^i$Pr)-NH$^i$Pr}(CN-2,6-C$_6$H$_3$Me$_2$)$_3$] (**9a−f**), in marked contrast to **3a−f**, they were completely inactive in the isomerization of 1-octen-3-ol, even when the reactions were performed in the presence of a base (KO$^t$Bu) or the chloride abstractor AgSbF$_6$. Although the electronic effects associated with the strong $\pi$-acceptor character of the isocyanide ligands cannot be discarded, the high steric congestion around the metal center imposed by the bulky 2,6-dimethylphenyl groups, which would prevent the coordination of the allylic alcohol, are possibly responsible for this disappointing result.

## ■ CONCLUSION

In summary, we have prepared and fully characterized the first examples of ruthenium(IV) complexes, namely [RuCl{$\kappa^2$(*N*,*N*′)-C(NR)(N$^i$Pr)-NH$^i$Pr}($\eta^3$:$\eta^3$-C$_{10}$H$_{16}$)] (**3a−f**), containing heteroallyl guanidinate monoanions as ligands. As previously observed with related half-sandwich ($\eta^6$-arene)-ruthenium(II) derivatives,[3] these Ru(IV) complexes are catalytically active in the base-free redox isomerization of allylic alcohols. In addition, they have also been shown to be useful precursors for the preparation of a new family of octahedral ruthenium(II) guanidinate complexes, i.e. *mer*-[RuCl{$\kappa^2$(*N*,*N*′)-C(NR)(N$^i$Pr)-NH$^i$Pr}(CN-2,6-C$_6$H$_3$Me$_2$)$_3$] (**9a−f**), via reductive elimination of the 2,7-dimethylocta-2,6-diene-1,8-diyl ligand (C$_{10}$H$_{16}$). Remarkably, despite the fact that several isomers are possible within both families of compounds, the reactions proceeded in all cases with complete stereoselectivity.

## ■ EXPERIMENTAL SECTION

Synthetic procedures were performed under an atmosphere of dry argon using vacuum-line and standard Schlenk techniques. Solvents were dried by standard methods and distilled under argon before use. All reagents were obtained from commercial suppliers and used without further purification, with the exception of the dimeric complexes [{RuCl($\mu$-Cl)($\eta^3$:$\eta^3$-C$_{10}$H$_{16}$)}$_2$] (**1**)[30] and [{RuCl($\mu$-Cl)($\eta^6$-*p*-cymene)}$_2$] (**6**)[31] and the guanidines ($^i$PrHN)$_2$C=NR (**2a−j**),[12a] which were prepared by following the methods reported in the literature. Infrared spectra were recorded on a PerkinElmer 1720-XFT spectrometer. GC measurements were made on a Hewlett-Packard HP6890 apparatus (Supelco Beta-Dex 120 column, 30 m length, 250 $\mu$m diameter). Elemental analyses were provided by the Analytical Service of the Instituto de Investigaciones Químicas (IIQ-CSIC) of Seville. NMR spectra were recorded on Bruker DPX300 and AV400 instruments. The chemical shift values are given in parts per million and are referenced to the residual peak of the deuterated solvent employed ($^1$H and $^{13}$C) or the CFCl$_3$ standard ($^{19}$F). DEPT experiments have been carried out for all of the compounds reported in this paper. The numberings employed for the protons and carbons of the 2,7-dimethylocta-2,6-diene-1,8-diyl skeleton are as follows:




**Reactions of the Dimer [{RuCl($\mu$-Cl)($\eta^3$:$\eta^3$-C$_{10}$H$_{16}$)}$_2$] (1) with Guanidines ($^i$PrHN)$_2$C=NR (R = Ph (2a), 4-C$_6$H$_4$F (2b), 4-C$_6$H$_4$Cl (2c), 4-C$_6$H$_4$Me (2d), 3-C$_6$H$_4$Me (2e) 4-C$_6$H$_4$$^t$Bu (2f)).** A solution of [{RuCl($\mu$-Cl)($\eta^3$:$\eta^3$-C$_{10}$H$_{16}$)}$_2$] (**1**; 0.308 g, 0.5 mmol) in 20 mL of tetrahydrofuran was treated with the appropriate guanidine **2a−f** (2 mmol) at room temperature for 5 h. A gradual color change from violet to red was observed. The solution was then evaporated to dryness, and 40 mL of pentane was added to the resulting oily residue, leading to the appearance of a white solid precipitate of the corresponding guanidinium chloride salt [($^i$PrHN)$_2$C(NHR)][Cl] (**4a−f**). The suspension was then filtered using a cannula and, once separated, the white solid was washed with hexanes (2 × 10 mL) and diethyl ether (5 mL) to afford **4a−f** in pure form. The filtrate was stored in freezer at −10 °C for 48 h, leading to the precipitation of the complexes [RuCl{$\kappa^2$(*N*,*N*′)-C(NR)(N$^i$Pr)-NH$^i$Pr}($\eta^3$:$\eta^3$-C$_{10}$H$_{16}$)] (**3a−f**) as orange-red solids, which were separated, washed with cold pentane (3 mL), and vacuum-dried.

Characterization data for complexes **3a−f** are as follows.

**3a**: yield 0.353 g (72%). Anal. Calcd for RuC$_{23}$H$_{36}$N$_3$Cl: C, 56.25; H, 7.39; N, 8.56. Found: C, 56.42; H, 7.44; N, 8.71. IR (KBr, cm$^{-1}$): $\nu$ 3336 (s, N−H). $^1$H NMR (C$_6$D$_6$): $\delta$ 7.08 (m, 2H, CH$_{arom}$), 6.94 (m, 1H, CH$_{arom}$), 6.82 (d, 2H, $^3J_{HH}$ = 7.2 Hz, CH$_{arom}$), 5.05, 4.71, 4.61, and 2.85 (s, 1H each, H$_1$, H$_2$, H$_9$ and H$_{10}$), 4.50 and 2.62 (m, 1H each, H$_3$ and H$_8$), 4.11 and 3.05 (m, 1H each, C*H*Me$_2$), 3.22 (d, 1H, $^3J_{HH}$ = 10.5 Hz, NH), 2.45 and 2.08 (s, 3H each, Me of C$_{10}$H$_{16}$), 2.37 and 2.12 (m, 1H and 3H respectively, H$_4$, H$_5$, H$_6$ and H$_7$), 1.73 (d, 3H, $^3J_{HH}$ = 6.0 Hz, CH*Me*$_2$), 1.62 (d, 3H, $^3J_{HH}$ = 6.9 Hz, CH*Me*$_2$), 0.87 (d, 3H, $^3J_{HH}$ = 6.6 Hz, CH*Me*$_2$), 0.62 (d, 3H, $^3J_{HH}$ = 6.8 Hz, CH*Me*$_2$) ppm. $^{13}$C{$^1$H} NMR (C$_6$D$_6$): $\delta$ 160.9 (s, CN$_3$), 149.1 (s, C$_{arom}$), 128.8, 125.4, and 121.6 (s, CH$_{arom}$), 120.5 and 110.6 (s, C$_2$ and C$_7$), 95.4 and 91.4 (s, C$_3$ and C$_6$), 78.2 and 73.0 (s, C$_1$ and C$_8$), 47.6 and 44.4 (s, *C*HMe$_2$), 33.8 and 31.2 (s, C$_4$ and C$_5$), 23.5, 23.4, 23.1, and 22.3 (s, CH*Me*$_2$), 19.9 and 19.0 (s, Me of C$_{10}$H$_{16}$) ppm.

**3b**: yield 0.381 g (75%). Anal. Calcd for RuC$_{23}$H$_{35}$N$_3$ClF: C, 54.27; H, 6.93; N, 8.25. Found: C, 54.41; H, 6.78; N, 8.40. IR (KBr, cm$^{-1}$): $\nu$ 3320 (s, N−H). $^{19}$F{$^1$H} NMR (C$_6$D$_6$): $\delta$ −120.9 (s) ppm. $^1$H NMR (C$_6$D$_6$): $\delta$ 6.75 (m, 2H, CH$_{arom}$), 6.60 (m, 2H, CH$_{arom}$), 5.04, 4.68, 4.12, and 2.74 (s, 1H each, H$_1$, H$_2$, H$_9$ and H$_{10}$), 4.59 and 2.50 (m, 1H each, H$_3$ and H$_8$), 4.05 and 2.95 (m, 1H each, C*H*Me$_2$), 3.12 (d, 1H, $^3J_{HH}$ = 9.9 Hz, NH), 2.52 and 2.12 (m, 1H and 3H respectively, H$_4$, H$_5$, H$_6$ and H$_7$), 2.46 and 2.08 (s, 3H each, Me of C$_{10}$H$_{16}$), 1.71 (d, 3H, $^3J_{HH}$ = 6.3 Hz, CH*Me*$_2$), 1.61 (d, 3H, $^3J_{HH}$ = 6.0 Hz, CH*Me*$_2$), 0.97 (d, 3H, $^3J_{HH}$ = 6.1 Hz, CH*Me*$_2$), 0.63 (d, 3H, $^3J_{HH}$ = 6.4 Hz, CH*Me*$_2$) ppm. $^{13}$C{$^1$H} NMR (C$_6$D$_6$): $\delta$ 160.8 (s, CN$_3$), 158.1 (d, $^1J_{CF}$ = 241.5 Hz, C$_{arom}$), 144.9 (d, $^4J_{CF}$ = 2.8 Hz, C$_{arom}$), 126.4 (d, $^3J_{CF}$ = 7.4 Hz, CH$_{arom}$), 120.2 and 110.3 (s, C$_2$ and C$_7$), 115.4 (d, $^2J_{CF}$ = 21.6 Hz, CH$_{arom}$), 95.4 and 91.2 (s, C$_3$ and C$_6$), 78.2 and 72.9 (s, C$_1$ and C$_8$), 47.7 and 44.5 (s, *C*HMe$_2$), 33.7 and 31.1 (s, C$_4$ and C$_5$), 23.4 (s, 2C, CH*Me*$_2$), 23.1 and 22.3 (s, CH*Me*$_2$), 19.9 and 19.1 (s, Me of C$_{10}$H$_{16}$) ppm.

**3c**: yield 0.368 g (70%). Anal. Calcd for RuC$_{23}$H$_{35}$N$_3$Cl$_2$: C, 52.57; H, 6.71; N, 8.00. Found: C, 52.64; H, 6.65; N, 8.21. IR (KBr, cm$^{-1}$): $\nu$ 3331 (s, N−H). $^1$H NMR (C$_6$D$_6$): $\delta$ 7.05 and 6.59 (d, 2H each, $^3J_{HH}$ = 9.6 Hz, CH$_{arom}$), 5.00, 4.66, 4.55, and 2.70 (s, 1H each, H$_1$, H$_2$, H$_9$ and H$_{10}$), 4.59 and 2.50 (m, 1H each, H$_3$ and H$_8$), 4.05 and 2.96 (m, 1H each, C*H*Me$_2$), 3.16 (d, 1H, $^3J_{HH}$ = 10.2 Hz, NH), 2.44 and 1.97 (s, 3H each, Me of C$_{10}$H$_{16}$), 2.35 and 2.07 (m, 1H and 3H respectively, H$_4$, H$_5$, H$_6$ and H$_7$), 1.69 (d, 3H, $^3J_{HH}$ = 6.6 Hz, CH*Me*$_2$), 1.59 (d, 3H, $^3J_{HH}$ = 6.5 Hz, CH*Me*$_2$), 0.84 (d, 3H, $^3J_{HH}$ = 5.7 Hz, CH*Me*$_2$), 0.59 (d, 3H, $^3J_{HH}$ = 7.0 Hz, CH*Me*$_2$) ppm. $^{13}$C{$^1$H} NMR (C$_6$D$_6$): $\delta$ 160.7 (s, CN$_3$), 147.8 and 126.4 (s, C$_{arom}$), 128.9 and 126.1 (s, CH$_{arom}$), 120.6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*Organometallics* XXXX, XXX, XXX−XXX

and 110.7 (s, $C_2$ and $C_7$), 95.6 and 91.4 (s, $C_3$ and $C_6$), 78.1 and 72.8 (s, $C_1$ and $C_8$), 47.7 and 44.4 (s, $CHMe_2$), 33.7 and 31.2 (s, $C_4$ and $C_5$), 23.5, 23.3, 23.1, and 22.2 (s, $CHMe_2$), 20.0 and 19.0 (s, Me of $C_{10}H_{16}$) ppm.

**3d**: yield 0.409 g (81%). Anal. Calcd for $RuC_{24}H_{38}N_3Cl$: C, 57.07; H, 7.58; N, 8.32. Found: C, 57.01; H, 7.64; N, 8.24. IR (KBr, $cm^{-1}$): $\nu$ 3332 (s, N−H). $^1H$ NMR ($C_6D_6$): $\delta$ 6.93 and 6.78 (d, 2H each, $^3J_{HH}$ = 8.1 Hz, $CH_{arom}$), 5.06, 4.71, 4.44, and 2.87 (s, 1H each, $H_1$, $H_2$, $H_9$ and $H_{10}$), 4.62 and 2.63 (m, 1H each, $H_3$ and $H_8$), 4.14 and 3.11 (m, 1H each, $CHMe_2$), 3.26 (d, 1H, $^3J_{HH}$ = 10.8 Hz, NH), 2.46 and 2.13 (s, 3H each, Me of $C_{10}H_{16}$), 2.35 and 2.18 (m, 1H and 3H respectively, $H_4$, $H_5$, $H_6$ and $H_7$), 2.12 (s, 3H, Me), 1.75 (d, 3H, $^3J_{HH}$ = 6.3 Hz, $CHMe_2$), 1.64 (d, 3H, $^3J_{HH}$ = 6.6 Hz, $CHMe_2$), 0.92 (d, 3H, $^3J_{HH}$ = 5.4 Hz, $CHMe_2$), 0.65 (d, 3H, $^3J_{HH}$ = 6.9 Hz, $CHMe_2$) ppm. $^{13}C\{^1H\}$ NMR ($C_6D_6$): $\delta$ 161.1 (s, $CN_3$), 146.1 and 130.9 (s, $C_{arom}$), 129.6 and 125.4 (s, $CH_{arom}$), 120.2 and 110.2 (s, $C_2$ and $C_7$), 95.4 and 91.4 (s, $C_3$ and $C_6$), 78.1 and 73.0 (s, $C_1$ and $C_8$), 47.7 and 44.4 (s, $CHMe_2$), 33.7 and 31.1 (s, $C_4$ and $C_5$), 23.5, 23.2, 22.7, and 22.3 (s, $CHMe_2$), 20.7 (s, Me), 20.0 and 19.1 (s, Me of $C_{10}H_{16}$) ppm.

**3e**: yield 0.424 g (84%). Anal. Calcd for $RuC_{24}H_{38}N_3Cl$: C, 57.07; H, 7.58; N, 8.32. Found: C, 57.15; H, 7.61; N, 8.14. IR (KBr, $cm^{-1}$): $\nu$ 3325 (s, N−H). $^1H$ NMR ($C_6D_6$): $\delta$ 7.03 (t, 1H, $^3J_{HH}$ = 7.8 Hz, $CH_{arom}$), 6.77 (m, 1H, $CH_{arom}$), 6.70 (d, 1H, $^3J_{HH}$ = 7.8 Hz, $CH_{arom}$), 5.07, 4.72, 4.45, and 2.90 (s, 1H each, $H_1$, $H_2$, $H_9$ and $H_{10}$), 4.63 and 2.69 (m, 1H each, $H_3$ and $H_8$), 4.13 and 3.15 (m, 1H each, $CHMe_2$), 3.27 (d, 1H, $^3J_{HH}$ = 9.9 Hz, NH), 2.46 and 2.20 (s, 3H each, Me of $C_{10}H_{16}$), 2.33 and 2.16 (m, 1H and 3H respectively, $H_4$, $H_5$, $H_6$ and $H_7$), 2.14 (s, 3H, Me), 1.74 (d, 3H, $^3J_{HH}$ = 6.6 Hz, $CHMe_2$), 1.63 (d, 3H, $^3J_{HH}$ = 6.0 Hz, $CHMe_2$), 0.90 (d, 3H, $^3J_{HH}$ = 6.5 Hz, $CHMe_2$), 0.65 (d, 3H, $^3J_{HH}$ = 6.3 Hz, $CHMe_2$) ppm. $^{13}C\{^1H\}$ NMR ($C_6D_6$): $\delta$ 161.1 (s, $CN_3$), 148.9 and 138.2 (s, $C_{arom}$), 128.8, 127.1, 126.0, and 122.6 (s, $CH_{arom}$), 120.5 and 110.4 (s, $C_2$ and $C_7$), 95.3 and 91.6 (s, $C_3$ and $C_6$), 78.1 and 73.0 (s, $C_1$ and $C_8$), 47.7 and 44.5 (s, $CHMe_2$), 33.8 and 31.3 (s, $C_4$ and $C_5$), 23.6, 23.5, 23.2, and 22.3 (s, $CHMe_2$), 21.2 (s, Me), 20.0 and 19.1 (s, Me of $C_{10}H_{16}$) ppm.

**3f**: yield 0.443 g (81%). Anal. Calcd for $RuC_{27}H_{44}N_3Cl$: C, 59.27; H, 8.11; N, 7.68. Found: C, 59.16; H, 8.24; N, 7.77. IR (KBr, $cm^{-1}$): $\nu$ 3341 (s, N−H). $^1H$ NMR ($C_6D_6$): $\delta$ 7.19 and 6.84 (d, 2H each, $^3J_{HH}$ = 8.5 Hz, $CH_{arom}$), 5.03, 4.69, 4.45, and 2.87 (s, 1H each, $H_1$, $H_2$, $H_9$ and $H_{10}$), 4.61 and 2.68 (m, 1H each, $H_3$ and $H_8$), 4.18 and 3.11 (m, 1H each, $CHMe_2$), 3.37 (d, 1H, $^3J_{HH}$ = 9.9 Hz, NH), 2.42 and 2.17 (s, 3H each, Me of $C_{10}H_{16}$), 2.36 and 2.15 (m, 1H and 3H respectively, $H_4$, $H_5$, $H_6$ and $H_7$), 1.74 (d, 3H, $^3J_{HH}$ = 5.7 Hz, $CHMe_2$), 1.65 (d, 3H, $^3J_{HH}$ = 5.6 Hz, $CHMe_2$), 1.30 (s, 9H, $CMe_3$), 0.93 (d, 3H, $^3J_{HH}$ = 6.6 Hz, $CHMe_2$), 0.67 (d, 3H, $^3J_{HH}$ = 6.7 Hz, $CHMe_2$) ppm. $^{13}C\{^1H\}$ NMR ($C_6D_6$): $\delta$ 161.2 (s, $CN_3$), 146.1 and 144.2 (s, $C_{arom}$), 125.6 and 125.1 (s, $CH_{arom}$), 120.3 and 110.3 (s, $C_2$ and $C_7$), 95.1 and 91.6 (s, $C_3$ and $C_6$), 78.0 and 72.9 (s, $C_1$ and $C_8$), 47.7 and 44.5 (s, $CHMe_2$), 34.0 (s, $CMe_3$), 33.8 and 31.3 (s, $C_4$ and $C_5$), 31.2 (s, $CMe_3$), 23.6, 23.5, 23.2, and 22.3 (s, $CHMe_2$), 20.0 and 19.1 (s, Me of $C_{10}H_{16}$) ppm.

Characterization data for the novel guanidinium chloride salts $[(^iPrHN)_2C(NHR)][Cl]$ (**4a**−**e**) are as follows.[15]

**4a**: yield 0.187 g (73%). Anal. Calcd for $C_{13}H_{22}N_3Cl$: C, 61.04; H, 8.67; N, 16.43. Found: C, 60.99; H, 8.62; N, 16.41. IR (KBr, $cm^{-1}$): $\nu$ 3240 (vs, N−H), 3187 (vs, N−H). $^1H$ NMR ($CDCl_3$): $\delta$ 9.78 (broad s, 1H, NH), 7.55 (broad s, 2H, NH), 7.39−7.19 (m, 5H, $CH_{arom}$), 3.93 (broad s, 2H, $CHMe_2$), 1.24 (d, 12H, $^3J_{HH}$ = 6.3 Hz, $CHMe_2$) ppm. $^{13}C\{^1H\}$ NMR ($CDCl_3$): $\delta$ 154.5 (s, $CN_3$), 137.2 (s, $C_{arom}$), 129.5, 125.7, and 122.7 (s, $CH_{arom}$), 45.8 (s, $CHMe_2$), 22.4 (s, $CHMe_2$) ppm.

**4b**: yield 0.191 g (70%). Anal. Calcd for $C_{13}H_{21}N_3ClF$: C, 57.03; H, 7.73; N, 15.35. Found: C, 55.88; H, 7.72; N, 15.29. IR (KBr, $cm^{-1}$): $\nu$ 3250 (vs, N−H), 3159 (vs, N−H). $^{19}F\{^1H\}$ NMR ($C_6D_6$): $\delta$ −115.7 (s) ppm. $^1H$ NMR ($CDCl_3$): $\delta$ 10.00 (broad s, 1H, NH), 7.56 (broad s, 2H, NH), 7.25 (m, 2H, $CH_{arom}$), 7.05 (m, 2H, $CH_{arom}$), 3.97 (broad s, 2H, $CHMe_2$), 1.20 (d, 12H, $^3J_{HH}$ = 6.4 Hz, $CHMe_2$) ppm. $^{13}C\{^1H\}$ NMR ($CDCl_3$): $\delta$ 160.5 (d, $^1J_{CF}$ = 246.7 Hz, $C_{arom}$), 154.7 (s, $CN_3$), 133.0 (s, $C_{arom}$), 124.8 (broad s, $CH_{arom}$), 116.5 (d, $^2J_{CF}$ = 22.8 Hz, $CH_{arom}$), 45.9 (s, $CHMe_2$), 22.6 (s, $CHMe_2$) ppm.

**4c**: yield 0.217 g (75%). Anal. Calcd for $C_{13}H_{21}N_3Cl_2$: C, 53.80; H, 7.29; N, 14.48. Found: C, 51.48; H, 7.15; N, 13.53. IR (KBr, $cm^{-1}$): $\nu$ 3244 (vs, N−H), 3193 (vs, N−H). $^1H$ NMR ($CDCl_3$): $\delta$ 10.04 (broad s, 1H, NH), 7.67 (broad s, 2H, NH), 7.31 and 7.22 (d, 2H each, $^3J_{HH}$ = 8.8 Hz, $CH_{arom}$), 3.96 (broad s, 2H, $CHMe_2$), 1.21 (d, 12H, $^3J_{HH}$ = 6.4 Hz, $CHMe_2$) ppm. $^{13}C\{^1H\}$ NMR ($CDCl_3$): $\delta$ 154.5 (s, $CN_3$), 135.8 and 131.2 (s, $C_{arom}$), 129.7 and 123.8 (s, $CH_{arom}$), 46.1 (s, $CHMe_2$), 22.6 (s, $CHMe_2$) ppm.

**4d**: yield 0.186 g (69%). Anal. Calcd for $C_{14}H_{24}N_3Cl$: C, 62.32; H, 8.97; N, 15.57. Found: C, 62.40; H, 8.88; N, 15.54. IR (KBr, $cm^{-1}$): $\nu$ 3239 (vs, N−H), 3201 (vs, N−H). $^1H$ NMR ($CDCl_3$): $\delta$ 9.77 (broad s, 1H, NH), 7.49 (broad s, 2H, NH), 7.06 (broad s, 4H, $CH_{arom}$), 3.96 (broad s, 2H, $CHMe_2$), 2.28 (s, 3H, Me), 1.12 (d, 12H, $^3J_{HH}$ = 6.6 Hz, $CHMe_2$) ppm. $^{13}C\{^1H\}$ NMR ($CDCl_3$): $\delta$ 154.5 (s, $CN_3$), 135.5 and 134.5 (s, $C_{arom}$), 130.1 and 123.0 (s, $CH_{arom}$), 45.8 (s, $CHMe_2$), 22.5 (s, $CHMe_2$), 20.9 (s, Me) ppm.

**4e**: yield 0.208 g (77%). Anal. Calcd for $C_{14}H_{24}N_3Cl$: C, 62.32; H, 8.97; N, 15.57. Found: C, 62.29; H, 9.11; N, 15.69. IR (KBr, $cm^{-1}$): $\nu$ 3242 (vs, N−H), 3227 (vs, N−H). $^1H$ NMR ($CDCl_3$): $\delta$ 9.71 (broad s, 1H, NH), 7.56 (broad s, 2H, NH), 7.21 (t, 1H each, $^3J_{HH}$ = 7.5 Hz, $CH_{arom}$), 7.02 (m, 3H, $CH_{arom}$), 3.98 (broad s, 2H, $CHMe_2$), 2.33 (s, 3H, Me), 1.20 (d, 12H, $^3J_{HH}$ = 6.1 Hz, $CHMe_2$) ppm. $^{13}C\{^1H\}$ NMR ($CDCl_3$): $\delta$ 154.6 (s, $CN_3$), 139.8 and 137.0 (s, $C_{arom}$), 129.4, 126.7, 123.4, and 119.8 (s, $CH_{arom}$), 46.0 (s, $CHMe_2$), 22.6 (s, $CHMe_2$), 21.4 (s, Me) ppm.

**Synthesis of $[RuCl_2(\eta^3{:}\eta^3\text{-}C_{10}H_{16})\{N{\equiv}C\text{-}4\text{-}C_6H_4\text{-}N{=}C(NH^iPr_2)_2\}]$ (5).** A solution of the dimer $[\{RuCl(\mu\text{-}Cl)(\eta^3{:}\eta^3\text{-}C_{10}H_{16})\}_2]$ (**1**; 0.308 g, 0.5 mmol) in 20 mL of tetrahydrofuran was treated with the guanidine $(^iPrHN)_2C{=}N\text{-}4\text{-}C_6H_4C{\equiv}N$ (**2j**; 0.244 g, 1 mmol) at room temperature for 15 min. An immediate color change from violet to orange was observed. The solution was then evaporated to dryness, and the resulting orange solid was washed twice with 3 mL of cold pentane and vacuum-dried. Yield: 0.503 g (91%). Anal. Calcd for $RuC_{24}H_{36}N_4Cl_2$: C, 52.17; H, 6.57; N, 10.14. Found: C, 52.21; H, 6.62; N, 10.20. IR (KBr, $cm^{-1}$): $\nu$ 3306 (m, N−H), 2237 (m, C≡N). $^1H$ NMR ($CD_2Cl_2$): $\delta$ 7.39 and 6.89 (d, 2H each, $^3J_{HH}$ = 8.7 Hz, $CH_{arom}$), 5.11 (m, 1H, $H_3$ or $H_8$), 5.06, 4.91, 4.61, and 4.03 (s, 1H each, $H_1$, $H_2$, $H_9$ and $H_{10}$), 4.58 (m, 3H, $H_3$ or $H_8$ and NH), 3.72 (m, 2H, $CHMe_2$), 3.08 and 2.53 (m, 2H each, $H_4$, $H_5$, $H_6$ and $H_7$), 2.41 and 2.38 (s, 3H each, Me of $C_{10}H_{16}$), 1.15 (d, 12H, $^3J_{HH}$ = 5.7 Hz, $CHMe_2$) ppm. $^{13}C\{^1H\}$ NMR ($CD_2Cl_2$): $\delta$ 157.2 (s, C=N), 151.9 and 98.9 (s, $C_{arom}$), 133.9 and 122.6 (s, $CH_{arom}$), 127.9 and 125.0 (s, $C_2$ and $C_7$), 127.5 (s, C≡N), 98.7 and 91.8 (s, $C_3$ and $C_6$), 83.2 and 79.6 (s, $C_1$ and $C_8$), 43.7 (s, $CHMe_2$), 37.6 and 36.8 (s, $C_4$ and $C_5$), 22.8 (s, $CHMe_2$), 20.5 and 20.0 (s, Me of $C_{10}H_{16}$) ppm.

**Synthesis of $[RuCl\{\kappa^2(N,N')\text{-}C(N\text{-}4\text{-}C_6H_4C{\equiv}N)(N^iPr)\text{-}NH^iPr\}(\eta^6\text{-}p\text{-cymene})]$ (7).** A solution of $[\{RuCl(\mu\text{-}Cl)(\eta^6\text{-}p\text{-cymene})\}_2]$ (**6**; 0.306 g, 0.5 mmol) in 20 mL of tetrahydrofuran was treated with the guanidine $(^iPrHN)_2C{=}N\text{-}4\text{-}C_6H_4C{\equiv}N$ (**2j**; 0.489 g, 2 mmol) at room temperature for 3 h. The solution was then evaporated to dryness, and 60 mL of pentane were added to the resulting oily residue, leading to the appearance of a white solid precipitate of the corresponding guanidinium chloride salt $[(^iPrHN)_2C(NH\text{-}4\text{-}C_6H_4C{\equiv}N)][Cl]$ (**4j**). The suspension was then filtered using a cannula and, once separated, the white solid was washed with hexanes (2 × 10 mL) and diethyl ether (5 mL) to afford 0.208 g of **4j** (74% yield). The filtrate was stored in freezer at −10 °C for 48 h, leading to the precipitation of the complex $[RuCl\{\kappa^2(N,N')\text{-}C(N\text{-}4\text{-}C_6H_4C{\equiv}N)(N^iPr)\text{-}NH^iPr\}(\eta^6\text{-}p\text{-cymene})]$ (**7**) as an orange solid, which was separated, washed with cold pentane (3 mL), and vacuum-dried. Yield: 0.427 g (83%). Anal. Calcd for $RuC_{24}H_{33}N_4Cl$: C, 56.07; H, 6.47; N, 10.90. Found: C, 56.18; H, 7.42; N, 10.98. IR (KBr, $cm^{-1}$): $\nu$ 3337 (m, N−H), 2213 (s, C≡N). $^1H$ NMR ($CD_2Cl_2$): $\delta$ 7.46 and 7.14 (d, 2H each, $^3J_{HH}$ = 9.0 Hz, $CH_{arom}$), 5.41, 5.19, 5.12, and 5.10 (d, 1H each, $^3J_{HH}$ = 5.7 Hz, CH of cymene), 3.55 (d, 1H, $^3J_{HH}$ = 10.8 Hz, NH), 3.35 and 3.17 (m, 1H each, $NCHMe_2$), 2.58 (m, 1H, $CHMe_2$ of cymene), 2.20 (s, 3H, Me of cymene), 1.32−0.96 (m, 18H, $CHMe_2$) ppm. $^{13}C\{^1H\}$ NMR ($CD_2Cl_2$): $\delta$ 160.7 (s, $CN_3$), 155.0 and 100.5 (s, $C_{arom}$), 132.6 and 121.1 (s, $CH_{arom}$), 120.4 (s, C≡N), 98.9 and 97.8 (s, C of cymene), 80.5, 79.3, 79.2, and 78.3 (s, CH of cymene), 45.9 and 45.4 (s, $NCHMe_2$), 31.3 (s, $CHMe_2$ of cymene), 25.2, 24.5, 24.0, 22.4, 22.2, and 22.1 (s, $CHMe_2$), 18.8 (s, Me of cymene) ppm.



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Organometallics XXXX, XXX, XXX−XXX

Characterization data for [($^i$PrHN)$_2$C(NH-4-C$_6$H$_4$C≡N)][Cl] (**4j**) are as follows. Anal. Calcd for $C_{14}H_{21}N_4Cl$: C, 59.88; H, 7.54; N, 19.95. Found: C, 59.93; H, 7.61; N, 20.10. IR (KBr, cm$^{-1}$): $\nu$ 3189 (vs, N−H), 2227 (s, C≡N). $^1$H NMR ($CDCl_3$): $\delta$ 10.2 (broad s, 1H, NH), 7.96 (broad s, 2H, NH), 7.56 and 7.37 (broad s, 2H each, $CH_{arom}$), 3.93 (broad s, 2H, C*H*Me$_2$), 1.19 (broad s, 12H, CH*Me*$_2$) ppm. $^{13}$C{$^1$H} NMR ($CDCl_3$): $\delta$ 154.1 (s, $CN_3$), 142.3 and 107.8 (s, $C_{arom}$), 133.6 and 121.2 (s, $CH_{arom}$), 118.3 (s, C≡N), 46.7 (s, *C*HMe$_2$), 22.6 (s, CH*Me*$_2$) ppm.

**Synthesis of the Dinuclear Ru(II)/Ru(IV) Complex 8.** A solution of the complex [RuCl{$\kappa^2$(*N*,*N*′)-C(N-4-C$_6$H$_4$C≡N)(N$^i$Pr)-NH$^i$Pr}($\eta^6$-*p*-cymene)] (7; 0.100 g, 0.194 mmol) in 10 mL of dichloromethane was treated with the dimer [{RuCl($\mu$-Cl)($\eta^3$:$\eta^3$-$C_{10}H_{16}$)}$_2$] (**1**) (0.060 g, 0.097 mmol) at room temperature for 30 min. The solution was then evaporated to dryness, and the resulting yellow solid was washed twice with 5 mL of diethyl ether and vacuum-dried. Yield: 0.147 g (92%). Anal. Calcd for $Ru_2C_{34}H_{49}N_4Cl_3$: C, 49.66; H, 6.01; N, 6.81. Found: C, 49.59; H, 6.06; N, 6.92. IR (KBr, cm$^{-1}$): $\nu$ 3307 (m, N−H), 2239 (m, C≡N). $^1$H NMR ($CD_2Cl_2$): $\delta$ 7.37 and 7.10 (d, 2H each, $^3J_{HH}$ = 8.4 Hz, $CH_{arom}$), 5.41 (d, 1H, $^3J_{HH}$ = 5.7 Hz, CH of cymene), 5.16−5.08 (m, 5H, CH of cymene, $H_3$ or $H_8$, and $H_1$, $H_2$, $H_9$ or $H_{10}$), 4.94, 4.63, and 4.05 (s, 1H each, $H_1$, $H_2$, $H_9$ or $H_{10}$), 4.59 (m, 1H, $H_3$ or $H_8$), 3.50 (d, 1H, $^3J_{HH}$ = 10.8 Hz, NH), 3.33 (m, 1H, NC*H*Me$_2$), 3.19−2.96 (m, 4H, NC*H*Me$_2$, C*H*Me$_2$ of cymene, and $H_4$, $H_5$, $H_6$ or $H_7$), 2.53 (2H, $H_4$, $H_5$, $H_6$ or $H_7$), 2.20 (s, 6H, Me of $C_{10}H_{16}$), 2.20 (s, 3H, Me of cymene), 1.31−1.00 (m, 18H, CH*Me*$_2$) ppm. $^{13}$C{$^1$H} NMR ($CD_2Cl_2$): $\delta$ 160.5 (s, $CN_3$), 156.6 and 99.1 (s, $C_{arom}$), 133.3 and 120.9 (s, $CH_{arom}$), 127.8 and 124.8 (s, $C_2$ and $C_7$), 127.5 (s, C≡N), 98.5 and 91.6 (s, $C_3$ and $C_6$), 98.2 and 97.8 (s, C of cymene), 83.3 and 79.7 (s, $C_1$ and $C_8$), 80.5, 79.4, 79.1, and 78.1 (s, CH of cymene), 46.1 and 45.6 (s, NCHMe$_2$), 37.6 and 36.9 (s, $C_4$ and $C_5$), 31.4 (s, *C*HMe$_2$ of cymene), 25.0, 24.4, 24.0, 22.4, 22.3, and 22.1 (s, CH*Me*$_2$), 20.5 and 20.0 (s, Me of $C_{10}H_{16}$), 18.8 (s, Me of cymene) ppm.

**Synthesis of *mer*-[RuCl{$\kappa^2$(*N*,*N*′)-C(NR)(N$^i$Pr)-NH$^i$Pr}(CN-2,6-C$_6$H$_3$Me$_2$)$_3$] (R = Ph (9a), 4-C$_6$H$_4$F (9b), 4-C$_6$H$_4$Cl (9c), 4-C$_6$H$_4$Me (9d), 3-C$_6$H$_4$Me (9e), 4-C$_6$H$_4$$^t$Bu (9f)).** A solution of the corresponding ruthenium(IV) guanidinate complex [RuCl{$\kappa^2$(*N*,*N*′)-C(NR)(N$^i$Pr)-NH$^i$Pr}($\eta^3$:$\eta^3$-$C_{10}H_{16}$)] (**3a−f**; 0.2 mmol) in 10 mL of toluene was treated with an excess of 2,6-dimethylphenyl isocyanide (0.314 g, 2.4 mmol) at room temperature for 12 h. A gradual color change from red to yellow was observed. Concentration of the resulting solution (ca. 3 mL) followed by the addition of hexanes (ca. 50 mL) precipitated a yellow solid, which was washed with hexanes (3 × 10 mL) and diethyl ether (5 mL) and vacuum-dried.

Characterization data for *mer*-[RuCl{$\kappa^2$(*N*,*N*′)-C(NR)(N$^i$Pr)-NH$^i$Pr}(CN-2,6-C$_6$H$_3$Me$_2$)$_3$] (**9a−f**) are as follows.

**9a**: yield 0.130 g (87%). Anal. Calcd for $RuC_{40}H_{47}N_6Cl$: C, 64.20; H, 6.33; N, 11.23. Found: C, 64.31; H, 6.24; N, 11.47. IR (KBr, cm$^{-1}$): $\nu$ 3326 (m, N−H), 2156 (m, C≡N), 2104 (vs, C≡N), 2055 (vs, C≡N). $^1$H NMR ($CD_2Cl_2$): $\delta$ 7.38−7.34 (m, 2H, $CH_{arom}$), 7.20−7.06 (m, 11H, $CH_{arom}$), 6.72 (m, 1H, $CH_{arom}$), 3.54 (m, 2H, C*H*Me$_2$ and NH), 3.42 (sept, 1H, $^3J_{HH}$ = 6.4 Hz, C*H*Me$_2$), 2.55 (s, 6H, C$_6$H$_3$*Me*$_2$), 2.43 (s, 12H, C$_6$H$_3$*Me*$_2$), 1.13 (d, 6H, $^3J_{HH}$ = 6.4 Hz, CH*Me*$_2$), 1.05 (d, 6H, $^3J_{HH}$ = 5.7 Hz, CH*Me*$_2$) ppm. $^{13}$C{$^1$H} NMR ($CD_2Cl_2$): $\delta$ 171.3 and 165.2 (s, C≡N), 158.8 (s, $CN_3$), 150.7, 135.4, 134.3, 130.4, and 126.2 (s, $C_{arom}$), 127.9, 127.8, 127.6, 127.5, 122.2, and 118.3 (s, $CH_{arom}$), 45.2 and 45.1 (s, C*H*Me$_2$), 24.3 and 23.3 (s, CH*Me*$_2$), 19.1 and 18.6 (s, C$_6$H$_3$*Me*$_2$) ppm.

**9b**: yield 0.115 g (75%). Anal. Calcd for $RuC_{40}H_{46}N_6ClF$: C, 62.69; H, 6.05; N, 10.97. Found: C, 62.76; H, 6.13; N, 11.10. IR (KBr, cm$^{-1}$): $\nu$ 3331 (m, N−H), 2165 (m, C≡N), 2108 (vs, C≡N), 2053 (vs, C≡N). $^{19}$F{$^1$H} NMR ($CD_2Cl_2$): $\delta$ −127.8 (s) ppm. $^1$H NMR ($CD_2Cl_2$): $\delta$ 7.33 (m, 2H, $CH_{arom}$), 7.21−7.09 (m, 9H, $CH_{arom}$), 6.85 (t, 2H, $^3J_{HH}$ = 9.0 Hz, $CH_{arom}$), 3.51 (m, 2H, C*H*Me$_2$ and NH), 3.39 (sept, 1H, $^3J_{HH}$ = 6.6 Hz, C*H*Me$_2$), 2.55 (s, 6H, C$_6$H$_3$*Me*$_2$), 2.43 (s, 12H, C$_6$H$_3$*Me*$_2$), 1.05 (d, 6H, $^3J_{HH}$ = 5.4 Hz, CH*Me*$_2$), 1.00 (d, 6H, $^3J_{HH}$ = 6.6 Hz, CH*Me*$_2$) ppm. $^{13}$C{$^1$H} NMR ($CD_2Cl_2$): $\delta$ 171.1 and 165.1 (s, C≡N), 158.8 (s, $CN_3$), 156.4 (d, $^1J_{CF}$ = 234.5 Hz, $C_{arom}$), 147.0, 135.3, 134.3, 130.4, and 127.8 (s, $C_{arom}$), 128.0, 127.6, 127.5, and 126.3 (s, $CH_{arom}$), 122.6 (d, $^3J_{CF}$ = 9.7 Hz, $CH_{arom}$), 114.0 (d, $^2J_{CF}$ = 22.6 Hz, $CH_{arom}$), 45.2 (s, 2C, C*H*Me$_2$), 24.3 and 23.3 (s, CH*Me*$_2$), 19.1 and 18.6 (s, C$_6$H$_3$*Me*$_2$) ppm.

**9c**: yield 0.130 g (80%). Anal. Calcd for $RuC_{40}H_{46}N_6Cl_2$: C, 61.37; H, 5.92; N, 10.74. Found: C, 61.46; H, 6.04; N, 10.91. IR (KBr, cm$^{-1}$): $\nu$ 3329 (m, N−H), 2164 (m, C≡N), 2108 (vs, C≡N), 2050 (vs, C≡N). $^1$H NMR ($CD_2Cl_2$): $\delta$ 7.35 (d, 2H, $^3J_{HH}$ = 8.4 Hz, $CH_{arom}$), 7.20−7.01 (m, 11H, $CH_{arom}$), 3.53 (m, 2H, C*H*Me$_2$ and NH), 3.40 (sept, 1H, $^3J_{HH}$ = 6.0 Hz, C*H*Me$_2$), 2.55 (s, 6H, C$_6$H$_3$*Me*$_2$), 2.42 (s, 12H, C$_6$H$_3$*Me*$_2$), 1.14 (d, 6H, $^3J_{HH}$ = 6.0 Hz, CH*Me*$_2$), 1.07 (d, 6H, $^3J_{HH}$ = 4.0 Hz, CH*Me*$_2$) ppm. $^{13}$C{$^1$H} NMR ($CD_2Cl_2$): $\delta$ 170.8 and 164.8 (s, C≡N), 158.8 (s, $CN_3$), 149.8, 135.3, 134.3, 130.3, 126.3, and 122.3 (s, $C_{arom}$), 128.0, 127.7, 127.5, and 123.0 (s, $CH_{arom}$), 45.2 and 45.1 (s, C*H*Me$_2$), 24.1 and 23.2 (s, CH*Me*$_2$), 19.1 and 18.6 (s, C$_6$H$_3$*Me*$_2$) ppm.

**9d**: yield 0.124 g (81%). Anal. Calcd for $RuC_{41}H_{49}N_6Cl$: C, 64.59; H, 6.48; N, 11.02. Found: C, 64.48; H, 6.53; N, 11.13. IR (KBr, cm$^{-1}$): $\nu$ 3335 (m, N−H), 2163 (m, C≡N), 2106 (vs, C≡N), 2042 (s, C≡N). $^1$H NMR ($CD_2Cl_2$): $\delta$ 7.25 and 6.96 (d, 2H each, $^3J_{HH}$ = 8.4 Hz, $CH_{arom}$), 7.20−7.01 (m, 9H, $CH_{arom}$), 3.52 (m, 2H, C*H*Me$_2$ and NH), 3.43 (sept, 1H, $^3J_{HH}$ = 6.4 Hz, C*H*Me$_2$), 2.55 (s, 6H, C$_6$H$_3$*Me*$_2$), 2.44 (s, 12H, C$_6$H$_3$*Me*$_2$), 2.27 (s, 3H, Me), 1.13 (d, 6H, $^3J_{HH}$ = 7.6 Hz, CH*Me*$_2$), 1.05 (d, 6H, $^3J_{HH}$ = 6.4 Hz, CH*Me*$_2$) ppm. $^{13}$C{$^1$H} NMR ($CD_2Cl_2$): $\delta$ 171.5 and 165.4 (s, C≡N), 158.7 (s, $CN_3$), 147.8, 134.3, 130.4, 128.6, 127.8, and 127.7 (s, $C_{arom}$), 135.4 128.4, 127.9, 127.6, 127.5, and 122.1 (s, $CH_{arom}$), 45.2 and 45.1 (s, C*H*Me$_2$), 24.3 and 23.3 (s, CH*Me*$_2$), 20.4 (s, C$_6$H$_4$*Me*), 19.1 and 18.6 (s, C$_6$H$_3$*Me*$_2$) ppm.

**9e**: yield 0.120 g (79%). Anal. Calcd for $RuC_{41}H_{49}N_6Cl$: C, 64.59; H, 6.48; N, 11.02. Found: C, 64.65; H, 6.50; N, 11.17. IR (KBr, cm$^{-1}$): $\nu$ 3343 (m, N−H), 2166 (m, C≡N), 2108 (vs, C≡N), 2068 (s, C≡N). $^1$H NMR ($CD_2Cl_2$): $\delta$ 7.21−7.01 (m, 12H, $CH_{arom}$), 6.56 (d, 1H, $^3J_{HH}$ = 8.7 Hz, $CH_{arom}$), 3.54 (m, 2H, C*H*Me$_2$ and NH), 3.40 (sept, 1H, $^3J_{HH}$ = 6.6 Hz, C*H*Me$_2$), 2.55 (s, 6H, C$_6$H$_3$*Me*$_2$), 2.44 (s, 12H, C$_6$H$_3$*Me*$_2$), 2.23 (s, 3H, Me), 1.13 (d, 6H, $^3J_{HH}$ = 6.6 Hz, CH*Me*$_2$), 1.05 (d, 6H, $^3J_{HH}$ = 5.4 Hz, CH*Me*$_2$) ppm. $^{13}$C{$^1$H} NMR ($CD_2Cl_2$): $\delta$ 171.5 and 165.4 (s, C≡N), 158.8 (s, $CN_3$), 150.5, 137.2, 135.4, 134.4, 130.5, and 127.8 (s, $C_{arom}$), 127.9, 127.6, 127.5, 127.4, 126.3, 122.7, 119.8, and 119.3 (s, $CH_{arom}$), 45.2 (s, 2C, C*H*Me$_2$), 24.2 and 23.2 (s, CH*Me*$_2$), 21.2 (s, C$_6$H$_4$*Me*), 19.1 and 18.6 (s, C$_6$H$_3$*Me*$_2$) ppm.

**9f**: yield 0.135 g (84%). Anal. Calcd for $RuC_{44}H_{55}N_6Cl$: C, 65.69; H, 6.89; N, 10.45. Found: C, 65.61; H, 7.02; N, 10.60. IR (KBr, cm$^{-1}$): $\nu$ 3334 (m, N−H), 2162 (m, C≡N), 2105 (vs, C≡N), 2041 (vs, C≡N). $^1$H NMR ($CD_2Cl_2$): $\delta$ 7.32−7.27 (m, 2H, $CH_{arom}$), 7.20−7.08 (m, 11H, $CH_{arom}$), 3.55 (m, 2H, C*H*Me$_2$ and NH), 3.43 (sept, 1H, $^3J_{HH}$ = 6.3 Hz, C*H*Me$_2$), 2.55 (s, 6H, C$_6$H$_3$*Me*$_2$), 2.42 (s, 12H, C$_6$H$_3$*Me*$_2$), 1.33 (s, 9H, CMe$_3$), 1.14 (d, 6H, $^3J_{HH}$ = 6.3 Hz, CH*Me*$_2$), 1.06 (d, 6H, $^3J_{HH}$ = 5.7 Hz, CH*Me*$_2$) ppm. $^{13}$C{$^1$H} NMR ($CD_2Cl_2$): $\delta$ 171.5 and 165.4 (s, C≡N), 158.9 (s, $CN_3$), 147.9, 140.9, 135.4, 134.3, 130.4, and 126.2 (s, $C_{arom}$), 127.9, 127.8, 127.6, 127.5, 124.5, and 121.6 (s, $CH_{arom}$), 45.2 and 45.1 (s, C*H*Me$_2$), 33.9 (s, *C*Me$_3$), 31.4 (s, C*Me*$_3$), 24.3 and 23.3 (s, CH*Me*$_2$), 19.1 and 18.7 (s, C$_6$H$_3$*Me*$_2$) ppm.

**General Procedure for the Catalytic Isomerization of 1-Octen-3-ol.** In a Teflon-capped sealed tube under an argon atmosphere, the corresponding ruthenium complex (0.01 mmol; 0.5 mol % of Ru) was added to a solution of 1-octen-3-ol (2 mmol) in tetrahydrofuran (10 mL), and the resulting mixture was stirred at 80 °C for the indicated time (see Table 1). The course of the reaction was monitored by regularly taking ca. 10 $\mu$L samples, which after dilution with THF (3 mL) were analyzed by GC. The identity of the resulting octan-3-one was assessed by comparison of its retention time with that of a commercially available pure sample (Aldrich Chemical Co.).

**X-ray Crystal Structure Determination of Compounds 3d, 4a−c, 7, and 9f.** Crystals of the ruthenium complexes **3d**, 7, and **9f** suitable for X-ray diffraction analysis were obtained by cooling (−10 °C) a saturated solution of the corresponding complex in hexane with some drops of dichloromethane. Crystals of the guanidinium chloride salts **4a−c** were grown by slow diffusion of pentane into saturated solutions of the salts in THF. The most relevant crystal and refinement data are collected in Tables S1 and S2 (see the Supporting Information). Data collection was performed with Oxford Diffraction Xcalibur Nova and Oxford Diffraction Gemini single crystal


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*Organometallics* XXXX, XXX, XXX−XXX

diffractometers, using Mo K$\alpha$ radiation ($\lambda$ = 0.71073 Å; **3d** and **9f**) and Cu K$\alpha$ radiation ($\lambda$ = 1.5418 Å; **4a−c** and **7**), respectively. Images were collected at a fixed crystal−detector distance of 45 mm for **3d**, **7**, and **9f**, 100 mm for **4a**, 63 mm for **4b**, and 65 mm for **4c**, using the oscillation method, with 1° oscillation and variable exposure time per image (37.22 s for **3d**, 7.28−30 s for **4a**, 1.5−2 s for **4b**, 1.5−4 s for **4c**, 1.27−5.08 s for **7**, and 43.68 s for **9f**). The data collection strategy was calculated with the program CrysAlis$^{Pro}$ CCD.[32] Data reduction and cell refinement was performed with the program CrysAlis$^{Pro}$ RED.[32] An empirical absorption correction was applied using the SCALE3 ABSPACK algorithm as implemented in the program CrysAlis$^{Pro}$ RED.[32] In all the cases, the software package WINGX[33] was used for space group determination, structure solution, and refinement. The structures were solved by direct methods using SIR2004 (**3d**, **7**, and **9f**)[34] or SIR92 (**4a−c**).[35]

Isotropic least-squares refinement on $F^2$ using SHELXL97[36] was performed in all cases. During the final stages of the refinements, all of 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. Atoms H2n and H5n (for **3d**), H1−6n (for **4a−b**), H1−3n (for **4c**), and H2n (**7** and **9f**) were found from the Fourier maps and included in a refinement with isotropic parameters. In the crystal of **3d** two independent molecules of the complex were found in the asymmetric unit per half hexane molecule of solvation. In crystals of **4a**,**b** two independent molecules of the salt and in the crystal of **4c** one molecule of the salt were found in the asymmetric unit. In the crystal of **7** one molecule of the complex was found in the asymmetric unit per half dichloromethane molecule of solvation. Finally, in the case of **9f** one molecule of the complex was found in the asymmetric unit per half hexane molecule of solvation. The function minimized was $[\sum w(F_o^2 - F_c^2)/\sum w(F_o^2)]^{1/2}$, where $w = 1/[\sigma^2(F_o^2) + (aP)^2 + bP]$ (values for $a$ and $b$ are collected in Tables S1 and S2 in the Supporting Information) with $\sigma(F_o^2)$ from counting statistics and $P = (\text{Max}(F_o^2 + 2F_c^2))/3$. In all the cases, the maximum residual electron density is located near heavy atoms. Atomic scattering factors were taken from ref 37. Geometrical calculations were made with PARST.[38] The crystallographic plots were made with ORTEP-3,[39] Mercury,[40] and POV-Ray.[41]

## ■ ASSOCIATED CONTENT

### Supporting Information

CIF files, tables, and figures giving crystallographic information on compounds **3d**, **4a−c**, **7**, and **9f**. The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.organomet.5b00070.

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### Notes

The authors declare no competing financial interest.

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*Organometallics* XXXX, XXX, XXX−XXX

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(21) Examples of dinuclear Ru(II)/Ru(IV) complexes combining ($\eta^6$-arene)ruthenium(II) fragments with the bis(allyl)ruthenium(IV) unit [RuCl$_2$($\eta^3$:$\eta^3$-C$_{10}$H$_{16}$)], through bridging halide, diphosphine, diamine, or cyanopyridine ligands, are known: (a) Toerien, J. G.; van Rooyen, P. H. *J. Chem. Soc., Dalton Trans.* **1991**, 2693−2702. (b) Steed, J. W.; Tocher, D. A. *Polyhedron* **1992**, *11*, 2729−2737. (c) Steed, J. W.; Tocher, D. A. *Inorg. Chim. Acta* **1995**, *229*, 87−93. (d) Sahay, A. N.; Pandey, D. S.; Walawalkar, M. G. *J. Organomet. Chem.* **2000**, *613*, 250−256. (e) Sahay, A. N.; Pandey, D. S. *Indian J. Chem.* **2001**, *40A*, 538−543.

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(27) We must point here that, although the dimer [{RuCl($\mu$-Cl)($\eta^3$:$\eta^3$-C$_{10}$H$_{16}$)}$_2$] (**1**) is itself one of the most active catalysts known for the redox isomerization of allylic alcohols in water, its effectiveness in THF is very low. Indeed, in the absence of base, it was only able to



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*Organometallics* XXXX, XXX, XXX−XXX

reach a TOF value of 20 $h^{-1}$ in the isomerization of 1-octen-3-ol. See ref 11a.

(28) (a) Other allylic alcohols, such as $CH_2$═CHCH(OH)R (R = H, Me, Et, $^n$Pr, $^n$Bu) and MeCH═CHCH(OH)Me, were subjected to the action of the complex [RuCl{$\kappa^2$(*N,N′*)-C(NR)(N$^i$Pr)-NH$^i$Pr}($\eta^3$:$\eta^3$-$C_{10}H_{16}$)] (**3f**) under identical reaction conditions, and quantitative formation of the corresponding carbonyl compounds was in all cases observed in short times (from 10 to 30 min; TOF = 400−1200 $h^{-1}$). (b) In complete accord with our previous results using compounds **D**, the novel (arene)ruthenium(II) complex **7** was also active in the base-free redox isomerization of 1-octen-3-ol. Using a ruthenium loading of 0.5 mol % and performing the catalytic reaction in THF at 80 °C, quantitative formation of octan-3-one was observed after 15 min (TOF = 800 $h^{-1}$). (c) As previously observed with the (arene)ruthenium(II) complexes **D**, the activity of the Ru(IV) complexes [RuCl{$\kappa^2$(*N,N′*)-C(NR)(N$^i$Pr)-NH$^i$Pr}($\eta^3$:$\eta^3$-$C_{10}H_{16}$)] (**3a−f**) decreases significantly when the catalytic reactions are performed in the presence of HCl. For example, 8 h was needed to quantitatively transform 1-octen-3-ol into octan-3-one with **3f** (0.5 mol %) when 1 mol % of HCl ($Et_2O$ solution) was introduced into the reaction medium (10 min required under acid-free conditions; see entry 6 in Table 1). This fact suggests that, as previously proposed for complexes **D** (see ref 3), the pendant amino NH$^i$Pr group of the guanidinate ligands acts as an internal base, facilitating the generation of the more coordinating oxo-allyl anion by deprotonation of the allylic alcohol.

(29) Evidence for the proposed chloride dissociation during catalysis has been gained by measuring the molar conductivities of complexes **3a−f** in THF/1-octen-3-ol (20/1 v/v) solvent mixtures. Thus, despite their neutral nature, molar conductivity values ranging from 10 (**3b**) to 18 (**3d**) $\Omega^{-1}$ $cm^2$ $mol^{-1}$ were observed. This fact strongly supports that partial dissociation of the chloride ligand to form cationic species takes place in solution.

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*Organometallics* XXXX, XXX, XXX−XXX