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Application of Electron-Withdrawing Coordinatively Unsaturated η^6-Arene β-Diketiminato−Ruthenium Complexes in Lewis Acid Catalyzed Diels−Alder Reactions

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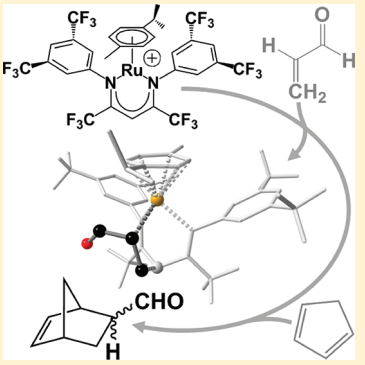
Supporting Information

ABSTRACT: Utilizing the aza-Wittig reaction involving the ylid 3,5-$(CF_3)_2C_6H_3NPPh_3$ and 1,1,1,5,5,5-hexafluoro-2,4-pentanedione, a highly fluorinated and electron-withdrawing β-diketiminate was obtained. Using strong bases, *n*BuLi, Ag_2O, or TlOEt, the corresponding β-diketiminato-Li, -Ag, or -Tl chelated complexes were prepared. Subsequent in situ transmetalation with $(Ru(\eta^6\text{-}C_6H_6)Cl_2)_2$ or $(Ru(\eta^6\text{-}p\text{-cymene})Cl_2)_2$ afforded the half-sandwich chloro-substituted Ru(II) β-diketimino complexes in high yield. The synthesis of the Lewis acidic catalysts featuring a vacant coordination site at the metal center was accomplished using [Na]BArF (BArF = tetrakis[3,5-bis(trifluoromethyl)phenyl]boron). These complexes are active for the Lewis acid catalyzed Diels−Alder reaction between α,β-unsaturated aldehydes, that is, methacrolein, acrolein, and dienes, that is, cyclopentadiene and 2,3-dimethyl-1,3-butadiene, with conversions in the range of 66−98% under mild conditions. Whereas the herein described catalysts generally promote exo selectivity of the [4 + 2] cycloaddition between methacrolein and cyclopentadiene, the reaction involving acrolein shows predominantly the formation of the endo adduct, similar to that observed for the noncatalyzed reaction. Importantly, the coordinatively unsaturated complexes demonstrate moderate Lewis acidity, which allows for the controlled reaction between methacrolein and 2,3-dimethyl-1,3-butadiene to 1,3,4-trimethyl-3-cyclohexene-1-carboxaldehyde without further isomerization to the bicyclic ketone, which is in contrast to strong Lewis acidic catalysts based on transition metals or main-group elements reported in the literature.



INTRODUCTION

Organic-based heterocycles containing at least one ring component now represent the vast majority of commercially available pharmaceuticals.[1] Concurrently, the number of synthetic methodologies for preparing cycloadducts has significantly increased. One widely utilized method to obtain functionalized six-membered rings is the highly atom efficient Lewis acid catalyzed Diels−Alder reaction. A number of metal- and nonmetal-based catalysts have been developed to promote the cyclization process and importantly afford selectivity between exo and endo products. Initial reports in the field describe the potential of Ru(II)-based Lewis acids in the catalysis of Diels−Alder type [4 + 2] cycloadditions.[2,3] The coordination complex $[Ru(salen)(NO)(H_2O)]SbF_6$ (salen = *N*,*N*′-ethylenebis(salicylimine)) showed increased selectivity and turnover numbers for the [4 + 2] cycloaddition between α,β-unsaturated aldheydes/ketones and various dienes, as compared to noncatalyzed cycloadditions.[3] The rationale behind introducing ruthenium as the active metal is based on high water tolerance,[4] moderate oxygen stability, increased rate of substrate−product exchange, and decreased side-product formation, as compared to the conventional simple, but strong, Lewis acids. More recently, Kündig et al. reported Lewis acid catalyzed Diels−Alder reactions of methacrolein and bromoacrolein with different types of dienes, employing a chiral η^5-cyclopentadienyl-substituted Ru(II) complex bearing a chelating diphosphinite with strongly electron-withdrawing fluorine substituents on the aryl groups. In all reactions, excellent conversion and selectivity was achieved, with predominant exo selectivity for the reaction between methacrolein and cyclopentadiene.[5] Furthermore, Kündig and co-workers studied the effect of different anions associated with the kinetics of ruthenium-catalyzed Diels−Alder reactions. If the organometallic-cationic component of the catalyst was combined with a weakly coordinating anion, such as SbF_6^-, higher activity was observed than if the stronger coordinating OTf^- and BF_4^- counterions were employed.[5−7] More recently, Oro et al.[8] reported the development of a potent asymmetric Ru(II)−pyridylamino half-sandwich complex. Interestingly, it was shown that, if the steric bulk of the η^6-arene capping group was increased from C_6H_6 to C_6Me_6, the enantiomeric excess of the formed product changed from (*R*) to (*S*).[8] Other important contributions to the field include the development of Ru(II) η^6-arene complexes with 4-isopropyl-2-(2-pyridyl)-1,3-oxazoline as a chiral ligand.[9] Currently, a wide range of chiral and achiral Ru(II) complexes capable of catalyzing the Diels−Alder reaction are known, including ligands, such as imidazolines,[10] bisoxazolines,[11]

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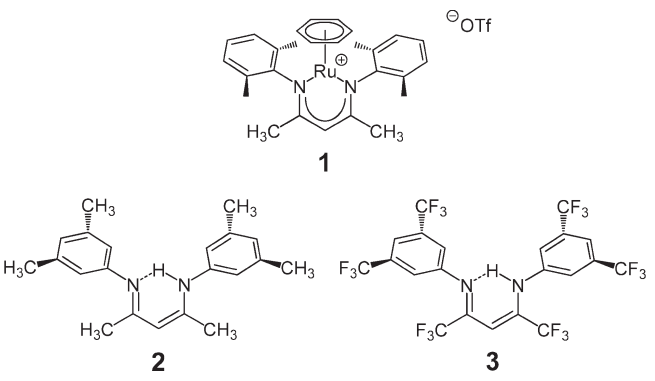
N-heterocyclic carbenes,[12] and chiral piano-stool complexes, with and without tethering of the capping arene group to the supporting chelating ligand.[12−15] To investigate the conformational stability of three-legged piano-stool complexes, Alezra et al. studied the temperature-dependent inversion of the geometry at the metal center of the diastereomeric [CpRu((R-BINOP-F)((CH$_3$)$_2$CO)]-SbF$_6$ complex, an active Lewis acid catalyst for the reaction between methacrolein and cyclopentadiene.[16] Moreover, Diàz-Àlvarez et al. prepared mono- and dicationic Ru(II) half-sandwich complexes bearing a tricyclic β-iminophosphine *P*,*N*-donor ligand demonstrating moderate to good enantio- and diastereoselectivity.[17] Further information regarding ruthenium Lewis acid catalyzed Diels−Alder reactions is available from the corresponding reviews.[18−20]

Initially, 1,3,5-triaza- and 1,5-diazapentadienyl systems were introduced as strategic ligands for the stabilization of low-coordinate and unusually bonded transition-metal and main-group complexes.[21−23] In the past two decades, however, it became apparent that these ligands possess a high degree of tunable steric and electronic properties that naturally impart application in catalysis. Consequently, there is an increasing number of reports describing the use of complexes bearing 1,3,5-triaza or 1,5-diazapentadienyl (β-diketiminate) ligands in homogeneous catalysis, especially in the fields of carbene and nitrene transfer,[24] polymerization,[25,26] hydroamination,[27,28] C−C bond formation,[29] hydrogenation,[30,31] and recently atom-transfer radical reactions.[32] In comparison to other chelating diazo ligands, such as amidinates, three-membered 1,2,3-triphenylguanidine, and four-membered α-diimines, the metal-coordinated β-diketiminate adopts a relatively unconstrained planar six-membered ring, resulting in a relatively smaller bite angle of less than 90°.[30,33−35] As a consequence, the substitution pattern of the flanking *N*-aryl substituents directly influences the steric environment around the metal center, forming a partially enclosed protective metal pocket with a structural analogy to the active sites found in metallo enzymes. Moreover, the β-diketiminate scaffold incorporates a wide range of steric and electronic modularity. Typically, flanking *N*-aryl groups are introduced through condensation of functionalized anilines with 2,4-pentanediones.[22,36−38] The backbone structure of this ligand class also offers three modular sites, two α- and one β-position. Recently, we have demonstrated that cationic η^6-arene β-diketiminato−ruthenium complexes **1** (Scheme 1) are well suited for the catalytic hydrogenation of highly substituted olefins, such as 1-methylcyclohexene. Moreover, the turnover activity is dependent on the substitution pattern at the α-positions; that is, electron-donating groups, such as methyl (**2**) and *t*-butyl, increase reactivity, whereas complexes containing ligand **3** with multiple electron-withdrawing CF$_3$ groups were catalytically inert (Scheme 1).[39] The latter finding suggests that the nature of **3** significantly reduces the electron density when bound to a Ru(II) metal center, leading to an overall Lewis acidic complex.

The research presented herein describes the first catalytic application of complexes featuring the heavily fluorinated β-diketiminate ligand **3**. In particular, emphasis is placed on the synthesis and characterization of novel cationic η^6-arene β-diketiminato−ruthenium(II) complexes and the evaluation of the efficiency and selectivity toward the Lewis acid mediated catalysis of Diels−Alder reactions between α,β-unsaturated aldehydes and various types of dienes.

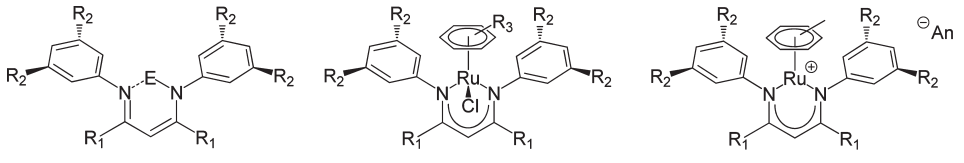
Scheme 1



RESULTS AND DISCUSSION

Synthesis of Ligand 3 and Corresponding Ru(II) Complexes. One advantage associated with β-diketiminate ligands is the straightforward synthesis, particularly when nonsterically demanding electron-donating groups are substituted at the flanking *N*-aryls and the α-positions, that is, ligand **2** (Scheme 2). The preparation of **2** and related analogues involves acid-catalyzed thermal condensation of two equivalents of aniline derivatives onto 2,4-pentanedione.[36,40−42] However, the particular substitution pattern of **2** does not afford β-diketiminato−Ru(II) complexes, that is, **1**, with the required Lewis acidity at the metal center to promote Diels−Alder-type cycloadditions. Therefore, the supporting ligands must be endowed with strongly electron-withdrawing substituents, such as fluorine or

Scheme 2



(**2**) E = H, R$_1$ = R$_2$ = CH$_3$
(**3**) E = H, R$_1$ = R$_2$ = CF$_3$
(**4**) E = Li, R$_1$ = R$_2$ = CH$_3$
(**5**) E = Li, R$_1$ = R$_2$ = CF$_3$

(**6**) R$_1$ = R$_2$ = CH$_3$, R$_3$ = C$_6$H$_6$
(**7**) R$_1$ = R$_2$ = CF$_3$, R$_3$ = C$_6$H$_6$
(**8**) R$_1$ = R$_2$ = CF$_3$, R$_3$ = C$_{10}$H$_{14}$

(**9**) R$_1$ = R$_2$ = CH$_3$, R$_3$ = C$_6$H$_6$, An = OTf
(**10**) R$_1$ = R$_2$ = CH$_3$, R$_3$ = C$_6$H$_6$, An = BArF
(**11**) R$_1$ = R$_2$ = CF$_3$, R$_3$ = C$_6$H$_6$, An = OTf
(**12**) R$_1$ = R$_2$ = CF$_3$, R$_3$ = C$_6$H$_6$, An = BArF
(**13**) R$_1$ = R$_2$ = CF$_3$, R$_3$ = C$_{10}$H$_{14}$, An = BArF

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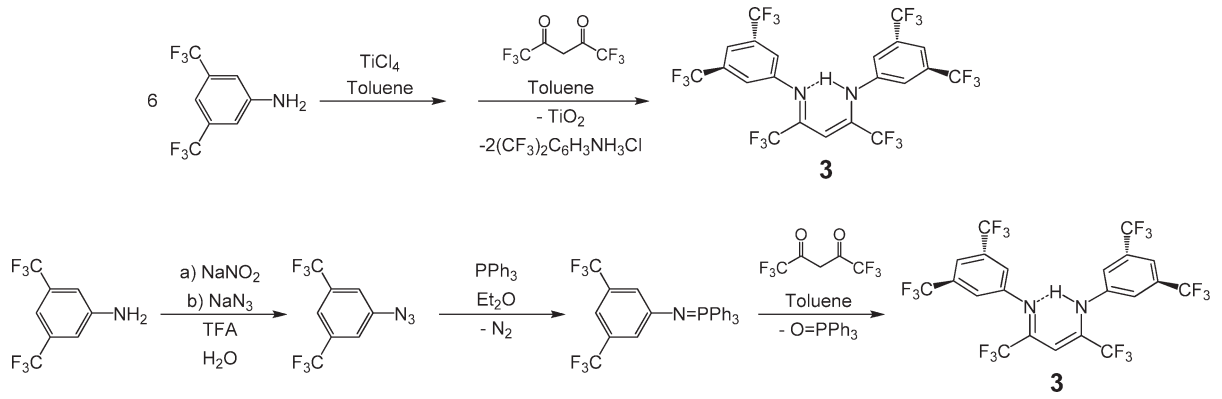

Figure 1. Two different synthetic pathways for accessing the heavily fluorinated β-diketiminate **3**, using a highly Lewis acidic metal mediated coupling method (top) or through an aza-Wittg ylid substitution reaction (bottom).

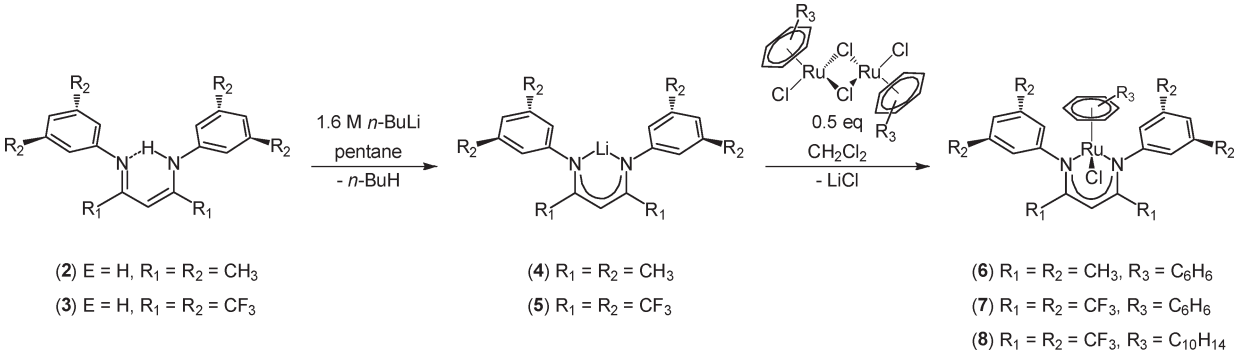

Figure 2. General synthetic transmetalation route for accessing chloro-η^6-arene β-diketiminato ruthenium complexes (**6**−**8**), using lithiated β-diketiminates (**4** and **5**) obtained through deprotonation of **2** or **3** using *n*-BuLi in pentane.

trifluoromethyl groups.[5,6] The heavily fluorinated β-diketiminate **3**, first reported by Sadighi et al., represents an ideal candidate for formulating a series of Lewis acidic Ru(II) complexes (Scheme 2).[43]

In contrast to **2**, the synthesis of **3** requires a different synthetic methodology, where activation of the electron-deficient bis-3,5-trifluoromethyl-aniline is necessary prior to coupling with the 1,1,1,5,5,5-hexafluoro-2,4-pentanedione. This is achieved through the use of the highly Lewis acidic $TiCl_4$ (Figure 1),[38,44] or through a stoichiometric aza-Wittig reaction involving a ylid derivative $(3,5\text{-}(CF_3)_2C_6H_3)N{=}PPh_3$ and hexafluoroacetylacetone (Figure 1).[43] In our hands, both procedures afforded **3** in high yield. However, the $TiCl_4$-based method has disadvantages, including the use of a large excess of aniline and the required strict anhydrous conditions. Using the slow vapor diffusion method, single crystals of **3** were obtained and characterized by X-ray diffraction techniques; see the Supporting Information for a more detailed discussion.

The previously reported synthesis of β-diketiminato−Ru(II) complexes bearing an η^6-arene ligand utilized a transmetalation procedure with the lithium complex **4**.[37,38,45,46] Similarly, lithiation of the heavily fluorinated β-diketiminate **3** is accomplished by the addition of 1.6 M *n*-BuLi at low temperatures, resulting in the precipitation of complex **5** from *n*-pentane (Figure 2).[47,48] The bright orange solid **5** is highly air- and moisture-sensitive, soluble in dry and degassed Et_2O, and stable in chlorinated hydrocarbons. Characterization of **5** was performed using solution ^1H, ^{13}C, and ^{19}F NMR. Coordination of the β-diketiminato ligand with an η^6-arene ruthenium(II) fragment is achieved following the methodology previously established by Phillips et al.[30] In this step, $((\eta^6\text{-}C_6H_6)RuCl_2)_2$ is reacted with either the electron-donating ligand **4** or the electron-withdrawing ligand **5** over a 12 h period at room temperature in dichloromethane, affording the chloro-substituted complexes **6** and **7** in moderate to high yields (Figure 2). In contrast, the corresponding transmetalation reaction between the β-diketiminato−lithium derivative **5** and the *p*-cymene substituted dimer $((\eta^6\text{-}(C_{10}H_{14})RuCl_2)_2$ proceeds to form complex **8**, albeit at low yield. We hypothesize that, in this reaction, a competing nucleophilic attack on the coordinated η^6-*p*-cymene ligand by the anionic β-diketiminate **5** occurs in parallel with the transmetalation step, as evidenced by the recovery of a high amount of the reconstituted protonated ligand **3**, as observed by solution ^1H NMR. A similar reaction with a coordinated metal arene has been observed between a β-diketiminato−lithium complex and the η^6-$CF_3C_6H_5$-substituted β-diketiminato−ruthenium(II) complex.[47]

Subsequently, two alternative synthetic routes were explored for preparing **8** with increased yields. The first method involved initial formation of the dimeric acetonitrile β-diketiminato silver complex **14** as first characterized by Chiong et al., which does not require use of the lithiated β-diketiminate **5**.[49] Using a modified procedure, employing a microwave reactor, metalation of **3** with 0.5 equiv of Ag_2O in acetonitrile afforded **14** with yields of up to 69%. Subsequent transmetalation between **14** and $((\eta^6\text{-}C_{10}H_{14})RuCl_2)_2$ in dichloromethane, with strict exclusion of light, provided complex **8** in 80% yield (Figure 3).

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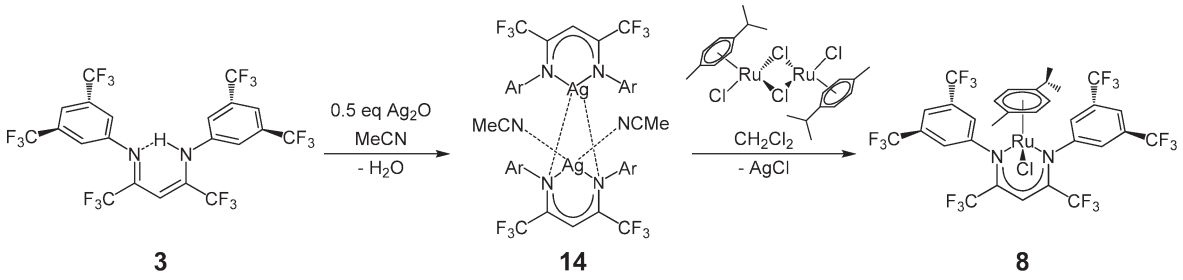

Figure 3. Synthesis of the dimeric silver β-diketiminate derivative **14** (Ar = $(CF_3)_2C_6H_3$) from **3** and the subsequent transmetalation to afford the corresponding η^6-*p*-cymene ruthenium half-sandwich chloride complex **8**.

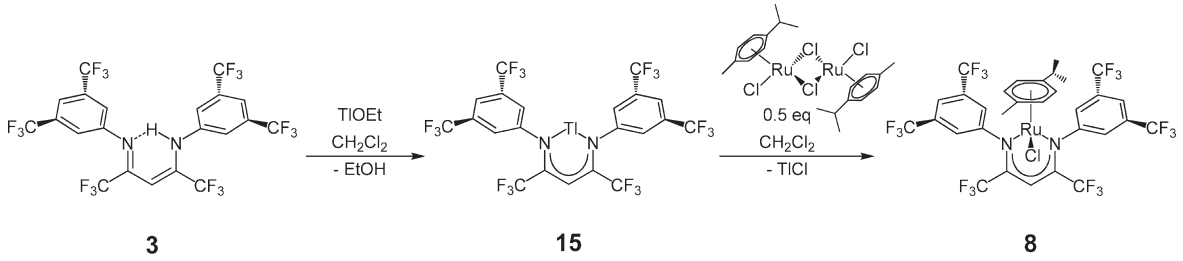

Figure 4. Synthesis of the thallium β-diketiminate derivative **15** from the in situ deprotonation of **3**. Subsequent transmetalation afforded the corresponding η^6-*p*-cymene ruthenium half-sandwich chloride complex **8**.

However, considering the entire synthetic route from **3** to **8**, the overall yield is only moderate (55%).

A third method was devised that involves the formation of the neutral β-diketiminato−thallium complex **15**. Transmetalation using Tl complexes represents one of the mildest routes for ligand transfer, and a number of precedents in the literature involving β-diketiminates have recently been reported. Although a limited number of thallium complexes are known, most synthetic procedures involve use of an alkaline metal precursor.[50−53] In contrast, we have employed a modified method based on the work reported by the groups of Chang et al., Tonzetich et al., and Dias et al.[4,54,55] TlOEt is used to quantitatively deprotonate the β-diketiminate **3** and directly form complex **15** in situ (Figure 4). In a separate reaction, the identity of **15** was validated using solution ^{1}H, ^{13}C, and ^{19}F NMR. Afterward, purification of **8** required column chromatography, using an eluent mixture of *n*-pentane, dichloromethane, and ethyl acetate (ratio of 4.5:4.5:1). The resulting dark red complex **8** was obtained in 86% yield. All of the isolated η^6-arene chloro-ruthenium(II) species bearing the heavily fluorinated β-diketiminate, **7** and **8**, were found to be air stable both in solution and in the solid state, in contrast to complex **6**, which decomposes to as yet an unidentified black powder within days upon exposure to air.

To obtain a catalytically active species, a vacant coordination site at the ruthenium center was generated via an anion metathesis reaction of the Cl substituent. This was accomplished using the corresponding sodium salt of a weakly coordinating anion, such as [Na]OTf or [Na]BArF (BArF = $[(3,5\text{-}(CF_3)_2C_6H_3)_4\text{-}B]^-$),[56] affording the coordinatively unsaturated complexes **9**, **10**, **12**, and **13** in yields of up to 70% (Figure 5).[30,31] In contrast to complex **9**, the Cl-anion metathesis reaction of **7** does not proceed if [Na]OTf is used, as the incorporation of **3** leads to a significantly stronger Ru−Cl bond. Therefore, Cl abstraction and subsequent anion exchange required the stronger metathesis reagent Me_3SiOTf, with the highly volatile Me_3SiCl formed as a byproduct. The corresponding red-colored triflate complex **11** is obtained in high yields of 87% (Figure 5), whereas complexes featuring the BArF counterion were prepared in yields of 60−70%. All of the cationic η^6-arene−ruthenium(II) β-diketiminate species demonstrated moderate sensitivity toward both oxygen and water and thus required storage and manipulation under an inert atmosphere. Complexes **9** and **10** are highly soluble in chlorinated solvents, such as CH_2Cl_2 and $CHCl_3$, over a wide temperature range. In contrast, especially **12** and, to some extent, **13** show reduced solubility at −20 to −50 °C. In particular, the triflate complex **11** is practically insoluble in dichloromethane, even at ambient temperatures.

Characterization in Solution. All isolated η^6-arene chloro-β-diketiminato−Ru(II) complexes were characterized by solution NMR (Table 1). The spectra reveal separate resonances for the *o*-CH and *o*-CH′ aryl protons associated with the Cl-substituted complexes **6**−**7**, bearing ligand **3**, consistent with C_s symmetry, whereas complex **6** with the *m*-CH_3 aryl-substituted ligand **2** adopts C_2 symmetry. The latter observation suggests that **6** is subject to either fast rotation (compared to NMR time scale) of the flanking aryl groups or an association−dissociation process of the Cl group. As complexes **6**−**8** possess a similar geometry, it is concluded that the lower symmetry observed in **6** originates from the difference in electronic character between ligands **2** and **3**. Hence, the complexes bearing the electron-withdrawing β-diketiminate **3** possess a stronger Ru−Cl bond, therefore, retaining the observed solid-state C_s symmetry even in solution. In particular, the C_s geometry found for the *p*-cymene-substituted complex **7** is even more defined in solution, as confirmed by a $\delta(^{13}C)$ difference for the two aryl *o*-C(H) positions. In contrast, the ^{1}H and ^{13}C NMR spectra of the cationic complexes **9**−**13** indicate the expected C_{2v} symmetry. A measure of the Lewis acidity associated with the Ru(II) complexes bearing β-diketiminate ligands **2** or **3** is provided by the highly diagnostic $\delta(^1H)$ associated with the β-H(C) group (Table 1). A comparison of

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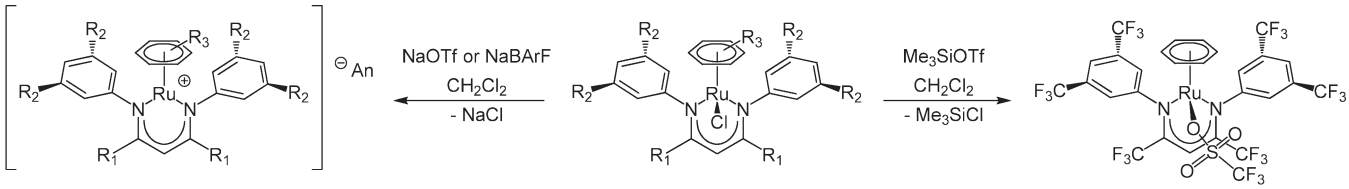

(**9**) $R_1 = R_2 = CH_3$, $R_3 = C_6H_6$, An = OTf
(**10**) $R_1 = R_2 = CH_3$, $R_3 = C_6H_6$, An = BArF
(**12**) $R_1 = R_2 = CF_3$, $R_3 = C_6H_6$, An = BArF
(**13**) $R_1 = R_2 = CF_3$, $R_3 = C_{10}H_{14}$, An = BArF

(**6**) $R_1 = R_2 = CH_3$, $R_3 = C_6H_6$
(**7**) $R_1 = R_2 = CF_3$, $R_3 = C_6H_6$
(**8**) $R_1 = R_2 = CF_3$, $R_3 = C_{10}H_{14}$

Figure 5. Cl-anion metathesis of the β-diketiminato−chloro-ruthenium complexes **6**−**8** with Na[OTf] or Na[BArF] to afford complexes **9**, **10**, **12**, and **13**. Use of the strong chlorine abstraction reagent Me_3SiOTf is required to obtain complex **11** in high yield.

Table 1. Selected Solution ^{1}H, ^{13}C, and ^{19}F NMR[a] Chemical Shifts (ppm) for Complexes 6−13

	compound							
	6	7	8	9	11	10	12	13
^{1}H NMR								
β-C*H*	4.48	5.40	5.46	6.37	6.11	6.39	7.53	7.41
arene-C*H*	4.56	4.57	3.79	5.20	5.31	5.11	5.41	4.67−4.69
aryl *o*-C*H*	7.02	7.61	7.60	6.98	8.35	6.92	8.08	8.01
aryl *o*-C*H*′		7.77	8.56					
aryl *p*-C*H*	6.84	8.3	7.85	7.09	8.13	7.11	8.24	8.25
^{13}C NMR								
β-CH	94.8	86.9	87.4	104.2	81.7	104.5	96.3	96.0
aryl *o*-CH	124.3	126.4	124.5	121.8	127.7	121.6	125.2	125.3
aryl *o*-CH′			130.0					
aryl *p*-CH	126.9	120.1	120.5	129.1	121.9	129.4	124.1	123.8
C═N	160	150.9	151.3	163.6	152.1	164	154.8	154.3
i-*C*	159.8	156.5	156.9	160.4	157.2	160.4	157.2	157.0
BArF C_B						162.4	162.3	162.3
^{19}F NMR								
α-CF_3		−59.25	−58.95		−57.50		−57.97	−57.96
m-CF_3		−63.27	−63.37		−63.77		−63.34	−63.36
m-CF_3′		−63.24	−63.30	−78.81	79.13			
OTf CF_3				−78.81	79.13			
BArF CF_3						−62.88	−62.91	−62.92

[a] Spectra were recorded in CD_2Cl_2, except complex **11**, which was measured in acetone-d_6.

the chloro-substituted complexes **6** and **7** shows increased shielding at the β-carbon position, consistent with an increase in electron density, which is in agreement with the observed $\delta(^1H)$ value in the uncoordinated ligand. The cationic β-diketiminato complexes **9**−**13** show substantially deshielded values for β-H(C), which corresponds to increased electron donation from the ligand to the Ru(II) center. Interestingly, a greater $\delta(^1H)$ difference was observed for the various types of anions used. For example, complexes with the weakly coordinating BArF, that is, **10**, **12**, and **13**, show $\delta(^1H)$ values greater than 7 ppm. Moreover, use of the electron-withdrawing ligand **3** further deshields β-H(C) and indicates an overall reduction of electron density in the core of the β-diketiminate. It is noteworthy that the chemical shifts for **9** and **10** are very similar, indicating that, in solution, both the triflate and the BArF components behave as noncoordinating anions. As indicated by the unchanged ^{13}C and ^{11}B chemical shifts of the BArF β-C and B center for complexes **10**, **12**, and **13**, it can be assumed that BArF is fully dissociated from the cationic complexes, leading to catalytic active species with the required vacant metal coordination site. In the context of hydrogenation reactions involving complexes similar to **10**, solution heteronuclear ^{1}H−^{19}F correlation and diffusion NMR studies revealed that the heavily fluorinated anion BArF weakly interacts with the cationic organometallic complex through a number of diffuse contacts involving all F groups. In contrast, the OTf and BF_4 counterions show strong localized interactions with specific regions of the cation, which can potentially interfere with substrate−metal coordination.[31]

Characterization in the Solid State. Using the liquid vapor-diffusion technique at either low temperatures, less than −10 °C, or at room temperature, single crystals suitable for X-ray diffraction studies were obtained for the majority of complexes (Figure 6). Indicative structural parameters are given in Table 2. The complexes **6**−**13**, depending on the substituent pattern of

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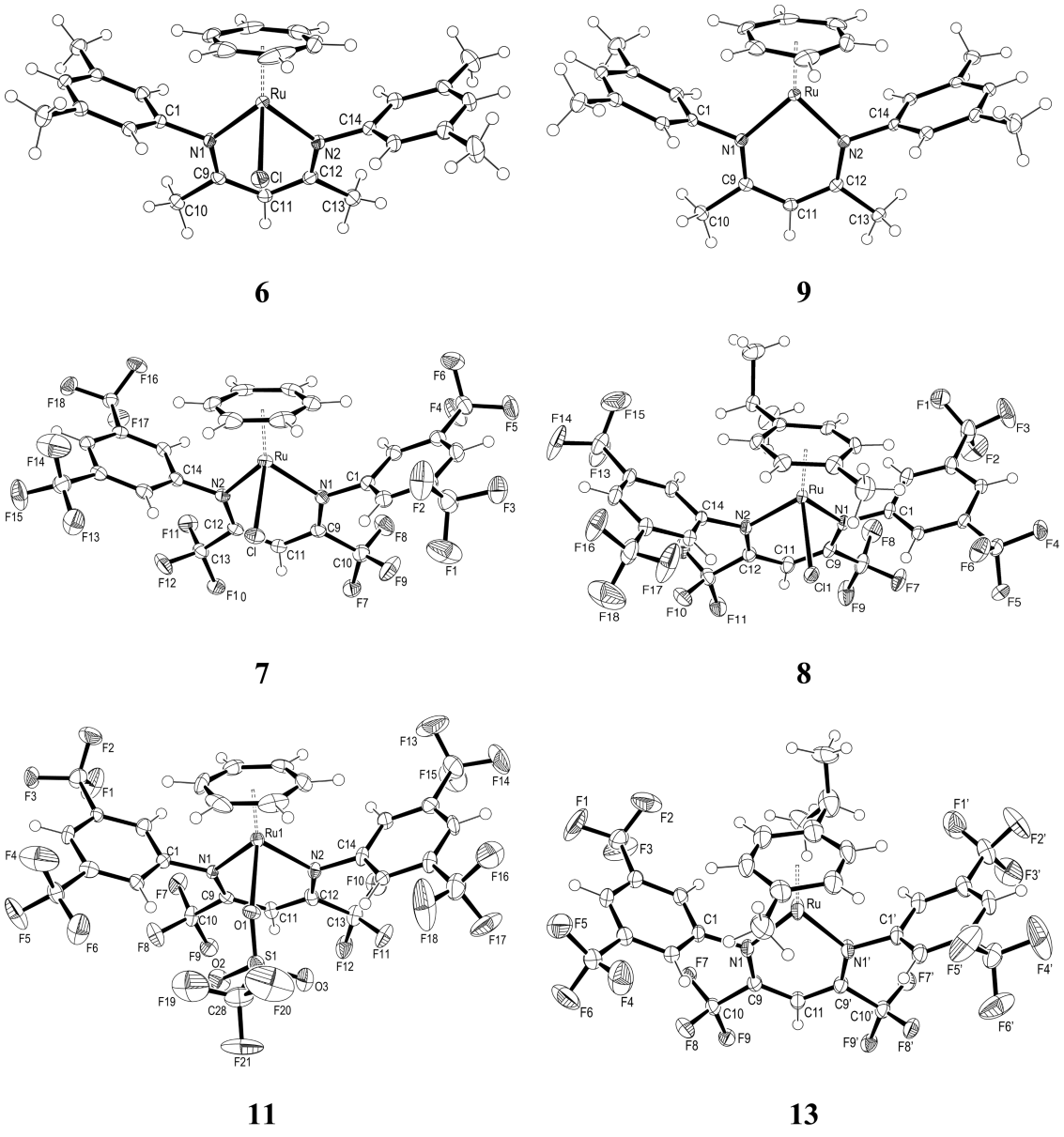

Figure 6. ORTEP diagrams of the chloro-substituted η^6-arene β-diketiminato−Ru(II) complexes **6**, **7**, and **8**; the triflate-coordinated complex **11**; and the coordinatively unsaturated species **13**. Thermal ellipsoids are drawn at 50% probability. Anions, solvates, and internal disorder have been omitted for clarity. In the case of complexes **9** and **11**, two crystallographically independent molecules are present within the unit cell, and the less disordered molecule is shown.

the β-diketiminate ligand, display either the standard three-coordinate piano-stool geometry about the Ru(II) center or, in cases where the organometallic component is cationic, a two-coordinate piano-stool geometry.

A comparison of complexes **6**−**8** featuring either ligand **2** or **3** reveals some key structural differences. Importantly, for ligand **2**, *meta*-substituted methyl groups on the flanking *N*-aryls were selected to minimize steric effects, thus highlighting the electronic properties derived from the substituent patterns of ligands and, in particular, the donor strength of the coordinated β-diketiminate. The most striking difference between **6** and **7** is the Ru−Cl bond length, which is a valuable measure of the Lewis acidity associated with the complex. Species **6** features an extremely long Ru−Cl bond of 2.453(1) Å; however, this bond is shorter than the 2.521(1) Å observed for the $(\eta^6\text{-}C_6H_6)$RuCl-$((2,6\text{-}(CH_3)_2C_6H_3NC(CH_3))_2CH$ complex,[30] which features an *ortho*-methyl *N*-aryl substitution pattern. In contrast, the heavily fluorinated complex **7** showed a considerably shortened Ru−Cl bond of 2.414(1) Å, which is increased slightly in **8**, 2.429(2) Å, where the sterically more demanding and electron-donating η^6-*p*-cymene is employed. However, the Ru(II)−Cl bond lengths of **7** and **8** are considerably shorter than those reported in other Lewis acidic (η^6-arene)Ru(II)Cl complexes.[8,10,15,57] Another measure of the Lewis acidity of the above complexes is the distance between the centroid of the η^6-arene and the metal center. Complex **6** with electron-donating methyl groups has the shortest distance, whereas both **7** and **8** feature a longer η^6-arene−metal distance. Moreover, smaller Ru−N−C-(ipso) angles were observed for **7** and **8** as a result of the greater steric interaction between the larger CF_3 substituents at the

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Table 2. Selected Bond Lengths (Å) and Angles (°) for η^6-Arene−β-diketiminato−Ru(II) Complexes, 6−9, 11, and 13

	complexes					
	6	7	8	9[a]	11[a]	13[b]
Ru−N	2.091(2)	2.108(2)	2.106(3)	2.005(2)	2.091(4)	2.022(3)
	2.098(2)	2.106(2)	2.118(3)	2.008(3)	2.101(4)	
				2.011(2)	2.088(4)	
				2.008(2)	2.092(4)	
Ru−Cl/O	2.453(1)	2.414(1)	2.429(2)		2.247(4)	
					2.252(4)	
Ru−C[c]	1.683(1)	1.703(1)	1.700(2)	1.704(2)	1.690(2)	1.714(1)
				1.698(1)	1.686(3)	
N−Ru−N	88.2(1)	87.8(1)	88.7(1)	89.1(1)	88.9(2)	89.0(1)
				88.8(1)	89.5(2)	
N−C_α−C_β	124.0(2)	126.1(2)	126.8(3)	122.4(2)	126.1(5)	125.0(3)
	124.6(2)	126.4(2)	126.6(4)	122.7(3)	126.4(6)	
				122.4(2)	125.5(6)	
				122.8(2)	125.7(5)	
N−Ru−Cl/O	85.4(1)	83.3(1)	83.7(1)		84.9(2)	
	84.2(1)	82.4(1)	83.0(1)		84.1(2)	
					81.8(2)	
					76.7(2)	
Cl/O−Ru−C[c]	126.3(1)	126.0(1)	126.5(1)		123.4(1)	
					128.8(2)	
C[c]−Ru−N[d]	150.8(1)	154.0(1)	152.8(1)	177.2(1)	154.3(2)	180.0[e]
				178.8(1)	156.4(2)	
Ru−N[d]−C_β	171.6(1)	170.5(1)	173.4(2)	175.5(1)	179.2(3)	180.0[e]
				176.2(2)	170.0(3)	

[a] Two crystallographically independent molecules are present in the unit cell. [b] Disorder is present within the molecule. [c] Refers to the centroid point of the η^6-arene ligand. [d] Refers to the midpoint distance between the two nitrogen centers of the β-diketiminato ligand. [e] No esd is possible due to placement of atoms on special positions.

α-position of the β-diketiminate and the flanking *N*-aryls. Interestingly, the N−Ru−N bond angle (Table 2), remains constant in the entire series and is independent of chloro substitution or the substituent pattern of the β-diketiminate or η^6-arene.

For complexes bearing the *meta*-methyl-substituted β-diketiminate **2**, a comparison of the covalently bonded chloro-substituted species **6** with the cationic species **9** containing a noncoordinating triflate counterion shows a number of important differences. These include an increased η^6-arene−metal interaction and shortened Ru−N bonds in the cationic species **9**, consistent with increased β-diketiminato σ- and π-bonding interactions to support the electron-deficient metal center. Similarly, a comparison of **8** and **13** shows that the latter has increased η^6-*p*-cymene−metal interaction in parallel with a shortening of the Ru−N bond distances. A key structural difference associated with the β-diketiminato ligand between the chloro complexes **6** and **7** and the cationic complexes **9** and **13** is the folding back of the β-diketiminate component, as indicated by η^6-arene(centroid)−Ru−N(midpoint) angles of 154.0(1), 152.8(1), and 154.1(2)°, respectively, for **6**, **7**, and **8**. Thus, the flanking *N*-aryl groups rotate in order to minimize steric interaction with the η^6-arene. In contrast, the coordinatively unsaturated complexes **9** and **13** with weakly coordinating anions show angles of 178.8(1)° and 180.0°, respectively; and thus the centroid point η^6-arene group, the Ru center, and the β-diketiminate backbone atoms are positioned within a common plane.

Structural analysis of the β-diketiminato fragment in the above-discussed complexes shows an overall shortening of the N−C_α bonds for those species featuring **3**, as compared with those with **2**. An important measure of the nucleophilic character of the β-C position is given by the C_α−C_β−C_α bond angle, which is decreased by 2.4° in complexes bearing **3**, indicating decreased s-orbital contribution to the sp^2 σ-hybridization of the β-C carbon.[47] The presented solid-state structures demonstrate that the choice of substituents on the β-diketiminate ligand can be used to effectively modulate the Lewis acidity of the metal center. Complexes with an electron-withdrawing β-diketiminate **3**, as opposed to **2**, show significantly increased Lewis acidity. This is well illustrated by the fact that, for **11**, a covalent Ru−O-(SO_2CF_3) interaction is observed in the solid state, which is absent in the analogous complex **9**, featuring the electron-donating ligand **2**. The Ru−O bond length is 2.250(4) Å and is slightly longer than the mean Ru−O(SO_2CF_3) distance of 2.234 Å reported for the 66 currently known examples.[58] In comparison, the shortest Ru−O bond involving a triflate group is 2.099(2) Å, as reported by Krause et al.[59] In contrast to the 18-electron configuration of complex **11**, the 16-electron configuration of the RuCl(=CH-*i*Pr-OC_6H_4)($IMesH_2$)(OTf) species results in a very short metal−oxygen bond. On the other hand, the closest cation−triflate interaction in **9** is 2.399 Å, which involves a close contact between a triflate oxygen and a hydrogen associated with the η^6-C_6H_6 group.

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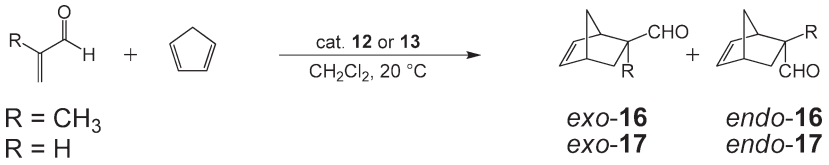


Figure 7. Catalytic Diels–Alder [4 + 2] cycloaddition between methacrolein or acrolein (0.5 mmol) and cyclopentadiene (9 equiv) mediated by 5 mol % of either complex **12** or **13** to yield the bicyclic exo- or endo-2-methyl-bicyclo[2.2.1]hept-5-ene-2-carboxaldehyde **16** and exo- or endo-bicyclo[2.2.1]hept-5-ene-2-carboxaldehyde **17**.

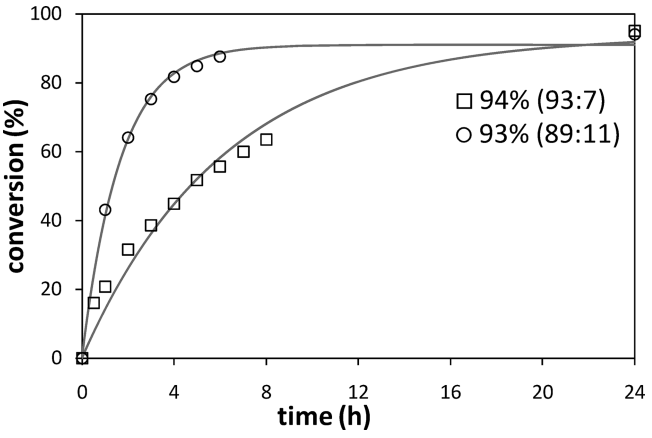


Figure 8. Plot of product conversion **16** (including exo/endo isomer ratio), as a function of reaction time catalyzed by complex **12** (□) and **13** (○), with methacrolein (0.5 mmol) and cyclopentadiene (9 equiv) at −20 °C for 24 h.

Lewis Acid Mediated Diels–Alder Catalysis Using β-Diketiminato–Ru(II) Complexes. To determine if complexes **9**, **10**, **12**, and **13** feature the required Lewis acidity to efficiently catalyze the [4 + 2] cycloaddition between methacrolein and cyclopentadiene (Figure 7), a series of room-temperature NMR experiments were performed. Employing similar conditions used in the literature,[5,60−62] species **9** and **10**, bearing the β-diketiminate **2**, are catalytically inert. In contrast, when methacrolein was added to CH_2Cl_2 solutions containing 5 mol % of either complex **12** or **13**, an immediate color change from brown-yellow to red was observed. This change is consistent with the color of the triflate complex **11** in CH_2Cl_2, indicating the presence of a Ru(II)–oxygen bond. Subsequent addition of excess cyclopentadiene to the complexes **12** and **13** in the presence of methacrolein resulted in the efficient formation of 2-methyl-bicyclo-[2.2.1]hept-5-ene-2-carboxaldehyde (**16**) within a period of 0.5 h at 20 °C. Product **16** was obtained with a exo/endo selectivity of 88–92% regardless of which catalyst was employed.

To understand the effect of using different η^6-arene ligands; benzene for **12** and *p*-cymene for **13**, the above reaction was repeated at −20 °C with NMR aliquots sampled over a period of 24 h (Figure 8). A noteworthy observation is the difference in the conversion rate between complexes **12** and **13** at −20 °C, which was not observed at room temperature. The increased activity of **13** is particularly surprising. On the basis of the structural data, increased Lewis acidity would be attributed to **12**. Furthermore, **12** shows a slight increased exo selectivity as compared to the reaction at 20 °C. Interestingly, the exo selectivity induced by **13** shows minor differences with changes in temperature, suggesting that **13** is inherently a highly rigid complex.

Table 3. Comparison of Conversions in Diels–Alder Cycloaddition Reactions Using HC(O)C(R)C=CH_2, Where R = H is Acrolein and R = Me is Methacrolein as the Dieneophile and Cyclopentadiene[a]

catalyst	arene	substrate R	time (h)	conversion (%)	yield[b] (%)	exo/ endo
12	η^6-C_6H_6	CH_3	2	80[c]	70	88:12[c]
12	η^6-C_6H_6	H	2	99[d]	81	17:83[d]
13	η^6-^{i}PrC$_6$H$_4$Me	CH_3	2	83	74	89:11
13	η^6-^{i}PrC$_6$H$_4$Me	H	2	99	84	26:74

[a] Reaction conditions: Dienophile (0.5 mmol) and cyclopentadiene (9 equiv) using 2 mol % of catalysts **12** and **13** at 20 °C in dichloromethane (6 mL) at 20 °C. [b] Isolated yield after column chromatography. [c] Without catalyst added, the conversion to **16** is 16% after 24 h with an exo/endo ratio of 78:22. [d] Without catalyst added, the conversion to **17** is 44% after 2 h with an exo/endo ratio of 23:77.

To further quantify the ability of **12** and **13** to catalyze a range of [4 + 2] cycloadditions, reactions with different dienophiles (i.e., methacrolein and acrolein) and cyclopentadiene were performed at 20 °C using a lower catalyst loading of 2 mol % (see Table 3).

Similar to the reactions employing 5 mol % of either complex **12** or **13**, the latter proved more active for [4 + 2] cycloadditions. Interestingly, **12** shows an increased endo selectivity in the reaction involving acrolein and cyclopentadiene, as compared to **13**. To study the interaction between α,β-unsaturated aldehydes and **13**, a series of solution NMR studies were performed. In contrast to other catalytically active Ru(II) species used in Diels–Alder reactions, both ^{1}H and ^{19}F NMR measurements provided no evidence of the formation of a methacrolein-**13** adduct, even in the presence of an excess of methacrolein (1–50 equiv).[5,60−62] However, the addition of an excess of acrolein (10 equiv) to a solution of **13** in CH_2Cl_2 resulted in the formation of complex **18**. Figure 9 shows the acrolein concentration-dependent formation of **18**, as monitored by ^{19}F NMR.

Upon closer examination of the reaction between **13** and acrolein, the splitting pattern observed in the ^{19}F NMR associated with the 3,5-$(CF_3)_2C_6H_3$ flanking aryl groups reveals that complex **18** does not feature the C_{2v} symmetry associated with **13**. Moreover, ^{1}H NOE measurements of **18** did not correspond to a presumed structure **18′**, which, based on literature precedents, should feature a Ru–O(CH(CHCH$_2$)) bond; see the Supporting Information for further details. In particular, the expected NOE interaction between the β-CH hydrogen and the aldehyde CHO proton was absent. Furthermore, the NOE experiment indicated a close proximity of the H(CO) group and the aromatic hydrogens of *p*-cymene. Fortunately, single crystals were obtained from the mixture of **13** and **18** when an excess of

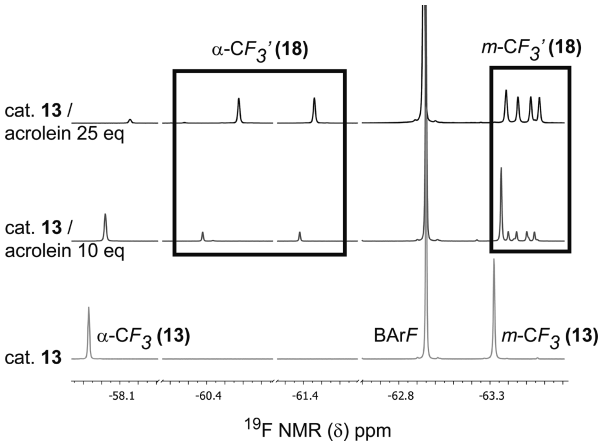
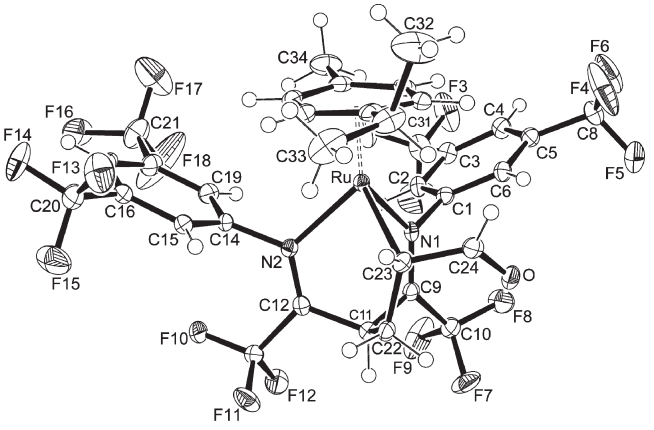


Figure 9. Solution ^{19}F NMR spectrum of complex **13**, and spectra of mixtures containing **13** with different ratios of acrolein in CD_2Cl_2. Complex **18** represents the product formed from the reaction of **13** and acrolein.



18

Figure 10. ORTEP diagram of the acrolein-**13** adduct, **18**. Thermal ellipsoids are drawn at 50% probability. The anion, BArF, was omitted for clarity. Selected bond distances (Å) and angles (°): Ru−N(1), 2.090(2); Ru−N(2), 2.100(2); Ru−C(23), 2.220(2); C(11)−C(22), 2.553(4); C(22)−C(23), 1.509(4); Ru−C^b, 1.767(1); N(1)−Ru−N(2), 82.8(1); N(1)−C(9)−C(11), 120.2(2); N(2)−C(12)−C(11), 119.4(2); N(1)−Ru−C(23), 81.9(1); N(2)−Ru−C(23), 86.0(1); C(23)−Ru−C^b, 125.2(1); C^b−Ru−N^c, 152.8(1); Ru−N^c−C(11), 127.8(1). C^b centroid formed between atoms C(25)−C(30) of the *p*-cymene ring. N^c centroid formed between atoms N(1) and N(2).

acrolein (25:1) was added. X-ray diffraction techniques identified **18** as a metal−ligand bridged metallocycle adduct, whereby the vinyl group of acrolein has undergone a [4 + 2] cycloaddition with the Ru(II) center and the β-carbon of the β-diketiminate (Figure 10).[63] This particular reversible mode of bonding has been observed between alkenes, such as ethylene or styrene, and η^6-arene Ru(II) complexes bearing electron-rich β-diketiminate ligands, similar in nature to complex **10**.[30,47] Nevertheless, it is surprising to observe the formation of **18** in the presence of an electron-withdrawing fluorinated β-diketiminate ligand, in which the nucleophilicity of the β-carbon is significantly reduced.[47] Moreover, this particular bonding mode of an α,β-unsaturated aldehyde has not been reported to date. Besides the common

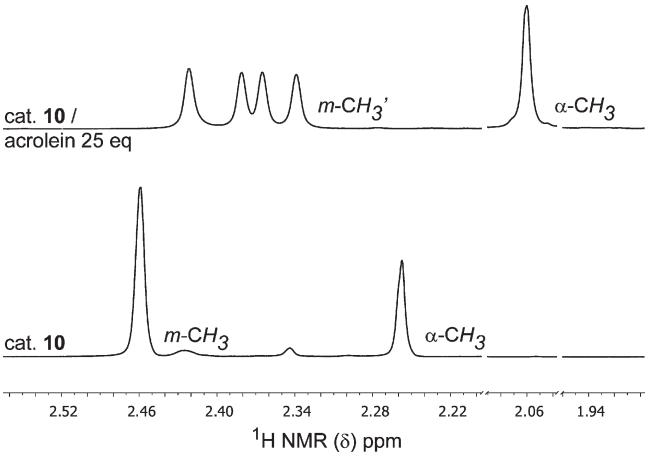


Figure 11. Solution ^1H NMR of **10** in CD_2Cl_2 with (top) and without (bottom) an excess of acrolein added. The change in symmetry is indicated by the *m*-CH_3 signals that form multiple inequivalent resonances upon formation of the acrolein-**10** adduct.

η^1-metal−oxygen coordination of such C═O containing substrates, only one other coordination mode of α,β-unsatuated aldehydes to transition metals is known from the literature. Hiraki and co-workers described the insertion of 2-methyl-2-propen-1-ol onto a [RuClH(CO)(PPh_3)$_3$] complex, forming a (η^4-enone)Ru(0) complex. The latter insertion is accompanied by the reductive elimination of hydrogen.[64]

The rate of appearance of the yellow-colored adduct **18** is correlated with the concentration of acrolein; that is, the greater the excess of acrolein, the faster the formation of **18**. The latter observations strongly suggest that the formation of **18** is subject to an equilibrium process involving **13** and acrolein. Importantly, no red-to-yellow color change was observed during the catalysis reaction of **13** involving acrolein and cyclopentadiene. Hence, the formation of **18** probably represents a resting state of the catalyst. To confirm the latter hypothesis, an excess of acrolein (25 equiv) was added to the catalytically inactive complex **10**, bearing the electron-donating ligand **2** with α-methyl substituents. As shown in Figure 11, the formation of an adduct acrolein-**10**, structurally similar to **18**, was observed after a short period of time.

By similarity, these findings suggest that complex **18** is not the catalytically active species in Lewis acid mediated cycloadditions. It is proposed that only the Ru(II)−O coordinated adduct **18′** is catalytically active in the herein described Diels−Alder reactions, as reported in the literature (Figure 12).[65]

Lewis acidic Ru(II) complexes are known to catalyze a range of various inter- and intramolecular Diels−Alder reactions.[66] To explore the applicability of complex **13** toward additional types of dienes, cycloaddition reactions between methacrolein and 1,3-cyclohexadiene or 2,3-dimethyl-buta-1,3-diene were performed using 2 mol % catalyst loadings at 20 °C in CH_2Cl_2 (Figure 13).

The reaction between methacrolein and 1,3-cyclohexadiene does not afford the bicyclic product 2-methyl-bicyclo[2.2.2]oct-5-ene-2-carboxaldehyde **19** in the presence of **13**, even after an extended period of 24 h at room temperature. In contrast to cyclopentadiene, 1,3-cyclohexadiene is a bulky, less strained cyclic dienophile, which is generally considered a poor substrate for cycloadditions,[67] especially when the Lewis acidity of the

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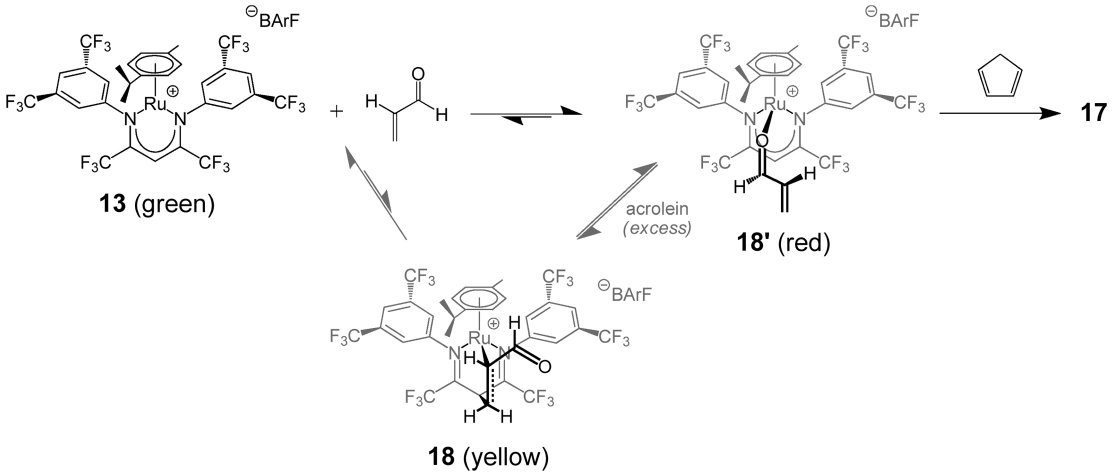

Figure 12. Proposed species and associated equilibria involved in the Diels–Alder reaction of α,β-unsaturated aldehydes and cyclopentadiene in the presence of **13**, involving formation of complex **18**.

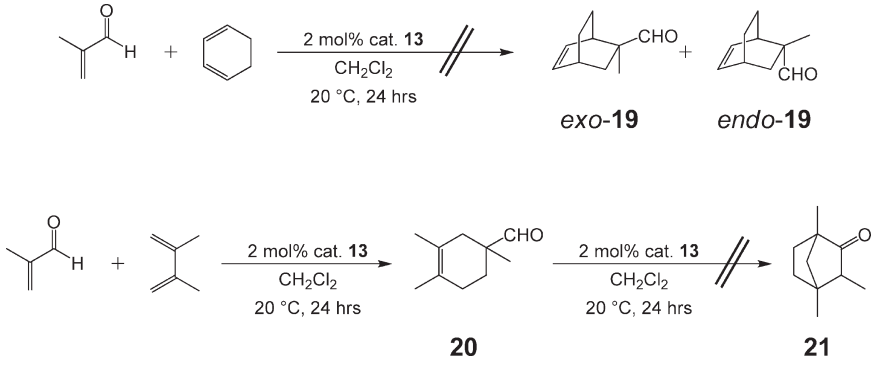

Figure 13. (top) The reaction between methacrolein (0.5 mmol) and 1,3-cyclohexadiene (9 equiv) in the presence of **13** (2 mol %) does not yield **19**. (bottom) Reaction of methacrolein (0.5 mmol) and 2,3-dimethyl-buta-1,3-diene (9 equiv) in the presence of **13** (2 mol %) shows formation of **20** without isomerization to **21**.

catalyst is mild, and the active space for substrate binding is sterically restricted, as in the case of **12** and **13**. In contrast, the reaction between methacrolein and 2,3-dimethyl-buta-1,3-diene proceeds readily at 20 °C to afford 1,3,4-trimethyl-3-cyclohexene-1-carboxaldehyde **20** in 24 h with 66% conversion. In the presence of strongly Lewis acidic catalysts, such as $[Ir(CO)(Me)(DIM)((R)\text{-}(+)\text{-}BINAP)]^{2+}$, where DIM is diethyl isopropylidenemalonate, **20** is a transient intermediate, and the catalyst actively isomerizes this substrate to the bicycle 1,3,3,4-tetramethyl-bicyclo[2.2.1]heptan-2-one **21** (Figure 13).[68,69] Solution ^{1}H NMR data recorded with an aliquot of the catalytic reaction mediated by **13** in the presence of methacrolein and 2,3-dimethyl-buta-1,3-diene showed exclusively formation of the monocyclic product **20**. In fact, no trace formation of **21** was detected, even after a prolonged reaction period of 24 h. Thus, **13** appears to be of similar Lewis acid strength compared to $[Ru(salen)(NO)(H_2O)]SbF_6$, which also exclusively forms **20**.[3] However, the Ru–Cl bond length measured for $[Ru(salen)(NO)(Cl)]SbF_6$ is 2.354(2) Å, considerably shorter than the 2.429(2) Å measured for **13**.[70] As previously described, the Ru–Cl bond length is an appropriate measure of the Lewis acidity at the Ru(II) center. Therefore, **13** is clearly one of the mildest Lewis acid catalysts known that can still efficiently catalyze a variety of [4 + 2] cycloadditions.

CONCLUSION

Employing the heavily fluorinated β-diketiminate ligand **3**, a series of different substituted η^6-arene ruthenium(II) complexes have been prepared using a variety of synthetic routes. The corresponding coordinatively unsaturated cationic complexes **12** and **13** are obtained through Cl abstraction using the weakly coordinating anion BArF. Consequently, these complexes were found to be robust Lewis acidic catalysts for the Diels–Alder reaction between α,β-unsaturated aldehydes (methacrolein, acrolein) and dienes (cyclopenatdiene, 2,3-dimethyl-1,3-butadiene). The structurally rigid β-diketiminate ligand **3** not only provides the required Lewis acidity at the metal center but also enhances the selectivity of the herein discussed Diels–Alder reactions. In the presence of 5 mol % of **13**, methacrolein and cyclopentadiene form the bicyclic carboxaldehyde product **16** almost quantitatively with an increase in exo selectivity, as compared to the reaction in the absence of catalyst. Importantly, species **12** and **13** enable the use of mild reaction conditions, reducing the risk of side reactions. As a direct result, the catalyzed formation of 1,3,4-trimethyl-3-cyclohexene-1-carboxaldehyde **20** proceeds with good yield and without subsequent Lewis acid mediated isomerization of the product. Further types of Diels–Alder reactions with heteronuclear substrates are currently being explored.

EXPERIMENTAL SECTION

General Procedures. The synthesis of the starting materials and the catalysts was carried out under a purified N_2 atmosphere using standard Schlenk techniques, whereas subsequent synthesis and manipulations of all products and reagents were performed in an Innovative Technologies glovebox with a N_2 atmosphere containing less than 1 ppm of O_2 and H_2O. All glassware was predried, and the flasks underwent several purge/refill cycles before the introduction of solvents or reagents. All solvents were dried according to literature procedures involving distillation over the appropriate drying agents and stored in Schlenk flasks equipped with a Teflon stopcock.[71] Celite for filtration was kept in an oven at 130 °C and degassed prior to use. All other reagents and gases (technical grade) were purchased from commercial sources and used as received if not specified otherwise. The synthesis of the bis(dichloro(η^6-arene)ruthenium(II)) (arene = benzene and *p*-cymene) dimers was carried out by a slightly modified procedure according to Bennett et al.,[72] whereas anhydrous sodium tetrakis(3,5-bis(trifluoromethylphenyl)borate, [Na]BArF (BArF = B(3,5-$(CF_3)_2$-$C_6H_3)_4$), was synthesized according to Reger et al.[73] NMR spectra were recorded using a Varian VNMRS 300, 400 and a Varian INOVA 500 instrument. Where necessary, ^{1}H (COSY, NOE, NOESY), ^{19}F, ^{10}B, and ^{13}C (HMBC and HSQC) one- and two-dimensional spectra were used to assign molecular connectivity and conformation in solution. Deuterated dichloromethane was distilled over CaH_2 and stored over 4 Å molecular sieves. Chemical shifts for ^{1}H and ^{13}C spectra were referenced to the relevant solvent peaks. ^{19}F NMR spectra were referenced to the relevant residual solvent peak and CCl_3F. Infrared spectra were recorded on a Varian 3100FT-IR Excalibur spectrometer. Samples were prepared as nujol mulls on KBr discs. Elemental microanalyses were obtained using an Exeter Analytical EA-1110 elemental analyzer. Mass spectra were recorded using either a solution or a nano-electrospray ionization (ESI) technique on a Waters alliance HT Micromass Quattro LCT (MeOH/H_2O, 60/40) TOF instrument with a cone voltage of 35 V and a capillary voltage of 2800 V (+) and 2500 V (−). Mass spectra for **9** and **11** were recorded using electrospray or nanoelectrospray techniques on a ThermoFinnigan LCQ DECA XP Plus quadrupole ion trap instrument set in positive mode: flow rate, 5 μL per min; spray voltage, 5 kV; capillary temperature, 100 °C; capillary voltage, 20 V. Conditions were used as described previously.[74] Microwave reactions were carried out using a Biotage Initiator 2.0 operating at 400 MW.

Synthesis and Characterization of Ligand 2 (3,5-$(CH_3)_2$-$C_6H_3NC(CH_3))_2CH_2$. The synthesis of the title compound was performed using the methodology established for *N*,*N*′-bis(2,6-dimethylphenyl)-2,4-pentanediimine as published by Feldman et al.[36] Yield: 1.2 g (20% based on 2,4-pentanedione). Elemental analysis found [calculated]: C, 82.28 [82.31]; H, 8.61 [8.55]; N, 9.37 [9.14]. ^{1}H NMR (30 °C, 400 MHz, $CDCl_3$) δ(ppm): 1.99 (s, 6H, α-CH_3), 2.28 (s, 12H, *o*-CH_3), 4.82 (s, 1H, β-*CH*), 6.58 (m, 2H, Ar *p*-*CH*), 6.69 (m, 4H, Ar *m*-*CH*), 12.58 (s, 1H, N*H*N). ^{13}C NMR (30 °C, 101 MHz, $CDCl_3$) δ(ppm): 21.1 (s, α-CH_3), 21.6 (s, *m*-CH_3), 97.3 (s, β-CH), 120.5 (s, Ar *o*-CH), 125.0 (s, Ar *p*-CH), 138.5 (s, Ar *m*-CCH_3), 146.0 (s, Ar *i*-*C*), 159.4 (s, α-CH_3C). TOF MS-ES positive (25 °C, MeCN) (*m*/*z*): 307.2177 [parent + H^+, 100%, calc. 307.2174]. FT-IR (25 °C, nujol mull, KBr discs), υ(cm^{-1}): 2953 (vs), 2923 (vs), 2854 (vs), 1628 (m), 1603 (m), 1550 (vs), 1489 (m), 1463 (s), 1377 (m), 1362 (m), 1313 (m), 1272 (m), 1218 (v), 1144 (m), 1030 (v), 1021 (w), 999 (vw), 960 (vw), 889 (vw), 877 (vw), 865 (vw), 850 (m), 746 (w), 722 (w), 685 (w).

Synthesis and Characterization of Ligand 3 (3,5-$(CF_3)_2C_6$-$H_3NC(CF_3))_2CH_2$. The synthesis was carried out according to a modified literature procedure as described by Laitar et al.,[43] which involved the reaction of 2.1 equiv of 3,5-dis(trifluoromethyl)phenyl azide with $CF_3C(O)CH_2C(O)CF_3$ in dry and degassed toluene. Yield: 3.60 g (90% based on 1,1,1,5,5,5-hexafluoro-2,4-pentanedione). Elemental analysis found [calculated]: C, 53.10 [53.07]; H, 4.68 [4.93]; N, 4.33 [4.42]. Crystals suitable for X-ray diffraction analysis were grown by slow evaporation of a saturated *n*-pentane solution of **3**. ^{1}H NMR (300 MHz, 30 °C, CD_2Cl_2) δ(ppm): 6.07 (s, 1H, β-*CH*), 7.52 (s, 4H, Ar *o*-*CH*), 7.75 (s, 2H, Ar *p*-*CH*), 11.70 (s, 1H, N*H*N). ^{13}C NMR (30 °C, 101 MHz, CD_2Cl_2) δ(ppm): 90.9 (m, $^3J_{CF}$ = 4.7 Hz, β-CH), 118.9 (q, $^1J_{CF}$ = 283.2 Hz, α-CF_3), 120.1 (m, Ar *p*-*CH*), 123.0 (q, $^1J_{CF}$ = 273 Hz, *m*-CF_3), 123.4 (s, br, Ar *o*-*CH*), 133.0 (q, $^2J_{CF}$ = 33.9 Hz, Ar *m*-CCF_3), 143.7 (s, Ar *i*-*C*), 150.8 (q, $^1J_{CF}$ = 30.7 Hz, α-CH_3C). ^{19}F NMR (30 °C, 188.2 MHz, CD_2Cl_2) δ(ppm): −63.17 (s, 12F, *o*-CF_3), −62.92 (s, 6F, α-CF_3). TOF MS-ES (25 °C, MeCN), positive mode (*m*/*z*): 631.0455 [parent + H^+, 100%, calcd. 631.0478]. FT-IR (25 °C, nujol mull, KBr discs), υ(cm^{-1}): 2917 (vs), 2856 (vs), 1817 (vw), 1649 (w), 1579 (s), 1328 (m), 1288 (s), 1224 (m), 1175 (s, br), 1134 (m), 947 (w), 899 (vw), 844 (vw), 801 (vw), 703 (vw), 628 (wv).

Synthesis and Characterization of Complex 6 (η^6-C_6H_6)-RuCl(3,5-$(CH_3)_2C_6H_3NC(CH_3))_2CH$. The title complex was synthesized using a method modified from that previously described.[30] A 1.14 g (3.74 mmol) portion of (3,5-$(CH_3)_2C_6H_3NC(CH_3))_2CH_2$ was added to a dried 50 mL Schlenk flask under inert conditions. A 20 mL portion of dried and nitrogen-saturated *n*-pentane was added. The solution was cooled to −60 °C, and 2.6 mL (4.11 mmol) of a 1.6 M *n*BuLi solution was added dropwise over a period of 5 min. After the addition, the reaction was stirred at −60 °C for 2 h. Volatile components were removed in vacuo, leaving a crude off-white solid, which was suspended in 10 mL of dried and degassed dichloromethane. This suspension was added to 0.92 g (0.5 equiv) of ((η^6-C_6H_6)RuCl)$_2Cl_2$ under a flow of nitrogen. The reaction was stirred overnight under nitrogen. The precipitated LiCl was removed by filtration over a plug of Celite under nitrogen, and the solvent was removed in vacuo. After drying under high vacuum, 1.54 g (80%) of a dark purple solid was obtained. Elemental analysis found [calculated with 1/4 CH_2Cl_2 solvate]: C, 60.71 [60.46]; H, 5.86 [5.87]; N, 5.00 [5.18]. Crystals suitable for X-ray diffraction analysis were grown by slow vapor diffusion of *n*-pentane into a saturated CH_2Cl_2 solution of **6** at room temperature. ^{1}H NMR (300 MHz, 30 °C, CD_2Cl_2) δ(ppm): 1.67 (s, 6H, α-CH_3), 2.36 (s, 12H, *m*-CH_3), 4.48 (s, 1H, β-*CH*), 4.56 (s, 6H, C_6H_6), 6.84 (m, 2H, *p*-*CH*), 7.02 (m, 4H, *o*-*CH*). ^{13}C NMR (30 °C, 100.6 MHz, CD_2Cl_2) δ(ppm): 21.8 (s, *m*-CH_3), 24.5 (s, α-CH_3), 86.3 (s, C_6H_6), 94.8 (s, β-CH), 124.3 (s, *o*-CH), 126.9 (s, *p*-CH), 138.7 (s, *m*-CCH_3), 159.8 (s, *i*-*C*), 160.0 (s, α-CH_3C). TOF MS-ES (25 °C, MeCN), positive mode (*m*/*z*): 485.1508 [parent M^+, 100%, calcd. 485.1531]. FT-IR (25 °C, nujol mull, KBr discs), υ(cm^{-1}): 2953 (vs), 2925 (vs), 2854 (vs), 2360 (w), 2340 (w), 1601 (vw), 1589 (vw), 1561 (w), 1524 (w), 1461 (s), 1407 (m), 1377 (m), 1308 (w), 1150 (vw), 1026 (vw), 977 (vw), 916 (vw), 850 (vw), 825 (w), 722 (w), 696 (vw).

Synthesis and Characterization of Complex 7 (η^6-C_6H_6)-RuCl(3,5-$(CF_3)_2C_6H_3NC(CF_3))_2CH$. To a 50 mL Schlenk flask, 0.255 g of ((η^6-C_6H_6)$RuCl_2)_2$ (orange-red powder) was added to 10 mL of CH_2Cl_2. Subsequently, 2 equiv of the corresponding β-diketiminate ligand **3** (0.642 g, 1.02 mmol) was dissolved in 10 mL of pentane. The solution was cooled to −78 °C, and 0.7 mL (1.1 equiv) of a 1.6 M *n*BuLi solution was added dropwise over a time of 10 min. After the addition, the reaction was stirred at −78 °C for 2 h. Volatile components were removed in vacuo, leaving a crude orange solid, which was suspended in 10 mL of dried and degassed dichloromethane. This suspension was slowly added to the ((η^6-C_6H_6)$RuCl_2)_2$ solution over a period of approximately 0.5 h. The flask was capped, and the reaction mixture was stirred for 14 h. Afterward, the resulting magenta solution was filtered through a 1 cm Celite-Schlenk frit combination, and the solution was reduced under vacuum to a volume of ca. 1 mL. While stirring, 25 mL of *n*-pentane was added, causing the formation of a magenta color solid. This solid was collected using a Schlenk frit and washed 3 × 5 mL of *n*-pentane. For further pruification, the complex was dissolved in a

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minimum amount of acetone, and *n*-pentane was slowly added until the majority of the compound had precipitated. The resulting purple microcrystalline solid was filtered and washed with 10 mL of *n*-pentane and dried for 14 h under high vacuum.Yield: 385 mg (89% based on $((\eta^6\text{-}C_6H_6)RuCl)_2Cl_2$). Elemental analysis found [calculated]: C, 39.17 [38.43]; H, 1.46 [1.55]; N, 3.23 [3.32]. Crystals suitable for X-ray diffraction analysis were grown by slow vapor diffusion of *n*-pentane into a saturated CH_2Cl_2 solution of **7** at room temperature. ^{1}H NMR (30 °C, 400 MHz, CD_2Cl_2) δ(ppm): 4.57 (s, 6H, C_6H_6), 5.40 (s, 1H, β-*CH*), 7.61 (s, 2H, Ar *o*-*CH*), 7.77 (s, 2H, Ar *o*-*CH*′), 8.30 (s, 2H, Ar *p*-*CH*). ^{13}C NMR (30 °C, 100.6 MHz, CD_2Cl_2) δ(ppm): 86.9 (s, β-*CH*), 87.0 (s, C_6H_6), 119.1 (q, $^1J_{CF}$ = 285 Hz, α-CF_3), 120.1 (sept, $^3J_{CF}$ = 3.69 Hz, Ar *p*-*CH*), 123.0 (q, $^1J_{CF}$ = 258 Hz, Ar *m*-CF_3), 126.4 (s, Ar *o*-*CH*), 131.6 (m, $^2J_{CF}$ = 33.9 Hz, Ar *m*-CCF_3), 150.9 (q, $^2J_{CF}$ = 26.9 Hz, α-CCF_3), 156.5 (s, Ar *i*-*C*). ^{19}F NMR (30 °C, 282 MHz, CD_2Cl_2) δ(ppm): −63.27 (s, 6F, *m*-CF_3), −63.24 (s, 6F, *m*-CF_3′), −59.25 (s, 6F, α-CF_3). TOF MS-ES (25 °C, CH_2Cl_2), positive mode (*m*/*z*): 809.00 [parent + H^+, 100%, calcd. 808.99]. FT-IR (25 °C, nujol mull, KBr discs), υ(cm^{-1}): 2953 (vs), 2925 (vs), 2854 (vs), 1584 (vw), 1557 (vw), 1465 (s), 1375 (s), 1312 (w), 1283 (m), 1224 (m), 1196 (m), 1184 (m), 1175 (m), 1137 (m), 1119 (m), 964 (w), 895 (vw), 847 (vw), 829 (vw), 779 (vw), 722 (w), 709 (vw), 683 (w).

Synthesis and Characterization of Complex 8 (η^6-^{i}PrC$_6$H$_4$-Me)RuCl(3,5-(CF$_3$)$_2$C$_6$H$_3$NC(CF$_3$))$_2$CH. *Method A.* The synthesis of the title compound was carried out following a similar method as for the η^6-C_6H_6 analogue **7**. To a nitrogen-filled 50 mL Schlenk tube containing 122.4 mg (0.2 mmol) of $((\eta^6\text{-}C_{10}H_{14})RuCl)_2Cl_2$, a solution of 275 mg of Li(3,5-$(CF_3)_2C_6H_3NC(CF_3)$)$_2$CH (0.4 mmol) in dichloromethane was added by cannula. The reaction was stirred at room temperature under nitrogen overnight. Afterward, the mixture was filtered over Celite under nitrogen to separate the product from LiCl. The solvent was removed in vacuo, and the solid was washed with dried and degassed pentane. The product was extracted with degassed diethyl ether and filtered over Celite under nitrogen. The solid was purified by column chromatography on silica gel using a pentane/dichloromethane eluent (1:1) and dried under vacuum to afford 20 mg (6%) of the title compound.

Method B. In modification of the procedure described by Chiong et al.,[49] the silver complex **14** of (3,5-$(CF_3)_2C_6H_3NC(CF_3)$)$_2$$CH_2$ (**3**) was prepared by a microwave reaction. In a 20 mL microwave vial equipped with a magnetic stir bar, 92 mg (0.4 mmol) of silver oxide Ag_2O was added, and the vial was sealed. A 250 mg (0.4 mmol) portion of **3** was added to a 50 mL Schlenk flask and purged with nitrogen and dissolved in 10 mL of dried and degassed acetonitrile. The bright yellow solution was then transferred to the nitrogen-purged microwave vial by cannula. The microwave reaction was performed at 80 °C for 30 min. A gradual color change from orange to red was observed. The reaction mixture was filtered over Celite under nitrogen to remove excess Ag_2O. The filtrate was evaporated to dryness and washed with dried and nitrogen-saturated pentane to remove excess **3**. The resulting red solid was dried under vacuum to afford 204 mg (69%) of $[Ag(CH_3CN)_2$-(3,5-$(CF_3)_2C_6H_3NC(CF_3)$)$_2$$CH_2]_2$ (**14**). ^{1}H NMR (30 °C, 300 MHz, C_6D_6) δ(ppm): 5.79 (s, 1H, β-*CH*), 7.24 (s, 4H, Ar *o*-*CH*), 7.52 (s, 2H, Ar *p*-*CH*). ^{13}C NMR (30 °C, 75 MHz, C_6D_6) δ(ppm): 84.7 (br), 117.0 (br), 117.3, 120.8 (q, $^1J_{CF}$ = 288.4 Hz), 122.8 (br), 124.3 (q, $^1J_{CF}$ = 272.9 Hz), 132.7 (q, $^2J_{CF}$ = 33.3 Hz), 153.5 (q, $^2J_{CF}$ = 25.0 Hz), 154.0. ^{19}F NMR (30 °C, 282.9 MHz, C_6D_6) δ(ppm): −59.1 (s, 12F, *m*-CF_3), −56.7 (s, 6F, α-CF_3). Under inert conditions, 83 mg (0.136 mmol) of $[(\eta^6\text{-}C_{10}H_{14})RuCl]_2Cl_2$ and 200 mg (0.136 mmol) of $[Ag(CH_3CN)_2$-(3,5-$(CF_3)_2C_6H_3NC(CF_3)$)$_2$$CH_2]_2$ (**14**) were loaded into a 50 mL Schlenk flask, and 25 mL of dried and degassed dichloromethane was added. The reaction mixture was stirred with the exclusion of light for 14 h under nitrogen. The precipitated AgCl was removed by filtration over a 1 cm Celite pad. Afterward, the solvent was removed under high vacuum. The crude solid was washed twice with degassed *n*-pentane and dried to afford 196 mg (80%, 55% overall from **3**) of the red colored title compound.

Method C. Using a modified procedure published by Tonzetich et al.,[54] a solution of thallium ethoxide (79 mg, 0.317 mmol) in dried and nitrogen-saturated dichloromethane was prepared under inert conditions. Likewise, 200 mg (0.317 mmol) of **3** dissolved in dichloromethane was added dropwise to the TlOEt solution at 0 °C while stirring. After the addition, the solution was allowed to warm to room temperature and stirred in the exclusion of light for several hours under a flow of nitrogen. The clear yellow solution was directly added by cannula to a solution containing 97 mg (0.158 mmol) of $[(\eta^6\text{-}C_{10}H_{14})$-$RuCl]_2Cl_2$ in 10 mL of CH_2Cl_2. The reaction was stirred overnight in the dark. Subsequently, the solvent was removed in vacuo and the crude product was extracted with dried and nitrogen-flushed Et_2O and filtered over a plug of Celite. After the removal of solvent under reduced pressure, the solid was purified by column chromatography on silica gel using dichloromethane/pentane/ethyl acetate in a ratio of 19:90:0 to 48:48:4. The purified title compound was obtained in 86% yield as a dark red solid. Yield: 610 mg (86% based on **3**). Elemental analysis found [calculated]: C,: 41.67 [41.37]; H, 2.63 [2.35]; N, 2.88 [3.11]. Suitable crystals were grown from a concentrated chloroform solution by pentane diffusion at −30 °C. ^{1}H NMR (30 °C, 400 MHz, CD_2Cl_2) δ(ppm): 1.25 (d, $^3J_{HH}$ = 6.9 Hz, 6H, 1,4-^{i}PrC$_6$H$_4$Me CH(*CH*$_3$)$_2$), 2.05 (s, 3H, 1,4-^{i}PrC$_6$H$_4$*Me* *CH*$_3$), 2.62 (sept, $^3J_{HH}$ = 6.9 Hz, 1H, 1,4-^{i}PrC$_6$H$_4$Me C*H*(CH$_3$)$_2$), 3.79 (m, 2H, 1,4-^{i}PrC$_6$H$_4$Me *CH*CMe), 4.22 (m, 1,4-^{i}PrC$_6$H$_4$Me *CH*C^{i}Pr), 5.46 (s, 1H, β-*CH*), 7.60 (s, 2H, Ar *o*-*CH*), 7.84 (s, 2H, Ar *p*-*CH*), 8.56 (s, 2H, Ar *o*-*CH*′). ^{13}C NMR (30 °C, 100.6 MHz, CD_2Cl_2) δ(ppm): 19.2 (s, 1,4-^{i}PrC$_6$H$_4$Me *CH*$_3$), 23.2 (s, 1,4-^{i}PrC$_6$H$_4$Me CH(*CH*$_3$)$_2$), 31.3 (s, 1,4-^{i}PrC$_6$H$_4$Me *CH*-(*CH*$_3$)$_2$), 84.4 (m, 1,4-^{i}PrC$_6$H$_4$Me Ar *CH*CMe), 87.4 (m, β-CH), 89.7 (m, 1,4-^{i}PrC$_6$H$_4$Me Ar *CH*C^{i}Pr), 103.8 (m, 1,4-^{i}PrC$_6$H$_4$Me Ar *C*^{i}Pr), 104.8 (m, 1,4-^{i}PrC$_6$H$_4$Me Ar *C*Me), 119.8 (q, $^1J_{CF}$ = 284.9 Hz, α-CF_3), 120.5 (m, Ar *p*-*CH*), 123.6 (q, $^1J_{CF}$ = 272.9 Hz, *m*-CF_3′), 123.7 (q, $^1J_{CF}$ = 272.5 Hz, *m*-CF_3), 124.5 (s br, Ar *o*-CH), 130.0 (s br, Ar *o*-*CH*′), 131.0 (q, $^2J_{CF}$ = 33.6 Hz, *m*-CCF_3′), 132.6 (q, $^2J_{CF}$ = 33.5 Hz, *m*-CCF_3), 151.3 (q, $^2J_{CF}$ = 26.1 Hz, α-CH_3C), 156.9 (s, Ar *i*-*C*). ^{19}F NMR (30 °C, 376 MHz, CD_2Cl_2) δ(ppm): −63.37 (s, 6F, *m*-CF_3), −63.30 (s, 6F, *m*-CF_3′), −58.95 (m br, 6H, α-CF_3). TOF MS-ES (25 °C, MeCN), positive mode (*m*/*z*): 865.0504 [parent M^+, 100%, calcd. 865.0461]. FT-IR (25 °C, nujol mull, KBr discs), υ(cm^{-1}): 2924 (vs), 2856 (vs) 1558 (vw), 1462 (s), 1371 (m), 1310 (w), 1280 (m), 1224 (w), 1180 (m), 1134 (m, br), 959 (w), 898 (vw), 848 (vw), 779 (vw), 720 (w), 681 (vw).

Synthesis and Characterization of Complex 9 [(η^6-C$_6$H$_6$)-Ru(3,5-(CH$_3$)$_2$C$_6$H$_3$NC(CH$_3$))$_2$CH]OTf. To a 100 mL Schlenk flask, 400 mg (0.770 mmol) of $[(\eta^6\text{-}C_6H_6)RuCl(3,5\text{-}(CH_3)_2C_6H_3NC$-$(CH_3))_2CH]Cl$ (**6**) and 159 mg (1.2 equiv) of [Na]OTf were dissolved in 10 mL of dried and nitrogen-saturated dichloromethane under an inert atmosphere. The reaction mixture was stirred for 12 h. Afterward, the solution was filtered to remove NaCl and excess [Na]OTf, and the solvent was removed in vacuo. The resulting orange-brown crude solid was washed several times with dried and degassed pentane and dried in vacuo to afford 390 mg (81%) of the dark brown title compound. Yield: 390 mg (81% based on **6**). Elemental analysis found [calculated +3/4 CH_2Cl_2 solvate]: C, 49.60 [49.51]; H, 4.65 [4.70]; N, 3.91 [4.02]. Crystals suitable for X-ray diffraction analysis were grown by slow vapor diffusion of *n*-pentane into a saturated CH_2Cl_2 solution of **9** at room temperature. ^{1}H NMR (400 MHz, 30 °C, CD_2Cl_2) δ(ppm): 2.26 (s, 6H, α-CH_3), 2.47 (s, 12H, m-CH_3), 5.20 (s, 6H, C_6H_6), 6.37 (s, 1H, β-*CH*), 6.98 (m, 4H, *o*-*CH*), 7.09 (m, 2H, *p*-*CH*). ^{13}C NMR (30 °C, 101 MHz, CD_2Cl_2) δ(ppm): 21.7 (s, *m*-CH_3), 24.5 (s, α-CH_3), 83.7 (s, C_6H_6), 104.2 (s, β-CH), 121.8 (s, *o*-*CH*), 129.1 (s, *p*-CH), 139.6 (s, *m*-CCH_3), 160.4 (s, *i*-*C*), 163.6 (s, α-CH_3C). ^{19}F NMR (30 °C, 376 MHz, CD_2Cl_2)

δ(ppm): −78.81 (s, $^1J_{FC}$ = 321.6 Hz, $CF_3SO_3^-$). TOF MS-ES (25 °C, MeCN), positive mode (m/z): 485.1521 [parent M^+, 100%, calcd. 485.1531]. TOF MS-ES (25 °C, MeCN), negative mode (m/z): 148.9492 [parent OTf^-, 100%, calcd. 148.9520]. FT-IR (25 °C, nujol mull, KBr discs), υ(cm^{-1}): 2953 (vs), 2925 (vs), 2854 (vs), 2361 (w), 2340 (w), 1605 (vw), 1589 (vw), 1552 (w), 1462 (s), 1377 (m), 1347 (w), 1262 (m), 1223 (w), 1151 (m), 1030 (m), 843 (vw), 722 (w), 697 (vw), 637 (m).

Synthesis and Characterization of Complex 10 [(η^6-C_6H_6)-Ru(3,5-$(CH_3)_2C_6H_3NC(CH_3))_2CH$]BArF. To a 50 mL Schlenk flask, 48 mg (0.09 mmol) of [(η^6-C_6H_6)RuCl(3,5-$(CH_3)_2C_6H_3NC(CH_3))_2CH$]Cl (**6**) and 90 mg (1.1 equiv) of [Na]BArF were dissolved in 10 mL of dried and nitrogen-saturated dichloromethane under an inert atmosphere. The reaction mixture was stirred for 12 h, after which the solution was filtered to remove NaCl and the solvent was removed in vacuo. The golden-brown crude solid was washed several times with dried and degassed *n*-pentane and dried under high vacuum to afford 85 mg (93%) of the dark brown title compound. Elemental analysis found [calculated +1.5 CH_2Cl_2 solvate]: C, 50.18 [49.26]; H, 3.06 [3.14]; N, 1.56 [1.90]. ^{1}H NMR (400 MHz, 30 °C, CD_2Cl_2) δ(ppm): 2.26 (s, 6H, α-CH_3), 2.46 (s, 12H, *m*-CH_3), 5.11 (s, 6H, C_6H_6), 6.39 (s, 1H, β-C*H*), 6.92 (s br, 4H, *o*-C*H*), 7.11 (s br, 2H, *p*-C*H*), 7.56 (s br, 4H, B(ArF)$_4$ *p*-C*H*), 7.72 (s br, 8H, B(ArF)$_4$ *o*-C*H*). ^{13}C NMR (30 °C, 101 MHz, CD_2Cl_2) δ(ppm): 21.7 (s, *m*-CH_3), 24.5 (s, α-CH_3), 83.6 (s, C_6H_6), 104.5 (s, β-CH), 118.1 (s br, B(ArF)$_4$ *p*-CH), 121.6 (s, Ar *o*-CH), 125.2 (q, $^1J_{CF}$ = 272.2 Hz, B(ArF)$_4$ *m*-CF_3), 129.4 (s, Ar *p*-CH), 135.4 (s, B(ArF)$_4$ *o*-CH), 139.8 (s, *m*-CCH_3), 160.4 (s, *i*-C), 162.4 (q, $^1J_{BC}$ = 49.4 Hz, B(ArF)$_4$), 164.0 (s, α-CH_3C). ^{19}F NMR (30 °C, 376 MHz, CD_2Cl_2) δ(ppm): −62.88 (s, $^1J_{FC}$ = 272.4 Hz, B(ArF)$_4$ *m*-CF_3). ^{11}B NMR (25 °C, 128.4 MHz, CD_2Cl_2) δ(ppm): −6.61 (s, $^1J_{BC}$ = 49.5 Hz, *B*(ArF)$_4$). TOF MS-ES positive (25 °C, MeCN) (m/z): 484.1515 [parent M^+, 100%, calcd. 485.1531]. FT-IR (25 °C, nujol mull, KBr discs), υ(cm^{-1}): 2953 (vs), 2925 (vs), 2854 (vs), 1609 (vw), 1555 (vw), 1462 (s), 1377 (m), 1356 (w), 1278 (w), 1124 (w, br), 1043 (vw), 888 (vw), 839 (vw), 722 (w), 682 (vw), 670 (vw).

Synthesis and Characterization of Complex 11 (η^6-C_6H_6)-RuOTf(3,5-$(CF_3)_2C_6H_3NC(CF_3))_2CH$. This reaction was performed in a glovebox. To a 50 mL round-bottom flask, 125 mg (0.148 mmol) of complex **7** was added and dissolved with 15 mL of dry and degassed dichloromethane. Rapidly, 0.300 g of $Me_3SiO_3SCF_3$ (colorless liquid) was added, and within 5 min, the solution rapidly changed to a dark orange-brown color. After stirring for 2 h, all volatiles were removed under reduced pressure. The resulting orange-brown solid was transferred to a frit and washed 3 × 10 mL with dry and degassed *n*-pentane, then dried for 4 h under high vacuum. Yield: 144 mg (0.144 mmol, 97.2%). Elemental analysis found [calculated]: C, 34.14 [35.12]; H, 1.33 [1.37]; N, 2.54 [2.93]. Crystals suitable for X-ray diffraction analysis were grown by slow vapor diffusion of *n*-pentane into a saturated acetone solution of **11** at room temperature. ^{1}H NMR (30 °C, 400 MHz, acetone-d_6) δ(ppm): 5.61 (s, 6H, C_6H_6), 6.11(s, 1H, β-C*H*), 8.13 (s, 2H, Ar *p*-C*H*), 8.35 (s, 4H, Ar *o*-C*H*). ^{13}C NMR (25 °C, 101 MHz, acetone-d_6) δ(ppm): 81.7 (s, β-CH), 87.3 (s, C_6H_6), 120.4 (q, $^1J_{CF}$ = 287.1 Hz, α-CF_3), 121.9 (m, Ar *p*-CH), 124.2 (q, $^1J_{CF}$ = 272.3 Hz, *m*-CF_3), 127.7 (s br, Ar *o*-CH), 132.6 (q, $^2J_{CF}$ = 34.0 Hz, *m*-CCF_3), 152.1 (q, $^2J_{CF}$ = 27.4 Hz, α-CH_3C), 157.2 (s, Ar *i*-C). ^{19}F NMR (30 °C, 282 MHz, acetone-d_6) δ(ppm): −79.13 (s, 3F, $^1J_{CF}$ = 320.8 Hz, $CF_3SO_3^-$), −63.77 (s, 12F, *m*-CF_3), −57.50 (s, 6F, α-CF_3). TOF MS-ES (25 °C, MeCN), positive mode (m/z): 808.76 [parent + H^+, 100%, calcd. 808.99]. ESI-MS (25 °C, CH_2Cl_2), (m/z) positive mode 557.231 [parent, 100%], negative mode 149.214 [parent, 100%]. FT-IR (25 °C, nujol mull, KBr discs), υ(cm^{-1}): 2953 (vs), 2925 (vs), 2854 (vs), 1566 (vw), 1462 (s), 1376 (s), 1284 (m, br), 1226 (m), 1184 (m), 1138 (m), 1030 (w), 1020 (w), 965 (w), 906 (vw), 849 (w), 802 (vw), 723 (w), 683 (vw), 637 (w).

Synthesis and Characterization of Complex 12 [(η^6-C_6H_6)-Ru(3,5-$(CF_3)_2C_6H_3NC(CF_3))_2CH$]BArF. A 100 mL Schlenk flask was charged with 100 mg (0.120 mmol) of complex **7** with 111 mg (0.125 mmol, 1.05 equiv) of [Na]BArF in 5 mL of dried and degassed dichloromethane. The mixture was stirred overnight and filtered over a plug of Celite to remove sodium chloride. Subsequently, the solvent was removed in vacuo. The crude solid was washed three times with dry and degassed *n*-pentane and dried under high vacuum for 24 h to afford 120 mg (60%) of a brown-green solid. Elemental analysis found [calculated]: C, 42.48 [42.39]; H, 1.45 [1.51]; N, 1.63 [1.68]. ^{1}H NMR (30 °C, 300 MHz, CD_2Cl_2) δ(ppm): 5.41 (s, 6H, C_6H_6), 7.53 (s, 1H, β-C*H*), 7.54 (s, 4H, B(ArF)$_4$ *p*-C*H*), 7.70 (m, 8H, B(ArF)$_4$ *o*-C*H*), 8.08 (s, 4H, Ar *o*-C*H*), 8.24 (s, 2H, Ar *p*-C*H*). ^{13}C NMR (30 °C, 101 MHz, CD_2Cl_2) δ(ppm): 86.4 (s, C_6H_6), 96.3 (m, β-CH), 118.1 (sept, $^3J_{CF}$ = 4.2 Hz, B(ArF)$_4$ *p*-CH), 119.1 (q, $^1J_{CF}$ = 283.6 Hz, α-CF_3), 122.9 (q, $^1J_{CF}$ = 273.6 Hz, *m*-CF_3), 124.1 (m, *p*-CH), 125.2 (q, $^1J_{CF}$ = 272.3 Hz, B(ArF)$_4$ *m*-CF_3), 125.3 (s, *o*-CH), 129.4 (q, $^2J_{CF}$ = 31.4 Hz, B(ArF)$_4$ *m*-CCF_3), 133.2 (q, $^2J_{CF}$ = 34.9 Hz, *m*-CCF_3), 135.4 (s br, B(ArF)$_4$ *o*-CH), 154.8 (m, α-CH_3C), 157.2 (s, *i*-C), 162.3 (q, $^1J_{CB}$ = 49.9 Hz, B(ArF)$_4$ *i*-C). ^{19}F NMR (30 °C, 282 MHz, CD_2Cl_2) δ(ppm): −63.34 (s, $^1J_{CF}$ = 273.6 Hz, 12F, *m*-CF_3), −62.91 (s, 24F, B(ArF)$_4$ *m*-CF_3), −57.97 (s, $^1J_{CF}$ = 283.6 Hz, 6F, α-CF_3). ^{11}B NMR (25 °C, 128 MHz, CD_2Cl_2) δ(ppm): −6.64 (m, $^1J_{BC}$ = 49.9 Hz, $^3J_{BH}$ = 2.57 Hz, *B*(ArF)$_4$). TOF MS-ES positive (25 °C, MeCN) (m/z): 808.9821 [parent M^+, 100%, calcd. 808.9835]. TOF MS-ES negative (25 °C, MeCN) (m/z): 863.0640 [parent $BArF^-$, 100%, calcd. 863.0649]. FT-IR (25 °C, nujol mull, KBr discs), υ(cm^{-1}): 2921 (vs), 2856 (vs), 1612 (vw), 1282 (m), 1189 (m br), 1144 (m br), 961 (vw), 894 (vw), 842 (vw), 719 (w), 680 (vw).

Synthesis and Characterization of Complex 13 [(η^6-$C_{10}H_{14}$)Ru(3,5-$(CF_3)_2C_6H_3NC(CF_3))_2CH$]BArF. In a 100 mL Schlenk flask, 197 mg (0.219 mmol) of complex **8** and 214 mg (1.1 equiv) of Na[BArF] were dissolved in dried and degassed dichloromethane under inert conditions and stirred for 12 h. Afterward, the reaction mixture was filtered through a 1 cm Celite pad under nitrogen and the solvent was removed in vacuo from the resulting solution. The brown-colored crude solid was washed several times with dried and nitrogen-saturated *n*-pentane and dried under high vacuum overnight. The resulting yield was 241 mg (64%) of a dark green-brown solid. Elemental analysis found [calculated]: C, 44.20 [43.80]; H, 2.00 [1.93]; N, 1.36 [1.62]. X-ray quality crystals were grown from a concentrated dichloromethane solution by diffusion with *n*-pentane at −30 °C. ^{1}H NMR (30 °C, 500 MHz, CD_2Cl_2) δ(ppm): 1.19 (d, $^3J_{HH}$ = 6.9 Hz, 6H, 1,4-^{i}PrC$_6$H$_4$Me CH(CH_3)$_2$), 2.04 (s, 3H, 1,4-^{i}PrC$_6$H$_4$Me CH_3), 2.36 (sept, 1H, 1,4-^{i}PrC$_6$H$_4$Me C*H*(CH$_3$)$_2$), 4.67−4.69 (m, 2H, 1,4-^{i}PrC$_6$H$_4$Me C*H*C^{i}Pr), 4.76−4.78 (m, 1,4-^{i}PrC$_6$H$_4$Me C*H*CMe), 7.41 (s, 1H, β-C*H*), 7.54 (s, 4H, B(ArF)$_4$ Ar *p*-C*H*), 7.70 (m, 8H, B(ArF)$_4$ *o*-C*H*), 8.01 (s, 4H, Ar *o*-C*H*), 8.25 (s, 2H, Ar *p*-C*H*). ^{13}C NMR (30 °C, 126 MHz, CD_2Cl_2) δ(ppm): 20.2 (s, 1,4-^{i}PrC$_6$H$_4$Me CH_3), 23.0 (s, 1,4-^{i}PrC$_6$H$_4$Me CH(CH_3)$_2$), 32.3 (s, 1,4-^{i}PrC$_6$H$_4$Me CHMe$_2$), 87.6 (s, 1,4-^{i}PrC$_6$H$_4$Me Ar *C*HCMe), 90.1 (s, 1,4-^{i}PrC$_6$H$_4$Me Ar *C*HC^{i}Pr), 96.0 (s, br, β-CH), 96.5 (s, 1,4-^{i}PrC$_6$H$_4$Me Ar *C*CH$_3$), 106.6 (s, 1,4-^{i}PrC$_6$H$_4$Me Ar *C*^{i}Pr), 118.0 (s br, B(ArF)$_4$ *p*-CH), 119.2 (q, $^1J_{CF}$ = 283.6 Hz, α-CF_3), 122.9 (q, $^1J_{CF}$ = 273.5 Hz, *m*-CF_3), 123.8 (m, Ar *p*-CH), 125.2 (q, $^1J_{CF}$ = 272.4 Hz, B(ArF)$_4$ *m*-CF_3), 125.3 (s br, Ar *o*-CH), 129.4 (q br, $^2J_{CF}$ = 31.5 Hz, B(ArF)$_4$ *m*-CCF_3), 132.9 (q, $^2J_{CF}$ = 34.9 Hz, Ar *m*-CCF_3), 135.4 (s, B(ArF)$_4$ Ar *o*-CH), 154.3 (q, $^2J_{FC}$ = 30.0 Hz, α-CH_3C), 157.0 (s, Ar *i*-C), 162.3 (q, $^1J_{CB}$ = 49.8 Hz, B(ArF)$_4$ *i*-C). ^{19}F NMR (30 °C, 282 MHz, CD_2Cl_2) δ(ppm): −63.36 (s, 12F, *m*-CF_3), −62.92 (s, 24F, B(ArF)$_4$ *m*-CF_3), −57.96 (s, 6F, α-CF_3). ^{11}B NMR (25 °C, 128 MHz, CD_2Cl_2) δ(ppm): −6.64 (m, $^1J_{BC}$ = 49.9 Hz, $^3J_{BH}$ = 2.57 Hz, B(ArF)$_4$). TOF MS-ES (25 °C, MeCN), positive mode (m/z): 865.0440 [parent M^+, 100%, calcd. 865.0461]. FT-IR (25 °C, nujol mull, KBr discs), υ(cm^{-1}): 2918 (vs), 2856 (vs), 1612 (vw), 1459 (m), 1372

(m), 1282 (m), 1132 (m br), 962 (vw), 891 (vw), 843 (vw), 719 (w), 681 (vw).

Synthesis and Characterization of Complex 18 {[(η^6-$C_{10}H_{14}$)Ru(3,5-$(CF_3)_2C_6H_3NC(CF_3)$)$_2$CH][$CH_2CH(CHO)$]}BArF. In a 4 mL vial, 30 mg (0.017 mmol) of [(η^6-$C_{10}H_{14}$)Ru(3,5-$(CF_3)_2$-$C_6H_3NC(CF_3)$)$_2$CH]BArF (**13**) and 30 μL (25 equiv, 0.43 mmol) of acrolein were dissolved in 1.5 mL of CH_2Cl_2. After a reaction period of 48 h, crystals suitable for X-ray analysis were grown by diffusion of pentane into the above described mixture at −10 °C. Solution NMR data were obtained by repeating the above procedure in an NMR sample tube, using only CD_2Cl_2 as a solvent. ^{1}H NMR (30 °C, 500 MHz, CD_2Cl_2) δ(ppm): 1.03 (d, $^3J_{HH}$ = 6.9 Hz, 3H, 1,4-^{i}PrC$_6$H$_4$Me CH-$(CH_3)_2$), 1.22 (d, $^3J_{HH}$ = 6.9 Hz, 3H, 1,4-^{i}PrC$_6$H$_4$Me CH$(CH_3)_2$′), 1.35 (dd, $^3J_{HH}$ = 9.7 Hz, $^2J_{HH}$ = 12.6 Hz, 1H, C$H_{acrolein,\beta}$), 2.09 (sept, 1H, 1,4-^{i}PrC$_6$H$_4$Me CH(CH$_3$)$_2$), 2.14 (s, 3H, 1,4-^{i}PrC$_6$H$_4$Me CH_3), 2.29−2.37 (m, 1H, C$H'_{acrolein,\beta}$), 4.06 (d, $^3J_{HH}$ = 6.3 Hz, 1H, 1,4-^{i}PrC$_6$H$_4$Me Ar CHCMe), 4.19 (m, 1H, 1,4-^{i}PrC$_6$H$_4$Me Ar CHCCMe$_2$), 4.21 (m, 1H, C$H_{acrolein,\alpha}$), 5.14 (d, $^3J_{HH}$ = 6.3 Hz, 1,4-^{i}PrC$_6$H$_4$Me Ar CH'CCHMe$_2$), 5.35−5.40 (m, 1H, β-CH), 5.48 (d, $^3J_{HH}$ = 6.4 Hz, 1,4-^{i}PrC$_6$H$_4$Me Ar CH'CMe), 7.33 (s, 1H, Ar o-CH), 7.54 (s, 4H, BArF Ar p-CH), 7.58 (s, 1H, Ar o-CH'), 7.71 (m, 8H, BArF Ar o-CH), 7.81 (s, 1H, Ar o-CH''), 8.02 (s, 1H, Ar p-CH), 8.11 (s br, 1H, Ar o-CH'''), 8.11 (s br, 1H, Ar p-CH'), 9.93 (s, br, 1H, CO$H_{acrolein}$). ^{13}C NMR (30 °C, 126 MHz, CD_2Cl_2) δ(ppm): 18.8 (s, 1,4-^{i}PrC$_6$H$_4$Me CH_3), 20.7 (s, $C_{acrolein,\beta}$), 22.3 (s, 1,4-^{i}PrC$_6$H$_4$Me CH$(C'H_3)_2$), 23.1 (s, 1,4-^{i}PrC$_6$H$_4$Me CH$(CH_3)_2$), 31.2 (s, 1,4-^{i}PrC$_6$H$_4$Me CHMe$_2$), 31.7 (s, $C_{acrolein,\alpha}$), 47.4 (s, β-CH), 87.2 (s, 1,4-^{i}PrC$_6$H$_4$Me Ar CHCMe), 87.5 (s, 1,4-^{i}PrC$_6$H$_4$Me Ar C'HCMe), 88.9 (s, 1,4-^{i}PrC$_6$H$_4$Me Ar CHCCHMe$_2$), 90.1 (s, 1,4-^{i}PrC$_6$H$_4$Me Ar C'HCCHMe$_2$), 110.3 (s, 1,4-^{i}PrC$_6$H$_4$Me Ar CCH$_3$), 117.1 (q, $^1J_{CF}$ = 284.9 Hz, α-CF_3), 117.4 (q, $^1J_{CF}$ = 285.6 Hz, α-CF_3'), 118.1 (s br, BArF Ar p-CH), 120.6 (s, 1,4-^{i}PrC$_6$H$_4$Me Ar CH(CH$_3$)$_2$), 121.4 (s br, Ar o-CH), 121.7 (s br, Ar o-C′H), 122.2 (s br, Ar o-C″H), 122.9 (s br, Ar o-C‴H), 123.8 (m, Ar p-CH), 124.0 (m, Ar p-C′H), 125.2 (q, $^1J_{CF}$ = 272.0 Hz, BArF m-CF_3), 129.5 (q br, $^2J_{CF}$ = 31.3 Hz, BArF Ar m-CCF_3), 132.33−134.43 (m, Ar m-CCF_3), 135.4 (s, BArF Ar o-CH), 153.0 (s, Ar i-C), 153.2 (s, Ar i-C'), 162.4 (q, $^1J_{CB}$ = 50.1 Hz, BArF BC), 166.0 (q, $^2J_{FC}$ = 33.0 Hz, α-CH_3C), 166.8 (q, $^2J_{FC}$ = 32.7 Hz, α-CH_3C'), 198.5 (s, O=C$_{acrolein}$). The m-CF_3 groups were not observed due to overlapping signals between 120 and 130 ppm. ^{19}F NMR (30 °C, 282 MHz, CD_2Cl_2) δ(ppm): −63.57 (s, 3F, m-CF_3), −63.52 (s, 3F, m-CF_3'), −63.45 (s, 3F, m-CF_3''), −63.39 (s, 3F, m-CF_3'''), −62.94 (s, 24F, BArF m-CF_3), −61.46 (s, 3F, α-CF_3), −60.58 (s, 3F, α-CF_3'). Additional 2D NMR data and an in-depth characterization of **18** are provided in the Supporting Information.

Typical Procedure for Lewis Acid Catalyzed Diels−Alder Cycloadditions. The dienophiles, methacrolein and acrolein, were dried over molecular sieves (Linde 4 Å) and stored under N_2 at 0−4 °C. Cyclopentadiene was freshly cracked and kept under a N_2 atmosphere prior to each series of catalytic tests. 2,3-Dimethyl-buta-1,3-diene and 1,3-cyclohexadiene were degassed and stored under N_2 at 0−4 °C. Dichloromethane was dried over CaH_2, degassed, and kept under N_2 in a Teflon stopcock-sealed flask. Experimental temperatures lower than 20 °C were maintained using a Thermo Scientific HAAKE EK90 immersion cooler. The appropriate amount of catalyst **9**, **10**, **12**, and **13** was dissolved in 6 mL of dichloromethane containing 0.5 mmol of dienophile. The solution was allowed to equilibrate to the experimental temperature for at least 15 min, after which, an excess of diene was then added (4.6 mmol) dropwise over a period of 1 min to the catalyst−dienophile solution. The reaction was left stirring under N_2 for the required reaction time. Aliquots for solution NMR (0.2 mL) were sampled at regular time intervals and added to a solution of 4-DMAP (10 equiv to catalyst) in CD_2Cl_2. The conversion of the desired cycloadducts was measured through solution NMR. To integrate the corresponding ^{1}H signals, a relaxation delay of 25 s was chosen to allow for full spin recovery of the methacrolein aldehyde proton and the product aldehyde proton. The corresponding T_1 was measured by a standard inversion recovery experiment, which showed both compounds to have a similar T_1 of approximately 10.4 ± 0.2 s. For full characterization of the resulting products, n-pentane or n-hexanes was added to precipitate the catalyst and the mixture was filtered over a small plug of Celite and the solvent was removed in vacuo. The crude products were purified over a short column of silica gel using ratios of n-pentane/dichloromethane of either 3:1 or 2:1.

■ ASSOCIATED CONTENT

Supporting Information. An in-depth discussion regarding the 2D NOE experiments for complex **18** is provided. Structural details concerning β-diketiminate **3** and supplementary kinetic data for the Diels−Alder reactions with the catalysts are also given. Crystallographic details (CIF) for all relevant complexes are provided. This material is available free of charge via the Internet at http://pubs.acs.org.

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