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The Lewis Acidic Ruthenium-Complex-Catalyzed Addition of β-Diketones to Alcohols and Styrenes Is in Fact Brønsted Acid Catalyzed

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Abstract: The perchlorate salt of the dicationic bipy–ruthenium complex *cis*-$[Ru(6,6'\text{-}Cl_2bipy)_2(H_2O)_2]^{2+}$ effectively catalyzes addition of β-diketones to secondary alcohols and styrenes to yield the α-alkylated β-diketones. In a catalytic addition reaction of acetylacetone to 1-phenylethanol, the κ^2-acetylacetonate complex $[Ru(6,6'\text{-}Cl_2bipy)_2(\kappa^2\text{-}acac)]ClO_4$ was isolated after the catalysis; this complex is readily synthesized by reacting *cis*-$[Ru(6,6'\text{-}Cl_2bipy)_2(H_2O)_2](ClO_4)_2$ with acetylacetone. $[Ru(6,6'\text{-}Cl_2bipy)_2(\kappa^2\text{-}acac)]ClO_4$ is unreactive toward 1-phenylethanol in the presence of $HClO_4$; it also fails to catalyze the addition of acetylacetone to 1-phenylethanol. On the basis of these observations, it is proposed and confirmed by independent experiments that the catalytic addition of β-diketones to the secondary alcohols is in fact catalyzed by the Brønsted acid $HClO_4$, which is generated by the reaction of *cis*-$[Ru(6,6'\text{-}Cl_2bipy)_2(H_2O)_2](ClO_4)_2$ with the β-diketone.

Keywords: beta-diketones · addition reaction · alcohols · Brønsted acids · ruthenium

Introduction

Alkylation of β-dicarbonyl compounds is one of the most common methodologies for C–C bond construction; the addition of β-dicarbonyl compounds to olefins, which yields alkylated dicarbonyls and is a highly atom-economical process,[1] has attracted much attention in recent years. Widenhoefer and co-workers reported several cases of Pd-catalyzed intramolecular addition of β-diketones and β-ketoesters to olefins to form six-membered ring compounds.[2] Similar Pd-catalyzed cyclization reactions of alkenyl β-keto esters and amides to give six-, seven-, or eight-membered-ring carbocycles were found to be promoted by lanthanide triflate.[3] Intermolecular addition of β-dicarbonyl compounds to ethylene and propylene catalyzed by Pd and Pt complexes has recently been published.[4] Moreover, Pd-catalyzed intermolecular addition of the α-C–H bond of monocarbonyl and β-dicarbonyl compounds to dienes has also been developed.[5]

Li and coworkers have employed silver salts or combinations of silver and gold salts as catalysts for the addition of β-dicarbonyl compounds to styrenes, dienes, trienes, and cyclic enol ethers;[6] coinage metals have not been common catalysts of choice in synthesis. More recently, the same group has developed a new route to fused lactones, the synthesis of which are based on a cascade addition of β-ketoesters to a cyclic diene followed by an in situ lactonization; the reactions are catalyzed by a combination of Lewis acid and Brønsted acid, $Ga(OTf)_3$/HOTf.[7]

Most of the recent studies of the catalytic addition of β-dicarbonyl compounds to olefins or polyenes are based on palladium, coinage metals, such as silver and gold, and gallium; however, the catalytic activities of other transition metals for this reaction have scarcely been investigated. Reported here is our work on the ruthenium-catalyzed addition of β-diketones to alcohols and styrenes. This study, however, demonstates that the addition reactions are in fact catalyzed by the Brønsted acid $HClO_4$ generated by the reaction of the Lewis acidic ruthenium complex with the β-diketone; the ruthenium complex merely acts as a precatalyst.

Results and Discussion

We studied the catalytic activities of several dicationic ruthenium complexes containing bipyridine (bipy) ligands. We hoped that by virtue of the complexes being able to pro-

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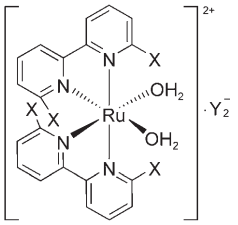


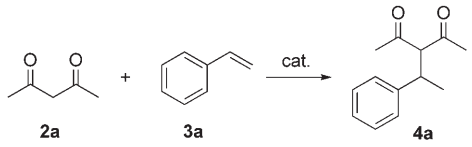
1a: X = Cl, Y = OTf
b: X = Br, Y = OTf
c: X = Me, Y = OTf
d: X = Cl, Y = ClO_4

vide two *cis* vacant sites readily and the high Lewis acidity of the metal centers, dual activation of the two substrates, that is, the olefin and the β-dicarbonyl compound, might be possible. The design and synthesis of electrophilic transition-metal complexes has been an important area in organometallic chemistry catalysis.[8]

It can be seen from Table 1 that the dicationic bipy–ruthenium complexes are active for the catalytic addition reaction of acetylacetone (**2a**) to styrene to afford **4a** with similar activity. The systems are efficient as a catalyst loading of only 0.4 mol% is needed, while 10 mol% of AgOTf or 5 mol% $AuCl_3$/15 mol% AgOTf was needed in an earlier report.[6] The reaction can be performed in air and no solvent is needed; addition of solvent does not seem to be beneficial (entries 2–4). No desired product was yielded when 1,4-dioxane was used as solvent and a complex mixture of products were formed. Yao and Li also reported that in their study of the AgOTf-catalyzed addition of acetylacetone to styrenes, no addition product was obtained when using dioxane.[6a] Lowering the temperature (to 80 °C) resulted in a lower yield (entry 9). The catalytic system was still efficient even when the substrate/catalyst (S/C) ratio was increased to 1000, a 34% yield could be obtained after 16 h (entry 10).

At this stage, we were also interested to see if the dicationic bipy–ruthenium complexes were also active for the catalytic addition of acetylacetone to 1-phenylethanol (**5a**) instead of styrene; we anticipated that this reaction might yield the same product of the addition of **2a** to styrene. It has been reported that benzylation of active methylenes, such as β-diketones and β-keto esters, with benzhydryl alcohols are promoted by a stoichiometric amount of Lewis acid, BF_3·OEt_2.[9] In a more recent communication, Bi(OTf)$_3$-catalyzed addition of acetylacetone to 1-phenylethanol has been presented.[10] Reactions of β-diketones or β-keto esters with benzylic or allylic alcohols in the presence of $InCl_3$, *p*-toluenesulfonic acid, and surfactant type or solid Brønsted acid catalysts have also been described.[11] No example of transition-metal-catalyzed addition of β-dicarbonyl compounds to benzylic alcohols has, however, been reported. Table 2 shows that the ruthenium complexes (0.4 mol%) are effective for the catalytic addition of acetylacetone to neat 1-phenylethanol (**5a**) to give **4a**; the yield of product in each case is higher than that of the corresponding addition reaction to styrene. Among the complexes containing the triflate anion, the one containing the 6,6′-dichloro-2,2′-bipyridine (6,6-Cl_2bipy) ligand gave the highest yields (entries 1–3, Table 2). Changing the anion of the (6,6′-Cl_2bipy)-complex to ClO_4^- further increases the catalytic activity of the dicationic complex (entry 4, Table 2). The complex *cis*-[Ru(6,6′-Cl_2bipy)$_2$(H_2O)$_2$](ClO_4)$_2$ (**1d**) is therefore used throughout the study. It is, however, strange to find that the tetrafluoroborate complex *cis*-[Ru(6,6′-Cl_2bipy)$_2$(H_2O)$_2$](BF_4)$_2$ (**1e**) is totally inactive for the addition reaction. Yao and Li found that while AgOTf is an active catalyst for the addition of acetylacetone to styrene, $AgBF_4$ is totally inactive.[6c] The same authors also learned that changing the counterion of the silver salt in the bimetallic system $AuCl_3$/

Table 1. Catalytic addition of acetylacetone (**2a**) to styrene (**3a**) with bipy–ruthenium complexes.[a]

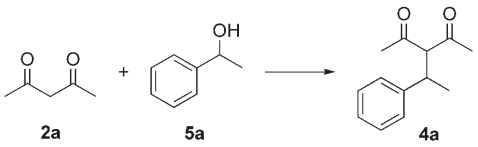


2a **3a** **4a**

Entry	Catalyst	Solvent	Yield [%][b]
1	**1a**	neat	47
2[c]	**1a**	DCE	46
3[c]	**1a**	$CHCl_3$	47
4[c]	**1a**	CH_2Cl_2	34
5	**1a**	dioxane	0
6	**1b**[d]	neat	46
7	**1c**	neat	39
8	**1d**	neat	49
9[e]	**1d**	neat	37
10[f]	**1d**	neat	34

[a] Reaction conditions: catalyst (0.004 mmol), **2a** (1.5 mmol), **3a** (1.0 mmol), 90 °C, 8 h, 2.0 mL of solvent was added if noted. [b] Based on the amount of **3a** used, which was determined by ^{1}H NMR spectroscopy with CH_3NO_2 as the internal standard. [c] In reflux. [d] Compound **1b** contains traces of an impurity (see the Experimental Section). [e] Reaction temperature 80 °C. [f] Reaction conditions: catalyst (0.002 mmol), **2a** (3.0 mmol), **3a** (2.0 mmol), 100 °C, 16 h.

Table 2. Catalytic addition of acetylacetone (**2a**) to 1-phenylethanol (**5a**) with bipy–ruthenium complexes.[a]



2a **5a** **4a**

Entry	Catayst	Solvent	Yield [%][b]
1	**1a**	neat	71
2	**1b**[c]	neat	66
3	**1c**	neat	59
4	**1d**	neat	86
5[d]	**1d**	neat	61
6	**1d**	DCE	72
7	**1d**	$CHCl_3$	52
8	**1d**	dioxane	0
9[e]	**1d**	neat	21

[a] Reaction conditions: catalyst (0.004 mmol), **2a** (1.5 mmol), **5a** (1.0 mmol), 80 °C, 6 h, 2.0 mL of solvent was added if noted. [b] Based on the amount of **3a** used, which was determined by ^{1}H NMR spectroscopy with CH_3NO_2 as the internal standard. [c] Compound **1b** contains traces of an impurity (see the Experimental Section). [d] Reaction temperature: 70 °C. [e] Reaction conditions: catalyst (0.002 mmol), **2a** (3.0 mmol), **5a** (2.0 mmol), 80 °C, 17 h.

AgOTf, which is an active catalyst for the addition of acetylacetone to styrene, from OTf^- to BF_4^-, resulted in a very substantial loss of catalytic activity in the system; no explanation was provided for this phenomenon.[6b] A lower yield was obtained at lower temperature (entry 5, Table 2). The reactions performed in 1,2-dichloroethane (DCE) and $CHCl_3$ could also afford the product **4a**, with slightly lower yields; however, the reaction in dioxane gave no yield of **4a** (entries 6–8). It is noteworthy that when the S/C ratio was increased to 1000, a product yield of 21% was obtained after 17 h (entry 9).

Subsequently, the addition reaction was examined on more substrates by using **1d** as the catalyst. β-Diketones were added to various alcohols at 80°C (Table 3). Benzylation of β-diketones **2a–c** with benzylic alcohols **5a–f** and **5j** are highly effective (entries 1–6, 10–14). The allylation reactions of **2a** and **2c** with allyl alcohols **5g** and **5h** are also effective, the yields of allyl product **4g**, **4h**, **4o**, and **4p** are comparable to those of the reaction with benzyl alcohols (entries 7, 8, 15, and 16). It is noteworthy that the reaction of **2a** with the heterocycle alcohol **5i** gives the functionalized heterocycle product **4i**, although the yield is relatively

Table 3. Catalytic addition of β-diketones to alcohols with *cis*-$[Ru(6,6'\text{-}Cl_2bipy)_2(H_2O)_2](ClO_4)_2$ (**1d**).[a]

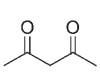
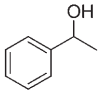
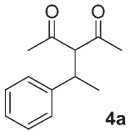
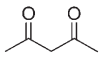
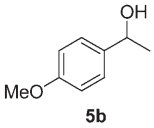
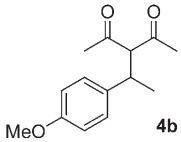
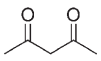
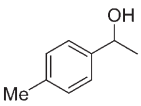
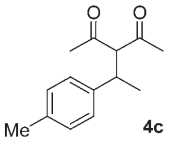
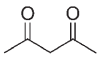
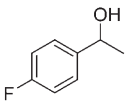
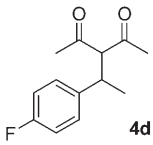
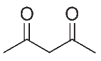
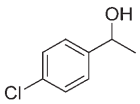
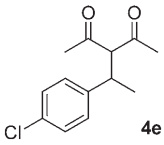
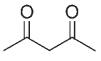
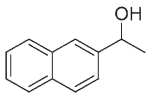
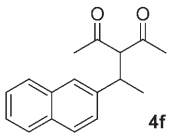
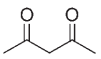
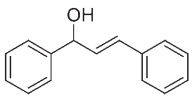
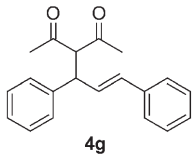
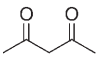
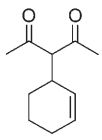
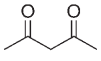
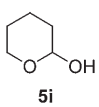
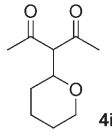
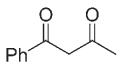
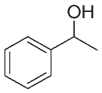
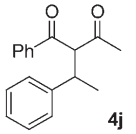
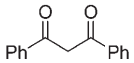
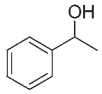
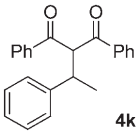
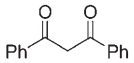
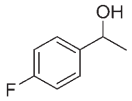
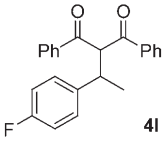
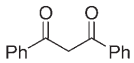
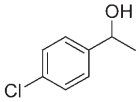
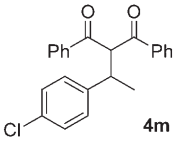
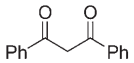
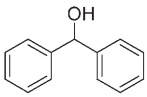
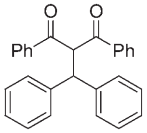
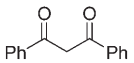
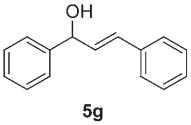
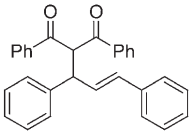
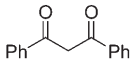
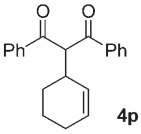
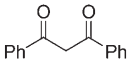
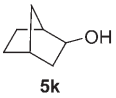
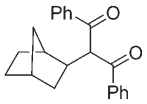
Entry	β-Diketone	Alcohol	Product	Yield [%][b]
1	 **2a**	 **5a**	 **4a**	82
2	 **2a**	 **5b**	 **4b**	82
3	 **2a**	 **5c**	 **4c**	90
4	 **2a**	 **5d**	 **4d**	86
5	 **2a**	 **5e**	 **4e**	72
6[c]	 **2a**	 **5f**	 **4f**	81
7[c]	 **2a**	 **5g**	 **4g**	86
8	 **2a**	 **5h**	 **4h**	73
9	 **2a**	 **5i**	 **4i**	41

Table 3. (Continued)

Entry	β-Diketone	Alcohol	Product	Yield [%][b]
10[c]	 **2b**	 **5a**	 **4j**	92 (1:0.8)[d]
11[c]	 **2c**	 **5a**	 **4k**	92
12[c]	 **2c**	 **5d**	 **4l**	91
13[c]	 **2c**	 **5e**	 **4m**	97
14[c]	 **2c**	 **5j**	 **4n**	86[e]
15[c]	 **2c**	 **5g**	 **4o**	61
16[c]	 **2c**	 **5h**	 **4p**	71
17[c]	 **2c**	 **5k**	 **4q**	65[f]

[a] Reaction conditions: catalyst (0.004 mmol), β-diketone (1.5 mmol), alcohol (1.0 mmol), 80 °C, 6–17 h, no solvent was used unless noted. [b] Based on the amount of alcohol used (isolated yield). [c] DCE added (2.0 mL). [d] The ratio of diastereomers was determined by ^{1}H NMR spectroscopy. [e] Reaction time: 20 h. [f] Reaction time: 42 h.

low (entry 9). The reaction of **2c** with norbornyl alcohol **5k** affords a moderate yield and a much longer reaction time is needed (entry 17). The **1d**-catalyzed addition of β-keto esters and β-diester to the secondary alcohols that we used in this study was, unfortunately, not successful under the present reaction conditions; neither was the addition of β-diketones to primary alcohols.

For comparison purposes, **1d**-catalyzed addition reactions of β-diketones to styrene and styrene derivatives have also been performed (Table 4); it was found that the yields of the addition products are, in general, lower than those of the reactions with the corresponding alcohols. In each catalytic reaction, the styrene dimer 1,3-diarylbut-1-ene and higher oligomers of the styrene are formed.

It is known that Lewis acids could act as promoters for the conversion of alcohols to symmetrical ethers;[12] we also found that the symmetrical ether PhMeHC–O–CHMePh (**6**) was present in a **1d**-catalyzed addition of acetylacetone (**2a**) to 1-phenylethanol (**5a**) to yield **4a**. The following **5a**/**6**/**4a** ratios were found at different times of the catalytic reaction: 0.37:1.73:1 (1 h), 0.09:0.42:1 (2 h), 0:0:1 (3 h); these results show that the symmetrical ether **6** was formed and later consumed in the course of the catalysis.

After the conclusion of the **1d**-catalyzed reaction of **2a** with **5a**, in which larger sample sizes of reactants and complex were used, diethyl ether was added to precipitate a deep-red solid; the solid was filtered and washed several times with Et_2O. The solid was characterized by ^{1}H NMR,

Table 4. Catalytic addition of β-diketones to alkenes with *cis*-[Ru(6,6′-Cl_2bipy)$_2$(H_2O)$_2$](ClO_4)$_2$ (**1d**).[a]

Entry	β-Diketone	Alkene	Product	Yield [%][b]
1	**2a**	**3a**	**4a**	46
2	**2a**	**3b**	**4c**	35
3	**2a**	**3c**	**4d**	52
4[c]	**2b**	**3a**	**4j**	37 (1:0.8)[d]
5[c]	**2c**	**3a**	**4k**	52
6[c]	**2c**	**3c**	**4l**	72
7[c]	**2c**	**3d**	**4m**	90

[a] Reaction conditions: catalyst (0.004 mmol), β-diketone (1.5 mmol), styrene (1.0 mmol), 90 °C, 15 h, no solvent was used unless noted. [b] Based on the amount of styrene used, isolated yield. [c] DCE added (2.0 mL). [d] Ratio of diastereomers was determined by ^{1}H NMR spectroscopy.

$^{13}C\{^1H\}$ NMR, IR, and mass spectroscopic analyses. After these analyses, the solid was identified as the κ^2-acetylacetonate (κ^2-acac) complex [Ru(6,6′-Cl_2bipy)$_2$(κ^2-acac)]ClO_4 (**7**). In the ^{1}H NMR spectrum of **7**, the acac group gives rise to a methyl singlet and a methylene singlet at 1.64 and 5.16 ppm, respectively. The $^{13}C\{^1H\}$ NMR spectrum shows one singlet each for the two equivalent methyl groups and the methylene carbon, respectively, at $\delta = 27.3$ and 98.7 ppm, while the acac C=O resonance appears as a singlet at $\delta = 187.4$ ppm. The IR spectrum of **7** shows two strong bands, characteristic of bidentate O-bonded acac, at $\tilde{\nu} = 1592$ and 1556 cm^{-1}.[13] The mass spectrum shows the parent peak of cation *cis*-[Ru(6,6′-Cl_2bipy)$_2$(κ^2-acac)]$^+$ (**7**$^+$) with *m*/*z* equal to 648.8417 (calcd: 648.9300).

Complex **7** was independently prepared by reacting **1d** with **2a** at 90 °C for 1 h. Single crystals of **7** suitable for X-ray crystallographic study were readily obtained by vapor diffusion of Et_2O into an acetone solution of **7** kept in a sealed vessel. Figure 1 shows the X-ray structure of **7**. The crystal data and refinement details are given in Table 5. The coordination geometry of **7**$^+$ is essentially octahedral al-

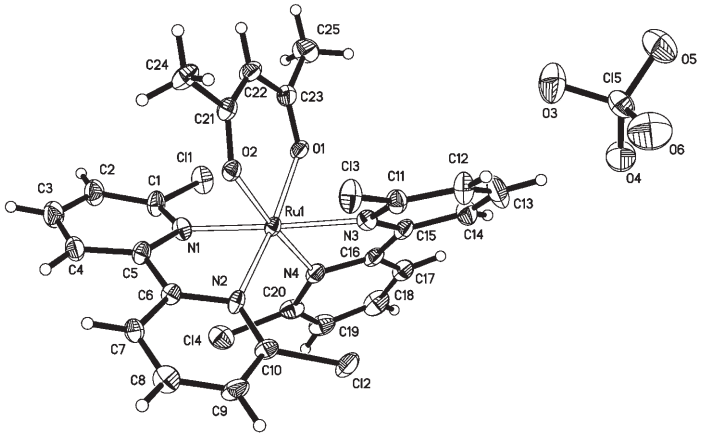


Figure 1. ORTEP diagram of [Ru(6,6′-Cl_2bipy)$_2$(κ^2-acac)]ClO_4.

Table 5. Crystal data and structure refinement for **7**.

	7
Empirical formula	$Ru(C_5H_7O_2)(C_{10}H_6N_2Cl_2)_2ClO_4$
F_w	749.76
T [K]	294(2)
λ [Å]	0.71073
crystal system	rhombohedral
space group	$R\bar{3}$
unit cell dimensions	
a [Å]	34.201(3)
b [Å]	34.201(3)
c [Å]	15.425(3)
α [°]	90
β [°]	90
γ [°]	120
V [Å^3]	15626(4)
Z	18
ρ_{calcd} [Mg m^{-3}]	1.434
μ [mm^{-1}]	0.876
$F(000)$	6732
crystal size [mm^3]	$0.32\times0.24\times0.12$
θ range [°]	2.25–27.57
index ranges	$-44\le h\le 42$
	$-44\le k\le 43$
	$-20\le l\le 19$
no. of reflns collected	48089
no. of independent reflns	7947 ($R_{int}=0.0342$)
completeness to $\theta=27.57°$ [%]	98.9
absorption correction	semi-empirical from equivalents
max. and min. transmission	1.000 and 0.817
refinement method	full-matrix least-squares on F^2
data/restraints/parameters	7947:56:363
GOF on F^2	1.010
final R indices [$I>2\sigma(I)$]	$R_1=0.0838$, $wR_2=0.2533$
R indices (all data)	$R_1=0.1489$, $wR_2=0.3300$
largest diff peak and hole [e Å^{-3}]	1.091 and −0.914

though the two bipyridines sustain relatively small angles at the metal center due to ligand constraints. The Ru–O (acac) bond lengths (2.04 and 2.05 Å) are similar to those of other Ru^{II}–acac complexes.[14] The structure of **7** as a whole is quite unremarkable; selected bond lengths and bond angles are shown in Table 6. Complex **7** did not react with 1-phenylethanol (**5a**), in the absence or presence of $HClO_4$; it also did not catalyze the addition of **2a** to **5a**.

On the basis of these observations, we are prompted to propose the following mechanism (Scheme 1) for the addition of β-diketones (using acetylacetone and 1-phenylethanol as examples) to secondary alcohols. It is seen that the addition reaction is in fact a Brønsted acid catalyzed reaction.[15] The catalytic process begins with **1d** reacting with acetylacetone (**2a**) to form **7** and concomitantly yield an equivalent of H^+, which then protonates the alcohol and generates the carbocation. The carbocation could attack an alcohol molecule to give the symmetric ether **6** or it can undergo electrophilic attack at the α-carbon center of the β-diketone (probably the enol form) to give the addition product with regeneration of a proton. It has been reported that the symmetrical ether **6** is formed as an intermediate in the Lewis acid catalyzed benzylation reaction of active methylenes with benzyl alcohol.[9a] The perchlorate anion might also play a role in the catalysis, probably in stabilizing the carbocation; the analogous Cl_2bipy–Ru complex containing tetrafluoroborate anion, **1e**, is totally inactive for the addition reaction. The fact that the **1d**-catalyzed benzylation of **2a** with **5a** was quenched by base, namely triethyl amine or K_2CO_3, is a strong indication that the addition reaction is Brønsted acid catalyzed. The fact that benzylation of **2c** with (*S*)-1-phenylethanol leads to the isolation of completely racemized product (Scheme 2) lends support to the proposed mechanism involving the intermediacy of the carbocation.

Table 6. Selected bond lengths [Å] and angles [°] in [Ru(6,6′-Cl_2bipy)$_2$-(κ^2-acac)]$^+$ (**7**$^+$).

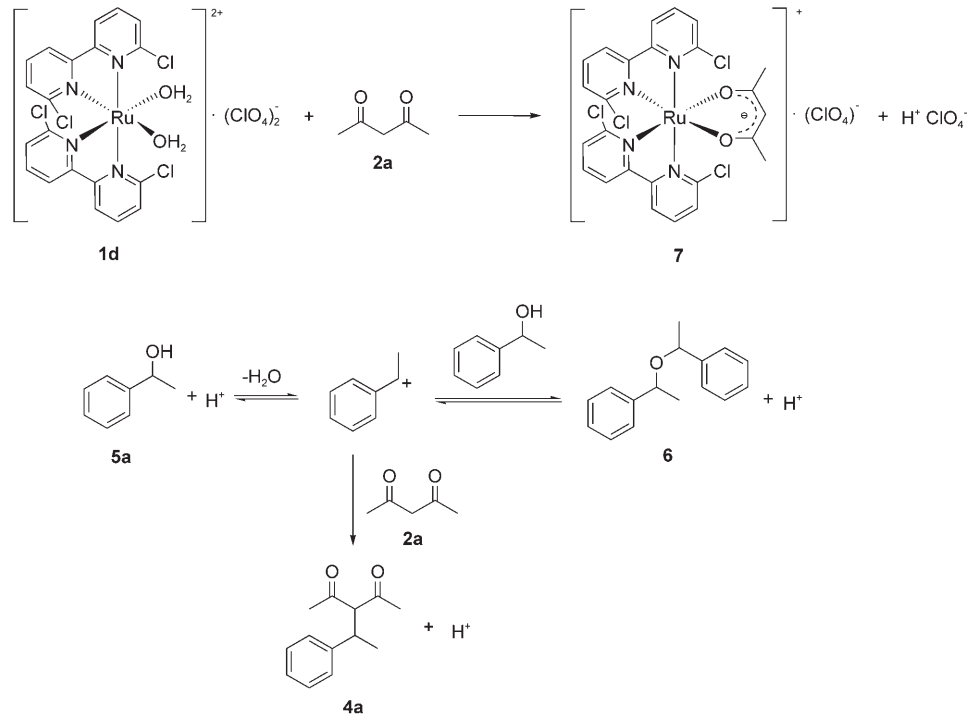
Ru(1)–O(1)	2.0531(19)	Ru(1)–O(2)	2.043(2)
O(1)–C(23)	1.241(4)	O(2)–C(21)	1.254(4)
C(21)–C(22)	1.380(5)	C(22)–C(23)	1.453(6)
Ru(1)–N(1)	2.043(3)	Ru(1)–N(2)	2.071(2)
Ru(1)–N(3)	2.058(3)	Ru(1)–N(4)	2.047(3)
O(1)-Ru(1)-O(2)	91.00(8)	N(1)-Ru(1)-N(2)	78.35(9)
N(3)-Ru(1)-N(4)	78.36(11)	N(4)-Ru(1)-N(2)	101.36(9)
O(1)-Ru(1)-N(2)	173.17(9)	O(2)-Ru(1)-N(4)	175.63(9)
N(1)-Ru(1)-N(3)	177.60(8)	O(1)-Ru(1)-N(4)	85.14(9)
O(2)-Ru(1)-N(2)	82.57(9)		

Hartwig et al. have suggested that addition of a broad range of O–H and N–H bond donors to unactivated alkenes catalyzed by metal triflates might not be truly metal-catalyzed reactions; the metal might simply generate a protic acid which is the real catalytic species.[16] It has also been reported that in the Lewis acidic metal complex catalyzed hetero-Michael addition reactions, the proton, rather than the metal ion is the true catalyst.[17] On the other hand, He et al. reported that the gold-mediated addition reactions of phenols, carboxylic acids, and tosylamides to simple olefins are truly metal-catalyzed; they do not support the possibility of these reactions being catalyzed by acid generated from the reaction of the gold(I) catalyst with the nucleophile.[18]

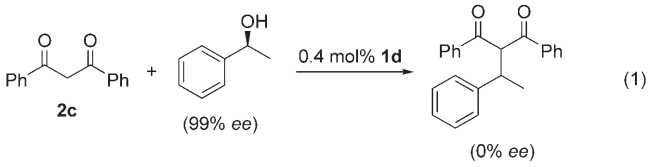
For comparison purposes, we carried out the $HClO_4$-catalyzed addition reactions of acetyacetone to two of the alcohols and styrene. The results collected in Table 7 show that the yields of the addition products are basically identical to those of the corresponding **1d**-catalyzed reactions. We have carried out a more comprehensive study on the acid-catalyzed addition reactions of β-diketones to 1-phenylethanols and styrenes, the results of which will be published elsewhere.

In two separate addition reactions of **2a** to **5a** under identical reaction conditions, one of which is catalyzed by 0.4 mol% of **1d** and the other by the same concentration of $HClO_4$, the yields of the addition products with times were measured. Figure 2 shows that the yields versus time graphs of the two catalytic processes are basically identical, therefore strongly implicating that the two reactions might have a common catalytic species, which is probably the protic acid.

A catalytic self-condensation reaction of 1-phenylethanol (**5a**) to form the symmetrical ether **6** with **1d**/**2a** was moni-



Scheme 1. Proposed mechanism for the catalytic addition of β-diketone to 1-phenylethanol with **1d**.



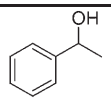
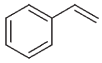
Scheme 2. Benzylation of **2c** with (*S*)-1-phenylethanol.

tored and comparison with an identical reaction with $HClO_4$ was made. As shown in Figure 3, the plots of percent conversion to the ether with times for the reactions are also basically identical, again indicating a common catalytic species (the proton) in both reactions.

Finally, we have demonstrated that reaction of **2a** with the symmetrical ether **6** instead of 1-phenylethanol (**5a**) in the presence of a catalytic amount of **1d** yields the addition product **4a**. Figure 4 shows that the results of the $HClO_4$-catalyzed reaction are identical to that of the **1d**-catalyzed one.

The postulate (Scheme 1) that the addition product is finally generated by attack of the carbocation on the free β-diketone rather than the bidentate acac ligand of **7** is supported by the fact that **7** fails to react with 1-phenylethanol (**5a**) or the ether **6** in the presence of $HClO_4$, which protonates **5a** or **6** and generates the benzyl carbocation in situ.

Table 7. Catalytic addition of acetylacetone (**2a**) to alcohols and styrene with $HClO_4$ and **1d**.

Entry	Addition reaction	Product	Yield with $HClO_4$ [%][a]	Yield with **1d** [%][a]
1	**2a** +  **5a**	**4a**[b]	87	82
2	**2a** +  **5h**	**4h**[b]	70	73
3	**2a** +  **3a**	**4a**[c]	42	46

[a] Based on alcohol or stryrene used (isolated yield). [b] Reaction conditions were same as those in Table 3. [c] Reaction conditions were same as those in Table 4.

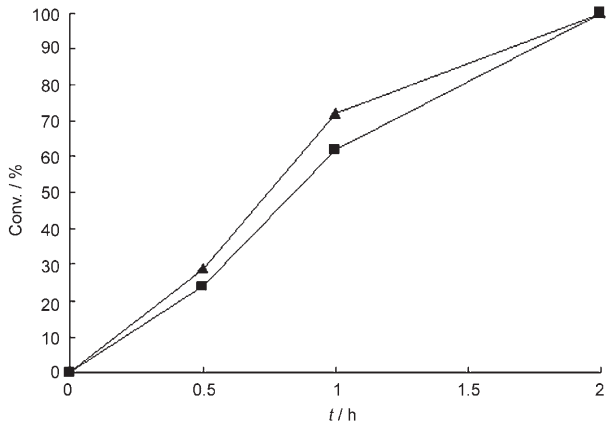


Figure 2. Conversion (to **4a**, based on **5a**) versus time plots of the catalytic addition of **2a** to **5a** with **1d** (■, 0.4 mol%) and $HClO_4$ (▲, 0.4 mol%).

A mechanism very similar to that depicted in Scheme 1 is believed to be operative for the **1d**-catalyzed addition of β-diketones to styrenes (Scheme 3, with **2a** and styrene as examples). Again, the crucial species is the carbocation; it attacks the β-diketone to yield the addition product or it reacts with styrene to yield the dimer and higher oligomers as byproducts.

Conclusion

In Lewis acidic metal catalysis, one has to caution against the true catalytic species not being the metal complex but

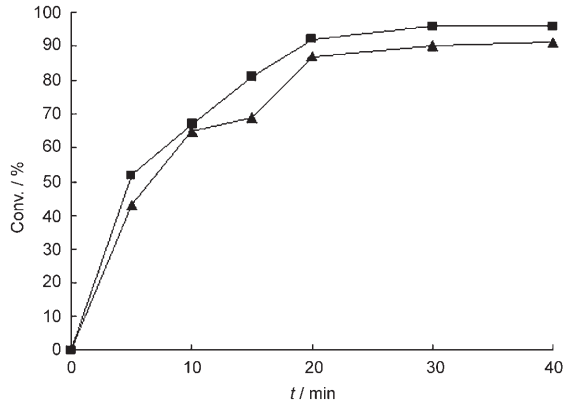


Figure 3. Conversion versus time plots for catalytic self-condensation of **5a** to the symmetrical ether **6** with **1d**/**2a** (■, 0.4/0.8 mol%) and $HClO_4$ (▲, 0.4 mol%).

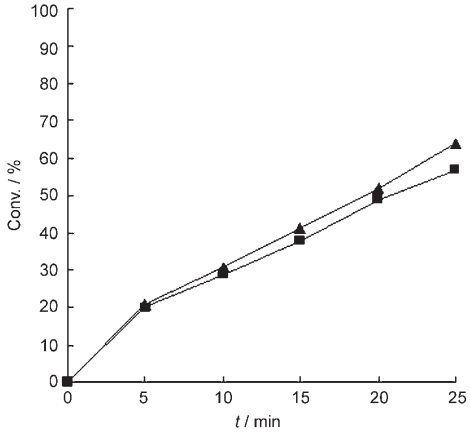
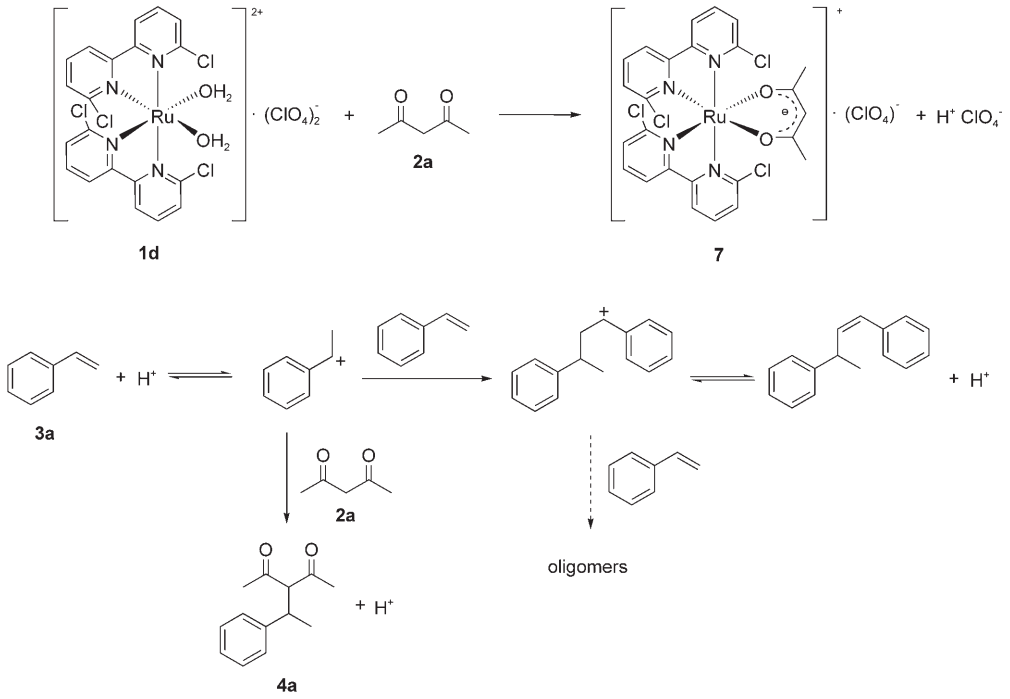


Figure 4. Conversion to **4a** (based on **6**) versus time plots for the catalytic reactions between **2a** and **6** with **1d** (■, 0.4 mol%) and $HClO_4$ (▲, 0.4 mol%).

the proton generated by the reaction of the metal with the substrate. Our work on the dicationic Cl_2bipy–Ru-complex-catalyzed addition of β-diketones to alcohols and styrenes constitutes a good example which unequivocally illustrates this phenomenon. Addition of β-diketones to 1-phenylethyl alcohols generally gives higher yields of benzylated β-diketones than addition to the corresponding styrenes because the former does not generate styrene dimer and oligomer byproducts.

Experimental Section

General: Complexes **1a** and **1d** were prepared according to the literature method.[19] The complex *cis*-[Ru(6,6′-Me_2bipy)$_2$(H_2O)$_2$](OTf)$_2$ (**1c**) was synthesized by using the same procedure as for the preparation of **1a**, except that 6,6′-Me_2bipy was used in place of 6,6′-Cl_2bipy; ^{1}H NMR spectrum of **1c** was found to be identical to that of the perchlorate salt *cis*-[Ru(6,6′-Me_2bipy)$_2$(H_2O)$_2$](ClO_4)$_2$ which has been reported.[20] 1-(4-Methylphenyl)ethanol (**5c**), 1-(4-fluorophenyl)ethanol (**5d**), 1-(4-chlorophenyl)ethanol (**5e**), and 1,3-diphenyl-2-propen-1-ol (**5g**) were prepared by reduction of the corresponding ketone precursors with $NaBH_4$ in methanol. The other reagents were obtained from Aldrich and used without further purification. ^{1}H NMR spectra were obtained from a Bruker DPX-400 spectrometer at 400 MHz; chemical shifts (δ, ppm) were reported by using TMS as the internal standard. ^{13}C NMR spectra were recorded with a Bruker DPX-400 spectrometer at 100 MHz; chemical shifts were internally referenced to $CDCl_3$ ($\delta = 77.0$ ppm). IR spectra were obtained from a Bruker Vector 22 FTIR spectrophotometer. Mass spectrometry was carried out with a Finnigan MAT 95S mass spectrometer with the samples dissolved in dichloromethane or acetone. HRMS was



Scheme 3. Proposed mechanism for the catalytic addition of β-diketone to styrene with **1d**.

carried out with Waters Micromass Q-Tof-2. Elemental analyses were performed by M-H-W Laboratories, Phoenix, AZ (USA). Melting points were determined on a Barnstead Electrothermal 9100 apparatus and were uncorrected.

***cis*-[Ru(6,6′-Br$_2$bipy)$_2$(H$_2$O)$_2$](OTf)$_2$ (1b)**: Ethylene glycol (3 mL) was added to $RuCl_3 \cdot 3H_2O$ (99 mg, 0.38 mmol), 6,6′-Br$_2$bipy (250 mg, 0.80 mmol), and LiCl (1.0 g, 23 mmol). The mixture was heated at 140 °C for 4 h under N_2. After the mixture had been cooled to room temperature, H_2O (3 mL) was added. The precipitated dark solid was collected by filtration; it was then washed twice with water (2×5 mL). The solid was dissolved in water (16 mL) and AgOTf (0.16 g, 0.62 mmol) was added. The resulting mixture was heated at 60 °C for 30 min, followed by filtration. The volume of the filtrate was reduced to 3 mL under reduced pressure and trific acid (0.5 mL) was added. The solution was placed in the refrigerator for 1 day, after which time, a thick oil separated. Chloroform (1 mL) was added to the solution and the mixture was stirred vigorously to enable the solidification of the oily substance. The mixture was filtered and a tacky brown solid was collected and recrystallized with THF/$CHCl_3$. The product, which remained a tacky brown solid, was dried in vacuo for 5 h. Yield: 0.05 g (13 %). ^{1}H NMR spectrum of the product shows two triplets and four doublets in the $\delta = 7.72$–8.50 ppm region; this pattern is very similar to those found in the ^{1}H NMR spectra of **1a** and **1c**. Some very small multiplets at $\delta = 7.36$–7.41 and 7.93–8.04 ppm indicate that minute amounts of impurities are present. It was found to be very difficult to completely remove these impurities from the product due to the tacky nature of **1b**. ^{1}H NMR (400 MHz, D_2O, 25 °C): $\delta = 7.72$ (d, $J = 7.7$ Hz, 2H; dbbp-5,5′-*H*), 7.85 (t, $J = 7.9$ Hz, 2H; dbbp-4,4′-*H*), 7.97 (d, $J = 7.5$ Hz, 2H; dbbp-5,5′-*H*), 8.04 (t, $J = 7.9$ Hz, 2H; dbbp-4,4′-*H*), 8.38 (d, $J = 8.0$ Hz, 2H; dbbp-3,3′-*H*), 8.50 ppm (d, $J = 8.2$ Hz, 2H; dbbp-3,3′-*H*); MS (+ESI): *m*/*z*: 382.8 $[M]^{2+}$ (23), 364.7 $[M-2H_2O]^{2+}$ (89).

***cis*-[Ru(6,6′-Cl$_2$bipy)$_2$(κ^2-acac)]ClO$_4$ (7)**: Complex **1d** (150 mg, 2.0 mmol) was added to acetylacetone **2a** (2 mL) and the solution was stirred under N_2 for 1 h at 90 °C. After cooling to room temperature, the volatile material was removed under vacuum to afford a deep-red solid. The residue was washed with diethyl ether (3×10 mL) and hexane (10 mL) and then dried under vacuum for 5 h. ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): $\delta = 1.64$ (s, 6H; C*H*$_3$C(O)CHC(O)C*H*$_3$), 5.16 (s, 1H; CH$_3$C(O)C*H*C(O)C*H*$_3$), 7.62–7.67 (m, 4H), 8.10–8.14 (m, 4H), 8.63–8.68 ppm (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C): $\delta = 27.3$ (*C*H$_3$C(O)CHC(O)*C*H$_3$), 98.7 (CH$_3$C(O)*C*HC(O)CH$_3$), 187.4 (CH$_3$*C*(O)CH*C*(O)CH$_3$), other signals due to the bipyridine ligands: 122.6, 123.4, 125.5, 125.7, 138.7, 139.8, 158.7, 160.0, 160.9, 162.3 ppm; IR (KBr): $\tilde{\nu} = 3096$, 1592 (C=O of acac$^-$), 1556 (C=O of acac$^-$), 1455, 1435, 1410, 1368, 1240, 1187, 1144, 1113, 1090, 856, 785, 741, 626 cm^{-1}; HRMS (+ESI): calcd for $C_{25}H_{19}Cl_4N_4O_2Ru^+$: 648.9300; found: 648.8417 $[M]^+$; elemental analysis calcd (%) for $C_{25}H_{19}Cl_5N_4O_6Ru$: C 40.05, H 2.55, N 7.47; found: C 40.25, H 2.38, N 7.21.

Typical procedure for the catalytic reaction of β-diketone with alcohol (or styrene): To a mixture of β-diketone (1.5 mmol) and alcohol (or styrene, 1.0 mmol) was added the catalyst **1d** (0.004 mmol). The resulting solution was stirred at 80 °C (90 °C for styrene) and monitored by TLC or ^{1}H NMR spectroscopy. When the maximum conversion had been reached, the desired product was isolated by flash column chromatography on silica gel. (**4d** and **4l** are new compounds and the other products **4a**–**c**, **4e**–**k**, **4m**–**q**, and **6** are known compounds).

3-[1-(4-Fluorophenyl)ethyl]pentane-2,4-dione (4d): M.p. 57–58 °C; ^{1}H NMR (400 MHz, $CDCl_3$) $\delta = 1.20$ (d, $J = 6.9$ Hz, 3H, ArCHC*H*$_3$), 1.86 (s, 3H; C*H*$_3$C(O)CHC(O)CH$_3$), 2.26 (s, 3H; CH$_3$C(O)CHC(O)C*H*$_3$), 3.58–3.63 (m, 1H; ArC*H*CH$_3$), 4.01 (d, $J = 11.3$ Hz, 1H; CH$_3$C(O)C*H*C(O)CH$_3$), 6.96–7.00 (m, 2H; Ar*H*), 7.15–7.19 ppm (m, 2H; Ar*H*); ^{13}C NMR (100 MHz, $CDCl_3$) $\delta = 20.7$ (ArCH*C*H$_3$), 29.5 (*C*H$_3$C(O)CHC(O)CH$_3$), 29.7 (CH$_3$C(O)CHC(O)*C*H$_3$), 39.5 (Ar*C*HCH$_3$), 76.6 (CH$_3$C(O)*C*HC(O)CH$_3$), 115.4, 115.6, 128.6, 128.7, 138.7, 160.3, 162.7 (Ar–C), 202.9 (CH$_3$*C*(O)CHC(O)CH$_3$), 203.1 ppm (CH$_3$C(O)CH*C*(O)CH$_3$); IR (KBr): $\tilde{\nu} = 2968$, 2934, 1724, 1699, 1511, 1363, 1292, 1225, 1161, 1148, 835, 542 cm^{-1}; MS (+ESI): *m*/*z* (%): 245.05 $[M+Na]^+$ (100); HRMS (+ESI): *m*/*z*: calcd for $C_{13}H_{15}FNaO_2^+$: 245.0948; found: 245.0972 $[M+Na]^+$.

1,3-Diphenyl-2-[1-(4-fluorophenyl)ethyl]propane-1,3-dione (4l): M.p. 110–112 °C; ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 1.34$ (d, ArCHC*H*$_3$, $J = 7.0$ Hz, 3H), 4.06–4.14 (m, ArC*H*CH$_3$, 1H), 5.66 (d, $J = 10.0$ Hz, 1H; PhC(O)C*H*C(O)Ph), 6.81–6.86 (m, 2H), 7.23–7.28 (m, 4H), 7.39–7.43 (m, 3H), 7.51–7.53 (m, 1H), 7.77 (d, $J = 7.3$ Hz, 2H), 8.06 ppm (d, $J = 7.6$ Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 20.2$ (ArCH*C*H$_3$), 40.4 (Ar*C*HCH$_3$), 64.4 (PhC(O)*C*HC(O)Ph), 114.8, 115.1, 128.3, 128.4, 128.6, 128.7, 129.1, 129.2, 133.1, 133.5, 136.6, 136.9, 139.3, 160.0, 162.5, 194.4 (CH$_3$*C*(O)CHC(O)CH$_3$), 194.6 ppm (CH$_3$C(O)CH*C*(O)CH$_3$); IR (KBr): $\tilde{\nu} = 3065$, 2970, 1687, 1595, 1510, 1447, 1265, 1219, 971, 838, 684, 604, 544 cm^{-1}; HRMS (+ESI): *m*/*z*: calcd for $C_{23}H_{19}FNaO_2^+$: 369.1261; found: 369.0547 $[M+Na]^+$.

Comparison of the catalytic addition of acetylacetone (2a) to 1-phenylethanol (5a) with HClO$_4$ and 1d: $HClO_4$ (60 % solution, 0.4 μL, 0.004 mmol) or **1d** (3.2 mg, 0.004 mmol) was added to a mixture of **2a** (154 μL, 1.5 mmol) and **5a** (122 mg, 1.0 mmol), the resulting solution was stirred at 80 °C; samples removed by the use of a microsyringe at different time intervals were analyzed by ^{1}H NMR spectroscopy to give the percentage conversions.

Comparison of catalytic self-condensation of 1-phenylethanol (5a) to the symmetrical ether 6 with 1d/2a and HClO$_4$: $HClO_4$ (60 % solution, 0.4 μL, 0.004 mmol) or **1d**/**2a** (3.2 mg, 0.004 mmol/0.8 μL, 0.008 mmol) was added to a sample of **5a** (122 mg, 1.00 mmol), the resulting solution was stirred at 80 °C. Samples removed by the use of a microsyringe at different time intervals were analyzed by ^{1}H NMR spectroscopy to give the percentage conversions.

Comparison of the catalytic reactions between acetylacetone (2a) and ether 6 with 1d and HClO$_4$: $HClO_4$ (60 % solution, 0.4 μL, 0.004 mmol) or **1d** (3.2 mg, 0.004 mmol) was added to a mixture of **2a** (154 μL, 1.50 mmol) and ether **6** (113 mg, 0.5 mmol), the resulting solution was stirred at 80 °C. Samples removed by the use of a microsyringe at different time intervals were analyzed by ^{1}H NMR spectroscopy to give the percentage conversions.

Crystallographic structure analysis of [Ru(6,6′-Cl$_2$bipy)$_2$(κ^2-acac)]ClO$_4$ (7): Deep-red crystals were obtained by slow infusion of diethyl ether into an acetone solution of [Ru(6,6′-Cl_2bipy)$_2$(κ^2-acac)]ClO_4 kept in a sealed vessel. A suitable crystal with dimensions of 0.32×0.24×0.12 mm^3 was mounted on a Bruker CCD area detector diffractometer by using $Mo_{K\alpha}$ radiation ($\lambda = 0.71073$ Å) from a generator operating at 50 kV, 30 mA condition. The intensity data were collected and corrected for SADABS (Sheldrick, 1996) program. The structure was solved by direct methods, expended by difference Fourier syntheses and refined by full-matrix least squares on F^2 by using the Bruker Smart and Bruker SHELXT1 program packages. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were placed in ideal positions and refined as riding atoms. The final cycle of the full-matrix least-squares refinement based on 7947 observed reflections ($I > 2\alpha(I)$) and 363 parameters converged to the R and R_w values of 0.0838 and 0.2533 for [Ru(6,6′-Cl_2bipy)$_2$(κ^2-acac)]ClO_4. Further details of the data collection are summarized in Table 5, and selected bond distances and angles are listed in Table 6. CCDC-646248 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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