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Catalytic Activity of Mono- and Bimetallic Rhodium(I) and Iridium(I) Complexes Bearing Carbon-Ether-Carbon (COC) Ligand for the Intramolecular Cyclization of 4-Pentynoic Acid

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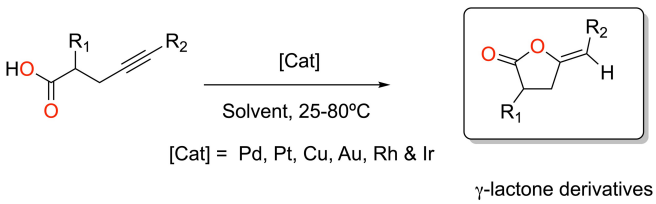
The catalytic performance of a series of mono- and bimetallic Ir(I) and Rh(I) complexes bearing the (COC) bis-triazolylidene ligand, coordinated in a bridging or chelating fashion, was evaluated in the cyclization of 4-pentynoic acid. The chelated mononuclear cationic complex [Ir(cod)(COC)]PF_6 (cod = 1,5-cyclooctadiene; COC = biscarbene ether) displayed the highest reaction rate for 4-pentynoic acid to form γ-methyl-ene-γ-butyrolactone (5-methylenedihydrofuran-2(3*H*)-one). Density Functional Theory calculations were carried out to rationalize the reaction mechanism which proceeds in three steps, namely coordination of the alkyne to the active catalyst followed by intramolecular cyclization and final reductive elimination. Its catalytic performance was further assessed against different substituted 4-pentynoic acid derivatives.

Introduction

The structural pattern of lactones makes these organic molecules important commodities for multiple synthetic applications. They are important intermediates in neurodegenerative diseases,[1] synthesis of natural products,[2–7] controlled drug release strategies,[8] flavors and fragrances,[3] production of carbon fibers[9] and more recently were also employed in the production of fuels and chemicals based on renewable feedstocks.[10–13] The development of atom-economical methods for the preparation of lactones via intramolecular functionalization of alkynes has thus attracted much interest in recent years. In this context, several transition metal complexes based on Pd,[14–20] Pt,[21,22] Cu,[23] Au,[24–31] Rh,[32–34] and Ir,[32,35–37] have been shown to be competent catalysts for this transformation (Scheme 1).

Inspired by the success in catalysis demonstrated by metal complexes containing aliphatic ligands, we recently reported the synthesis of a series of Rh(I) and Ir(I) complexes based on 1,2,3-triazole-5-ylidenes (mesoionic carbenes, MICs)[38–44] (Figure 1), which can be readily prepared from the ether-bridged bis(triazolium) ligand precursor.[45]

Their catalytic performance was evaluated in the hydrothiolation of terminal alkynes, resulting in very efficient and selective formation of the α-vinyl sulfide product.[46] Seeking to expand their applicability in a different alkyne transformation we have focused on the intramolecular cyclization of acetylenic carboxylic acids to alkylidene lactones. As mentioned earlier, this reaction is relevant to the pharmaceutical industry since it



Scheme 1. Cyclization of acid-alkynes catalyzed by different transition metal complexes to generate lactone derivatives.

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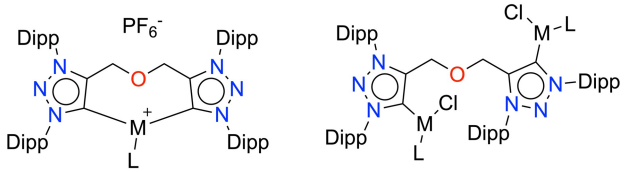
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[M(L)(**COC**)]PF_6

1a M = Ir; L = cod
1b M = Rh; L = cod
2a M = Ir; L = $(CO)_2$
2b M = Rh; L = $(CO)_2$

[$M_2(L)_2Cl_2$(μ-**COC**)]

3a M = Ir; L = cod
3b M = Rh; L = cod
4a M = Ir; L = $(CO)_2$
4b M = Rh; L = $(CO)_2$

cod = 1,5-cyclooctadiene; Dipp = 2,6-diisopropylphenyl

Figure 1. Mono- and bimetallic Ir(I) and Rh(I) complexes **1**–**4** used in this study.

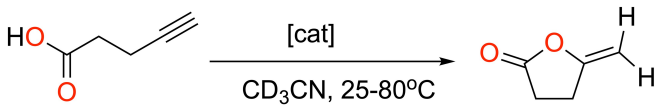
provides access to five-membered oxygen-containing heterocycles.

Thus, we herein report the catalytic activity of cationic monometallic Ir(I) and Rh(I) **1**–**2** with formula [M(L)(**COC**)]PF_6 (M=Ir, Rh; L=cod, $(CO)_2$) and neutral dinuclear Ir(I) and Rh(I) metal complexes **3**–**4** with formula [$M_2(L)_2Cl_2$(μ-**COC**)] (M=Ir, Rh; L=cod, $(CO)_2$) towards the intramolecular cyclization of 4-pentynoic acid to form γ-methylene-γ-butyrolactone. Among them, the monometallic iridium catalyst **1a** [Ir(cod)(**COC**)]PF_6 outperformed the related metal complexes in the series. Its catalytic activity was further explored towards the intramolecular cyclization of different acetylenic carboxylic acid derivatives and the involved mechanism elicited by the means of computational and experimental tools.

Results and Discussion

A perusal of the literature reveals that most reported examples dealing with this transformation involved rhodium(I) complexes, whereas only a few iridium(I) catalysts have been studied.[32,35,36] However a recent study demonstrated that a tetranuclear iridium(I) complex containing a tetra-NHC ligand based on a pyrene core could efficiently catalyze the reaction at 80 °C in CD_3CN, outperforming its related rhodium(I) derivative.[32] On this basis, we initially studied the performance of monometallic complexes **1a** [Ir(cod)(**COC**)]PF_6 and **2a** [$Ir(CO)_2$(**COC**)]PF_6 (1 mol% catalyst loading) towards the catalytic cyclization of 4-pentynoic acid to form γ-methyl-ene-γ-butyrolactone, under these reaction conditions, at 80 °C in CD_3CN for 1 hour (Table 1, entries 1–2). Full conversion of the alkynoic acid was observed

Table 1. Cyclization of 4-pentynoic acid **5a** catalyzed by **1a** and **2a**.[a]



5a **6a**

Entry	Catalyst	Ir (mol%)	Temp (°)	Time (h)	Yield (%)[c]
1	**1a**	1	80	1	>99
2	**2a**	1	80	1	>99
3	**1a**	1	60	2.75	>99
4	**2a**	1	60	3	>99
5	**1a**	1	40	7.25	>99
6	**2a**	1	40	8.75	>99
7	**1a**	1	25	54	>99
8	**2a**	1	25	127	96
9	**1a**	0.5	80	2	>99
10	**2a**	0.5	80	3	>99
11[b]	**1a**	0.25	80	2.4	>99
12[b]	**2a**	0.25	80	3	>99
13	**1a**	0.25	80	3.5	>99
14	**2a**	0.25	80	6	>99
15	**1a**	0.1	80	10.5	>99
16	**2a**	0.1	80	31	93
17	**1a**	0.01	80	110	72
18	**2a**	0.01	80	110	62

[a] Reaction Conditions: J. Young NMR tube loaded with 4-pentynoic acid **5a** 0.5 mmol, CD_3CN (0.75 mL). [b] 1 mmol substrate. [c] Yields were determined by ^1H NMR spectroscopy using 1,3,5-trimethoxybenzene as internal standard.

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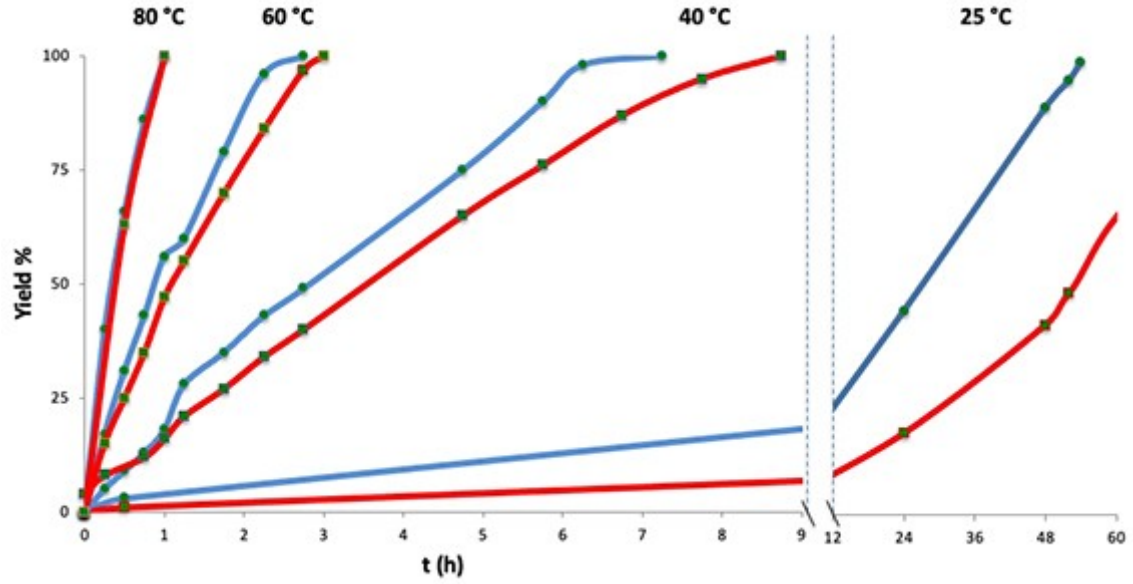


Figure 2. Time-dependent reaction profile for the catalytic formation of γ-methylene-γ-butyrolactone at different temperatures 25, 40, 60 and 80 °C, using catalyst **1 a** (blue lines) and **2 a** (red lines) (1 mol % Ir).

for both after one hour. Encouraged by the improved rates of formation of the alkylidene lactone product compared to the tetranuclear Ir(I) derivative,[31] we studied the reaction at lower temperatures. In this case, longer reaction times were required when shifting from 80 °C down to 60 °C, 40 °C and 25 °C respectively (Table 1, entries 3–8). As graphically shown in Figure 2, **1 a** [Ir(cod)(**COC**)]PF_6 outperformed catalyst **2 a** with dicarbonyl ancillary ligands, in all cases.

Confirmation of the superior catalytic performance of **1 a** over **2 a** was found when decreasing the catalyst loading to 0.5 mol %. Full conversion was achieved by catalyst **1 a** in 2 hours (Table 1, entry 9), whereas complex **2 a** required 3 hours. When the substrate amount was doubled while keeping catalyst loading constant to afford a final catalyst concentration of 0.25 mol %, full conversion was achieved after 2.4 hours for catalyst **1 a**, in contrast to the 3 hours needed for complex **2 a** to reach full conversion (Table 1, entries 11 and 12). Similarly, at catalyst loading of 0.25 mol %, **1 a** achieved full conversion after 3.5 hours while catalyst **2 a** required 6 hours (entries 13 and 14). With a catalyst loading of 0.1 mol %, full conversion was attained after 10.5 hours for catalyst **1 a**, which is almost a third of the time needed by catalyst **2 a** to reach the 93 % yield (Table 1, entries 15 and 16). Finally, reducing the catalyst loading to 0.01 % with respect to the metal for both metal complexes prolonged the reaction time significantly achieving only 74 and 60 % yield for **1 a** and **2 a**, respectively, after 110 hours.

Once we had found the optimal reaction conditions (Table 1, entries 15 and16), we then evaluated the catalytic performance of the Rh(I) analogues [Rh(L)(**COC**)]PF_6 **1 b** (L = cod) and **2 b** (L = $(CO)_2$) along with the dimetallic Ir(I) and Rh(I) **3** – **4** with formula [$M_2(L)_2Cl_2$(μ-**COC**)] (M = Ir, Rh; L = cod, $(CO)_2$) depicted in Figure 1, under the optimal reaction conditions of 80 °C and 0.1 mol % (metal content) catalyst loading.

From inspection of Table 2, it can be concluded that the cationic monometallic Rh(I) complexes **1 b** [Rh(cod)(**COC**)]PF_6 and **2 b** [$Rh(CO)_2$(**COC**)]PF_6 are less effective than their iridium counterparts; requiring 40 and 60 hours, respectively, to reach 82 % yield (entries 2 and 4).

Next, we tested the dinuclear Ir(I) and Rh(I) complexes **3 a,b** and **4 a,b** at 0.05 mol % catalyst loading (0.1 mol with respect to the metal). In this case, the iridium complex **3 a** [$Ir_2(cod)_2Cl_2$(μ-**COC**)] achieved full conversion after 16 hours while the tetracarbonyl derivative **4 a** [$Ir_2(CO)_4Cl_2$(μ-**COC**)] required 31 hours to reach 82 % yield (entries 5 and 7). In line with the previous observations, both dinuclear rhodium derivatives resulted in less effective catalytic conversion than the related

Table 2. Catalytic cyclization of 4-pentynoic acid **5 a** catalyzed by **1**–**4**[a]

Entry	Catalyst	Time (h)	Yield[b]
1	**1 a** [Ir(cod)(**COC**)]PF_6	10.5	> 99
2	**1 b** [Rh(cod)(**COC**)]PF_6	40	82
3	**2 a** [$Ir(CO)_2$(**COC**)]PF_6	31	93
4	**2 b** [$Rh(CO)_2$(**COC**)]PF_6	60	82
5	**3 a** [$Ir_2(cod)_2Cl_2$(μ-**COC**)]	16	> 99
6	**3 b** [$Rh_2(cod)_2Cl_2$(μ-**COC**)]	40	56
7	**4 a** [$Ir_2(CO)_4Cl_2$(μ-**COC**)]	31	82
8	**4 b** [$Rh_2(CO)_4Cl_2$(μ-**COC**)]	40	38

[a] Reaction Conditions: J. Young NMR tube loaded with 4-pentynoic acid **5 a** 0.5 mmol, CD_3CN (0.75 mL). [b] Yields were determined by ^1H NMR spectroscopy using 1,3,5-trimethoxybenzene as internal standard.

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iridium derivatives and their respective monometallic counterparts.

These results indicate that greater reaction rates were observed for **1a** [Ir(cod)(**COC**)]PF_6 when compared to the Rh(I) and Ir(I) examples previously described in the literature.[32–35] In addition, it is important to highlight that for this particular transformation, and in contrast to our previous findings for the alkyne hydrothiolation, monometallic complex **1a** bearing the bidentate carbon-ether-carbon (COC) ligand outperformed its dinuclear derivative **3a** [Ir_2(cod)$_2Cl_2$(μ-**COC**)]. Based on these results, we decided to evaluate the activity of the four iridium(I) complexes **1a**–**4a** towards the cyclization of 5-hexynoic acid (see Table S1 ESI). Unfortunately, none of them were efficient in catalyzing the formation of the expected six-membered cyclic product. This outcome is in line with the previously described iridium-catalyzed examples.[34,47,48] The improved catalytic performance of the mononuclear iridium catalyst **1a** compared to the dinuclear derivative (**3a**) prompted us to explore the reaction profiles dependence upon catalyst concentration **1a** within the range (1, 0.5, 0.25 and 0.1 mol%) (see Figure 3). As expected, the representation clearly indicates that the reaction outcome depends directly on catalyst concentration.

Finally, given the observed catalytic performance of **1a** towards the 4-pentynoic acid **5a** to form the five-membered cyclic product γ-methyl-ene-γ-butyrolactone **6a** (Table 3, entry 1), the tolerance of different other substituents at the α position of the acid group like esters **5b-c** (entries 2 and 3), benzyl **5d** (entry 4) and a propargyl group **5e** was evaluated (entry 5). In most cases, the corresponding products **6b-e** were obtained in good to quantitative yields except for substrate **5c** bearing a methyl group at the alkyne that bucks the trend. The latter result confirms that the process is limited to the use of terminal alkynes. Furthermore, a tandem reaction was attempted using the double acid-double alkyne **5f** that led to the double spiro-lactone compound **6f** in 23% yield as the minor product (entry 6) along with the decarboxylated product **7f** in 68% yield as the major product. Decarboxylation of **5f** to **7f** has previously been observed for the copper-catalyzed cyclization under basic conditions.[23]

The kinetic profile of this catalyzed reaction is similar to that of the two previously reported iridium-catalyzed alkynoic acid cyclizations, where the reaction is order is 1 with respect to the catalyst and is accompanied by a zeroth order dependence with respect to the substrates.[16–19] This leads to the presumption that a similar reaction mechanism could be operative in this case with the substrate coordinated to the coordination sphere of the metal in the resting state of the catalytic cycle (see Scheme 2).[19]

For rhodium-catalyzed intermolecular cyclizations with bimolecular substrates carboxylic acids and alkynes, a corresponding kinetic profile was demonstrated and it was shown that this substrate coordination involves firstly alkyne coordination to the metal center, followed by electrophilic attack of the terminal carbon at the metal-bound alkyne; in contrast to previously accepted mechanisms involving oxidative addition of the carboxylic acid O–H to the metal. In the case of iridium-catalyzed cyclizations, a similar first step of alkyne-coordination (**A** in Scheme 2) has been confirmed by both experimental and computational investigations.[32,36] However, the mechanism of propargylic protonation, namely intramolecular oxidative addition of acid O–H bond to form Ir[III]-hydride intermediate **B**, or alternatively, direct protonation of terminal alkyne carbon with carboxylic acid proton to yield intermediate **C** on the way to iridium(III) catalytic intermediate **D** (Scheme 2), remains ambiguous for iridium-based catalyzed intramolecular cyclization.[36]

Density functional theory (DFT) calculations at the dispersion corrected PCM(CH_3CN)-B3LYP–D3/def2-TZVPP//PCM(CH_3CN)-B3LYP–D3/def2-SVP level (see computational details in the supporting information) were carried out to gain more insight into the mechanism involved in the transformation. To this end, we computed the reaction profile for the conversion of the **5a** into **6a** catalyzed by a model of Ir(I)-

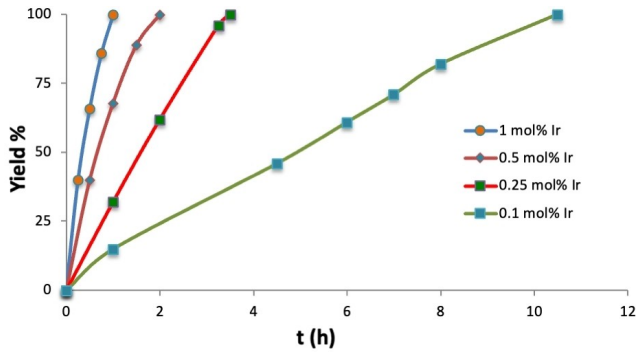
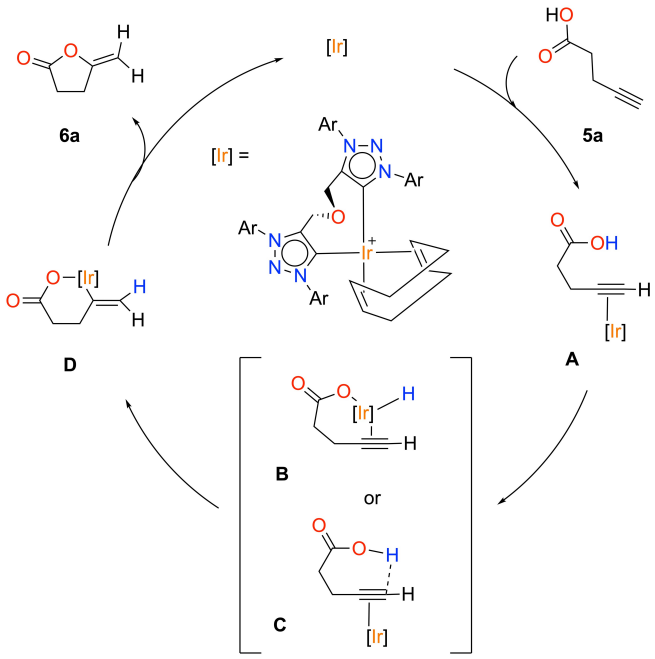


Figure 3. Time-dependent reaction profile for the catalytic formation of γ-methylene-γ-butyrolactone using catalyst **1a** at different catalyst loading (0.1–1 mol%).



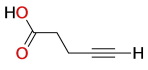
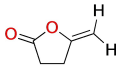
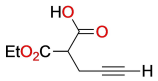
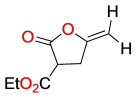
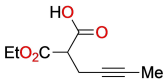
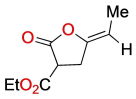
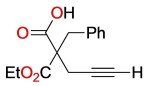
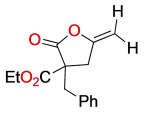
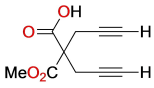
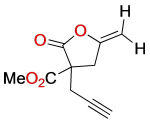
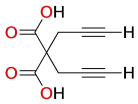
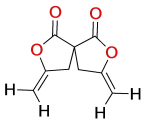
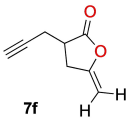
Scheme 2. Previously proposed catalytic cycle for intramolecular alkynoic acid cyclisation mediated by rhodium and iridium(I) catalyst precursors.[36,49,50]

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Table 3. Substrate scope for the cyclization of acid-alkynes catalyzed by **1a** to generate lactone derivatives.[a,b,c]

Entry	Substrate	Product	Time (h)	Yield (%)[b]
1	 **5a**	 **6a**	10.5	>99
2	 **5b**	 **6b**	24	73
3	 **5c**	 **6c**	24	<2
4	 **5d**	 **6d**	24	>99
5	 **5e**	 **6e**	24	98
6	 **5f**	 **6f**  **7f**	24	23 for **6f** and 68 for **7f**

[a] Reaction Conditions: NMR tube loaded with substrate 0.5 mmol, CD_3CN (0.75 mL) and catalyst **1a** (0.1 mol%), and reaction performed at 80 °C under stirring. [b] Yields were determined by ^1H NMR spectroscopy using 1,3,5-trimethoxybenzene as internal standard and on an average of two duplicates.

catalyst **1a** where the bulky Dipp substituents were replaced by phenyl groups (Figure 4).

Our calculations confirm that the reaction begins with the coordination of the triple bond of the alkyne to the active catalyst **INT1** to produce intermediate **INT2** in a highly exergonic step ($\Delta G = -12.1$ kcal/mol). This species evolves into Ir(III)-intermediate **INT3** (species **B** in Scheme 2) through **TS1**, a saddle point associated with the intramolecular oxidative addition of the O–H bond of the carboxylic acid moiety. All our attempts to locate the transition state associated with the formation of species **C** (Scheme 2) were fruitless. Both the computed barrier ($\Delta G^{\neq} = 21.2$ kcal/mol) and reaction energy ($\Delta G = -7.8$ kcal/mol) are compatible with the reaction conditions used in the experiments. From **INT3**, two alternative pathways can be envisaged, namely (i) cyclization (i.e. C–O bond formation) followed by reductive elimination or (ii) C–H bond formation followed by cyclization (forming intermediate **D** as outlined in Scheme 2). Our calculations indicate that the latter pathway is unfeasible given the rather high computed barrier for the hydride migration ($\Delta G^{\neq}$ ca. 40 kcal/mol kcal/mol). Instead, we found that the **INT3** can be easily transformed in **INT4** via **TS2**, a saddle point associated with the formation of the five-membered ring, with a feasible barrier of 21.7 kcal/mol. Finally, facile reductive elimination through **TS3** ($\Delta G^{\neq} = 12.0$ kcal/mol) produces the lactone **6a** with concomitant release of the active catalyst, which may enter a new catalytic cycle. The exergonicity of the last step ($\Delta G = -4.9$ kcal/mol) compensates for the slight endergonicity of the previous cyclization reaction, thus driving the transformation forward.

Conclusions

The catalytic activity of a series of mono-and bimetallic rhodium(I) and iridium(I) complexes bearing the carbon-ether-carbon (COC) ligand was evaluated against the cyclization of 4-

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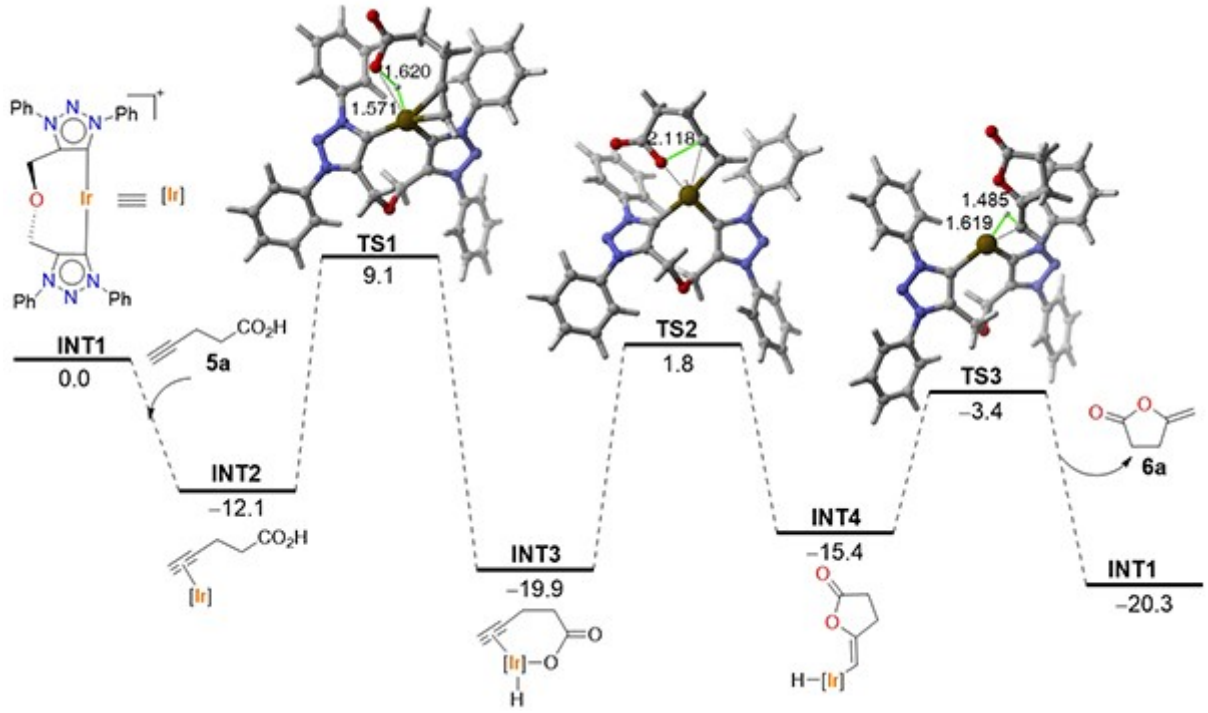


Figure 4. Computed reaction profile for the conversion of **5a** into **6a** catalyzed by Ir(I)-complex **INT1**. Relative free energies (ΔG) and bond distances are given in kcal/mol and angstroms, respectively. All data have been computed at the PCM(CH_3CN)-B3LYP–D3/def2-TZVPP//PCM(CH_3CN)-B3LYP–D3/def2-SVP level.

pentynoic acid to form γ-methylene-γ-butyrolactone. In this case, and in contrast to the previously reported related rhodium(I) derivatives, monometallic **1a** complex [Ir(cod)(**COC**)]PF_6 resulted as the best-performing catalyst, outperforming its dinuclear counterparts and those rhodium and iridium catalysts reported in the literature to date. The transformation is compatible with different functional groups in the initial substrate but limited to terminal alkynes. According to the DFT calculations, the process begins with the coordination of the alkyne moiety to the active catalyst followed by intramolecular cyclization and final reductive elimination.

Experimental

The standard operating procedure for the cyclization of 4-pentynoic acid reactions performed in this study is as follows:

To a J. Young NMR tube loaded with 4-pentynoic acid **5a** 0.5 mmol, 1,3,5-trimethoxybenzene as internal standard and the corresponding catalyst **1**–**4** or **5**--**6** at 0.1 mol% catalyst loading was added CD_3CN (0.75 mL). After ^1H NMR spectroscopy was performed at t = 0, then, a stirring bar was added under inert atmosphere, the J. Young NMR tube was placed in an oil bath and heated to 80 °C. The stirring bar was removed, and the yields were determined by ^1H NMR spectroscopy using 1,3,5-trimethoxybenzene as the internal standard.

Supporting Information Summary

The authors have cited additional references within the Supporting Information.

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Conflict of Interests

The authors declare no conflict of interest.

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Data Availability Statement

The data that support the findings of this study are available in the supplementary material of this article.

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