Homogeneous Catalyst

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Exploring Bis(cyclometalated) Ruthenium(II) Complexes as Active Catalyst Precursors: Room-Temperature Alkene–Alkyne Coupling for 1,3-Diene Synthesis**

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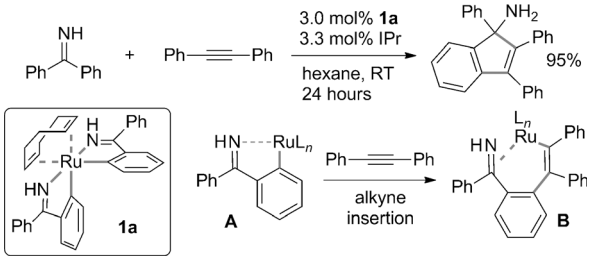
Abstract: *Described is the development of a new class of bis(cyclometalated) ruthenium(II) catalyst precursors for C–C coupling reactions between alkene and alkyne substrates. The complex [(cod)Ru(3-methallyl)$_2$] reacts with benzophenone imine or benzophenone in a 1:2 ratio to form bis(cyclometalated) ruthenium(II) complexes (**1**). The imine-ligated complex **1a** promoted room-temperature coupling between acrylic esters and amides with internal alkynes to form 1,3-diene products. A proposed catalytic cycle involves C–C bond formation by oxidative cyclization, β-hydride elimination, and C–H bond reductive elimination. This Ru^{II}/Ru^{IV} pathway is consistent with the observed catalytic reactivity of **1a** for mild tail-to-tail methyl acrylate dimerization and for cyclobutene formation by [2+2] norbornene/alkyne cycloaddition.*

Late-transition-metal-mediated C–H bond activation has become a popular method to generate metal–carbon σ bonds in metallacycle synthesis. These cyclometalation reactions are usually facilitated by a heteroatom (X)-based functional group nearby the target C–H bond.[1] Such directed C–H bond activation strategies have been widely used to generate cyclometalated late-transition-metal catalysts and catalyst precursors in various homogeneous catalytic processes.[2] Among reported metallacycles as catalyst precursors, a dominant majority feature one five- or six-membered chelating ring with a η^2-[C,X] ligand as both an anionic carbon donor and neutral heteroatom donor. By contrast, bis(cyclometalated) late-transition-metal complexes with two η^2-[C,X] ligands[3] are rarely exploited as organometallic catalysts.[4–6] We herein report the synthesis, structural characterization, and catalytic applications of several bis(cyclometalated) ruthenium(II) complexes with η^2-[C,N] and η^2-[C,O] ligands. The potential of these ruthenacycles as catalyst precursors is demonstrated by a catalytic room-temperature alkene–alkyne coupling to synthesize α,β,γ,δ-unsaturated esters and amides.

We recently reported a bis(cyclometalated) octahedral ruthenium(II) complex, [Ru(η^4-cod){η^2-HN=C(C_6H_5)C_6H_4}$_2$] (**1a**), as a catalyst precursor in ruthenium(II)-catalyzed [3+2] carbocyclization between NH ketimines and alkynes using the N-heterocyclic carbene ligand IPr (Scheme 1).[7] The proposed mechanism involves carbon–carbon bond formation by alkyne insertion into the Ru–C σ bond of a ruthenacycle intermediate (**A**→**B**), presumably facilitated by the IPr ligand which has replaced the cod ligand on the ruthenium center. Thus, the substrate-derived η^2-[C,N] imine ligands appear to play the dual role of a ligand and spectator ligand, eventually incorporated into the cyclization product and replaced by incoming ketimine substrates by cyclometalation. It is noteworthy that **1a** did not react with alkyne substrates without the added IPr ligand, thus suggesting significant ligand effect on its stability and reactivity. We envision that **1a** and its structural analogues can be further explored as ruthenium(II) catalyst precursors with η^2-[C,X] ligands solely as spectator ligands which occupy four of the six coordination sites and affect reactions occurring at the other two *cis* coordination sites (Scheme 2; **C**). In particular, ancillary ligands (L) can be replaced by alkene/alkyne substrates through π complexation (**C**→**D**), thus setting the stage for C–C bond formation by oxidative cyclization (**D**→**E**).[8] The latter transformation is a key step in a number of ruthenium-catalyzed C–C coupling reactions such as alkene–alkyne (enyne) couplings for diene synthesis,[9] [2+2] or [2+2+2] cycloadditions,[10] and [2+2+1] cycloadditions such as the Pauson–Khand reaction.[11] With easily accessible η^2-[C,X] ligands through C–H activation, bis(cyclometalated) ruthenium(II) complexes may serve as an attractive alternative to existing ruthenium catalysts,[12] thus allowing modular catalyst design and tunable ligands for catalyst efficiency and selectivity.



Scheme 1. Proposed C–C bond formation by alkyne insertion into Ru–C bond of ruthenacycle intermediates for ruthenium(II)-catalyzed [3+2] imine/alkyne carbocyclization.[7]

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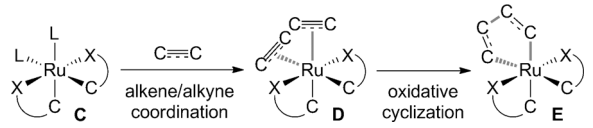
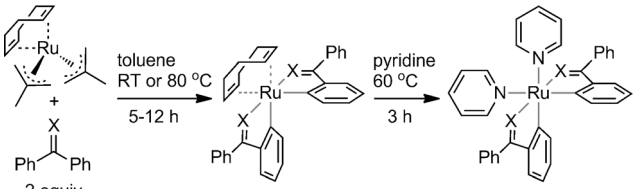


Scheme 2. Envisioned C–C bond formation by oxidative cyclization with bis(cyclometalated) ruthenium(II) complexes having two η^2-[C,X] ligands.

As reported previously,[7] the complex **1a** was synthesized by room-temperature cyclometalation of benzophenone imine with the commercially available ruthenium(II) π-allyl complex [(cod)Ru(η^3-methallyl)$_2$] in a 2:1 ratio (Scheme 3).



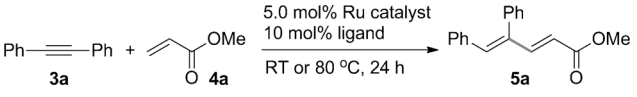
Scheme 3. Synthesis of bis(cyclometalated) ruthenium(II) complexes with η^2-[C,N] benzophenone imine and η^2-[C,O] benzophenone ligands.

The bis(cyclometalated) ketone analogue [Ru(η^4-cod){η^2-OC(C_6H_5)C_6H_4}$_2$] (**1b**) was synthesized using benzophenone in a similar fashion, albeit with lower reactivity and requiring heating at 80 °C for complete conversion. The chelating cod ligand in both **1a** and **1b** could be replaced by two pyridine ligands by heating in neat pyridine at 60 °C to form the bis(pyridine)-ligated **2a** and **2b**, respectively. The solid-state structures of **1a**,[7] **1b**, **2a**, and **2b** were determined by single-crystal X-ray diffraction (see the Supporting Information for details). All four of these bis(cyclometalated) ruthenium(II) complexes displayed a near-octahedral ruthenium(II) center with two *cis* η^2-[C,X] ligands, where the two N or O atoms were *trans* to each other and the two Ru–C σ bonds were *cis* to each other.[7,13]

The catalytic activity of bis(cyclometalated) ruthenium(II) complexes was evaluated by intermolecular alkene–alkyne coupling between diphenylacetylene (**3a**) and methyl acrylate (**4a**) to form the (2*E*,4*Z*)-1,3-diene product **5a** (Table 1).[9,14–16] By using 5 mol % of [(cod)Ru(η^3-methallyl)$_2$] (**6**) as a catalyst precursor, with no added ligands, led to only 12 % conversion after heating at 80 °C for 24 hours in toluene (entry 1). By contrast, the in situ generated ruthenacycle **1a**, from preactivation of **6** with 2 equivalents of benzophenone imine, effectively promoted formation of **5a** in quantitative yield (entry 2). Compared to the benzophenone imine ligand, much lower reactivity was observed when catalyst preactivation was carried out using other aromatic compounds which are capable of generating bis(cyclometalated) ruthenium(II) complexes.[13] For example, using 2-phenylpyridine and benzophenone ligands both resulted in lower than 10 % conversion (entries 3 and 4; see the Supporting Information for complete results).

Gratifyingly, the in situ formed **1a** was sufficiently active at room temperature, thus promoting quantitative formation of **5a** after 24 hours with a 5 mol % catalyst loading (Table 1, entry 5). To the best of our knowledge, this reaction is the first example of catalytic room-temperature acrylate–alkyne coupling to form α,β,γ,δ-unsaturated esters, and complements other catalyst systems for mild enyne couplings.[15,16] Notably, skipping the 80 °C preactivation led to much lower catalyst reactivity (entry 6). Thus, the isolated **1a** was used as a catalyst precursor to further evaluate the solvent effect, with the highest reactivity observed in toluene and THF (entries 7–11). Under optimized reaction conditions, room-temperature coupling between **3a** (1.0 equiv) and **4a** (2.0 equiv)[17] proceeded smoothly in toluene with 5.0 mol % **1a**, thus giving **5a** in quantitative yield as determined by GC analysis (entry 7). The pyridine-ligated bis(imine) complex **2a** was less stable than **1a** in solution phase, but displayed comparable catalytic activity (entry 13). By contrast, the bis(ketone) analogues **1b** and **2b** were virtually unreactive as catalyst precursors (entries 12 and 14). Such reactivity distinction is consistent with the mechanistic hypothesis that cod or pyridine ligands can be be replaced by alkene/alkyne substrates (Scheme 2; **C**→**D**), thus having little effect on catalytic activity beyond the initial stage of catalyst preactivation. In contrast, the η^2-[C,X] imine or ketone ligands are expected to stay on the ruthenium center throughout catalytic cycles and play a dominant role on catalyst activity.

Table 1: Development of the catalytic reactions.[a]

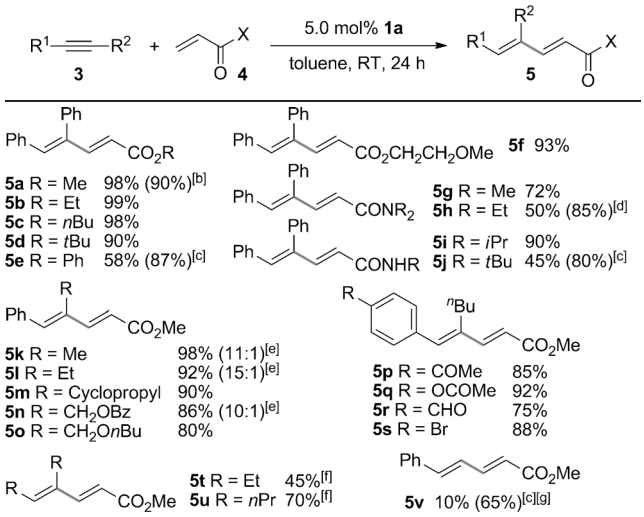


Entry	[Ru]	Ligand	Solvent	Method[b]	*T* [°C]	Yield [%][c]
1	**6**	none	toluene	A	80	12
2	**6**	Ph_2C=NH	toluene	B	80	>98
3	**6**	2-phenylpyridine	toluene	B	80	8
4	**b**	Ph_2C=O	toluene	B	80	<5
5	**6**	Ph_2C=NH	toluene	B	RT	>98
6	**6**	Ph_2C=NH	toluene	A	RT	15
7	**1a**	none	toluene	A	RT	>98
8	**1a**	none	THF	A	RT	96
9	**1a**	none	DME	A	RT	66
10	**1a**	none	DMF	A	RT	93
11	**1a**	none	hexane	A	RT	82
12	**1b**	none	toluene	A	RT	<2
13	**2a**	none	toluene	A	RT	>98
14	**2a**	none	toluene	A	RT	<2

[a] Reaction conditions: **3a** (0.20 mmol, 1 equiv), **4a** (2.0 equiv), Ru catalyst (0.05 equiv), ligand (0.10 equiv), solvent (0.5 mL), room temperature (20–22 °C) or 80 °C, 24 h. [b] Mixing methods: A: All components were mixed without pre-activation; B: The ruthenium precursor **6** and the ligand were added to toluene and stirred at 80 °C for 30 min; the mixture was then cooled to room temperature and then **3a** and **4a** were added. [c] Yields determined by GC using *n*-dodecane as an internal standard. DMF = *N*,*N*-dimethylformamide, THF = tetrahydrofuran.

With the standard reaction conditions established, various internal alkynes and acrylic esters or amides were studied for ruthenium-catalyzed room-temperature alkene–alkyne coupling (Table 2). Coupling between **3a** and unsubstituted alkyl acrylates proceeded smoothly to form the 1,3-diene products **5a–d** and **5f** in over 90 % yield and with exclusive stereoselectivity for the 2*E*,4*Z* isomers. For the phenyl acrylate

Table 2: Scope of the catalytic alkene–alkyne coupling.[a]

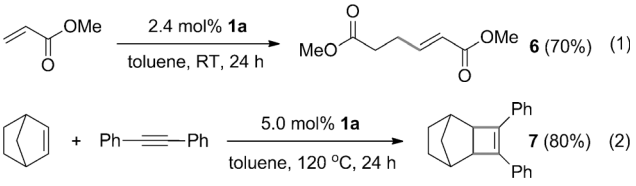


[a] Reaction conditions: **3** (0.20 mmol, 1.0 equiv), **4** (2.0 equiv), **1a** (0.050 equiv), toluene (0.5 mL), 20–22 °C, 24 h. The reported yields are an average of the yields of the isolated products from two runs. [b] Yield of isolated product under scale-up conditions: **3** (20 mmol, 1.0 equiv), **4** (2.0 equiv), **1a** (0.010 equiv), toluene (6.0 mL), 22 °C, 48 h. [c] Using **2a** as catalyst precursor. [d] Reactions at 60 °C. [e] Combined yield of two regioisomers (ratios determined by NMR analysis). The structure of the major isomer is shown. [f] Using 0.20 mmol methyl acrylate as limiting reagent and 2.0 equiv of alkyne. [g] Yield of the isolated major stereoisomer, which was isolated from a 5:1 mixture; minor isomer was not purified.

coupling product **5e**, the yield was improved from 58% to 87% by replacing **1a** with **2a** as the catalyst precursor. Such reactivity enhancement is likely due to facile catalyst activation by substrate replacement of the more labile pyridine ligands compared to the chelating diene ligand. When coupling between **3a** and **4a** was scaled up from 0.2 mmol to 20 mmol, the loading of **1a** could be reduced to 1.0 mol% to acquire **5a** in 90% yield upon isolation (4.8 gram purified product) after a reaction time of 48 h. Coupling between **3a** and *N*,*N*-dimethyl acrylamide gave the product **5g** in 72% yield, but heating at 60 °C was needed to improve the yield of the *N*,*N*-diethyl product **5h** to 85%. Compared to less reactive *N*,*N*-dialkylacrylamides, *N*-isopropyl- and *N*-*tert*-butylacrylamide reacted with **3a** in good reactivity to form the products **5i** and **5j**, respectively, although the latter required **2a** as the catalyst precursor for satisfactory yield. The scope of alkyne substrates was studied by coupling reactions with methyl acrylate (**4a**) to give the products **5k**–**v**. High reactivity and regioselectivity was observed for phenylacetylene derivatives with alkyl substituents (**5k**–**s**), thus favoring the formation of the 4-alkyl-5-aryl regioisomer in greater than 10:1 selectivity. The mild reaction conditions allow good compatibility with functional groups such as acyl, formyl, and Br substituents (**5p**, **5r** and **5s**), thus providing synthetic handles for further functional-group transformations. Aliphatic internal alkynes such as 3-hexyne and 4-octyne displayed lower reactivity than aromatic alkynes, and a 2:1 alkyne/acrylate stoichiometry was used to obtain the coupling products **5t** and **5u** in moderate yields. Coupling between **4a** and terminal alkynes generally suffered from low reactivity and gave a complex mixture of products.[18] Nevertheless, coupling between **4a** and phenylacetylene was effectively catalyzed by **2a** to form **5v** with *E*,*E* stereoselectivity in 65% yield upon isolation.[14b]

Three types of reaction mechanisms have been proposed for ruthenium-catalyzed alkene–alkyne couplings to form 1,3-dienes:[14,19] 1) C–C bond formation by alkene–alkyne oxidative cyclization (Scheme 2), followed by β-hydride elimination and C–H reductive elimination (Path 1); 2) alkyne insertion into a ruthenium hydride, followed by alkene insertion into the resulting ruthenium–alkenyl bond and subsequent β-hydride elimination (Path 2); 3) sp^2 C–H bond activation of an alkene, followed by alkyne insertion into the ruthenium–alkenyl bond, and C–H bond formation by either reductive elimination or protonation of the Ru–C bond (Path 3). Although the latter two pathways cannot be completely ruled out, the oxidative cyclization mechanism (Path 1) is most consistent with the observed regio- and stereochemistry in coupling products. In particular, high regioselectivity with nonsymmetric alkyne substrates (**5k**–**s**) supports C–C bond formation by either oxidative cyclization (Path 1) or alkyne insertion into a ruthenium–alkenyl bond (Path 3), and not by alkyne insertion to Ru–H (Path 2).[19] The complete lack of 2*Z* stereoisomers as coupling products also argues against the proposed alkene C–H activation stereochemistry in Path 3, which should favor 2*Z* isomers by ester- or amide-directed C–H activation/cyclometalation.

The proposed oxidative cyclization pathway has prompted us to extend our study to other mechanistically related C–C couplings using the current catalyst system. Thus, **1a** was found to catalyze the room-temperature dimerization of methyl acrylate with high efficiency and exclusive tail-to-tail regioselectivity [Eq. (1)].[17] In addition, a [2+2] norbornene/alkyne cycloaddition was effectively catalyzed by **1a** at 120 °C [Eq. (2)], which further supports the proposed Ru^{II}/Ru^{IV} catalytic cycle involving oxidative cyclization.[19,20]



In summary, we have developed a new class of bis(cyclometalated) ruthenium(II) catalyst precursors with readily available η^2-[C,X] ligands derived from aromatic NH ketimines and ketones. The catalytic activity of the bis(imine) complex **1a** was evaluated in several catalytic C–C coupling reactions which are proposed to proceed by $Ru^{II}/Ru(IV)$ catalytic cycles involving oxidative cyclization. A room-temperature alkene–alkyne coupling was promoted to form α,β,γ,δ-unsaturated esters and amides with high regio- and stereoselectivities, good functional-group tolerance, and very high catalyst efficiency in a representative gram-scale synthesis. The major limitation of the current catalyst system is the limited scope of alkene substrates,[21,22] and we aim to improve this scope through a more systematic study on structure–reactivity correlations of bis(cyclometalated) ruthenium(II) complexes with various η^2-[C,X] ligands.

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[22] Preliminary results from DFT calculations suggest involvement of hydrogen-bonding interactions between cyclometalated imine NH moieties and carbonyl groups from the acrylate substrates, and could contribute to the reactivity dependence on alkene substrates and classes of η^2-[C,X] ligands. Results of this computational study on proposed catalytic mechanisms will be reported separately.