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Ruthenium-catalyzed oxidation of a carbon–carbon triple bond: facile syntheses of alkenyl 1,2-diketones from alkynes†

Ting-Chuan Hu, Pei-I Hsiao, Tsang-Hsiu Wang, Yu-Wen Yang, Chih-Yun Chang, Yuan-Hsun Wu, Wei-Chen Sun, Ming-Shiuan Yu, Ching-Yu Lee and Yih-Hsing Lo*

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A new oxidation procedure of alkynes catalyzed by $Tp(PPh_3)(CH_3CN)Ru$ -Cl is presented, which provides an efficient way to obtain alkenyl 1,2-diketones *via* ruthenium alkenyl 1,2-diketone intermediates. In contrast, the analogous reactions with $Tp(PPh_3)(PhCN)Ru$ -Cl gave rise to the ruthenium metallacycle complexes.

1,2-Diketones are very important structural moieties in many biologically interesting compounds¹ and are versatile building blocks in organic synthesis.² The synthesis of simple alkyl- and aryl-substituted 1,2-diketones has been extensively investigated, and most popular methods are the oxidations of alkynes.³ By contrast, there are relatively few reports on the synthesis of alkenyl 1,2-diketones. A fairly general method of alkenyl 1,2-diketone is condensation of 2,3-butanedione with aldehydes;⁴ nevertheless, it only provides acceptable results for the condensation of 2,3butanedione with activated aldehydes such as enals. Starting from benzotriazole derivatives, some alkenyl 1,2-diketones have been obtained in a few steps.⁵ So far, there is no general way to synthesise alkenyl 1,2-diketones, which start from simple precursors, and is generally useful for preparative purpose.

Ruthenium complexes play significant roles in many catalytic reactions, such as olefin metathesis,⁶ polymerization⁷ and asymmetric hydrogenation.⁸ A better understanding of the mechanism of these reactions revealed the role of the metal and led to extensive applications of ruthenium in organic synthesis. To further expand the scope of these applications, it is important to explore new reactivity of various complexes of ruthenium. Recently, we have reported the ruthenium-catalyzed dimerization of some terminal alkynes HC=CR in organic and aqueous media.⁹ As a continuation of this previous work, we report a new catalytic transformation of alkynes into alkenyl 1,2-diketones by using Tp(CH₃CN)(PPh₃)Ru–Cl¹⁰ {Tp = HB(pz)₃, pz = pyrazolyl} catalyst.

 Table 1
 Catalytic transformation under various conditions^a

H- -Ph	H Ph	0 0 → Ph H CH ₃ CN ^{\\\\} 2a	Tp Ru_CI PPh ₃ 1a
Entry	Solvent	Conditions	Yield (%) ^b
1 2 3 4 5	$\begin{array}{c} CH_2Cl_2\\ Toluene\\ CH_3OH\\ CH_2Cl_2\\ CH_2Cl_2\\ CH_2Cl_2 \end{array}$	Air Air Air N ₂ Air, in the dark	99 81 32 Dimer ^e 99

^{*a*} A mixture of Tp(PPh₃)(CH₃CN)Ru–Cl (**1a**) (2.0 mol %) and alkyne (0.06 M) in the selected boiling solvent was stirred for 4 h. ^{*b*} Yields are for isolated products. Product has been determined by NMR spectroscopy. ^{*c*} The head to head dimmer: (*E*)-1,4-diphenyl-1-buten-3-yne.

First, we examined the effect of solvents and gases on catalytic reactions. Treatment of the ruthenium chloride complex $Tp(PPh_3)(CH_3CN)Ru-Cl$ (1a) with an excess of HC=CPh in CH₂Cl₂ at reflux under atmosphere for 4 h exclusively produced the alkenyl 1,2-diketone product (E)-1,4-diphenylbut-3-ene-1,2dione (2a) (Table 1). Under similar conditions, the conversion decreases from 99% in CH_2Cl_2 to 81% in toluene and 32% in CH₃OH (entries 1-3) respectively. The high conversion in CH₂Cl₂, could be due to the high solubility of the catalyst. Significantly, a similar reaction was performed under nitrogen instead of atmosphere (entry 4) revealing oxygen as an oxidant and gave the head to head dimmer (E)-1,4-diphenyl-1-buten-3yne¹¹ Commonly, hydrocarbons reacting with O₂ are required for the photo-activation of O₂ in free radical oxidation, and a number of ruthenium complexes have been used as sensitizers in photo reactions involving O₂.¹² However, we carried out the reaction in the dark and found no effect on the formation of 2a (entry 5). Thus, this oxidation was not a free radical oxidation. The ruthenium metal center may assist this oxidation by possibly providing a coordination site for O_2 .

Moreover, we prepared various alkynes to examine the scope of catalytic reactions. These catalytic reactions are applicable to the replacement of the substrates of R groups including electron-withdrawing groups (R = 4-CF₃Ph and 4-FPh). The corresponding

Department of Applied Physics and Chemistry, Taipei Municipal University of Education, Taipei, 10610, Republic of China. E-mail: yhlo@tmue.edu.tw; Fax: (886)-2-2389-7641

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alkenyl 1,2-diketones **2b–c** were obtained in good yields; however, possessing electron-donating groups (R = 4-CH₃Ph and 4-CH₃OPh) were poor substitutes to give the corresponding alkenyl 1,2-diketones **2d–e** in low yields (Scheme 1).



Scheme 1

We also carried out the reaction at room temperature for 1 h to give a coordinatively unsaturated complex Tp(PPh₃)Ru–Cl (**3**) as monitored by ³¹P{¹H} NMR spectroscopy (Scheme 2), and a resonance was at δ 34.5 (*cf.* **1a** exhibits a signal at δ 51.1).¹³ Unfortunately, complex **3** could not be isolated from the mixture of the product due to its thermal instability. Furthermore, we carried out the catalytic reactions for 3 h at room temperature, and then it afforded the ruthenium alkenyl 1,2-diketone complex Tp(PPh₃)Ru-{C(Ph)=CHC(O)}C(O)(Ph) (**4a**) (Scheme 2). The reaction of **4a** with protic acid breaks the Ru–C bond and yields compound **2a**, revealing that **4a** is an intermediate in this formation.



The spectroscopy data was sufficient to unequivocally assign the structures of **2a** and **4a**. The ¹H NMR spectrum of **2a** displays well-resolved doublets at δ 7.82 with $J_{\text{H-H}} = 16.2$ Hz and δ 6.87 with $J_{\text{H-H}} = 16.2$ Hz. The ¹³C {¹H} NMR exhibits two carbonyl carbons at δ 194.2 and 193.8 and exhibits two olefinic carbons at δ 151.3 and 149.5. In the EI-MS mass spectrum, the parent peak is observed at m/z = 236.1 indicating the molecular weight of **2a**. In addition, the IR spectrum of **4a** shows two strong bands at 1642 and 1612 cm⁻¹ due to two C=O groups, and a medium intensity absorption is assigned at 1537 cm⁻¹ resulting from the C=C. Owing to the vinylic proton, the ³¹P{¹H} NMR spectrum shows a singlet

resonance at δ 58.3 and the ¹H NMR spectrum displays a singlet resonance at δ 6.71 respectively. In the ¹³C NMR spectrum, the doublet resonance at δ 167.4 with ² $J_{P,C}$ = 12.3 Hz is assigned to the vinyl C α . Similarly, the *p*-tolyl derivative Tp(PPh₃)Ru-{C(C₆H₄Me)=CHC(O)}C(O)(C₆H₄Me) (**4b**) was also isolated, and the single crystal was obtained from a mixture of solvent (CH₂Cl₂/MeOH). X-Ray analysis revealed that the ruthenium atom connected with the triphenylphosphine, and the carbon and oxygen atoms in the alkenyl diketone were moiety (Fig. 1).‡ The bond lengths of C(37)–C(38) (1.400(5) Å), C(28)–O(1) (1.285(4) Å) and C(29)–O(2) (1.215(5) Å) are typical of double bonds.



Fig. 1 An ORTEP drawing of **4b** with thermal ellipsoids shown at the 50% probability level. Selected distances (Å) and angles (°): Ru(1)–O(1) 2.060(2), O(1)–C(28) 1.285(4), C(28)–C(37) 1.385(5), C(37)–C(38) 1.400(5), C(38)–Ru(1) 1.986(3), O(2)–C(29) 1.215(5); Ru(1)–O(1)–C(28) 112.6(2); O(1)–C(28)–C(37) 119.4(3), C(28)–C(37)–C(38) 115.3(3), C(37)–C(3)–Ru(1) 112.5(2), C(38)–Ru(1)–O(1) 80.35(11).

A rational and simplified mechanism for the formation of 2a is proposed in Scheme 2. The catalytic cycle begins by losing the CH₃CN ligand and then forms a coordinatively unsaturated species 3. Subsequent a coordinatively unsaturated alkyne complex A is formed by the liberation of the HCl. The next process proceeds with A that is transformed into an intermediate B [cisalkynyl(π -alkyne)] via π -coordination of a second terminal alkyne to the Ru. Intramolecular migration of the alkynyl ligand to the π -alkyne in **B** forms an enyne (intermediate **C**). Followed by oxidation of C, the ruthenium metal center may serve to assist this oxidation by possibly providing a coordination site leading to **D**. Then the intermediate **D** transforms to the ruthenium alkenyl 1,2-diketone product 4a. Protonation of 4a with HCl causes the Ru-C bond cleavage and then affords complex 3 and alkenyl 1,2diketone 2a, respectively. The detailed mechanism is currently under investigation.

On the other hand, we examined two other catalysts to assess the effect of the ligands on the catalysts. Intriguingly, the reaction of Tp(PPh₃)(PhCN)RuCl (1b)¹⁴ with excess HC==CPh in CH₃OH at reflux for 4 h did not yield the expected compound 2a but gave the yellow ruthenium alkenyl imine complex Tp(PPh₃)Ru{C(OCH₃)=C(Ph)C(Ph)=NH} (5) in 46% yield (Scheme 3) instead. Furthermore, no reaction was observed in CH₂Cl₂, THF and CHCl₃. The IR spectrum of 5 shows



the disappearance of a strong CN (2214 cm⁻¹) band and the appearance of the characteristic bands at 3252 cm⁻¹, assigning to v(NH). The ¹H NMR spectrum displays a characteristic singlet resonance at δ 12.68 and assigns to the NH proton of the imine group; in addition, a singlet resonance at δ 3.77 is attributed to the three methoxyl protons. The ³¹P NMR spectrum of the complex **5** displays a singlet at δ 57.7; in the EI-MS mass spectrum, the parent peak is observed at m/z = 812.2 indicating an additional CH₃OH and an eliminated HCl from **1b**.

The structure of **5** was further confirmed by a solid-state singlecrystal X-ray diffraction analysis (Fig. 2).‡ It is apparent that the C–C bond formation between C_β of vinylidene moiety and the carbon of benzylnitrile has occurred. The N(7)–Ru(1)–C(42) bite angle is 76.79(8)°. The Ru(1)–N(7) and Ru(1)–C(42) bond lengths are 2.0334(18) and 2.032(2) Å, respectively. The C(42)–C(35) and C(28)–N(7) bond lengths are 1.404(3) and 1.307(3) Å, respectively, compared with those found for the C–C and C–N double bond lengths.



Fig. 2 An ORTEP drawing of 5 with thermal ellipsoids shown at the 50% probability level. Selected distances (Å) and angles (°): Ru(1)–N(7) 2.0334(18), N(7)–C(28) 1.307(3), C(28)–C(35) 1.422(3), C(35)–C(42) 1.404(3), C(42)–Ru(1) 2.032(2); Ru(1)–N(7)–C(28) 118.79(13); N(7)–C(28)–C(35) 115.3(2), C(28)–C(35)–C(42) 112.68(19), C(35)–C(42)–Ru(1) 116.32(16), C(42)–Ru(1)–N(7) 76.79(8).

The formation of **5** can be accounted for by the mechanism depicted in Scheme 4. The reaction of **1b** with phenylacetylene gives the cationic vinylidene complex **D**, and chloride is the counteranion of the complex **D**. It is well-known that C_{α} of a vinylidene ligand is susceptible to nucleophilic attack¹⁵ particularly



by a nitrogen or an oxygen donor and then gives a Fischer type carbene complex. The nucleophilic attack of MeOH is followed by formation of a C_{β} -C bond, and then an intramolecular coordination of the iminyl nitrogen to the Ru generates the carbene intermediate E. Finally, the HCl is eliminated form E and affords the complex **5**. Compared to CH₃CN, PhCN ligand is apt to expose the C_{α} atom of the ruthenium vinylidene complex that leads to much easier attack at C_{α} by other nucleophiles.

Moreover, the reaction of 1b with excess of HC = C(p-MeC₆H₄) in MeOH at reflux for 4 h did not yield the expected alkenyl imine complex $Tp(PPh_3)Ru\{C(OCH_3)=C(p-1)\}$ MeC_6H_4)C(Ph)=NH} but gave the alkenyl ketone $Tp(PPh_3)Ru\{C(p-MeC_6H_4)=CHC(O)CH_2(p-MeC_6H_4)\}$ (6)in high yields (Scheme 3) instead. Characterization of 6 was performed on the basis of ¹H and ¹³C {¹H} NMR, IR, FAB-MS, elemental analysis and X-ray diffraction analysis. The IR spectrum shows the presence of a C=C and C=O group at ca. 1567 and 1618 cm⁻¹, respectively. The ³¹P NMR spectrum displays a singlet at δ 57.1. The ¹H NMR spectrum displays two doublet resonances at δ 3.45 and 3.73 with a coupling constant of $J_{\text{H-H}} = 16.2$ Hz, it is assigned to the CH₂Ph group. Another singlet resonance is at δ 6.72 and is assigned to the CH group. In the ¹³C NMR spectrum, the doublet resonance at δ 168.1 with ${}^{2}J_{P-C} = 14.0$ Hz is assigned to the vinyl C_{α}. A similar alkenyl ketone structure with a five-membered ring has also been reported recently.¹⁶ Recently, there have been considerable efforts devoted to the understanding of the origins of the selectivity and the development of alkynes coupling.¹⁷ The solid state structure of 6 contains two crystallographically distinct molecules, although there is no essential structural difference between them (Fig. 3).‡ The bond lengths of C(37)-C(38) (1.397(5) Å) and C(28)-O(1)(1.278(4) Å) are typical double bonds.

In conclusion, the treatment of Tp(PPh₃)(CH₃CN)Ru–Cl with terminal alkynes afforded the alkenyl 1,2-diketone products *via* ruthenium alkenyl 1,2-diketone intermediates, whereas the analogous reactions with Tp(PPh₃)(PhCN)Ru–Cl gave rise to the ruthenium metallacycle complexes. To our knowledge, this is the first example that the ruthenium chloride complex with terminal alkynes yields an alkenyl 1,2-diketone product. A new oxidation of alkynes has been developed. This transformation showed high efficiency. Further investigations on mechanistic understanding and substrate scope expanding are ongoing



Fig. 3 An ORTEP drawing of 6 with thermal ellipsoids shown at the 50% probability level. Selected distances (Å) and angles (°): Ru(1)–O(1) 2.086(3), O(1)–C(28) 1.278(4), C(28)–C(37) 1.404(5), C(37)–C(38) 1.397(5), C(38)–Ru(1) 1.999(3); Ru(1)–O(1)–C(28) 113.5(2); O(1)–C(28)–C(37) 118(3), C(28)–C(37)–C(38) 115.3(3), C(37)–C(38)–Ru(1) 113.4(3), C(38)–Ru(1)–O(1) 79.4(13).

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Notes and references

‡ Data for **4b**: $C_{45}H_{40}BN_6O_2PRu\cdot0.79(C_7H_8)$, M = 912.29, triclinic, space group $P\overline{1}$, a = 10.1964(4) Å, b = 12.4327(4) Å, c = 18.4795(7) Å, $\alpha = 89.086(2)^\circ$, $\beta = 77.852(2)^\circ$, $\gamma = 83.264(2)^\circ$, V = 2274.27(14) Å³, T = 200(2)K, Z = 2, 15791 reflections collected, 7759 unique ($R_{int} = 0.0365$) which were used in all calculations. $R_1 = 0.0392$ for $I > 2\sigma$. The final wR_2 was 0.0915 (all data). Data for **5**: $C_{43}H_{39}BN_7OPRu$, M = 812.66, monoclinic, space group P21/n, a = 11.7013(7) Å, b = 14.1739(9) Å, c = 23.4437(13) Å, $\beta = 104.301(2)^\circ$, V = 3767.7(4) Å³, T = 200(2)K, Z = 4, 21592 reflections collected, 6479 unique ($R_{int} = 0.0310$) which were used in all calculations. $R_1 = 0.0285$ for $I > 2\sigma$. The final wR^2 was 0.0737 (all data). Data for **6**: $C_{45}H_{42}BN_6OPRu$, M = 825.70, monoclinic, space group P21/n, a = 24.6370(10) Å, b = 10.0656(4) Å, c = 32.0278(13) Å, $\beta = 91.513(2)^\circ$, V = 7939.7(6) Å³, T = 200(2)K, Z = 8, 53461 reflections collected, 13970 unique ($R_{int} = 0.0574$) which were used in all calculations. $R_1 = 0.0457$ for $I > 2\sigma$. The final wR_2 was 0.148 (all data).

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