

Electronic Supporting Information

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

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Contents

Experimental Procedures

Table S1. Crystallographic data for **4b**

Table S2. Crystallographic data for **5**

Table S3. Crystallographic data for **6**

Experimental Procedures

General Procedure. All manipulations were performed under nitrogen using vacuum-line, drybox, and standard Schlenk techniques. CH_3CN and CH_2Cl_2 were distilled from CaH_2 and diethyl ether and THF from Na/ketyl. All other solvents and reagents were of reagents grade and were used without further purification. NMR spectra were recorded on a Bruker AC-300 instrument at 300 MHz (^1H), 121.5 MHz (^{31}P), 267.45 MHz (^{11}B) or 75.4 MHz (^{13}C) using SiMe_4 , $\text{BF}_3 \cdot \text{Et}_2\text{O}$ or 85% H_3PO_4 as standard or on an Avance 500 FT-NMR spectrometer. FAB mass spectra were recorded on a JEOL SX-102A spectrometer. Elemental analyses and X-ray diffraction studies were carried out at the Regional Center of Analytical Instrument at National Taiwan Normal University.

General Procedure of the Ruthenium-Catalyzed Oxidation of $\text{RC}\equiv\text{CH}$ ($\text{R} = \text{Ph}$ and *p*-tolyl).

In a 25 mL Schlenk tube equipped with a Teflon stopcock, the ruthenium catalyst **1a** (2 mol %) in 10 mL of CH_2Cl_2 . Excess alkyne (0.60 mmol) was added to the solution, and the reaction mixture was heated under an air atmosphere for 4 h. After that time, the solution was evaporated under high vacuum. The residue was extracted with Et_2O , and the Et_2O solution was chromatographed on silica gel (*n*-hexane/ Et_2O) in air. The rotary evaporation led to the products as a pale-yellow oil. For (*E*)-1,4-diphenylbut-3-ene-1,2-dione (**2a**, 99 % yield): δ 8.10-6.80 (m, Ph), 7.82 (d, $J = 16.2$ Hz, =CHPh), 6.87 (d, $J = 16.2$ Hz, =CH-C=O). ^{13}C NMR (CDCl_3): δ 194.2 (CO), 193.8 (CO), 151.3(=CH(CO)), 149.5 (=CHPh), 137.3, 132.2, 129.7, 129.4, 129.2, 127.3, 124.4 (Ph carbons). GC-MS m/z 236.1 (M^+).

For (*E*)-1,4-di(4-trifluorotoluene)but-3-ene-1,2-dione (**2b**, 87 % yield): ^1H NMR (CDCl_3): δ 8.02-7.13 (m, Ph), 7.94 (d, $J = 16.0$ Hz, =CHPh), 6.43 (d, $J = 16.0$ Hz, =CH-C=O). GC-MS m/z 372.1 (M^+).

For (*E*)-1,4-di(4-fluorotoluene)but-3-ene-1,2-dione (**2c**, 81 % yield): ^1H NMR (CDCl_3): δ 7.94-6.98 (m, Ph), 7.86 (d, $J = 16.1$ Hz, =CHPh), 6.38 (d, $J = 16.1$ Hz, =CH-C=O). GC-MS m/z 270.1 (M^+).

For (*E*)-1,4-di(*p*-tolyl)but-3-ene-1,2-dione (**2d**, 43 % yield): ^1H NMR (CDCl_3): δ 7.97-6.80 (m, Ph), 7.82 (d, $J = 16.1$ Hz, =CHPh), 6.30 (d, $J = 16.1$ Hz, =CH-C=O), 2.34 (s, 3H, CH_3), 2.30 (s, 3H, CH_3). ^{13}C NMR (CDCl_3): δ 189.1 (CO), 187.2 (CO), 151.1 (=CH(CO)), 149.6 (=CHPh), 139.1, 134.6, 128.9, 128.1, 127.4, 127.1, 124.3 (Ph carbons). GC-MS m/z 264.1 (M^+).

For (*E*)-1,4-di(anisole)but-3-ene-1,2-dione (**2e**, 32 % yield): ^1H NMR (CDCl_3): δ 7.87-6.76 (m, Ph), 7.81 (d, $J = 16.3$ Hz, =CHPh), 6.26 (d, $J = 16.3$ Hz, =CH-C=O), 3.54 (s, 3H, CH_3), 3.49 (s, 3H, CH_3). GC-MS m/z 296.1 (M^+).

Preparation of $\text{Tp}(\text{PPh}_3)\text{Ru}\{-\text{C}(\text{Ph})=\text{CHC}(\text{O})\}\text{C}(\text{O})(\text{Ph})$ (4a**).** To a CH_2Cl_2 (20 mL) solution of **1a** (0.1 g, 0.15 mmol) was added phenylacetylene (0.14 mL, 1.3 mmol) at room temperature. The reaction mixture turned yellow in 4 h and starting material disappeared as indicated by ^{31}P NMR spectrum. The solvent was evaporated under reduced pressure to 5 mL. To the solution was added 20 mL of *n*-hexane, whereupon a yellow compound was precipitated. The precipitate was filtered, washed with 10 mL of *n*-hexane and dried under vacuum to yield $\text{Tp}(\text{PPh}_3)\text{Ru}\{-\text{C}(\text{Ph})=\text{CHC}(\text{O})\}\text{C}(\text{O})(\text{Ph})$ (**4a**) (0.10 g, 84 % yield). Spectroscopic data for **4a** are as follows: ^1H NMR (CDCl_3): δ 8.41

(d, 1H, $J_{\text{H-H}} = 2.0$ Hz, Tp), 6.31-7.75 (m, Ph, Tp), 6.71 (s, 1H, =CH), 6.31 (d, 1H, $J_{\text{H-H}} = 2.0$ Hz, Tp), 5.86 (t, 1H, $J_{\text{H-H}} = 2.0$ Hz, Tp), 5.71 (d, 1H, $J_{\text{H-H}} = 2.1$ Hz, Tp), 5.59 (t, 1H, $J_{\text{H-H}} = 2.0$ Hz, Tp). ^{13}C NMR (CDCl_3): δ 203.7 (s, CO), 195.3 (s, CO), 167.4 (d, $J_{\text{P-C}} = 12.3$ Hz, Ru-C=), 148.9 -129.8 (m, PPh_3 , Tp, C_β). ^{31}P NMR (CDCl_3): δ 58.3. MS (m/z , Ru102): 812.1 (M^+), 577.1 ($\text{M}^+ - \text{PhCCHCOCOPh}$). Anal. Calcd for $\text{C}_{43}\text{H}_{36}\text{BN}_6\text{O}_2\text{PRu}$ (812.1): C, 63.63; H, 4.47; N, 10.35. Found: C, 63.50; H, 4.38; N, 10.28.

Preparation of $\text{Tp}(\text{PPh}_3)\text{Ru}\{-\text{C}(\text{C}_6\text{H}_4\text{Me})=\text{CHC}(\text{O})\}\text{C}(\text{O})(\text{C}_6\text{H}_4\text{Me})$ (4b**).** In a similar manner as above, solution of **1a** (0.1 g, 0.15 mmol) was added 4-ethynyltoluene (0.1 mL, 0.8 mmol) at room temperature, the reaction was performed to afford complex $\text{Tp}(\text{PPh}_3)\text{Ru}\{-\text{C}(\text{C}_6\text{H}_4\text{Me})=\text{CHC}(\text{O})\}\text{C}(\text{O})(\text{C}_6\text{H}_4\text{Me})$ (**4b**) (0.05 g, 40 % yield). Spectroscopic data for **4b** are as follows: ^1H NMR (CDCl_3): δ 8.42 (d, 1H, $J_{\text{H-H}} = 2.1$ Hz, Tp), 6.33-7.68 (m, Ph, Tp), 6.68 (s, 1H, =CH), 6.32 (d, 1H, $J_{\text{H-H}} = 1.9$ Hz, Tp), 5.82 (t, 1H, $J_{\text{H-H}} = 2.1$ Hz, Tp), 5.67 (d, 1H, $J_{\text{H-H}} = 2.1$ Hz, Tp), 5.58 (t, 1H, $J_{\text{H-H}} = 1.9$ Hz, Tp), 2.08 (s, 3H, Me), 2.07 (s, 3H, Me). ^{13}C NMR (CDCl_3): δ 202.4 (s, CO), 197.6 (s, CO), 163.6 (d, $J_{\text{P-C}} = 12.3$ Hz, Ru-C=), 148.1-126.3 (m, PPh_3 , Tp), 21.4 (s, CH_3), 21.3 (s, CH_3). ^{31}P NMR (CDCl_3): δ 58.1. MS (m/z , Ru102): 840.1 (M^+), 577.1 ($\text{M}^+ - \text{MeC}_6\text{H}_4\text{CCHCOCOC}_6\text{H}_4\text{Me}$). Anal. Calcd for $\text{C}_{45}\text{H}_{40}\text{BN}_6\text{O}_2\text{PRu}$ (840.2): C, 64.37; H, 4.80; N, 10.01. Found: C, 64.21; H, 4.69; N, 10.01.

Synthesis of $\text{Tp}(\text{PPh}_3)\text{Ru}\{\text{C}(\text{OCH}_3)=\text{C}(\text{Ph})\text{C}(\text{Ph})=\text{NH}\}$ (5**).**

Methanol (20 mL) was added to a round-bottomed flask charged with complex **1b** (0.10 g,

0.14 mmol) and phenylacetylene (0.14 mL, 1.3 mmol). The reaction mixture was stirred at reflux for 4 h. The solvent was evaporated under reduced pressure to 5 mL. To the solution was added 20 mL of *n*-hexane, whereupon a yellow compound was precipitated. The precipitate was filtered, washed with 10 mL of *n*-hexane and dried under vacuum to yield $\text{Tp}(\text{PPh}_3)\text{Ru}\{\text{C}(\text{OCH}_3)=\text{C}(\text{Ph})\text{C}(\text{Ph})=\text{NH}\}$ (**5**) (0.048 g, 42 % yield). Spectroscopic data for **5** are as follows: ^1H NMR (CDCl_3): δ 12.68 (s, 1H, HN), 7.86 (d, $J_{\text{H-H}} = 2.1$ Hz, 1H, Tp), 7.38 (d, $J_{\text{H-H}} = 2.1$ Hz, 2H, Tp), 7.21-6.84 (m, PPh₃), 6.68 (d, $J_{\text{H-H}} = 2.1$ Hz, 2H, Tp), 5.72 (t, $J_{\text{H-H}} = 2.1$ Hz, 2H, Tp), 5.16 (t, $J_{\text{H-H}} = 2.1$ Hz, 1H, Tp), 5.12 (d, $J_{\text{H-H}} = 2.1$ Hz, 1H, Tp), 3.77 (s, 3H, CH₃). ^{13}C NMR (CDCl_3): δ 198.4 (C=O), 171.3 (d, $J_{\text{P-C}} = 14.1$ Hz, Ru-C=), 167.8 (s, N=C), 145.6-121.8 (m, Ph, PPh₃, Tp, C_β), 56.1 (s, OCH₃). ^{31}P NMR (CDCl_3): δ 57.7. MS (FAB) *m/z*: 812.2 (M⁺), 577.1 (M⁺ - HNCPhCPhCOCH₃). Anal. Calcd for C₄₅H₄₀BN₉P₂Ru (812.2): C, 63.55; H, 4.84; N, 12.06. Found: C, 63.43; H, 4.79; N, 11.95.

Synthesis of $\text{Tp}(\text{PPh}_3)\text{Ru}\{\text{C}(p\text{-MeC}_6\text{H}_4)=\text{CHC}(\text{O})\text{CH}_2(p\text{-MeC}_6\text{H}_4)\}$ (6**).**

Methanol (20 mL) was added to a round-bottomed flask charged with complex **1b** (0.10 g, 0.14 mmol) and 4-ethynyltoluene (0.1 mL, 0.8 mmol). The reaction mixture was stirred at reflux for 4 h. The solvent was evaporated under reduced pressure to 5 mL. To the solution was added 20 mL of *n*-hexane, whereupon a yellow compound was precipitated. The precipitate was filtered, washed with 10 mL of *n*-hexane and dried under vacuum to yield $\text{Tp}(\text{PPh}_3)\text{Ru}\{\text{C}(p\text{-MeC}_6\text{H}_4)=\text{CHC}(\text{O})\text{CH}_2(p\text{-MeC}_6\text{H}_4)\}$ (**6**) (0.10 g, 86 % yield). Spectroscopic data for **6** are as follows: ^1H NMR (CDCl_3): δ 8.06 (br, 1H, Tp), 7.89 (br, 1H, Tp), 7.81 (br, 1H, Tp), 7.71 (br, 1H, Tp), 7.45 - 7.10 (m, Ph), 6.72 (s, 1H, CH), 6.53

(br, 1H, Tp), 6.24 (br, 1H, Tp), 6.12 (br, 1H, Tp), 5.89 (br, 1H, Tp), 5.51 (br, 1H, Tp), 3.73 (d, $J_{\text{H-H}} = 16.8$ Hz, 1H, *CHHP*h), 3.42 (d, $J_{\text{H-H}} = 16.8$ Hz, 1H, *CHHP*h). ^{13}C NMR (CDCl_3): δ 204.2 (C=O), 168.1 (d, $J_{\text{P-C}} = 14.0$ Hz, Ru-C=), 147.2-123.4 (m, Ph, PPh_3 , Tp, C_β), 52.1 (CH_2Ph). ^{31}P NMR (CDCl_3): d 57.1. MS (FAB) m/z : 825.1 (M^+), 577.1 ($\text{M}^+ - \text{OCH}_2\text{C}_6\text{H}_4\text{CH}_3\text{CHCC}_6\text{H}_4\text{CH}_3$). Anal. Calcd for $\text{C}_{45}\text{H}_{42}\text{BN}_6\text{P}_2\text{Ru}$ (825.7): C, 65.46; H, 5.13; N, 10.18. Found: C, 65.41; H, 5.09; N, 10.05.

Table 1. Crystal data and structure refinement for **4b. squeezed 0.79 toluene**

Empirical formula	C50.53 H46.32 B N6 O2 P Ru
Formula weight	912.29
Temperature	200(2) K
Wavelength	0.71073 Å
Crystal system	Triclinic
Space group	P -1
Unit cell dimensions	a = 10.1964(4) Å • = 89.086(2)°. b = 12.4327(4) Å • = 77.852(2)°. c = 18.4795(7) Å • = 83.264(2)°.
Volume	2274.27(14) Å ³
Z	2
Density (calculated)	1.332 Mg/m ³
Absorption coefficient	0.426 mm ⁻¹
F(000)	943
Crystal size	0.24 x 0.15 x 0.05 mm ³
Theta range for data collection	1.13 to 24.93°.
Index ranges	-10<=h<=12, -14<=k<=12, -21<=l<=21
Reflections collected	15791
Independent reflections	7759 [R(int) = 0.0365]
Completeness to theta = 24.93°	97.5 %
Absorption correction	multi-scan
Max. and min. transmission	0.9790 and 0.9046
Refinement method	Full-matrix least-squares on F ²
Data / restraints / parameters	7759 / 0 / 505
Goodness-of-fit on F ²	0.947
Final R indices [I>2sigma(I)]	R1 = 0.0392, wR2 = 0.0856
R indices (all data)	R1 = 0.0583, wR2 = 0.0915
Largest diff. peak and hole	0.849 and -0.331 e.Å ⁻³

Table S2. Crystal data and structure refinement for **6**.

Empirical formula	C ₄₃ H ₃₉ B N ₇ O P Ru
Formula weight	812.66
Temperature	200(2) K
Wavelength	0.71073 Å
Crystal system	Monoclinic
Space group	P 2 ₁ /n
Unit cell dimensions	a = 11.7013(7) Å • = 90°. b = 14.1739(9) Å • = 104.301(2)°. c = 23.4437(13) Å • = 90°.
Volume	3767.7(4) Å ³
Z	4
Density (calculated)	1.433 Mg/m ³
Absorption coefficient	0.504 mm ⁻¹
F(000)	1672
Crystal size	0.62 x 0.30 x 0.21 mm ³
Theta range for data collection	1.69 to 25.00°.
Index ranges	-13<=h<=13, -16<=k<=10, -27<=l<=27
Reflections collected	21592
Independent reflections	6479 [R(int) = 0.0310]
Completeness to theta = 25.00°	97.9 %
Absorption correction	multi-scan
Max. and min. transmission	0.9016 and 0.7453
Refinement method	Full-matrix least-squares on F ²
Data / restraints / parameters	6479 / 0 / 487
Goodness-of-fit on F ²	1.027
Final R indices [I>2sigma(I)]	R1 = 0.0285, wR2 = 0.0704
R indices (all data)	R1 = 0.0341, wR2 = 0.0737
Largest diff. peak and hole	0.648 and -0.399 e.Å ⁻³

Table S3. Crystal data and structure refinement for **7**.

Empirical formula	C ₄₅ H ₄₂ B N ₆ O P Ru
Formula weight	825.70
Temperature	200(2) K
Wavelength	0.71073 Å
Crystal system	Monoclinic
Space group	P 2 ₁ /n
Unit cell dimensions	a = 24.6370(10) Å • = 90°. b = 10.0656(4) Å • = 91.513(2)°. c = 32.0278(13) Å • = 90°.
Volume	7939.7(6) Å ³
Z	8
Density (calculated)	1.382 Mg/m ³
Absorption coefficient	0.479 mm ⁻¹
F(000)	3408
Crystal size	0.42 x 0.18 x 0.05 mm ³
Theta range for data collection	1.03 to 25.03°.
Index ranges	-29<=h<=29, -11<=k<=9, -34<=l<=37
Reflections collected	53461
Independent reflections	13970 [R(int) = 0.0574]
Completeness to theta = 25.03°	99.8 %
Absorption correction	multi-scan
Max. and min. transmission	0.9765 and 0.8243
Refinement method	Full-matrix least-squares on F ²
Data / restraints / parameters	13970 / 0 / 995
Goodness-of-fit on F ²	1.064
Final R indices [I>2sigma(I)]	R1 = 0.0457, wR2 = 0.0951
R indices (all data)	R1 = 0.0758, wR2 = 0.1137
Largest diff. peak and hole	0.751 and -0.556 e.Å ⁻³