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Cent. Eur. J. Chem. • 9(4) • 2011 • 728-736
DOI: 10.2478/s11532-011-0055-1

Central European Journal of **Chemistry**

Metathesis transformations of unsaturated derivatives of β-diketones

Research Article

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Received 3 March 2011; Accepted 11 April 2011

Abstract: Selected β-diketones bearing unsaturated derivatives have been demonstrated to undergo homo-metathesis and cross-metathesis with selected olefins in the presence of Grubbs catalysts. The reactions led to respective homo- and cross-metathesis products mainly with good yields and selectivities.

Keywords: *Cross-metathesis • β-diketones • Homogeneous catalysis • Homo-metathesis • Grubbs' catalysts*

1. Introduction

Olefin metathesis has become an important synthetic tool in organic and polymer chemistry. The family of ruthenium-based catalysts (**1**-**4**, Fig. 1) tolerant of normal organic and polymer processing conditions and preserving their catalytic properties in the presence of the majority of functional groups have allowed a great number of new applications [1].

A vast number of examples of efficient metathesis transformations of unsaturated derivatives bearing functional groups have been published [1]. A variety of available W, Mo, and especially Ru-based alkylidene complexes have enabled transformation of unsaturated derivatives bearing nearly all types of functionalities [1]. Among metathetic methods the cross-metathesis is the one that offers great opportunities in organic synthesis [1,2]. Pentane-2,4-dione as well as other β-diketones and their derivatives attract much interest because of a broad spectrum of applications, especially those of its metal derivatives, *e.g.* in analytical chemistry, as molecular precursors in chemical vapour deposition techniques, and in medicine [3]. Chelates of β-diketones with transition metals are often used as catalysts in a number of catalytic processes such as hydroformylation, oxidation, hydrogenation, addition to unsaturated bonds and C-C bond formation [3]. The metathesis reactivity of unsaturated derivatives of β-diketones is nearly unexplored. Efficient microwave irradiation assisted cross-metathesis of β-oxoesters with ethyl acrylate was reported by Murray [4]. Recently cross-metathesis of unsaturated derivatives of β-oxoamides or β-oxoesters with selected olefins were tested under thermal and microwave irradiation conditions [5]. Relatively good yields were obtained for cross-metathesis of β-oxoderivatives with acrylonitrile performed under thermal and microwave irradiation conditions in the presence of catalyst **4** [6].

Herein we report on the efficient homo-metathesis of unsaturated derivatives of selected β-diketones and their cross-metathesis with selected olefins in the presence of Grubbs type ruthenium alkylidene complexes.

2. Experimental Procedure

2.1. General

All manipulations were carried out under dry argon using standard Schlenk techniques. ^{1}H- and ^{13}C-NMR spectra were recorded on a Varian Gemini 300 at 300 and 75 MHz, respectively. ^{31}P NMR spectra were recorded on a Mercury 300 operating at 121.5 MHz. The GC/MS analyses were performed on a Varian Saturn 2100T

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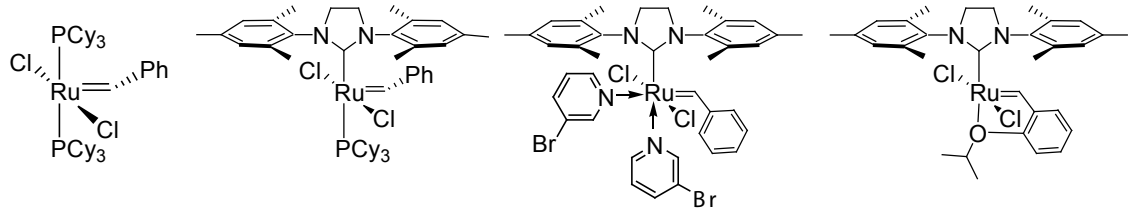


Figure 1. Well-defined ruthenium-based catalysts of olefin metathesis

equipped with a DB-5 column (30 m I.D. 0.23 mm) and Ion Trap Detector. GC analyses were carried out on a Varian CP-3800 equipped with a Rtx-5 column (30 m, I.D. 0.53 mm) and TCD. Elemental analyses were performed at the Faculty of Chemistry, Adam Mickiewicz University, on Elemental Analyser Vario EL III. The chemicals were obtained from the following sources: catalysts **1**, **2** and **4**, allyl diethylmalonate, 2-allyl-2-methyl-1,3-cyclopentanedione, vinylsilanes, styrene, dichloromethane, benzene-d_6, chloroform-d, decane, dodecane, calcium hydride and triethylamine were obtained from Aldrich, toluene, acetone, ethyl acetate, *n*-hexane, *n*-pentane and THF from Chempur. Catalyst **3** [7], diketone derivatives **5a**, **9** [8], **6b** and **6c** [9] were prepared according to the literature procedures. All solvents were dried prior to use over CaH_2 and stored under argon. CH_2Cl_2 was additionally passed through a column with alumina and after that it was degassed by repeated freeze-pump-thaw cycles.

2.2. Catalytic tests (typical procedures)

Homo-metathesis: The oven dried 10 mL glass reactor equipped with a reflux condenser was charged under argon with CH_2Cl_2 2 mL, 3-allyl-pentane-2,4-dione (10 µL, 6.8×10^{-5} mol) and decane or dodecane 5 µL (internal standard). The reaction mixture was stirred and heated in an oil bath to maintain a gentle reflux. Then a ruthenium complex (1-5 mol% in relation to diketone) was added under argon. The reaction progress was monitored by gas chromatography.

Cross-metathesis: The oven dried 10 mL glass reactor equipped with a condenser and a magnetic stirring bar was charged under argon with CH_2Cl_2 2 mL, **5a** (10 µL, 6.8×10^{-5} mol), decane or dodecane 5 µL (internal standard) and **11a** (140 µL, 6.8×10^{-4} mol). The reaction mixture was stirred and heated in an oil bath to maintain a gentle reflux. Then a ruthenium complex (1-5 mol% in relation to diketone) was added under argon. The reaction progress was monitored by gas chromatography.

2.3. Synthetic procedures

2.3.1. 3,8-diacetyldec-5-ene-2,9-dione (6a)

Round 25 mL flask equipped with reflux condenser was charged under argon with methylene chloride (5 mL) and **5a** (0.3 mL, 2.04×10^{-3} mol) and heated to reflux in an oil bath. Then the second generation Grubbs catalyst (0.087 g, 1.02×10^{-4} mol) was added. The reaction was carried out at 40°C for 24h. After this time solvent was evaporated and the residue was purified by column chromatography on silica gel (hexane : THF = 5 : 1 as eluent) to afford **6a** as a yellow oil (0.211 g, 83%). Found C, 66.86; H, 7.86%. $C_{14}H_{20}O_4$ requires C, 66.65; H, 7.99%. ^{1}H NMR (C_6D_6; δ (ppm)): 1.73 (s, 12H, CH_3) (enol); 1.76 (s, 12H, CH_3) (keto); 2.23-2.31 (m, 4H, CH_2) (keto); 2.40-2.43 (m, 4H, CH_2) (enol); 3.08-3.19 (m, 2H, CHC=O) (keto); 5.03-5.05 (m, 2H, =CH) (enol); 5.08-5.12 (m, 2H, =CH) (keto); 17.42 (s, 2H, OH) (enol); ^{13}C NMR (C_6D_6; δ (ppm)) (enol form): 22.58 (CH_2); 29.81 (CH_3); 107.7 (C=COH); 128.12 (=CH); 191.24 (COH); MS m/z (rel. int.): 253(M^++1, 14), 211(3), 191(20), 153(20), 137(15), 109(100), 101(27), 81(17), 67 (43), 55 (12);

2.3.2. 4,9-dipropionyldodec-6-ene-3,10-dione (6b)

Synthesis of this compound was performed according to procedure described for **6a**: Grubbs catalyst (**2**) (0.087 g, 1.02×10^{-4} mol) was added to the boiling solution of **5b** (0.3 mL, 2.04×10^{-3} mol) in 5 mL of methylene chloride. The reaction was carried out at 40°C for 24 h. After this time solvent was evaporated and the residue was purified by column chromatography on silica gel (hexane : THF = 5 : 1 as eluent) to afford **6b** as yellow oil (0.086 g, 71%). Found: C, 70.25; H, 9.09%. $C_{18}H_{28}O_4$ requires C, 70.10; H, 9.15; O, 20.75%. ^{1}H NMR (C_6D_6; δ (ppm)): 0.91 (t, J=7.2 Hz, 12H, CH_3,) (keto form); 0.92 (t, J=7.2 Hz, 12H, CH_3) (enol form); 2.07 (q, J=7.2 Hz, 8H, CH_2) (keto form); 2.08 (q, J=7.2 Hz, 8H, CH_2,) (enol form); 2.32-2.39 (m, 4H, CH_2) (keto form); 2.40-2.43 (m, 4H, CH_2) (enol form); 3.28 (t, J=7.2 Hz, 2H, CH) (keto form); 5.15-5.20 (m, 2H, CH=) (enol form); 5.21-5.24 (m,

2H, CH=) (keto form); 17.59 (s, 2H, OH) (enol form); ^{13}C NMR (C_6D_6; δ (ppm)): (keto) 7.68 ($\underline{C}H_3CH_2$); 31.25 (CH_2); 35.38 ($CH_3\underline{C}H_2$); 66.52 (CH); 129.31 (CH=); 205.18 (C=O); MS m/z (rel. int.): 309 (M^++1, 5); 251(1); 223(1); 194(2); 181(5); 167(3); 153(3); 137(3); 129(28); 125(6); 123(44); 99(5); 67(12); 57(100)

2.3.3. 2,7-dibenzoyl-1,8-diphenyloct-4-ene-1,8-dione (6c)

Synthesis of this compound was performed according to procedure described for **6a**: Grubbs catalyst (**2**) 0.054 g (6.4×10^{-5} mol) was added to the boiling solution of 0.34 g (1.3×10^{-3} mol) 3-allyl-1,5-diphenyl-2,4-pentanodione (**5c**) in 20 mL of methylene chloride. The reaction was carried out at 40°C. for 24h. After this time the white solid was precipitated by vigorous mixing of concentrated (5 mL) reaction mixture with 20 mL of pentane, filtrated, washed 3×3 mL of methylene chloride/pentane (1:1) and dried under vacuum to afford **6c** as white microcrystalline powder (0.198 g, 61%). Found: C, 81.80; H, 5.54%. $C_{34}H_{28}O_4$ requires: C, 81.58; H, 5.64; O, 12.78%; ^{1}H NMR ($CDCl_3$; δ (ppm)) (one stereoisomer and exclusively keto form observed): 2.72-2.76 (m, 4H, CH_2); 5.16 (t, J=6.6 Hz, 2H, CHC=O); 5.58-5.60 (m, 2H, =CH); 7.39-7.90 (m, 20H, Ph); ^{13}C NMR ($CDCl_3$; δ (ppm)): 32.30 (CH_2); 56.90 (CH); 128.53 (CH aromatic); 128.78 (CH aromatic); 129.71 (=CH); 133.52 (CH aromatic); 135.87 (CH aromatic); 195.50 (C=O); MS m/z (rel. int.): 501 (M^++1, 1); 395(4); 290(1); 276(19); 263(1); 237(1); 224(5); 171 (8); 105 (100); 77(25); M.p. 209-210°C.

2.3.4. 2,2'-(but-2-ene-1,4-diyl)bis(2-methylcyclopentane-1,3-dione) (8)

Synthesis of this compound was performed according to procedure described for **6a**: Grubbs catalyst (**2**) 0.086g (1.01×10^{-4} mol) was added to the boiling solution of 0.30 mL (2.02×10^{-3} mol) 2-allyl-2-methyl-1,3-cyclopentanedione (**7**) in 20 mL of toluene. The reaction was carried out at 110°C for 24h. Then toluene was removed by evaporation, the content was washed 3×3 mL of pentane and dried under vacuum to afford **8** as white powder (0.220 g, 79%). The analytically pure sample of compound **8** was obtained by column chromatography on silica gel (hexane: ethyl acetate (2:1) as eluent). Found: C, 69.80; H, 7.20%. $C_{16}H_{20}O_4$ requires C, 69.54; H, 7.30; O, 23.16%; ^{1}H NMR (C_6D_6); δ (ppm)): 0.81 (s, 6H, CH_3); 1.98-2.08 (m, 8H, CH_2); 2.22-2.29 (m, 4H, $C\underline{H}_2CH$=CH); 5.11-5.15 (m, 2H, =CH); ^{13}C NMR (C_6D_6; δ (ppm)): 19.65 (CH_3); 35.27 (CH_2); 38.39 (CH_2); 56.36 (C); 128.81 (CH=); 215.13 (C=O); MS m/z (rel. int.): 277(M^++1, 1), 249(2), 164(100), 149(84), 137(18), 123(18), 109(50), 99(30), 67(22), 53(13)

2.3.5. (E)-3,3'-(4,4'-(ethene-1,2-diyl)bis(4,1-phenylene))bis(methylene)dipentane-2,4-dione (10)

Round 50 mL flask equipped with a reflux condenser was charged with 20 mL of methylene chloride and 0.6 mL (3.42×10^{-3} mol) of **9**. After 5 min 0.145 g (1.71×10^{-4} mol) of the second generation Grubbs catalyst was added. The reaction was carried out at 40°C for 24 h. After this time complete conversion of the substrate was observed by gas chromatography. Then solvent was evaporated and 10 mL of THF was added to the solid residue and the content was stirred intensively for 5 minutes. The solid was filtrated, washed several times with THF and dried under vacuum to afford **10** as white microcrystalline solid (0.257 g, 75%). Found: C, 77.41; H, 6.80%. $C_{26}H_{28}O_4$ requires: C, 77.20; H, 6.98; O, 15.82%; ^{1}H NMR ($CDCl_3$; δ (ppm)): 2.07 (s, 12H, CH_3) (keto); 1.99 (s, 12H, CH_3) (enol); 3.06 (d, J=7.5 Hz, 4H, CH_2) (keto); 3.51 (s, 4H, CH_2) (enol); 3.92 (t, J=7.5 Hz, 2H, CHC=O) (keto); 6.93 (s, 1H, =CH) (keto); 6.95(s, 1H, =CH) (enol) 7.05 (d, J=7.8 Hz, 4H, C_6H_4) (enol and keto overlapped); 7.32 (d, J=7.8 Hz, 4H, C_6H_4) (enol and keto overlapped); 16.75 (s, 1H, OH) (enol); ^{13}C NMR ($CDCl_3$; δ (ppm)) (keto form): 29.76 (CH_3); 33.99 (CH_2); 69.92 (CHC=O); 126.81 (Ph); 128.03 (=CH); 128.98 (Ph); 135.86 (C_6H_4); 137.46 (C_6H_4); 203.51 (C=O); MS m/z (rel. int.): 404 (M^+, 14), 361(100), 319(8), 305(7), 281(6), 261(48), 243(6), 207(15), 147(4), 113(10), 91(5), 73 (8), 45 (5); M.p. 184-186°C.

2.3.6. 3-(3-(triethoxysilyl)allyl)pentane-2,4-dione (12a)

Catalyst **2** (0.1443 g, 1.7×10^{-4} mol) was added to the boiling solution of **5a** (0.5 mL, 3.4×10^{-3} mol) and **11a** (7.18 mL, 3.4×10^{-2} mol) in 20 mL of toluene. The reaction was carried out under reflux for 24h. After this time benzene was removed by evaporation and the product was isolated by column chromatography on silica gel modified with NEt_3 (hexane : ethyl acetate (10:1) as eluent) to afford **12a** as yellow oil (0.52 g, 51%). ^{1}H NMR (C_6D_6; δ (ppm)): 1.18 (t, J=7.0 Hz, 9H, CH_3) (enol form); 1.20 (t, J=7.0 Hz, 9H, CH_3) (keto); 1.68 (s, 6H, CH_3) (keto); 1.71 (s, 6H, CH_3) (enol); 2.42-2.46 (m, 2H, CH_2) (keto); 2.58-2.63 (m, 2H, CH_2) (enol); 3.27 (t, J=7.5 Hz, 1H, CH) (keto); 3.82 (q, J=7.0 Hz, 6H, OCH_2) (enol); 3.84 (q, J=7.0 Hz, 6H, OCH_2) (keto); 5.52 (dt, J=18.7 Hz; J=2.0 Hz, 1H, =CHSi) (enol); 5.56 (dt, J=18.7 Hz, J=1.6 Hz, 1H, =CHSi) (keto); 6.40 (dt, J=18.7 Hz, J=6.4 Hz, 1H, =CHCH$_2$) (keto); 6.47 (dt, J=18.7 Hz, J=4.9 Hz, 1H, =CHCH$_2$) (enol); 17.47 (s, 1H, OH) (enol); ^{13}C NMR (C_6D_6; δ (ppm)): 18.56 (CH_3CH_2) (enol and keto); 22.57 (CH_3C=OH) (enol); 28.67 (CH_3C=O) (keto); 33.78 (CH_2C=C) (enol); 34.82 (CH_2C=C) (keto); 58.63 (OCH_2)

(enol); 58.67 (OCH_2) (keto); 67.18 (C=COH) (keto); 106.16 (CHC=O) (enol); 120.38 (=$CHCH_2$) (enol); 123.55 (=$CHCH_2$) (keto); 148.46 (=CHSi) (keto); 149.95 (=CHSi) (enol); 191.58 (COH) (enol); 202.26 (C=O) (keto); MS m/z (rel. int.): 303(M^++1, 4), 284(8), 269(28), 256(20), 241(55), 213(85), 177(20), 169(53), 163 (68), 135 (65), 127 (17), 107 (66), 79 (100), 45 (35)

2.3.7. 3-(3-(trimethoxysilyl)allyl)pentane-2,4-dione (12b)

Catalyst **2** (0.1443 g, 1.7×10^{-4} mol) was added in three portions within 0.5h to the boiling solution of **5a** (0.5 mL, 3.4×10^{-3} mol) and **11b** (5.1 mL, 3.4×10^{-2} mol) in 20 mL of CH_2Cl_2. The reaction was carried out under reflux for 24 h. After this time benzene was removed by evaporation and the product was isolated by vacuum distillation (b.p. 110-112°C / 0.1 mmHg) to afford **12b** as yellow oil (0.60 g, 68%). ^{1}H NMR (C_6D_6; δ (ppm)): 1.81 (s, 6H, CH_3) (enol); 1.90 (s, 6H, CH_3) (keto); 2.41-2.46 (m, 2H, CH_2) (keto), 2.58-2.61 (m, 2H, CH_2) (enol); 2.83 (t, J=7.3 Hz, 1H, CH) (keto); 3.44 (s, 9H, OCH_3) (enol); 3.45 (s, 9H, CH_3) (keto); 5.42(dt, J=1.9 Hz, J=18.8 Hz, 1H, =CHSi) (enol); 5.46 (dt, J=1.6 Hz, J=18.8 Hz, 1H, =CHSi) (keto); 6.34 (dt, J=6.4 Hz, J=18.6 Hz, 1H, =C<u>H</u>-CH_2) (keto); 6.39 (dt, J=4.9 Hz, J=18.8 Hz, 1H, =C<u>H</u>-CH_2) (enol); 17.42 (s, 1H, -OH); ^{13}C NMR (C_6D_6; δ (ppm)): 22.57 (<u>C</u>H_2C=C) (keto); 28.70 (<u>C</u>H_2C=C) (enol); 33.85 (CH_3) (enol); 34.83 (CH_3) (keto); 50.34 (OCH_3) (keto and enol overlapped); 68.16 (<u>C</u>H_2C=O) (keto), 106.46 (<u>C</u>=COH) (enol); 118.75 (=<u>C</u>HCH_2) (enol); 121.88 (=<u>C</u>HCH_2) (keto); 145.50 (=CHSi) (keto); 150.80 (=CHSi) (enol); 190.64 (COH) (enol); 202.24 (C=O) (keto); MS m/z (rel. int.): 261(M^++1, 4), 229(10), 217(26), 213(42), 185(99), 139(12), 121(100), 107(88), 91 (96), 77 (53), 45(19)

2.3.8. Diethyl 2-(3-(triethoxysilyl)allyl)malonate (12d)

The second generation Grubbs catalyst (**2**) (0.107 g, 1.25×10^{-4} mol) was added to the boiling solution of **5d** (0.5 mL, 2.5×10^{-3} mol) and **11a** (4.3 mL, 2.5×10^{-2} mol) in 20 mL of toluene. The reaction was carried out under reflux (110°C) for 24h. After this time benzene was removed by evaporation and the product was isolated by column chromatography on silica gel modified with NEt_3 (hexane : ethyl acetate (10:1) as eluent) to afford **12d** as yellow oil (0.715 g, 79%). ^{1}H NMR (C_6D_6; δ (ppm)): 0.92 (t, J=7.1 Hz, 6H, CH_3); 1.19 (t, J=7.0 Hz, 9H, CH_3); 2.77-2.85 (m, 2H, <u>C</u>H_2CH=CH); 3.44 (t, J=7.5 Hz, 1H, CH); 3.84 (q, J=7.0 Hz, 6H, CH_2); 3.93 (q, J=7.2 Hz, 4H, CH_2); 5.65-5.72 (1H, =CH), 6.53-6.60 (1H, =CH); ^{13}C NMR (C_6D_6; δ (ppm)): 14.04 (CH_3); 18.55 (CH_3); 35.84 (CH_2); 51.45 (CH); 58.62 (OCH_2); 61.23 (CH_2); 123.75 (=CH); 148.28 (=CH); 168.68 (C=O); MS m/z (rel. int.): 363(M^++1, 1), 347(1), 333(1), 316(7), 289(14), 271(7), 243(100), 215(15), 199(5), 163(10), 135(6), 107(7), 45(7).

2.3.9. (E)-3-(4-(2-(triethoxysilyl)vinyl)benzyl)pentane-2,4-dione (13)

Catalyst **1** (0.1399 g, 1.7×10^{-4} mol) was added to the boiling solution of **9** (0.6 mL, 3.4×10^{-3} mol) and **11a** (3.6 mL, 1.7×10^{-2} mol) in 20 mL of CH_2Cl_2. The reaction was carried out under reflux for 24h. After this time methylene chloride was removed by evaporation and the product was isolated by column chromatography on silica gel modified with NEt_3 (hexane:ethyl acetate (50:1) as eluent) to afford **13** as brown oil (0.67 g, 52%). ^{1}H NMR (C_6D_6; δ (ppm)): 1.24 (t, 9H, CH_3) (enol); 1.25 (t, 9H, CH_3) (keto); 1.64 (s, 6H, CH_3) (keto); 1.68 (s, 6H, CH_3) (enol); 2.91 (d, J=7.6 Hz, 2H, C<u>H</u>$_2$Ph) (keto); 3.12(s, 2H, C<u>H</u>$_2$Ph) (enol); 3.55 (t, J=7.16, 1H, CHC=O); 3.92 (q, 6H, OCH_2) (keto); 3.93 (q, 6H, OCH_2) (enol), 6.34 (d, J=19.3 Hz, 1H, =CHSi) (keto); 6.41 (d, J=19.2 Hz, 1H, =CHSi) (enol); 7.45 (d, J=19.3 Hz, 1H, =C<u>H</u>-CH_2) (keto); 7.52 (d, J=19.2 Hz, 1H, =C<u>H</u>-CH_2) (enol); 6.82 (d, J=8.4 Hz, 2H, C_6H_4) (enol); 6.87 (d, J=8.0 Hz, 2H, C_6H_4) (keto); 7.22 (d, J=8.0 Hz, 2H, C_6H_4) (keto); 7.28 (d, J=8.0 Hz, 2H, C_6H_4) (enol); 17.52 (s, 1H, OH); ^{13}C NMR (C_6D_6; δ (ppm)): 18.6 (OCH_2<u>C</u>H_3) (enol and keto overlapped); 22.90 (CH_3) (enol); 29.15 (CH_3) (keto); 32.77 (<u>C</u>H_2C=C) (enol); 34.02 (<u>C</u>H_2C=C) (keto); 58.78 (OCH_2) (enol and keto overlapped); 69.69 (<u>C</u>HC=O) (keto); 108.21 (<u>C</u>=COH) (enol); 118.58 (=<u>C</u>H) (enol); 118.80 (=<u>C</u>H) (keto); 127.36 (C_6H_4) (keto); 127.46 (C_6H_4) (enol); 127.90 (C_6H_4) (enol); 129.26 (C_6H_4) (keto); 136.44 (C_6H_4) (enol); 136.66 (C_6H_4) (keto);139.42 (C_6H_4) (keto); 140.92 (C_6H_4) (enol); 148.68 (=CHSi) (keto); 148.81 (=CHSi) (enol); 191.82 (COH) (enol); 202.18 (C=O) (keto); MS m/z (rel. int.): 378(M^+, 1), 335(100), 289(56), 263(5), 245(9), 217(27), 189(14), 163(20), 115 (12), 45 (12).

2.3.10. Dichlorobis(tricyclohexylphosphine){4-(2-acetyl-3-oxobutyl)benzylidene}ruthenium(II) (14) (Optimised procedure)

Schlenk flask (20 mL) was charged under argon with [$RuCl_2(PCy_3)_2$(=CHMe)] (0.114 g, 1.5×10^{-4} mol), 5 mL of CH_2Cl_2 and 24 µL (1.35×10^{-4} mol) of **9**. The mixture was stirred under reflux for 1h. Then, solvent was evaporated and the solid residue was treated with methanol. The precipitate was separated by canula filtration, washed three times with cold methanol and dried in vacuum to afford **14** as pink microcrystalline solid (0.112 g, yield 80%). Found: C, 63.19; H, 8.43%. $C_{49}H_{80}Cl_2O_2P_2Ru$ requires: C, 62.94; H, 8.62; Cl, 7.58; O, 3.42; P, 6.62; Ru, 10.81%. ^{1}H NMR (C_6D_6; δ (ppm)): 1.56-1.58, 1.63-1.68,

1.97-2.01, (m, 66H, Cy) (keto and enol overlapped); 1.72 (s, 3H, CH_3) (enol); 1.68 (s, 3H, CH_3) (keto); 2.73 (d, J=7.8 Hz, 2H, CH_2) (keto); 2.82 (s, 2H, CH_2) (enol); 3.64 (t, 1H, J=7.8 Hz, CHC=O) (keto); 8.69-8.72, 6.92-6.96 (m, 4H, C_6H_4) (keto and enol overlapped); 17.50 (s, 1H, OH) (enol); 20.55 (s, 1H, Ru=CH) (keto and enol overlapped); ^{31}P NMR (C_6D_6; δ (ppm)): 36.15; (keto); 36.05 (enol); ^{13}C NMR C_6D_6; δ (ppm)): 26.9 (CH_3) (keto); 30.2 (CH_3) (enol); 27.8-32.7 (Cy) (keto and enol); 33.8 (CH_2) (enol); 34.6 (CH_2) (keto); 68.7 (CHC=O) (keto); 107.6 (C=COH) (enol); 129.7 (C_6H_4) (enol); 130.1 (C_6H_4) (keto); 131.9 (C_6H_4) (keto); 132.1 (C_6H_4) (enol); 140.1 (C_6H_4) (keto); 141.6 (C_6H_4) (enol); 152.1 (C_6H_4) (enol); 152.2 (C_6H_4) (keto); 191.7 (COH) (enol); 201.8 (C=O) (keto); 293.4 (Ru=C) (keto and enol overlapped); M.p. 141-142°C (air)

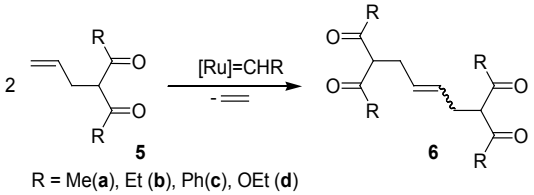
2.4. X-Ray structure determination

Diffraction data were collected at room temperature by the ω-scan technique on an Oxford Diffraction Xcalibur four-circle diffractometer with Eos CCD-detector with graphite-monochromatized MoK_α radiation (λ=0.71073 Å). The data were corrected for Lorentz-polarization as well as for absorption effects [10]. Accurate unit-cell parameters were determined by a least-squares fit of 9398 reflections of highest intensity, chosen from the whole experiment. The structures were solved with SIR92 [11] and refined with the full-matrix least-squares procedure on F^2 by SHELXL97 [12]. Scattering factors incorporated in SHELXL97 were used. The function $\Sigma w(|F_o|^2-|F_c|^2)^2$ was minimized, with $w^{-1}=[\sigma^2(F_o)^2+(0.0562P)^2+0.2776P]$ ($P = [Max(F_o^2, 0) + 2F_c^2]/3$). All non-hydrogen atoms were refined anisotropically. The hydrogen atoms were found in the difference Fourier maps and isotropically refined. Relevant crystal data are listed in Table 1, together with refinement details.

Crystallographic data (excluding structure factors) for the structures in this paper has been deposited with the Cambridge Crystallographic Data Centre as supplementary publication No. CCDC-799216. Copies of the data can be obtained free of charge, on application to CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK. Fax: +44-(0)1223-336033 or e-mail: deposit@ccdc.cam.ac.uk.

3. Results and Discussion

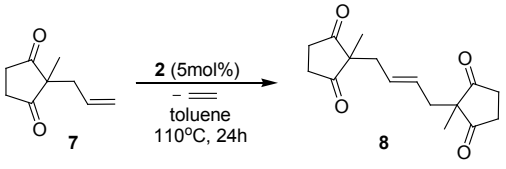
Treatment of 3-allyl-pentane-2,4-dione in refluxing methylene chloride with 5 mol% of the ruthenium complex **1** results in evolution of a gas. Analysis of the reaction mixture by GC and GC-MS proved substrate conversion and formation of three isomeric products of homo-metathesis (Eq. 1). ^{1}H NMR analysis of the reaction mixture indicated the formation of a mixture of tautomers. In equations 1, 3-5 only one tautomeric form is presented for clarity.



(1)

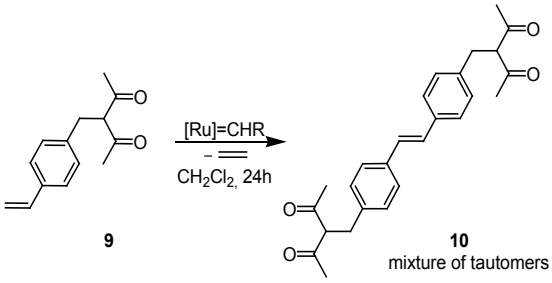
R = Me(**a**), Et (**b**), Ph(**c**), OEt (**d**)

Compound **5b** in the presence of **2** exhibits similar reactivity and forms four isomeric products (as indicated by GC-MS). In contrast, homo-metathesis of **5c** led to formation of a single product (as observed by GC). Reactivity of diketones was compared with that of allyl diethylmalonate (**5d**), known to readily undergo homo-metathesis [13]. In this case, nearly quantitative and selective transformation was observed (Table 1). Efficiency of the reactions was found to depend on the catalyst used. Low conversion of the substrates was observed in the presence of **1** irrespective of the reaction duration. In contrast, nearly complete conversions and high yields were observed when catalyst **2**, **3** or **4** was applied. Effective conversion in the presence of catalyst **4** required a higher reaction temperature (80°C). For all reagents tested, the reaction proceeded highly stereoselectively. When compound **5a**, **5b** or **5d** was used as reagent, analysis of the reaction mixtures by GC/MS and ^{1}H NMR spectroscopy indicated a high predominance of one stereoisomer. The homo-metathesis of allyl derivative of cyclic diketone **7** proceeded efficiently with the formation of two stereoisomers in a *E*/*Z* ratio exceeding 20/1 (Eq. 2) (Table 1).



(2)

Treatment of 3-[4-(ethenyl)benzyl]pentane-2,4-dione (**9**) with 5 mol% of **1** or **2** in boiling CH_2Cl_2 results in formation of homo-metathesis product (Eq. 3) (Table 1). While the first generation Grubbs catalyst (**1**) exhibited relatively low activity in the reaction, quantitative conversion was observed in the presence of **2**. Monitoring of the reaction by GC/MS showed formation of a single broad peak of the product. ^{1}H NMR analysis of the reaction mixture indicated the formation of single stereoisomer of stilbene derivative **10** being a mixture of tautomers (Eq. 3, Table 1).



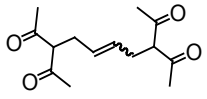
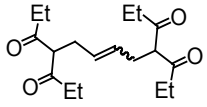
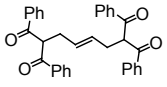
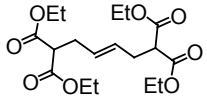
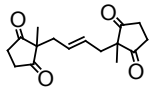
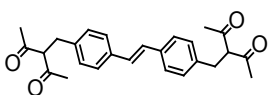
(3)

Products of all reactions were isolated and characterised spectroscopically. To the best of the authors' knowledge products **6b**, **6c**, **8** and **10** have not been reported in the literature. Compound **6a** was reported to be formed as a minor by-product during allylation of pentane-2,4-dione with *Z*-2-butene-1,4-diol [14]. Crystal structure of product **10** confirmed expected formation of *E*-stereoisomer. Fig. 2 shows the perspective view of the molecule (see supplementary data for the list of some relevant geometrical parameters). The molecule is symmetrical (C_i), the middlepoint of the central double bond lies in special position, at the center of symmetry. This symmetry enforces the *trans* disposition of the double bond and ideal coplanarity of the planar – within 0.016(1) Å - phenyl rings of the molecule.

Unsaturated derivatives of pentane-2,4-dione and diethylmalonate were tested in cross-metathesis with triethoxyvinylsilane and styrene in the presence of ruthenium benzylidene complexes. Trialkoxyvinylsilanes were selected as reaction partners because they are highly active in CM and do not undergo homo-metathesis [16]. Moreover they easily react with silica so that trialkoxysilyl derivatives can be readily immobilised on siliceous surfaces. On the other hand styrene is known to undergo homo-metathesis slowly in the presence of **1** and readily in the presence of second and further generations of Grubbs catalysts [17].

Treatment of a mixture of **5** and vinylsilane **11** in the presence of 5 mol% of Grubbs catalyst gives rise to conversion of reacting olefins and the evolution of ethene. To avoid homo-metathesis of **5**, vinylsilane was used in five- or tenfold excess. Examination of the reaction mixtures by ^{1}H NMR and GC-MS confirmed the

Table 1. Homo-metathesis of unsaturated derivatives of β-diketones and allyl diethylmalonate

Product(s)	Cat.	Solvent	Temp. [°C]	Yield [%] (isolated)	Stereoselectivity [%]	Tautomer ratio
 **6a**	1	CH_2Cl_2	40	37	90	1 / 4[a]
	2	CH_2Cl_2	40	99 (83)		1 / 4[a]
	3	CH_2Cl_2	40	99		1 / 4[a]
	4	benzene	80	85		1 / 4[a]
 **6b**	2	CH_2Cl_2	40	99 (71)	90	5 / 1[b]
 **6c**	2	CH_2Cl_2	40	74 (61)	100	keto[b]
 **6d**	1	CH_2Cl_2	40	69	100	keto[b]
	2	CH_2Cl_2	40	95		keto[b]
	3	CH_2Cl_2	40	99		keto[b]
	4	toluene	110	99		keto[b]
 **8**	2	toluene	110	90 (79)	95	-
 **10**	2	CH_2Cl_2	40	98 (75)	100	10 / 1[b]

Reaction conditions: 24 h, [diketone]:[Ru] = 1 : 5×10^{-2}; [a][total ketone form] / [total enol form] ratio determined by ^{1}H NMR in C_6D_6; [b][total ketone form] / [total enol form] ratio determined by ^{1}H NMR in $CDCl_3$;

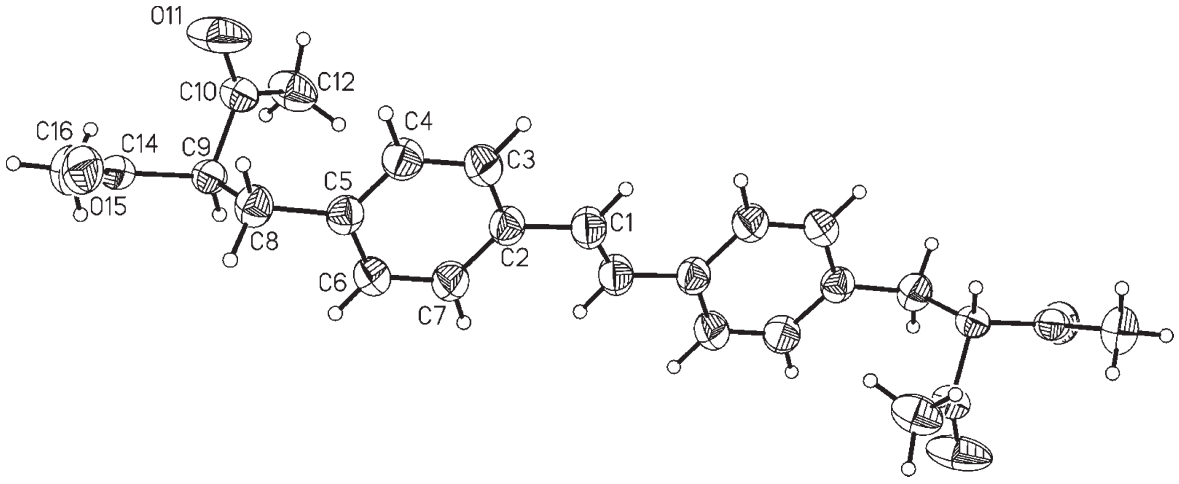
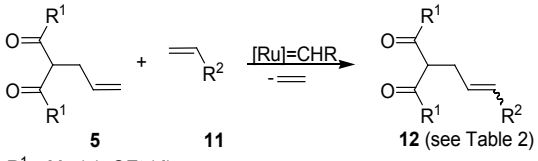


Figure 2. Perspective view of the molecule **10** with labeling scheme. The ellipsoids are drawn at the 50% probability level, hydrogen atoms are depicted as spheres of arbitrary radii [15]. The unlabelled part of the molecule is related with the labeled one by the symmetry operation -x,-y,-z. Some geometrical data: C1-C1(-x,-y,-z) 1.324(3) Å; C10-O11 1.1967(17) Å, C14-O15 1.2026(17) Å;

formation of CM products (Eq. 4). When compound **5a** was used as a reacting partner, the reaction results in formation of a mixture of tautomers.

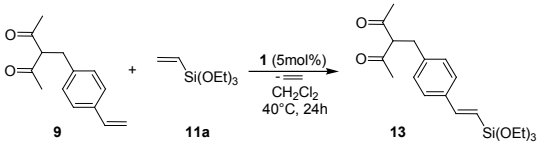


(4)

5 **11** **12** (see Table 2)

R^1 = Me (**a**), OEt (**d**);
R^2 = $Si(OEt)_3$ (**a**), $Si(OMe)_3$ (**b**), Ph (**c**)

CM requires more drastic reaction conditions than those of homo-metathesis. Relatively high yields were obtained for the reactions run in the presence of catalysts **2**, **3** or **4** in boiling benzene or toluene. Each time stereoselective formation of *E* isomer was observed and confirmed on the basis of ^{1}H NMR spectra. Selective synthesis of **12c** and **12e** by CM (Table 2) failed due to preference of **5a**, **5d** and styrene to form homo-metathesis products under conditions used. Products **12c** [18] and **12e** [19] can be more effectively synthesised by catalysed coupling of pentane-2,4-dione with an appropriate organic derivative. 3-[4-(ethenyl) benzyl]pentane-2,4-dione (**9**) was successfully tested in cross-metathesis with triethoxyvinylsilane (**11a**) (Eq. 5).

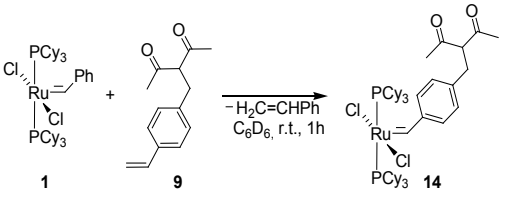


(5)

9 **11a** **13**

To avoid competitive homo-metathesis of **9**, triethoxyvinylsilane (**11a**) was used in tenfold excess. The reaction proceeded highly stereoselectively and led to exclusive formation of *E*-isomer of cross-metathesis product **13**, being a mixture of two tautomers. The results are presented in Table 2. To our knowledge, cross-metathesis products summarised in Table 2 except for **12c** and **12e** were not described in the literature.

To learn more on the reaction mechanism the interaction of benzylidene complex **1** with equimolar amount of **9** was monitored by ^{1}H NMR spectroscopy. Effective formation of styrene and new alkylidene complex (**14**) was observed, which indicates the stoichiometric metathesis according to Eq. 6.



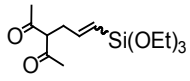
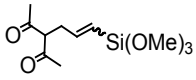
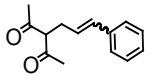
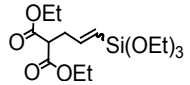
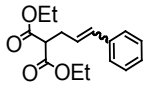
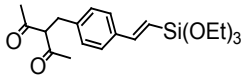
(6)

1 **9** **14**

yield = 95%
[ketone] / [enol] = 1 / 1.6

In C_6D_6 solution complex **14** is a mixture of tautomers. Keto to enol form ratio was calculated on the basis of ^{1}H NMR spectrum. Compound **14** was synthesised and characterised spectroscopically. Stoichiometric metathesis of second generation Grubbs catalyst (**2**) with **9** showed formation of minor amounts of a second generation analogue of **14**. However, in the presence of **2** homo-metathesis proceeds too fast for the propagative carbene to accumulate in the reaction mixture. Reaction of complex **14** with fivefold excess of compound **9** proceeds slowly and leads to formation of methylene complex and stilbene derivative **10**. After 6h of reaction in C_6D_6 at 40°C formation of 15% of methylene complex $[RuCl_2(PCy_3)_2(=CH_2)]$ and corresponding amount of **10** were observed by the ^{1}H NMR spectroscopy. The results of the equimolar reactions support metathesis mechanism of the reaction.

Table 2. Cross metathesis of unsaturated derivatives of β-diketones and allyl diethylmalonate

Product	Cat.	Solvent	Temp. [°C]	Time [h]	Yield (isolated) [%]	Tautomer ratio[a]	E / Z
 **12a**	2	CH_2Cl_2	40	24	80	1/ 2	>10 / 1
	2	toluene	110	24	90 (71)	1/ 2	
	4	toluene	110	24	90	1/ 2	
 **12b**	2	CH_2Cl_2	40	24	85 (67)[b]	1/ 1.3	>10 / 1
 **12c**	1	CH_2Cl_2	40	24	15	1/ 1.3	>10 / 1
 **12d**	2	toluene	110	24	90 (79)	-	>10 / 1
 **12e**	1	CH_2Cl_2	40	24	20	-	>10 / 1
 **13**	1	CH_2Cl_2	40	24	73 (52)[c]	1 / 1.8	E

Reaction conditions: 24h, [diketone]:[olefin]:[Ru]=1:10:5×10^{-2}; [a] [ketone form] / [enol form] ratio determined by ^{1}H NMR in C_6D_6; [b] [5a]:[11b] = 1:5; [c] [9]:[11a] = 1:5;

4. Conclusion

We have demonstrated that olefin metathesis catalysed by Grubbs type ruthenium alkylidene complexes can be conveniently used for synthesis and functionalisation of unsaturated derivatives of *β*-diketones. Conditions of efficient homo-metathesis of selected diketone derivatives and their cross-metathesis with vinyltrialkoxysilanes were demonstrated. Results of equimolar reactions support the expected carbene mechanism of the reaction.

Acknowledgement

Financial support from the Ministry of Science and Higher Education (Poland), (project No. N 204 1935 33) is gratefully acknowledged.

Supplementary data

Supplementary data associated with this article can be found separately.

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