Catalytic Performance of Ruthenium-Supported Ionic-Liquid Catalysts in Sustainable Synthesis of Macrocyclic Lactones

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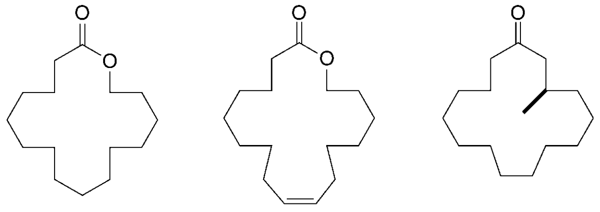
Thirteen- to eighteen-membered lactones were synthesized by ring-closing olefin-metathesis reactions of bis-olefins with heterogeneous *Grubbs*-supported ionic-liquid catalysts (SILCs), in which homogeneous *Grubbs* catalysts were confined in pores of alumina with the aid of an ionic liquid. The *Grubbs*-SILCs exhibited higher catalytic performance than their homogeneous counterparts and could be repeatedly recovered by simple filtration and re-used several times.

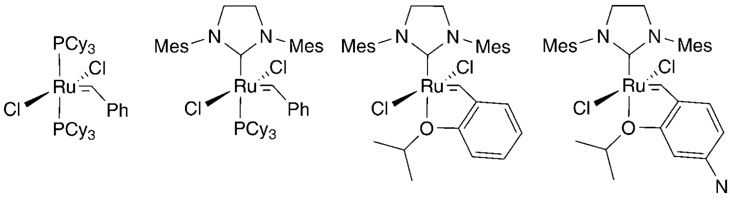
Introduction. – Macrocyclic lactones such as cyclopentadecano-15-lactone (=*Exaltolide*®; **1**) from angelica oil and cyclohexadec-9-eno-16-lactone (=ambrettolide; **2**) from ambrette oil (*Fig. 1*) are valuable and important perfumery ingredients for composing the bottom note of perfumery products [1]. These macrocyclic lactones have a strong musk scent in addition to preserving other scent ingredients in perfumes. Since compounds that are alternatives to natural muscone (=(3*R*)-3-methylcyclopentadecanone; **3**) such as aromatic nitro- and polycyclic musks are not currently used owing primarily to their low biodegradability, macrocyclic lactones are becoming increasingly important as alternative fragrance ingredients. However, a readily accessible supply of macrocyclic lactones cannot be easily obtained by intramolecular lactonization of long-chain hydroxy acids.



1 **2** **3**

Fig. 1. *Macrocyclic musk ingredients*

Since the development of carbeneruthenium and -molybdenum complexes (*Fig. 2*) by *Grubbs* and *Schrock*, respectively [2], olefin metathesis has emerged as a highly potent method for closing macrocyclic rings. Since these catalysts react almost exclusively with olefins and exhibit high tolerance toward a wide range of functional groups, metathesis reactions have been widely utilized as key steps in numerous total syntheses of complex natural products [3].



4 GR1 **5** GR2 **6** HG2 **7** AM-HG2

Fig. 2. Grubbs' *carbeneruthenium complex* **4** *and its congeners* **5**–**7**. PCy_3 = tricyclohexylphosphine; Mes = 2,4,6-trimethylphenyl.

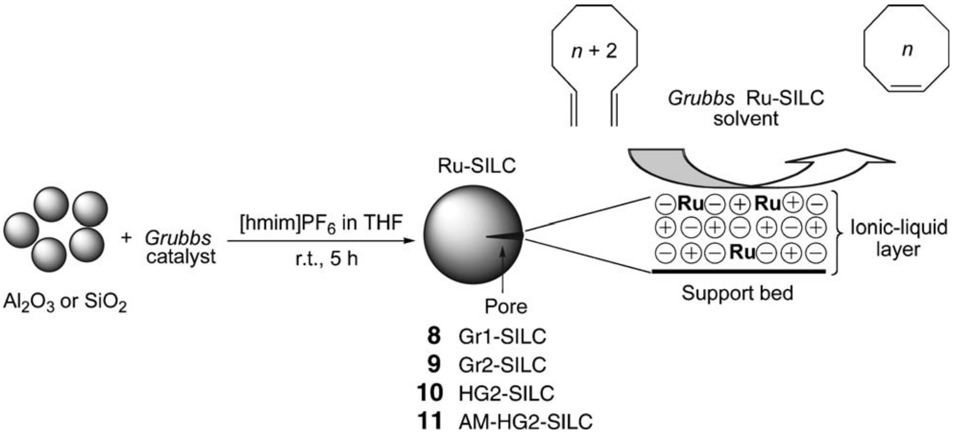
However, these exceptionally good catalysts are not without drawbacks. They easily deteriorate and are difficult to recycle when used in homogeneous catalysis. In addition, the catalytic turnover number is not high, and their high price and large molecular mass limit their use.

To solve these issues, considerable effort has been devoted to immobilize the *Grubbs* Ru catalysts on a variety of supports [4]. The *Grubbs* catalysts have been covalently immobilized on solid supports such as zirconium [5], silica [6], polymers [7], and dendrimers [8]. Covalent immobilization on liquid supports has been accomplished by anchoring ion-tagged *Grubbs* catalysts in ionic liquids [9], polyethylene glycol [10], and fluorous solvents [11]. More facile methods of noncovalent immobilization include dissolution in an ionic liquid [12], encapsulation in polymer beads [13], occlusion in polydimethylsiloxane [14], and ionic binding on sulfonated resin [15]. Although a plethora of immobilization methods have been developed, a limited number of these protocols have been successful in closing macrocyclic rings [6c][6e][7][15b], especially in terms of repeated use.

As part of our continuing efforts to immobilize homogeneous organometallic catalysts noncovalently, we have been investigating immobilization on supported ionic-liquid catalysts (SILCs), in which a homogeneous organometallic catalyst in an ionic liquid is confined within the pores of an inorganic solid support. The procedure is quite simple and uses commercially available catalysts without modifying their structures or requiring additional synthetic steps. The SILCs can be separated easily by filtration and recycled. With this protocol, Pd- [16], Cu- [17], and Ru-SILCs [18] (*Scheme*) have been developed and utilized as sustainable catalysts.

Results and Discussion. – Our investigation of the performance of Ru-SILCs as catalysts for macrolactonization was prompted by the lack of an efficient and sustainable method of macrolactonization in the presence of immobilized *Grubbs* catalysts, which we have successfully immobilized as SILCs [18], as well as our interest in developing efficient protocols for the synthesis of perfumery ingredients [19]. Inexpensive undec-10-enoic, oleic (=(9*Z*)-octadec-9-enoic) and erucic (=(13*Z*)-docos-13-enoic), acids were chosen as the acid moieties in the long-chain bis-olefinic esters **12**–**17** (*Table*), which were prepared by conventional methods with commercially available olefinic alcohols. The *Grubbs* first-generation (Gr1) and second-

Scheme. *Ring-Closing Olefin Metathesis Catalyzed by Ru*-SILC



generation (Gr2) catalysts **4** and **5** and the second-generation *Hoveyda-Grubbs* (HG2) catalyst **6** (*Fig. 2*) were immobilized as Gr1-SILC **8**, Gr2-SILC **9**, and HG2-SILC **10**, respectively, according to our previously reported procedure [18] (*Scheme*). The role of the ionic liquid in catalysis with Ru-SILCs is critical; Gr1 catalyst **4** did not exhibit any catalytic activity when immobilized by sintering without an ionic liquid. Moreover, HG2 catalyst **6** was transformed into the 4-(diethylamino) derivative **7** according to the procedure by *Kirschning*, *Grela*, and co-workers [15] and immobilized as AM-HG2-SILC **11** with the aid of 1-hexyl-3-methyl-1*H*-imidazolium hexafluorophosphate ([hmim]PF_6) on silica gel bearing propanesulfonic acid residues.

Ring-closing olefin metathesis reactions of bis-olefinic esters **12**–**18** were carried out in the presence of 0.2 equiv. of Ru-SILC in toluene at 100° under a N_2 atmosphere unless otherwise noted; the results are listed in the *Table*. In the case of allyl oleate (**12**), the reaction resulted in complete recovery of the starting ester **12** (*Entries 1–3*), which was likely due to the inherent difficulty of closing twelve-membered rings. No dimeric bis-lactone was obtained [18]. In contrast, thirteen- and fourteen-membered lactones **20** and **21** were synthesized from **13** and **14**, respectively, in good yield in the presence of Gr2-SILC **9** and HG2-SILC **10**, respectively (see *Entries 4–9*). Gr1-SILC **8** effectively closed pent-4-en-1-ylundec-10-enoate (**15**) into the fifteen-membered lactone **22** and was recycled five times by simple filtration without any pretreatment (*Entries 11–15*), while use of homogeneous Gr1 catalyst **4** resulted in recovery of a large amount of starting material (*Entry 10*). It is worth noting that heterogeneous Gr1-SILC **8** was more favorable for macrolactonization than the original homogeneous Gr1 catalyst **4**. A low catalytic performance was also observed when Gr1 catalyst **4** was immobilized with 1-butyl-2,3-dimethyl-1*H*-imidazolium hexafluorophosphate, which suggests activation of the Gr1 catalyst **4** in the SILC **8** by the intervention of the *N*-heterocyclic carbene at the ruthenium center [20] (*Entry 16*).

Cyclopentadecano-15-lactone (= *Exaltolide*®; **1**), a sixteen-membered lactone, has important commercial uses. Although this compound has been previously synthesized by olefin metathesis employing heterogeneous [7] as well as homogeneous *Grubbs*

Table. *Synthesis of Macrocyclic Lactones Catalyzed by Ru-SILC*[a])

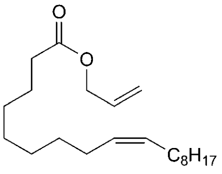
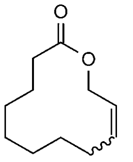
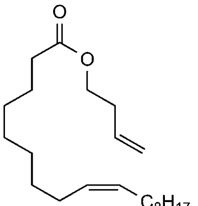
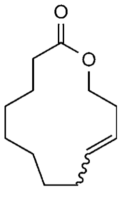
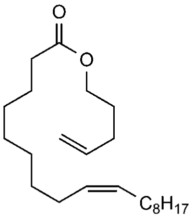
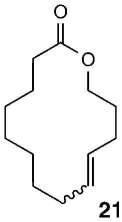
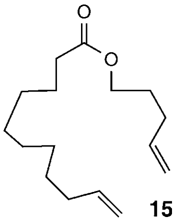
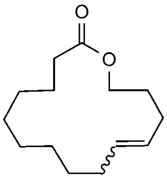
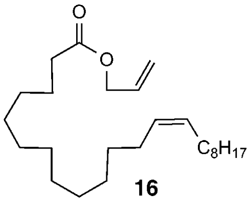
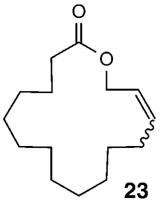
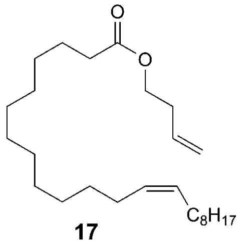
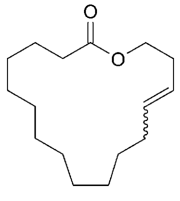
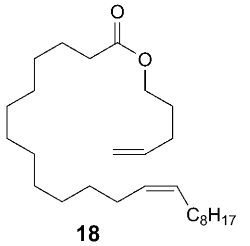
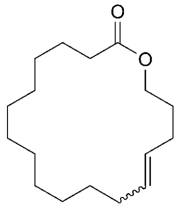
Entry	Substrate	Product	Catalyst	Time [h]	Yield [%][b])
1	 **12**	 **19**	Gr1 **4**	2	0
2			Gr1-SILC **8**	5	0
3			Gr2-SILC **9**	4.5	0
4	 **13**	 **20**	Gr1-SILC **8**	5	41 (62)
5			Gr2-SILC **9**	14	86 (98)
6	 **14**	 **21**	Gr1 **4**	2	43 (81)
7			Gr1-SILC **8**	1.5	60 (78)
8			Gr2-SILC **9**	4	60 (97)
9			HG2-SILC **10**	0.5	76 (76)
10	 **15**	 **22**	Gr1 **4**	1	42 (58)
11			Gr1-SILC **8**	0.75	66 (77)
12[c])				1.25	64 (77)
13[c])				2	61 (69)
14[c])				6	59 (59)
15[c])				18	39 (66)
16			Gr1-SILC **8**[d])	18	45 (45)
17	 **16**	 **23**	Gr1-SILC **8**	3	78 (94)
18[c])				36	46 (88)
19[e])			Gr1-SILC **8**	4.5	63 (78)
20[c])[e])				16	50 (68)
21[c])[e])				28	51 (74)
22			Gr2-SILC **9**	16	42 (86)
23[f])			HG2-SILC **10**	2	70 (91)
24[c])[f])				22	60 (85)
25			AM-HG2-SILC **11**	0.17	60 (65)
26[c])				0.17	51 (59)
27[c])				0.5	50 (60)
28[c])				18	41 (58)

Table (cont.)

Entry	Substrate	Product	Catalyst	Time [h]	Yield [%][b])
29	 **17**	 **24**	Gr1-SILC **8**	6	80 (98)
30			Gr2-SILC **9**	4	84 (84)
31	 **18**	 **25**	Gr1-SILC **8**	1.5	28 (35)
32			Gr2-SILC **9**	4	95

[a]) Reaction in the presence of 0.2 equiv. of Ru-SILC at 100° in toluene unless otherwise noted. [b]) Yield in parentheses based on recovered starting ester. [c]) The catalyst of the previous experiment was re-used. [d]) Gr1 catalyst **4** was immobilized with 1-butyl-2,3-dimethyl-1*H*-imidazolium hexafluorophosphate. [e]) Reaction in refluxing benzene. [f]) Reaction in refluxing toluene.

catalysts [21], to the best of our knowledge, there is no precedent for recycling the catalyst, particularly in the reaction of inexpensive allyl eruciate (**16**). The metathesis reaction of **16** catalyzed by Gr1-SILC **8** afforded the desired sixteen-membered lactone **23** when carried out in refluxing benzene to prevent rapid thermal decomposition of the catalyst. The catalyst was active until the third repeated use (*Entries 19–21*). Thermally more stable HG2-SILC **10** exhibited comparable catalytic activity (*Entries 23* and *24*). On the other hand, the reaction catalyzed by AM-HG2-SILC **11** proceeded more rapidly as shown by *Entries 25–28*, which is likely attributable to the electron-deficient nature of the aromatic ring of the AM-HG2 catalyst **7** as a result of protonation by acidic silica gel of the diethylamino group. Addition of titanium tetraisopropoxide was not effective in most of these experiments.

The much larger seventeen- and eighteen-membered lactones **24** and **25**, respectively, were also synthesized in high yield (*Entries 29–32*).

Conclusions. – In summary, homogeneous carbeneruthenium complexes **4**–**7** were immobilized as Ru-SILCs **8**–**11** in the pores of amorphous inorganic supports with the aid of the ionic liquid [hmim]PF_6. Ru-SILCs successfully catalyzed ring-closing olefin metathesis of bis-olefinic esters **13**–**18** to afford thirteen- to eighteen-membered macrocyclic lactones **20**–**25** in satisfactory yields and were used repeatedly several times after simple filtration without any pretreatment. The catalytic activity of the proposed catalysts was superior to that of their homogeneous counterpart Gr1 **4** for macrolactonization. The present protocol might be useful for the synthesis of macrocyclic perfumery ingredients since the starting bis-olefinic esters **13**–**18** are reasonably available, and catalytic hydrogenation of the macrocyclic lactones **20**–**25** proceeded smoothly. Immobilization of homogeneous organometallic catalysts as SILCs is simple and cost-effective, and is a mild method for immobilizing highly complex but unstable organometallic complexes on solid supports without changing their original catalytic activity.

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Experimental Part

General. IR Spectra: *Jasco-FT/IR-4200* spectrometer; in $CHCl_3$; $\tilde{\nu}$ in cm^{-1}. ^1H-NMR Spectra: *Jeol-EX-270* spectrometer at 270 MHz; in $CDCl_3$; δ in ppm rel. to Me_4Si as internal standard, J in Hz. MS: *Jeol-GCMate* (EI, 70 eV) instrument; in m/z (rel. %).

1-Oxacyclotridec-9-en-2-one (**20**). Gr2-SILC **9** was prepared according to the procedure reported previously [18]. A stirred suspension of Gr2-SILC **9** (1.252 g, 0.008 mmol/g) and pent-4-en-1-yl oleate (**13**; 16.9 mg) in toluene (10 ml) was heated at 100° for 14 h under N_2. After cooling to r.t., the Ru-SILC **9** was rinsed with Et_2O (4 ×). The combined org. phase was concentrated and the residue purified by medium-pressure LC (SiO_2, AcOEt/hexane 1:9): **20** (8.5 mg, 86%). IR: 3012, 2927, 2858, 1726. ^1H-NMR: 1.25–1.44 (*m*, 8 H); 1.63–1.68 (*m*, 2 H); 2.00–2.09 (*m*, 2 H); 2.27–2.39 (*m*, 4 H); 4.15 (*t*, J = 5.4, 2 H); 5.30–5.42 (*m*, 1 H); 5.46–5.62 (*m*, 1 H). EI-MS: 196 (7, M^+), 107 (31), 95 (38), 94 (44), 93 (62), 82 (29), 81 (67), 80 (73), 79 (100), 69 (29), 68 (53), 67 (76). HR-MS: 196.1463 ($C_{12}H_{20}O_2^+$; calc. 196.1457).

1-Oxacyclotetradec-10-en-2-one (**21**). IR: 3020, 2934, 2860, 1725. ^1H-NMR: 1.29–1.35 (*m*, 10 H); 1.62–1.81 (*m*, 4 H); 2.01–2.06 (*m*, 2 H); 2.01–2.28 (*m*, 2 H); 2.32–2.43 (*m*, 2 H); 4.10–4.15 (*m*, 2 H); 5.26–5.57 (*m*, 2 H). EI-MS: 210 (29, M^+), 109 (29), 96 (39), 95 (67), 83 (26), 82 (89), 81 (100), 80 (27), 79 (48), 69 (40), 68 (100), 67 (100). HR-MS: 210.1621 ($C_{13}H_{22}O_2^+$; calc. 210.1620).

1-Oxacyclopentadec-11-en-2-one (**22**). IR: 3016, 2932, 2858, 1725. ^1H-NMR: 1.34 (*m*, 10 H); 1.61–1.82 (*m*, 4 H); 2.01–2.02 (*m*, 2 H); 2.20–2.23 (*m*, 2 H); 2.31–2.39 (*m*, 2 H); 4.10–4.16 (*m*, 2 H); 5.27–5.45 (*m*, 2 H). EI-MS: 224 (17, M^+), 96 (32), 95 (48), 83 (29), 82 (63), 81 (99), 79 (37), 71 (69), 69 (34), 68 (100), 67 (93). HR-MS: 224.1758 ($C_{14}H_{24}O_2^+$; calc. 224.1776).

1-Oxacyclohexadec-14-en-2-one (**23**). IR: 3001, 2927, 2855, 1728. ^1H-NMR: 1.28 (*m*, 16 H); 1.56–1.65 (*m*, 2 H); 2.06–2.15 (*m*, 2 H); 2.32–2.39 (*m*, 2 H); 4.19 (*m*, 2 H); 5.53–5.78 (*m*, 2 H). EI-MS: 238 (27, M^+), 111 (28), 109 (34), 98 (56), 97 (40), 96 (62), 95 (73), 84 (25), 83 (54), 82 (87), 81 (100), 69 (72), 68 (86), 67 (100). HR-MS: 238.1937 ($C_{15}H_{26}O_2^+$; calc. 238.1933).

1-Oxacycloheptadec-14-en-2-one (**24**). IR: 3020, 2929, 2856, 1712. ^1H-NMR: 1.23–1.40 (*m*, 18 H); 1.59–1.67 (*m*, 2 H); 2.00–2.07 (*m*, 2 H); 2.26–2.40 (*m*, 4 H); 4.14 (*t*, J = 5.37, 2 H); 5.30–5.55 (*m*, 2 H). EI-MS: 252 (21, M^+), 96 (43), 95 (47), 83 (27), 82 (74), 81 (73), 69 (38), 68 (100), 67 (82). HR-MS: 252.2077 ($C_{16}H_{28}O_2^+$; calc. 252.2089).

1-Oxacyclooctadec-14-en-2-one (**25**). IR: 3008, 2929, 2855, 1723. ^1H-NMR: 1.26–1.29 (*m*, 18 H); 1.65–1.75 (*m*, 2 H); 2.00–2.10 (*m*, 4 H); 2.33 (*t*, J = 6.35, 2 H); 4.12 (*t*, J = 6.84, 2 H); 5.35–5.40 (*m*, 2 H). EI-MS: 266 (17, M^+), 96 (43), 95 (45), 82 (80), 81 (83), 69 (31), 68 (100), 67 (82). HR-MS: 266.2262 ($C_{17}H_{30}O_2^+$; calc. 266.2246).

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