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Communications

Water-Soluble Ruthenium Vinylidene and Allenylidene Complexes: Potential Catalysts for Ring-Opening Metathesis

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Summary: Reaction of the water-soluble ruthenium complex $[\{RuCl_2(TPPMS)_2\}Na_2]_2\cdot 4H_2O$ *with phenylacetylene and diphenylpropargyl alcohol in THF at room temperature gave the water-soluble unsaturated carbenes* $[\{RuCl_2\{C{=}C(H)Ph\}(TPPMS)_2\}]Na_2$ *and* $[\{RuCl(\mu\text{-}Cl)(C{=}C{=}CPh_2)(TPPMS)_2\}_2]Na_4$*, respectively. The ability of these complexes, which represents the first example of water-soluble vinylidenes and allenylidenes, to catalyze the ring-opening metathesis of cyclic olefins with methyl acrylate as chain transfer reagents is briefly discussed.*

Unsaturated carbenes, particularly the lower members vinylidenes[1] and allenylidenes,[2] are useful reagents in both organic synthesis and homogeneous catalysis. Recent applications reported by Ozawa,[3] Hill,[4,5] Nolan,[6] Dixneuf,[5,7] and their co-workers include the ring-opening metathesis polymerization of strained olefins and the ring-closing metathesis of different substrates. It is now apparent that unsaturated vinylidenes and allenylidenes of Ru(II) represent a valid alternative to Grubbs' catalysts[8] for olefin metathesis.[9]

Despite the ubiquitous character of transition-metal vinylidenes[1] and allenylidenes,[2] water-soluble complexes containing these ligands have not yet been reported, which is quite surprising given the intense research activity centered on this class of metal complexes[10] and the increasing demand for environmentally benign technologies in fine chemicals manufacturing.[10a,11] In this communication, we report the successful synthesis of water-soluble ruthenium(II) vinylidene and allenylidene species and show that these complexes are capable of promoting olefin metathesis reactions. In particular, we show that the selective ring-opening metathesis (ROM) of cyclopentene with methyl acrylate can be accomplished in aqueous biphasic systems, which

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(9) For recent reviews, see: Fürstner, A. *Top. Catal.* **1997**, *4*, 285. Schuster, M.; Blechert, S. *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 2036.

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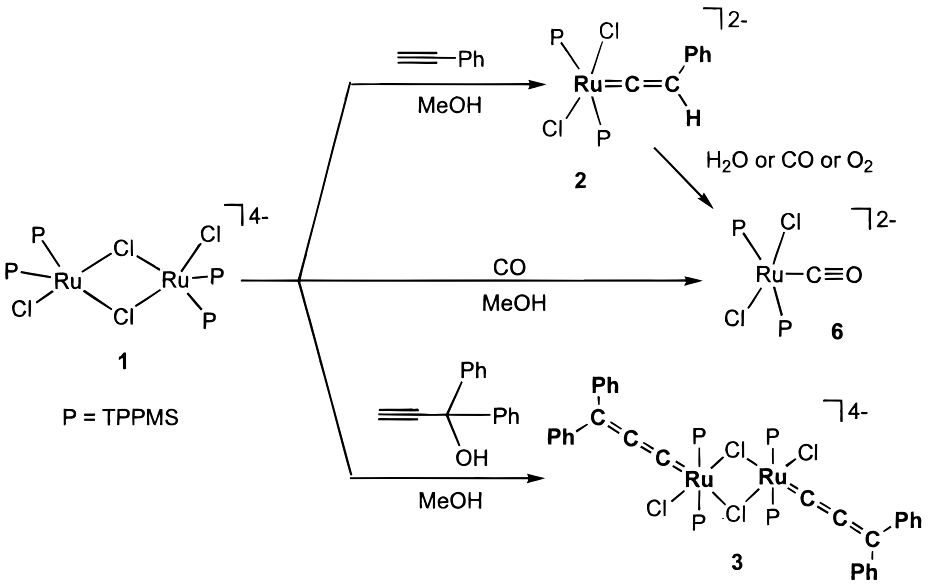
Scheme 1



is quite intriguing because Grubbs' carbene complexes do not catalyze the ROM of cycloalkenes with electron-poor olefins.[12]

$[RuCl_2(PPh_3)_3]$ is a suitable precursor for the preparation of the known pale green dimer $[\{RuCl_2(TPPMS)_2\}Na_2]_2\cdot 4H_2O$ (**1**) by reaction with TPPMS (TPPMS = $Ph_2P\{2\text{-}OS(O)_2C_6H_4\}^-Na^+$) in THF at reflux temperature.[13] The straightforward reaction of **1** at 40 °C (Scheme 1) in MeOH with $HC\equiv CPh$ or $HC\equiv CCPh_2OH$ affords in moderate to good yields either the yellow mononuclear vinylidene $[\{RuCl_2\{C=C(H)Ph\}(TPPMS)_2\}]Na_2$ (**2**) or the purple binuclear allenylidene $[\{RuCl(\mu\text{-}Cl)(C=C=CPh_2)(TPPMS)_2\}_2]Na_4$ (**3**).[14] Both compounds are soluble in MeOH and water and, to our knowledge, represent the first water-soluble unsaturated carbenes described so far ($S(H_2O)_{22\,°C} = 0.12$ g/mL (**2**); 0.04 g/mL (**3**)).

Complexes **2** and **3** exhibit spectroscopic features in agreement with the presence of an unsaturated C_2 and C_3 carbene ligand, respectively. Key pieces of evidence come from the $^{13}C\{^1H\}$ NMR spectra (CD_3OD, 22 °C), which show signals at 350.25 (C_α) and 123.68 ppm (C_β) for **2** and at 309.25 (C_α), 215.99 (C_β), and 158.63 ppm (C_γ) for **3**, and from the typical IR absorptions at 1621 cm^{-1} ($\nu_{C=C}$, **2**) and 1930 cm^{-1} ($\nu_{C=C=C}$, **3**). The FAB-MS spectra confirm the mononuclear nature of **2** and the binuclear structure of **3**. In addition to spectroscopic data, the nature of **2** and **3** is supported by their reactivity, which is in line with the known chemistry of vinylidenes[1] and allenylidenes,[2,15] respectively. Thus, **2** reacts with *n*-propylamine[16] and ethanethiol[17] to yield the corresponding amino- and thiocarbene derivatives $[\{RuCl_2\{C(NHPr)CH_2Ph\}(TPPMS)_2\}]Na_2$ (**4**) and $[\{RuCl_2\{C(SEt)CH_2Ph\}(TPPMS)_2\}]Na_2$ (**5**), respectively. Carbonylation of **2** in CH_3OH affords the carbonyl complex $[\{RuCl_2(CO)(TPPMS)_2\}]Na_2$ (**6**) via vinylidene to phenylacetylene retrotautomerization (GC-MS detected). Noticeably, **6** is formed also by hydrolysis of **2**[18] or by exposing **1** to a CO atmosphere. The allenylidene **3** reacts neither with water[19] nor with CO or O_2 (P_{CO} or $P_{O_2} = 1$ atm). However, **3** is endowed with reactivity toward primary amines and thiols. As an example, the reaction of **3** with *n*-propylamine gives the alkenylaminocarbene $[\{RuCl(\mu\text{-}Cl)\{C(NHPr)CH=CPh_2)(TPPMS)_2\}_2]$-

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[10] Some water-soluble ruthenium alkylidenes capable of initiating the olefin metathesis have already been described. See: (a) Grubbs, R. H. In *Aqueous Organometallic Chemistry and Catalysis*; Horváth, I. T., Joó, F., Eds.; NATO ASI Series 35; Kluwer Academic: Dordrecht, The Netherlands, 1995; p 15. (b) Mohr, B.; Lynn, D. M.; Grubbs, R. H. *Organometallics* **1996**, *15*, 4317. (c) Lynn, D. M.; Mohr, B.; Grubbs, R. H. *J. Am. Chem. Soc.* **1998**, *120*, 1627. (d) Lynn, D. M.; Mohr, B.; Grubbs, R. H.; Henling, L. M.; Day, M. W. *J. Am. Chem. Soc.* **2000**, *122*, 6601.

[11] *Aqueous-Phase Organometallic Catalysis*; Cornils, B., Herrmann, W. A., Eds.; Wiley-VCH: Weinheim, Germany, 1998.

[12] The catalytic metathesis of electron-poor olefins has recently been accomplished. See: Stüer, W.; Wolf, J.; Werner, H.; Schwab, P.; Schulz, M. *Angew. Chem., Int. Ed. Engl.* **1998**, *37*, 3421. Fürstner, A.; Thiel, O. R.; Ackermann, L.; Schanz, H.-J.; Nolan, S. P. *J. Org. Chem.* **2000**, *65*, 2204.

[13] Joó, F.; Kovacs, J.; Katho, A.; Benyei, A. C.; Decuir, T.; Darensbourg, D. J. *Inorg. Synth.* **1998**, *32*, 2.

[14] General procedure for the preparation of **2** and **3**: A solution of $[\{RuCl_2(TPPMS)_2\}Na_2]_2\cdot 4H_2O$ (**1**; 1.0 mmol) in MeOH (10 mL) was treated under nitrogen with a stoichiometric amount of neat $HC\equiv CPh$ or $HC\equiv CCPh_2OH$ and stirred at 40 °C for 15 min (**2**) or 1 h (**3**). The solution was filtered through silica and concentrated to ca. 2 mL under vacuum. Addition of acetone (**2**) or *n*-hexane (**3**) (10 mL) gave **2** or **3**, which was filtered off and washed with acetone (**2**) or *n*-hexane (**3**) (5 mL) before being dried under a vacuum. **2**: yellow, yield 45%. Anal. Calcd for $C_{44}H_{34}Cl_2O_6Na_2P_2RuS_2$: C, 52.70, H, 3.42. Found: C, 52.34, H, 3.59. IR: $\nu_{C=C}$ 1621 cm^{-1} (m). $^{31}P\{^1H\}$ NMR (22 °C, CD_3OD, 121.49 MHz): δ 23.87 (s). ^1H NMR (22 °C, CD_3OD, 300.13 MHz): $\delta_{C=CH}$ 3.65 (br s, 1H, disappears in 15 min by exchanging with the deuterated solvent), $\delta_{aromatic}$ 8.4−6.7 (m, 33H). $^{13}C\{^1H\}$ NMR (22 °C, CD_3OD, 75.47 MHz): $\delta_{C\alpha}$ 350.53 (t, $^2J(C,P) = 18.3$ Hz), $\delta_{C\beta}$ 123.68 (s). FAB-MS (*m/z* (%)): 845.2 (14) $HNa[\{(TPPMS)_2RuCl\}]^+$, 783 (70) $H[(TPPMS)_2Ru]^+$, 567.2 (100) $Na[\{(TPPMS)RuC=CPh\}]^+$. **3**: purple, yield 78%. Anal. Calcd for $C_{102}H_{76}Cl_4O_{12}Na_4P_4Ru_2S_4$: C, 56.15, H, 3.51. Found: C, 55.90, H, 3.72. IR: $\nu_{C=C=C}$ 1930 cm^{-1} (m). $^{31}P\{^1H\}$ NMR (22 °C, CD_3OD, 121.49 MHz): AB system, δ_A 43.78, δ_B 41.44, $^2J(P_A,P_B) = 29.2$ Hz. ^1H NMR (22 °C, CD_3OD, 300.13 MHz): $\delta_{aromatic}$ 8.3−6.8 (m, 76H). $^{13}C\{^1H\}$ NMR (22 °C, CD_3OD, 75.47 MHz): $\delta_{C\alpha}$ 309.27 (t, $^2J(C,P) = 19.7$ Hz), $\delta_{C\beta}$ 215.99 (s), $\delta_{C\gamma}$ 158.63 (s). FAB-MS (*m/z* (%)): 2146.5 (6) $Na_4[\{(TPPMS)_2RuCl_3(C=C=CPh_2)\}_2]^+$, 2123.5 (6) $HNa_3[\{(TPPMS)_2RuCl_3(C=C=CPh_2)\}_2]^+$, 2087.0 (10) $Na_3[\{(TPPMS)_2RuCl_2(C=C=CPh_2)\}_2]^+$, 2043.0 (21) $H_2Na[\{(TPPMS)_2RuCl_2(C=C=CPh_2)\}_2]^+$, 655.1 (100) $Na[\{(TPPMS)Ru(C=C=CPh_2)\}]^+$.

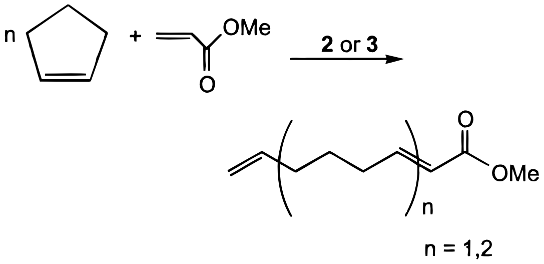
[15] Bis(allenylidene) diruthenium complexes of the formula $[(PPh_3)_4(\mu\text{-}Cl)_3Ru_2(C=C=CAr_2)]PF_6$ (Ar = Ph, *p*-C_6H_4Cl, *p*-C_6H_4F) were obtained from the reaction of $[RuCl_2(PPh_3)_3]$ with $HC\equiv CCAr_2OH$: Touchard, D.; Guesmi, S.; Bouchaib, M.; Haquette, P.; Daridor, A.; Dixneuf, P. H. *Organometallics* **1996**, *15*, 2579.

[16] Bianchini, C.; Peruzzini, M.; Masi, D.; Romerosa, A.; Zanobini, F. *Organometallics* **1999**, *18*, 4501.

[17] Boland-Lussier, B. E.; Hughes, R. *Organometallics* **1982**, *1*, 635. Bianchini, C.; Glendenning, L.; Peruzzini, M.; Romerosa, A.; Zanobini, F. *Chem. Commun.* **1994**, 2219.

Na_4 (**7**).[20] These and similar transformations involving **2** and **3** are at present under investigation and will be reported in due course.

A preliminary assessment of the catalytic performance of **2** and **3** in homogeneous ROM reveals that both unsaturated carbenes are active catalysts in promoting the cross-olefin metathesis of cyclopentene with methyl acrylate to give polyunsaturated esters (eq 1). Noticeably, the catalytic reactions proceed with good efficiency and selectivity under mild conditions (22 °C).[21]



(1)

With the vinylidene **2** as the catalyst, the selective formation of the ester $C_7H_{11}CO_2Me$ ($n = 1$ in eq 1) takes place after 2 h in a homogeneous methanolic system at room temperature (yield 64%). In contrast, **2** is catalytically inactive in the same process in a biphasic system. Replacing **2** with **3** does not provide a more efficient ROM catalyst but makes feasible a catalytic reaction also in the biphasic aqueous system. Thus, while the selective formation of the ester $C_7H_{11}CO_2Me$ occurs in the monophasic system (yield 56%), a 1:12 mixture of $C_7H_{11}CO_2Me$ ($n = 1$) and $C_{12}H_{19}CO_2Me$ ($n = 2$) is formed in the biphasic system Et_2O/H_2O (yield 42%).

In summary, the isolation and characterization of the first water-soluble Ru(II) vinylidene and allenylidene complexes has allowed us to demonstrate that such compounds could be successfully used to catalyze olefin metathesis. In particular, the use of vinylidenes and allenylidenes to bring about the selective ROM of electron-poor acyclic olefins is without precedent and worthy of further expansion. Current work in our laboratories is aimed at investigating the mechanism of the catalytic reactions as well as exploring the synthetic scope of these highly accessible water-soluble unsaturated carbenes. In this respect, particular attention is being paid to investigate the tolerability of the process to different polar functional groups.

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Supporting Information Available: Text giving experimental details describing (i) the stability of **2** and **3**, (ii) in situ NMR monitoring of the reaction between **1** and HC≡CPh or $HC{\equiv}CCPh_2OH$, and (iii) the synthesis and characterization of complexes **4**−**7**. This material is available free of charge via the Internet at http://pubs.acs.org.

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[18] The oxidative cleavage of the vinylidene in **2** in MeOH yields **6** and PhCHO. See: Bianchini, C.; Innocenti, P.; Peruzzini, M.; Romerosa, A.; Zanobini, F. *Organometallics* **1996**, *15*, 272. The hydrolysis of Ru(II) vinylidenes has been studied in detail. See: Bianchini, C.; Casares, J. A.; Peruzzini, M.; Romerosa, A.; Zanobini, F. *J. Am. Chem. Soc.* **1996**, *118*, 4585.

[19] Bianchini, C.; Peruzzini, M.; Lopez; C.; de los Rios, I.; Romerosa, A.; Zanobini, F. *Chem. Commun.* **1999**, *243*.

[20] Bernad, D. J.; Esteruelas, M. A.; Lopez, A. M.; Modrego, J.; Puerta, M. C.; Valerga, P. *Organometallics* **1999**, *18*, 4995.

[21] Selective ROM of cyclopentene with methyl acrylate was performed (catalyst:cyclopentene = 1:590). Catalysis with **2** was carried out as follows. (A) Monophasic system: A solution of **2** (38.5 mg, 0.039 mmol) in MeOH (2 mL) and 0.06 mL of $HBF_4{\cdot}OEt_2$ [10c] was added to a mixture of methyl acrylate (25 mL, 0.276 mol) and cyclopentene (2 mL, 0.023 mol) at room temperature (22 °C). After the solution was stirred for 2 h at this temperature under nitrogen, the solvent and the excess substrates were distilled off at atmospheric pressure. The residue was taken up in 30 mL of pentane/diethyl ether (1:5 v/v) and filtered through a column (3 × 2 cm) filled with aluminum oxide (neutral, activity grade I) to give a colorless solution. GC/MS analysis showed the presence of $C_7H_{11}CO_2CH_3$ (92%). Total yield: 64%. (B) Biphasic system: The catalytic tests were carried out by mixing 25 mL of methyl acrylate and 2 mL of cyclopentene with 25 mL of Et_2O and 5 mL of H_2O containing **2** (38.5 mg, 0.039 mmol) and 0.06 mL of $HBF_4{\cdot}OEt_2$. The mixture was vigorously stirred for 2 h under nitrogen, after which the organic layer was separated, washed with 2 mL of H_2O, and dried over $MgSO_4$. After evaporation of the solvent no organic product was detected, indicating that under these conditions the system was catalitycally inactive. Catalysis with **3**: Replacing **2** with **3** (84 mg, 0.039 mmol) as catalyst under similar experimental conditions gave the following results. (A) Monophasic system: $C_7H_{11}CO_2CH_3$ (87%). Total yield: 56%. (B) Biphasic system: $C_{12}H_{19}CO_2CH_3$ (83%) and $C_7H_{11}CO_2CH_3$ (7%). Total yield: 42%.