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Catalytic Oxidation of THF with homo and hetero metallic Mo/Ru complexes and molecular oxygen

Catalytic oxidation of THF with homo and hetero metallic Mo/Ru complexes and molecular oxygen ☆

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Abstract

The novel complex $Ind(CO)_3Mo–Ru(CO)_2Cp$ (**1**) ($Ind = \eta^5$-indenyl, $Cp = \eta^5$-cyclopentadienyl), as well as other hetero and homo metallic complexes of molybdenum and ruthenium are catalyst precursors in the aerobic oxidation of THF under ambient conditions. Selectivities towards γ-butyrolactone of up to 70% are obtained. For the first time in this transformation, propylformate is isolated besides the lactone.
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1. Introduction

During our reactivity studies of the novel hetero bimetallic complex $Ind(CO)_3Mo–Ru(CO)_2Cp$ (**1**) and $Cp(CO)_3Mo–Ru(CO)_2Cp$ (**2**) [1] towards carbon monoxide and carbon dioxide, respectively, we incidentally detected the formation of γ-butyrolactone in THF solutions of **1** and **2** when they were exposed to air. Since co-operative effects between the metals make **2** an exceptionally efficient catalyst in the hydrodesulphurisation of thiophene [2] and the aerobic oxidation of THF with ruthenium complexes as catalysts is only mentioned briefly in the literature [3], we were prompted to investigate the oxidation reaction in more detail.

The selective oxidation of ethers to their corresponding esters or lactones in presence of transition metal compounds is an important reaction and is well documented. Among the oxidants used in stoichiometric amounts are metal oxides such as CrO_3, $ZnCr_2O_7$, $KMnO_4$, $Zn(MnO_4)_2$, Mn_2O_7, and RuO_4 [4]. Together with terminal oxidants such as $NaIO_4$, $LiClO$ or organic peroxides, catalytic amounts of RuO_4 [5], $RuCl_3$ [6], $RuCl_2[1,3$-bis(diphenylphosphino)propane]$_2$ [7] or of the type $[Ru^{III}(L^x)(L^y)Cl]$ [8], promote this transformation. For more than a decade now, much research has been directed to employing molecular oxygen as a cheap, safe and clean, i.e., an environmentally more attractive, 'green,' alternative to the above mentioned oxidants [9]. For example, $CoCl_2$ [10], $Co(acac)$ [11], Pt [12], and dinuclear Cu [13] systems have been established in the oxygenation of THF with molecular oxygen, usually working at elevated temperatures. In presence of carbon monoxide [14] or carbon dioxide [15], this process is promoted by $PdCl_2/CuCl_2$ [14], $FeCl_2$ [15a], or Rh complexes [15a,15b]. Recently, a whole array of mono nuclear, late transition metal complexes have been reported to catalyse the selective oxidation of THF, yielding γ-butyrolactone as well as small quantities of 2-hydroxytetrahydrofuran and 4-hydroxybutanal [3]. Here we present some preliminary results concerning the catalytic aerobic oxidation of THF, using hetero and homo metallic Mo and Ru complexes as catalyst precursors.

2. Experimental

2.1. Materials and methods

All manipulations of air-sensitive materials were performed under a nitrogen atmosphere in conventional

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Schlenk apparatus. Solvents were distilled from Na benzophenyl ketyl under nitrogen. Hexane for column chromatography was deoxygenated but otherwise used as received. C_6D_6 was deoxygenated (three freeze-pump-thaw cycles) and stored under argon over molecular sieves. Indene, cyclopentadienyl sodium (2 M in THF), n-butyllithium (1.6 M in hexanes), $Mo(CO)_6$, $[Mo(CO)_3Cp]_2$ (**4**) (all purchased from Aldrich) and $RuCl_3 \cdot H_2O$ (Strem) were used as received. Silica gel 60 (0.063–0.200 mm, Merck) for column chromatography was kept under HV for 24 h and saturated with nitrogen before use. Column dimensions: 2×40 cm. Infrared spectra were measured on a Perkin Elmer Spectrum One FT-IR spectrometer in hexane or THF solution, respectively. ^1H and ^{13}C NMR spectra were recorded on a Bruker Avance 400 MHz spectrometer using C_6D_6 or $CDCl_3$ and acetone-d6 as solvents for the organometallics and the organic samples, respectively. Elemental analysis were performed with a Perkin Elmer Elemental Analyzer 2400 CHN. $Cp(CO)_3Mo–Ru(CO)_2Cp$ (**2**) [1], [CpRu$(CO)_2]_2$ (**3**) [16] and $CpRu(CO)_2Br$ [17] were prepared according to methods reported in the literature.

2.2. Synthesis of $Ind(CO)_3Mo–Ru(CO)_2Cp$ (**1**)

1.5 ml (2.4 mmol) of a 1.6 M solution of n-BuLi in hexanes were added dropwise to 300 μl (2.6 mmol) of freshly distilled indene in 20 ml THF at −78 °C. After stirring for 2 h at RT, 528 mg (2.0 mmol) $Mo(CO)_6$ were added and the mixture was refluxed for 18 h until the formation of $LiMo(CO)_3Ind$ is complete (IR). A solution of 604 mg (2.0 mmol) $CpRu(CO)_2Br$ in 20 ml THF was added dropwise at RT, the mixture refluxed until the starting materials were consumed (25 h, IR) and subsequently concentrated and separated into its components by column chromatography. Fraction 1 (eluent: hexane/THF 25/1): 495 mg (0.96 mmol, 48 %) red-orange cubes of $Ind(CO)_3Mo–Ru(CO)_2Cp$ (**1**) (from hexane/THF at −25 °C). IR (hexane) [cm^{-1}]: 2023 (vw), 2008 (vw), 1963 (vs), 1955 (vs), 1922 (vw), 1902 (w), 1884 (m), IR (THF) [cm^{-1}]: 2015 (vw), 2006 (vw), 1953 (vs), 1988 (sh), 1873 (m) [1]. ^1H-NMR (C_6D_6) [ppm]: 7.29 (m, 2 H, Ind, $H_{4,7}$), 6.75 (m, 2 H, Ind, $H_{5,6}$), 5.44 (d, 2 H, $^3J = 6.0$ Hz, Ind, $H_{1,3}$), 5.05 (t, 1 H, $^3J = 6.0$ Hz, Ind, H_2), 4.48 (s, 5 H, RuCp). ^{13}C-NMR (C_6D_6) [ppm]: 219.4 (s, CO), 124.1 (d, $^1J_{CH} = 160$ Hz, Ind, $C_{5,6}$), 123.4 (d, $^1J_{CH} = 165$ Hz, Ind, $C_{4,7}$), 109.4 (s, Ind, $C_{7a,7b}$), 91.8 (d, $^1J_{CH} = 175$ Hz, Ind, C_2), 87.5 (d, $^1J_{CH} = 179$ Hz, RuCp), 89.7 (d, $^1J_{CH} = 177$ Hz, Ind, $C_{1,3}$). Anal. Calcd. for $C_{19}H_{12}O_5MoRu$ (FW = 517.3108): C, 44.11; H, 2.34. Found C, 44.81; H, 2.43.

2.3. Catalytic runs

In a typical catalytic run, 0.1 mmol of the catalyst precursor was dissolved in 30 ml of dry THF and stirred under atmospheres of O_2, O_2/CO (1:1) and O_2/CO_2 (1:1), respectively, which were supplied by balloon. The control runs under Ar, CO and CO_2 were carried out in sealed Schlenk flasks under a pressure of 0.5 bar. The reactions were monitored by IR spectroscopy and the amounts of γ-butyrolactone formed were derived from reference calibration (area for the v-CO band at 1780 cm^{-1}). A rough quantitative approximation of the sum of all other products was obtained by reference to propylformate calibration (area for the v-CO band at 1726 cm^{-1}, relevant for all formed CO compounds other than γ-butyrolactone). Fractional distillation of the reaction mixture of a typical **3** + O_2 run allowed us to isolate the pure products γ-butyrolactone, succinic acid and propylformate as well as to quantify the sum of all other products. The formate acetal **6** [10] and others were detected in the mother solution and mixed fractions (NMR) but were not isolated. The organic compounds were identified by comparison of spectral data with literature results and/or authentic samples.

3. Results and discussion

$Ind(CO)_3Mo–Ru(CO)_2Cp$ (**1**) was synthesised in moderate yield (48%) by a metathesis of $LiMo(CO)_3Ind$ and $Cp(CO)_2RuBr$. The proton and carbon NMR spectra exhibit the expected pattern for the Cp and indenyl ligands. In the carbon NMR, a single resonance for the CO ligands is detected at room temperature, which indicates a facile and rapid interchange of all the carbonyl groups of the molecule in and between the two metal moieties in solution. In the IR spectra, the absence of bands correspondent to bridging carbonyls, suggests an all-terminal carbonyl structure, featuring an unbridged metal–metal bond (for a more detailed explanation of IR features of the isostructural **2**, see [1]).
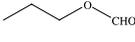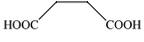
Treatment of 30 ml of a THF solution of 0.1 mmol of the catalyst precursors $Ind(CO)_3Mo–Ru(CO)_2Cp$ (**1**), $Cp(CO)_3Mo–Ru(CO)_2Cp$ (**2**), $Cp(CO)_2Ru–Ru(CO)_2Cp$ (**3**), $Cp(CO)_3Mo–Mo(CO)_3Cp$ (**4**) or $RuCl_3 \cdot H_2O$ (**5**), respectively, with molecular oxygen, leads to the formation of γ-butyrolactone in high turnover numbers (TON) and other organic products (Scheme 1). To the best of our knowledge, propylformate is isolated for the first time in an aerobic oxidation reaction of THF. It can be formed via an oxidative cleavage from the lactol or the formate acetal **6** [10,12b,18].

Upon exposure to oxygen, the orange solutions of **1** and **2** as well as the yellow solution of **3**, turned black with time and a black precipitate was formed, reflecting the formation of the active catalyst species by oxidative decomposition of the starting materials. Organic product formation was observed from the start of the reaction. It did not alter while and after **1–3** were oxidised (IR control). The red solution of **4** turned yellow, indicating the formation of oxo-complexes [19].
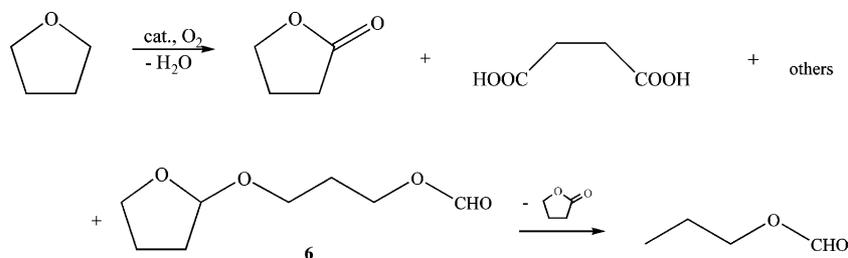
Scheme 1.

Table 1
Oxidation of THF under various conditions

Catalyst precursor	Atmosphere	TON (7 days)				TON (7) (15 days)
		γ-butyrolactone (7)	...O...CHO	HOOC...COOH	Other than 7, Σ^a	
Ind(CO)$_3$Mo–Ru(CO)$_2$Cp (1)	O_2	55			100	
Cp(CO)$_3$Mo–Ru(CO)$_2$Cp (2)	O_2	49			100	80
[Ru(CO)$_2$Cp]$_2$ (3)	O_2	100			77	155
[Ru(CO)$_2$Cp]$_2$ (3)	O_2	290[b]	48[b]	12[b]	120[b]	290[b]
[Ru(CO)$_2$Cp]$_2$ (3)	O_2/CO_2 1/1	80[c]			70[c]	80[c]
[Ru(CO)$_2$Cp]$_2$ (3)	O_2/CO 1/1	75			51	75
[Ru(CO)$_2$Cp]$_2$ (3)	CO_2	–			–	0
[Ru(CO)$_2$Cp]$_2$ (3)	CO	–			–	0
Cp(CO)$_3$Mo–Mo(CO)$_3$Cp (4)	O_2	5[d]			6[d]	5
RuCl$_3$ (5)	O_2	30			50	61

Reaction conditions: 30 ml THF, RT, 0.1 mmol cat., 7 days; [a]approximation; [c]8 days; [d]15 days. Amounts determined by IR; [b]isolated (30 days).

Since in control runs of THF/O_2 as well as THF solutions of **1**, **2**, or **3**, under Ar, CO, or CO_2 atmospheres, respectively, the formation of organic products could not be detected, it is evident that the combination of THF, a metal complex and oxygen is crucial to perform the oxidation reaction. A comparison of the TONs of catalytic runs with **1–5**, reveals that the dinuclear ruthenium complex **3** and oxygen yield the most active species of the series, with a TON of about 180 after 7 days (Table 1). In contrast, only a few turnovers were detected when the molybdenum compound **4** was used. With the dinuclear MoRu complexes **1** and **2** as precursors, TONs of about 150 are observed and the TON obtained for the mononuclear RuCl$_3$ (**5**) derived catalyst is about half of that. In either case, the catalyst could be recovered and used repeatedly. In contrast to reports for Pd/Cu [14] and Fe, Rh [15] systems, O_2/CO and O_2/CO_2 atmospheres did not enhance, but decrease the catalytic activity of **3**, likely as a result of the lower partial oxygen pressure in the system.

These trends are clearly reflected by the rate of formation of γ-butyrolactone (Fig. 1). Under oxygen atmosphere, **3** yields the most active promoter from the start of the reaction, while all other catalyst precursor/atmosphere combinations show lower activity which seems to be dependent mainly on the concentration of active ruthenium species. However, a comparison of the selectivities towards γ-butyrolactone shows that the
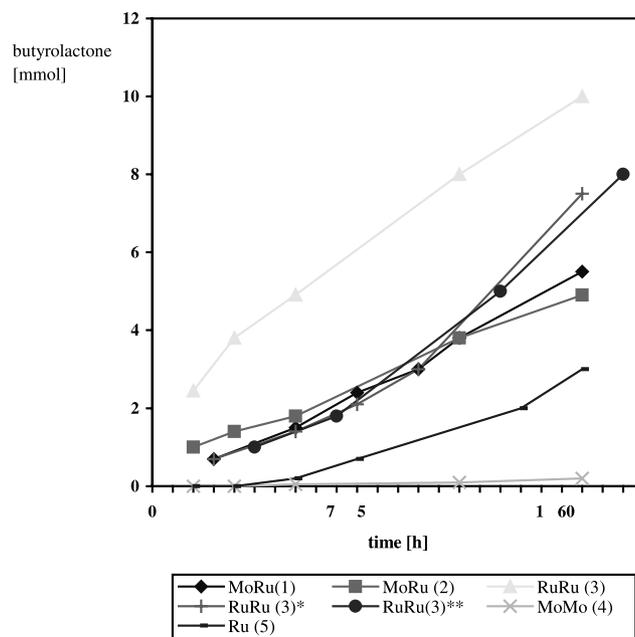

Fig. 1. Yield of γ-butyrolactone versus time. Conditions: 30 ml THF, RT, O_2, 0.1 mmol catalyst precursor. *O_2/CO, **O_2/CO_2 atmosphere.

oxidation product of **3** yields a significantly higher selectivity (up to 70%) than the other catalysts of the series. This shows that the nature of the catalyst precursor is a dominant factor and suggests that different active

species are formed upon their oxidation. The exceptionally low activity of RuCl$_3$ can partly be explained with an induction period (Fig. 1), as described for a K$_2$PtCl$_4$/D$_2$O system [12]. For the compounds presented here, the induction, i.e., the decomposition, of **1**–**3** proceeds faster than the formation of the active catalyst from RuCl$_3$. In addition, the solubility of the catalyst influences its performance.

We prepared and characterised the novel hetero bimetallic complex Ind(CO)$_3$Mo–Ru(CO)$_2$Cp (**1**) and could demonstrate that the homo and hetero dinuclear complexes **1**–**4** as well as RuCl$_3$ · H$_2$O (**5**) are catalyst precursors for the oxo-functionalisation of THF under ambient conditions using molecular oxygen. High turnover numbers and a selectivity towards γ-butyrolactone of up to 70% are observed. Further studies on the oxidation of other substrates and towards the understanding of the reaction mechanism are underway.

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