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Baeyer–Villiger oxidation of ketones catalysed by rhenium complexes bearing *N*- or oxo-ligands

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1. Introduction

Transition-metal-catalysed Baeyer–Villiger (BV) oxidations, viz. the transformation of cyclic and acyclic ketones into the lactones and esters, has become an important research topic in the last years [1–30] due to the wide applications of the products, *e.g.* in the gas and oil industry, for the production of gasoline additives [31], perfume components [32] and pharmaceutical materials (*e.g.* antiviral, antiproliferative and imunosupressor agents [33,34]).

Owing to economic and environmental reasons, a growing attention has been paid to the replacement of organic peroxy acids, traditionally used as stoichiometric oxidants in the BV oxidation, by more atom efficient and environmentally friendly oxidants, such as molecular oxygen [35–37] or hydrogen peroxide [3,11,13,17,23,38,39].

The application of transition metal catalysts for the BV reactions was started by Mares and co-workers, using Mo^{VI} picolinato and dipicolinato complexes in the presence of H_2O_2 (90%) as terminal oxidant [40]. Later, compounds of other metals, such as Co [23], Ni [30], Cu [24], Sn [14], W [2], Re [17,38,41] and V/Mo [26], were also shown to catalyse the BV oxidations. In particular, systems based

ABSTRACT

Rhenium (I, III–V or VII) complexes bearing *N*-donor or oxo-ligands catalyse the Baeyer–Villiger oxidation of cyclic and linear ketones (*e.g.* 2-methylcyclohexanone, 2-methylcyclopentanone, cyclohexanone, cyclopentanone, cyclobutanone and 3,3-dimethyl-2-butanone) into the corresponding lactones or esters, in the presence of aqueous H_2O_2 (30%). The effects of various reaction parameters are studied allowing to achieve yields up to 54%.

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on d⁸ metal centres such as Pd^{II} [42,43] and Pt^{II} [3,11–13,19] have been successfully explored in recent years.

The recognized application of the versatile complex [(Me)ReO₃] (MTO) in oxidation catalysis [44–47], including the BV oxidation of ketones [17,39,41], clearly demonstrates the ability of rhenium centres to form highly active catalysts for the oxidation reactions of olefins and other unsaturated substrates. However, the application of other Re complexes, apart from MTO, as catalysts for the BV oxidation is still very limited, although we have found that certain rhenium complexes with oxo- or *N*-ligands (such as scorpionates, pyrazoles, benzoyl-diazenido, -hydrazido) are capable of catalysing, in homogeneous systems, the oxidation and carboxylation of inert alkanes, under mild or moderate conditions [48–50].

Aiming at the extension of our oxidation studies to other substrates and catalytic transformations and to a further development of the catalytic applications of rhenium complexes, we embarked in evaluating the catalytic potential of various Re complexes of our interest, bearing the above types of ligands and with the metal in a wide range of oxidation states, for the Baeyer–Villiger oxidation of ketones. Hence, in the present work we report the BV oxidation, by aqueous H_2O_2 in 1,2-dichloroethane, of cyclic and linear ketones to the corresponding lactones and esters, catalysed by a number of Re complexes bearing *N*-ligands, namely a scorpionate [HC(pz)₃, pz = pyrazoly], pyrazole (Hpz), benzoyl-hydrazido and -diazenido [η^2 - or η^1 -N₂C(O)Ph], acetonitrile and dinitrogen,

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Scheme 1. Re catalyst precursors in this study for BV oxidation.

apart from the oxo-ligand (Scheme 1). Such ligands are expected to promote coordinative unsaturation at the metal, in view of their lability [N₂, NCMe, Hpz, η^3 - or η^2 -HC(pz)₃ towards lower denticity], and/or proton-transfer steps, in view of their basic character [Hpz, HC(pz)₃, N₂C(O)Ph, oxo], features that are favourable [50–54] to the occurrence of oxidation catalysis with H₂O₂.

2. Experimental

2.1. Materials and complexes

2-Methylcyclohexanone (Aldrich), 2-methylcyclopentanone (Aldrich), cyclopentanone (Aldrich), cyclohexanone (Aldrich), cyclobutanone (Aldrich), 3,3-dimethyl-2-butanone (pinacolone) (Aldrich), delta-hexalactone (Aldrich), epsilon-caprolactone (Aldrich), delta-valerolactone (Aldrich), beta-butyrolactone (Aldrich), tert-butylacetate (Aldrich), 1,2-dichloroethane (Aldrich), acetonitrile (Riedel-de-Haën), dichloromethane (Fluka), methanol



Scheme 2. BV oxidation of cyclic (reaction 1) and acyclic (reaction 2) ketones.

(Fluka) hydrogen peroxide (30%) (Fluka), Re₂O₇ **10** (Aldrich), cycloheptanone (Aldrich), diethyl ether (Riedel-de-Haën) and dinitrogen gas (Air Liquid Portugal) were used as received from the suppliers. The solvents were dried over appropriate drying agents and degassed by standard methods.

2.2. Instrumentation

Gas chromatographic (GC) measurements were carried out using a FISONS Instruments GC 8000 series gas chromatograph with a FID detector and a capillary column (DB-WAX, column length: 30 m; internal diameter: 0.32 mm). The temperature of injection was 240 °C. The initial temperature was maintained at 80 °C for 1 min, then raised 10 °C/min up to 140 °C (in the case of pinacolone oxidation) or 180 °C, and held at this temperature for 1 min. Helium was used as the carrier gas.

2.3. Typical procedures and product analysis

In typical conditions, Re catalysts were used as stock solutions (for this, 10.0 mg of the compound **1–10** were dissolved in 2.00 mL of 1,2-dichloroethane, 1,2 DCE). The required amount of this stock solution for the desired oxidant/catalyst molar ratio (1000:1) was transferred to a second flask containing 3.00 mL of 1,2-dichloroethane. 1.7 mmol of H₂O₂ as a 30% aqueous solution $(102 \,\mu\text{L})$ and 1.7 mmol of substrate were then added, and the reaction solution was stirred for 6 h at the desired temperature (typically 70 °C) and normal pressure (dinitrogen atmosphere). Then, 120 µL of cycloheptanone (internal standard) and 10.00 mL of diethyl ether (to extract the substrate and the organic products from the reaction mixture) were added. The obtained mixture was stirred during 10 min and then a sample (1 µL) was taken from the organic phase and analysed by GC using the internal standard method. Blank tests indicate that no oxidation takes place in the absence of the Re catalyst or the oxidant.

3. Results and discussion

We found that the rhenium complexes **1–10** (Scheme 1) can exhibit a remarkable catalytic activity (*e.g.* turnover numbers up to *ca.* 2450 for complex **1**, Table 2, entry 5) under relatively mild conditions for the partial oxidation of different simple cyclic (2methylcyclohexanone, 2-methylcyclopentanone, cyclohexanone, cyclopentanone, cyclobutanone) and acyclic (pinacolone) ketones to the respective lactones and esters, in a single-pot process (Scheme 2, Tables 1, 2, S1 and S2). The catalytic systems are based on the above Re compounds, hydrogen peroxide (30% aqueous solution) as the oxidizing agent, and 1,2-dichloroethane (1,2 DCE) as the solvent, under typical temperature of 70 °C and 6 h reaction time.

28

Table 1

Baeyer–Villiger oxidation of several ketones catalysed by Re complexes 1-10 (selected data).^a

Entry	Substrate	Catalyst	Yield ^b	TON ^c	Conv.	Select.	Product
1		1	42	416	68	61	
2 ^d		1	18	178	97	18	
3 ^e	0	1	5	45	>99	4	0
4	Ű	2	31	307	77	39	U II
5	CH₂	3	22	223	79	28	
6	ſŢ	4	18	177	74	24	
7		5	24	241	65	37	< /Сн₃
8	\sim	8	33	329	81	41	
9		9	39	393	67	58	
10		10	7	67	60	11	
11		1	27	270	42	67	
12		2	22	223	28	80	â
13	Ö	3	10	102	40	26	U II
14		4	21	209	37	57	
15	CH ₃	5	19	192	37	52	ې ´ `Q
16	$\langle \gamma \rangle$	6	37	365	77	47	l
17	\setminus /	7	13	131	58	22	
18		9	26	263	79	33	013
19		10	10	104	26	40	
20	0	1	17	172	57	30	
21	U U	2	16	158	24	69	Q.
22		3	7	74	47	16	
23	$\langle \rangle$	4	18	180	44	41	\sim $^{\circ}$
24		5	5	53	46	12	
25	\searrow	9	14	138	33	43	
26	•	10	3	27	55	5	
27	O II	2	23	231	63	37	O II
28		3	11	109	58	41	
29	$\langle \rangle$	9	31	306	36	85	
30	\setminus /	1	45	449	90	50	\searrow
31		2	40	401	98	49	0
32 ^f	\wedge	2	54	537	99	54	~ 0
33		3	18	178	65	28	14
34		4	33	329	78	42	\setminus 1
35	~	5	33	334	100	33	$\sum_{i=0}^{i}$
36		9	43	432	94	46	
37	0	1	11	109	73	15	
38	Ŭ	2	6	64	8	81	
39	н.с.	3	7	74	11	67	
40		4	12	118	69	17	
41		6	7	67	69	10	H ₃ C ^C CH ₂
42 ^g		9	9	92	32	29	3- U UI3
43		10	2	18	51	4	

^a Reaction conditions (unless stated otherwise): rhenium catalyst (1.7 μmol, used as a stock solution in 1,2-dichloroethane), 1.7 mmol of substrate, H₂O₂ (1.7 mmol, *i.e.* 1000:1 molar ratio of oxidant to Re catalyst), 1,2-dichloroethane (3.0 mL), 6 h, 70 °C, under dinitrogen; for more essays see Table S1 (supporting data). Percentage of yield, TON determined by GC analysis.

^b Molar yield (%) based on the ketone substrate, *i.e.* moles of lactone (or ester) per 100 mol of ketone.

^c Turnover number (moles of product per mol of Re catalyst).

^d Oxidant/substrate = 2:1.

^e Oxidant/substrate = 4:1. No substrate was observed in the end.

^f 30 h.

^g $T = 50 \circ C$.

All the tested Re complexes bearing *N*- or oxo-ligands exhibit higher activities than the simple Re^{VII} oxide Re₂O₇ **10** (Table 1). The Re^V complexes, *i.e.* the oxo-chloro [ReOCl₃(PPh₃)₂] **9** and the benzoyl-hydrazido [ReCl₂{ η^2 -*N*,O-C(O)Ph}(PPh₃)₂] **1**, provide the most active catalysts under the conditions of this study for the oxidation of 2-methylcyclohexanone, cyclopentanone and cyclobutanone, whereas the Re^{IV} acetonitrile complex [ReCl₄(NCMe)₂] **6** and the Re^{III} tris(pirazolyl)methane compound [ReCl₃{HC(pz)₃}] **4** are the most active catalysts for 2-methylcyclopentanone and cyclohexanone or pinacolone BV oxidations, respectively.

The reactions are cleaner (water is formed as the only byproduct) than those promoted by peroxy acids [3], also giving rather high yields (up to 45%, Table 1) in a relatively short reaction period (typically 6 h) using a low concentration (<30%) of hydrogen peroxide solution and without the utilization of any additive.

In the presence of the Re complexes **1–9**, the Baeyer–Villiger oxidation of cyclic ketones to the respective lactones proceeds more effectively than that of the acyclic pinacolone to *tert*-butylacetate, in accord with the steric hindrance of the latter substrate.

As expected [41,45], for the simplest cyclic ketones the highest reactivity was exhibited by the ring-strained cyclobutanone (conversions up to 99%, Table 1), that was easily converted into the γ -butyrolactone, followed by cyclopentanone and cyclohexanone (Table 1, entries 21, 22, 25, 27–29, 31, 33 and 36, for complexes **2**, **3** and **9**). The same tendency was reported in the case of the [(CH₃)ReO₃]/H₂O₂ catalysed BV oxidation of cyclic ketones in ionic liquids [21]. In this system, conversions (up to 98%) and yields (up

Table 2

Effect of the oxidant-to-catalyst molar ratio in the BV oxidation of 2methylcyclohexanone and 2-methycyclopentanone catalysed by complex **2**.^a

Entry	Substrate	$n(H_2O_2)/n(catalyst) \times 10^3$	Yield	TON
1	Ö	0.1	14	14
2		0.5	35	175
3	CH ₃	1	30	307
4		10	12	1167
5	\checkmark	40	6	2452
6	Q	0.1	8	8
7		0.5	15	75
8		1	22	223
9	$\langle \gamma \rangle$	10	7	653
10		40	4	1730

^a Reaction conditions: rhenium catalyst ($0.425-17 \mu$ mol, used as a stock solution in 1,2-dichloroethane), 1.7 mmol of substrate, H₂O₂ (1.7μ mol), 1,2-dichloroethane (3.0μ L), 6 h, 70 °C, under dinitrogen.

to 98% and 70%) for cyclobutanone and cyclopentanone, respectively [21], are higher those obtained in our Re catalytic systems, but for the 6-membered ring ketones, such as cyclohexanone and 2-methylcyclohexanone, we have achieved comparable or even better results.

Despite of high achieved conversions for some substrates (*e.g.* up to 99% in case of cyclobutanone oxidation, Table 1), the selectivities are moderate and depend on the type of the catalyst applied, *e.g.* catalysts **2** and **9** are usually the most selective ones.

We typically used one equivalent of H_2O_2 relatively to the substrate. Hence, the yields and selectivities concerning H_2O_2 correspond to those concerning the substrate. However, increasing the amount of H_2O_2 relatively to the substrate (up to 4:1), for a common amount of catalyst, leads to a decrease of product yield (possibly due to overoxidation) concomitant with an increase of the conversion and a lowering of selectivity (Table 1, entries 1–3).

In spite of structural similarities of the Re^{III} complexes **2** and **3**, the latter, *i.e.* the pyrazole-fluoro complex displays a considerably lower activity for the oxidation of cyclic ketones than the former, *i.e.* the analogous pyrazole-chloro compound (Table 1). Hence, the presence of a fluoride ligand in **3**, although particularly favourable for other oxidation reactions [49,57], reduces its catalytic activity, what eventually can be related to the stronger electron-donor character of the F⁻ ligand to the metal in **3** compared with Cl⁻ in **2** (the former ligand exhibits lower values of the electrochemical Lever E_L and Pickett P_L parameters, *i.e.* -0.42 V vs. NHE [64,65] and -1.3 V [66], respectively for F⁻, and -0.24 V vs. NHE [64,65] and -1.19 V [67] for Cl⁻) [68–70]. In accord, the fluoro-complex **3** is a weaker Lewis acid and therefore would, by coordination, activate less the carbonyl group of the ketones for a nucleophilic attack by H_2O_2 .

In the most active species, $[\text{ReCl}_2\{\eta^2-N,O-C(O)\text{Ph}\}(\text{PPh}_3)_2]$ **1** and $[\text{ReOCl}_3(\text{PPh}_3)_2]$ **9** the metal is in the 5+ oxidation state. However, they are conceivably oxidized by H_2O_2 to peroxo-complexes with the metal in a higher oxidation state. In fact, the formation of the η^2 -peroxo complex $[\text{ReCl}_2(\eta^2-O_2)\{\text{NNC}(O)OMe\}(\text{PPh}_3)_2]$ is reported [71] to occur in the reaction of the η^1 -diazenido compound $[\text{ReCl}_2\{\text{NNC}(O)OMe\}(\text{PPh}_3)_2(\text{dmf})]$ (dmf=N,N-dimethylformamide) with O_2 . Moreover, oxo- and peroxo-complexes of Re^{VII} , such as $[(CH_3)\text{ReO}_3(\text{bipy})]$ [72], $\text{ReO}_3[\{(CH_3)_2N-C_2H_4\}_2\text{NCH}_3,\text{ReO}_4]$ [72], $[(CH_3)\text{ReO}(O_2)_2]$ [73,74] and $[(CH_3)\text{ReO}(O_2)_2(H_2O)]$ [72] are known catalysts for various oxidation reactions of olefins and aromatics.

Similarly to an earlier proposed mechanistic pathway for MTO catalysed BV oxidation [18,20,21], the reaction can proceed *via* the formation of active peroxo-Re species derived from the starting complexes in the presence of H_2O_2 , which would undergo nucle-ophic attack to the polar carbonyl group of the ketone substrate.



Fig. 1. Effect of H_2O_2 amount $(H_2O_2/catalyst molar ratio)$ on TON in the BV oxidation of 2-methylcyclohexanone and 2-methylcyclopentanone catalysed by $[\text{ReCl}_2\{N_2C(O)\text{Ph}\}(\text{Hpz})_2(\text{PPh}_3)]$ **2.** Reaction conditions are those of Table 2 entries.

For the purpose of optimization of the reaction conditions, the effects of various reaction parameters were examined. Hence, the dependences of the yields of products and the TONs on the oxidant-to-catalyst molar ratio, reaction time, temperature and type of solvent were investigated for **1**, **2** and **9** (Tables 2, S1 and S2).

3.1. Effect of the oxidant-to-catalyst molar ratio

The influence of the peroxide-to-catalyst molar ratio was studied for the BV oxidation of 2-methylcyclohexanone and 2-methylcyclopentanone in the presence of **2**. Values of TON are given in Table 2 for typical essays, and the dependences for both substrates are shown in Fig. 1. The increase of the $n(H_2O_2)/n(catalyst)$ molar ratio, by decreasing the catalyst amount, results in higher TONs, *e.g.* the TON for the oxidation of 2-methylcyclohexanone in the presence of complex **2** enhances from 14 to 2452 upon changing that ratio from 100 to 40,000. However, the yield values decline after reaching a maximum on account of the deceleration of reaction rate upon lowering the catalyst concentration.

3.2. Effect of the reaction time and temperature

The effect of the reaction time was studied for complexes **1**, **2** and **9** using 2-methylcyclohexanone, 2-methylcyclopentanone, cyclohexanone, cyclopentanone and the acyclic pinacolone (Tables S1 and S2). It was observed, for the cyclic substrates, that the yield and TON sharply increase during the first 6 h, achieving a maximum before droping slightly, after *ca.* 10 h (Fig. 2), conceivably due to product overoxidation or hydrolysis [75,76]. For the cyclic 4-membered cyclobutanone, and in the presence of complex **2**, there is an increase of both yield and conversion upon prolonging the reaction time to 30 h (54% yield, 99% conversion). It is also noted for this substrate that the good yield of *ca.* 20% is achieved after 2 h, while for the larger ring ketones no significant reaction is observed in the first 2–3 h, what is consistent with the known higher reactivity of 4-membered ring ketones.

The temperature is also an important factor and the use of 70 °C appears to be the most adequate for the cyclic ketone oxidation. In fact, *e.g.* we failed the attempt of performing the oxidation of 2-methylcyclohexanone in the presence of **9** at room temperature (entry 10, Table S1) whereas the use of 50 °C resulted in the yield reduction to half (from 39% at 70 °C to 17% at 50 °C, entries 12 and 11, respectively, Table S1). The heating effect above 70 °C is less pronounced, corresponding to a slight yield decrease (*e.g.* from 39% at 70 °C to 35% at 100 °C, entries 12 and 13, respectively, Table S1)



Fig. 2. Effect of the reaction time on TON in the BV oxidation of 2-methylcyclohexanone (--), 2-methylcyclopentanone (---) and cyclopentanone (--), catalysed by $[ReOCl_3(PPh_3)_2]$ **9** and $[ReCl_2\{N_2C(O)Ph\}(Hpz)_2(PPh_3)]$ **2** (\blacklozenge). Reaction conditions are those of Table S2 entries.

conceivably due to the decomposition of the oxidant H_2O_2 and of any peroxo intermediates. For pinacolone, a different behaviour was observed, since medium temperatures are more preferable. Hence, 50 °C seems to be the most adequate temperature for this system (see entries 47–50, Table S1), whereas at 100 °C no products are observed. On the other hand, its oxidation at room temperature (although in a small extent, see entry 47, Table S1) can be performed.

3.3. Effect of type of solvent

1,2-Dichloroethane was chosen as the typical solvent for our systems due to its high resistance to oxidizing agents and also in view of the good solubility of both catalysts and substrates. It has also been used in other cases as the most appropriate solvent for similar Baeyer–Villiger oxidations [15].

Replacement of 1,2-dichloroethane by other solvents resulted, in general, in a decrease of activity. In the case of the 2methylcyclopentanone oxidation in the presence of **9**, the product yield lowered drastically from 26% (entry 18, Table S1) in 1,2-dichloroethane to 1%, 0.2%, 8% or 5% in acetonitrile, water, dichloromethane or methanol, respectively (entries 19–22, Table S1). Moreover, the use of acetonitrile for the oxidation of pinacolone results in a complete inhibiting effect.

4. Conclusions

This study has contributed towards the development of the still little explored application of Re compounds as catalyst and/or catalyst precursor for the oxidation of ketones to the respective esters or lactones, under relatively mild conditions and with an environmentally friendly oxidant (H₂O₂).

In general, it was observed that the Re compounds are more active for the oxidation of cyclic (4-, 5- and 6-membered rings) than for the acyclic ketones, consistent with the common lower reactivity of the latter ketones.

The Re^V benzoyl-hydrazido [ReCl₂{ η^2 -*N*,*O*-C(O)Ph}(PPh₃)₂] **1** and oxo-chloro [ReOCl₃(PPh₃)₂] **9** complexes are the most active catalysts under the studied conditions for the oxidation of 2-methylcyclohexanone, cyclopentanone and cyclobutanone, whereas the Re^{IV} acetonitrile complex [ReCl₄(NCMe)₂] **6** and the Re^{III} tris(pirazolyl)methane compound [ReCl₃{HC(pz)₃}] **4** are the most active ones for 2-methylcyclopentanone and cyclohexanone or pinacolone BV oxidations, respectively.

The use of 1,2-dichloroethane as solvent leads to the highest activity for all ketones, but compounds **1** and **9** (the most active ones) can even operate in water as the only solvent.

The replacement of 1,2 DCE solvent by a mixed organic/water medium deserves to be further explored by application of hydrosoluble compounds, since it is particularly important for the development of a green BV system.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.apcata. 2012.07.007.

References

- T. Seiser, T. Saget, D.N. Tran, N. Cramer, Angew. Chem. Int. Ed. 50 (2011) 7740–7752.
- [2] P. Jin, L. Zhu, D. Wei, M. Tang, X. Wang, Comput. Theor. Chem. 966 (2011) 207–212.
- [3] R.A. Michelin, P. Sgarbossa, A. Scarso, G. Strukul, Coord. Chem. Rev. 254 (2010) 646–660.
- [4] F. Cavani, K. Raabova, F. Bigi, C. Quarantelli, Chem. Eur. J. 16 (2010) 12962–12969.
- [5] A. Cavarzan, A. Scarso, P. Sgarbossa, R.A. Michelin, G. Strukul, ChemCatChem 2 (2010) 1296–1302.
- [6] A. Cavarzan, G. Bianchini, P. Sgarbossa, L. Lefort, S. Gladiali, A. Scarso, G. Strukul, Chem. Eur. J. 15 (2009) 7930–7939.
- [7] G. Bianchini, A. Cavarzan, A. Scarso, G. Strukul, Green Chem. 11 (2009) 1517-1520.
- [8] C. Jiménez-Sanchidrián, J.R. Ruiz, Tetrahedron 64 (2008) 2011–2026.
- [9] S. Xu, Z. Wang, X. Zhang, X. Zhang, K. Ding, Angew. Chem. Int. Ed. 47 (2008) 2840–2843.
- [10] A.O. Terent'ev, M.M. Platonov, A.S. Kashin, G.I. Nikishin, Tetrahedron 64 (2008) 7944–7948.
- [11] G. Greggio, P. Sgarbossa, A. Scarso, R.A. Michelin, G. Strukul, Inorg. Chim. Acta 361 (2008) 3230–3236.
- [12] P. Sgarbossa, M.F.C. Guedes da Silva, A. Scarso, R.A. Michelin, A.J.L. Pombeiro, Inorg. Chim. Acta 361 (2008) 3247–3253.
- [13] P. Sgarbossa, A. Scarso, E. Pizzo, A.M. Sbovata, A. Tassan, R.A. Michelin, G. Strukul, J. Mol. Catal. A: Chem. 261 (2007) 202–206.
- [14] Q.H. Zhang, S.F. Wang, Z.Q. Lei, Chin. Chem. Lett. 18 (2007) 4-6.
- [15] P. Sgarbossa, A. Scarso, R.A. Michelin, G. Strukul, Organometallics 26 (2007) 2714–2719.
- [16] Z.Q. Lei, Q.H. Zhang, J.J. Luo, Tetrahedron Lett. 46 (2005) 3505-3508.
- [17] V. Conte, B. Floris, P. Galloni, V. Mirruzzo, A. Scarso, D. Sordi, G. Strukul, Green Chem. 7 (2005) 262–266.
- [18] G.-J. ten Brink, I.W.C.E. Arends, R.A. Sheldon, Chem. Rev. 104(2004)4105-4123.
- [19] A. Brunetta, G. Strukul, Eur. J. Inorg. Chem. 43 (2004) 1030–1038.
- [20] A. Corma, M.T. Navarro, L. Nemeth, M. Renz, J. Catal. 219 (2003) 242-246.
- [21] R. Bernini, A. Coratti, G. Fabrizib, A. Goggiamani, Tetrahedron Lett. 44 (2003) 8991–8994.
- [22] G. Strukul, Top. Catal. 19 (2002) 33-42.
- [23] T. Uchida, T. Katsuki, Tetrahedron Lett. 42 (2001) 6911-6914.
- [24] Y. Peng, X. Feng, K. Yu, Z. Li, Y. Jiang, C.-H. Yeung, J. Org. Chem. 619 (2001) 204–208.
- [25] G. Strukul, Nature 412 (2001) 388-389.
- [26] M. Renz, B. Meunier, Eur. J. Org. Chem. 4 (1999) 737–750.
- [27] G. Strukul, Angew. Chem. 110 (1998) 1256–1267;
- G. Strukul, Angew. Chem. Int. Ed. 37 (1998) 1198-1209.
- [28] K. Kaneda, S. Ueno, ACS Symp. Ser. 638 (1996) 300-318.
- [29] M. Hamamoto, N. Nakayama, Y. Nishiyama, Y. Ishii, J. Org. Chem. 58 (1993) 6421.
- [30] C. Bolm, G. Schlingloff, K. Weickhardt, Tetrahedron Lett. 34 (1993) 3405–3408.
 [31] J.M. Robinson, "Lactones as new oxygenate fuel additives, fuels based thereon
- and methods for using same", US Patent Application 2006/0096,158 (2006). [32] P. Kraft, "Macrocyclic lactones as fragrances" World Intellectual Property Orga-
- nization, WO/2009/039675, European Patent EP 2205581 (2012). [33] M. Weigele, M.F. Loewe, "Lactones and their pharmaceutical applications", World Intellectual Property Organization, WO/1994/017056 (1994).
- [34] P. Magiatis, S. Mitaku, A. Skaltsounis, F. Tillequin, A. Pierré, G. Atassi, Nat. Prod. Lett. 14 (2000) 183–190.

- [35] K. Kaneda, S. Ueno, T. Imanaka, E. Shimotsuma, Y. Nishiyama, Y. Ishii, J. Org. Chem. 59 (1994) 2915-2917.
- [36] X. Li, F. Wang, H. Zhang, C. Wang, G. Song, Synthetic Commun. 26 (8) (1996) 1613-1616.
- [37] A. Chrobok, Tetrahedron 66 (2010) 2940-2943.
- [38] R. Bernini, E. Mincione, M. Cortese, G. Aliotta, A. Oliva, R. Saladina, Tetrahedron Lett. 42 (2001) 5401-5404.
- [39] A. Brunetta, P. Sgarbossa, G. Strukul, Catal. Today 99 (2005) 227-232.
- [40] S.E. Jacobson, R. Tang, F. Mares, Inorg. Chem. 17 (1978) 3055-3063.
- [41] M.M. Abu-Omar, J.H. Espenson, Organometallics 15 (1996) 3543-3549. [42] A.V. Malkov, F. Friscourt, M. Bell, M.E.S. Swarbrick, P. Kočovský, J. Org. Chem.
- 73 (2008) 3996-4003. [43] K. Ito, A. Ishii, T. Kuroda, T. Katsuki, Synlett 5 (2003) 643-646.
- [44] S.M. Bishof, M.-J. Cheng, R.J. Nielsen, T. Brent Gunnoe, W.A.A. Goddard, R.A. Periana, Organometallics 30 (2011) 2079-2082.
- [45] M. Crucianelli, R. Saladino, F. De Angelis, ChemSusChem 3 (2010) 524-540.
- [46] F.E. Kühn, W.A. Herrmann, J. Organomet. Chem. 689 (2004) 4149-4164.
- [47] C.C. Romão, F.E. Kühn, W.A. Herrmann, Chem. Rev. 97 (1997) 3197.
- [48] A.M. Kirillov, M. Haukka, M.V. Kirillova, A.J.L. Pombeiro, Adv. Synth. Catal. 347 (2005) 1435-1446.
- [49] E.C.B. Alegria, M.V. Kirillova, L.M.D.R.S. Martins, A.J.L. Pombeiro, Appl. Catal. A: Gen. 317 (2007) 43-52.
- [50] M.L. Kuznetov, A.J.L. Pombeiro, Inorg. Chem. 48 (2009) 307-318.
- [51] M.V. Kirillova, M.L. Kuznetsov, Y.N. Kozlov, L.S. Shul'pina, A. Kitaygorodskiy, A.J.L. Pombeiro, G.B. Shul'pin, ACS Catal. 1 (2011) 1511-1520.
- [52] R.R. Fernandes, J. Lasri, M.F.C.G. da Silva, J.A.L. da Silva, J.J.R.F. da Silva, A.J.L. Pombeiro, Appl. Catal. A 402 (2011) 110-120.
- [53] G.B. Shul'pin, M.V. Kirillova, J.N. Kozlov, L.S. Shul'pina, A.R. Kudinov, A.J.L. Pombeiro, J. Catal. 277 (2011) 164-172.
- [54] M.V. Kirillova, Y.N. Kozlov, L.S. Shul'pina, O.Y. Lyakin, A.M. Kirillov, E.P. Talsi, A.J.L. Pombeiro, G.G. Shul'pin, J. Catal. 268 (2009) 26-38.
- [55] J. Chatt, J.R. Dilworth, G.J. Leigh, V.D. Gupta, J. Chem. Soc. A 16 (1971) 2631.

- [56] E.C.B. Alegria, L.M.D.R.S. Martins, M.F.C.G. da Silva, A.J.L. Pombeiro, J. Organomet. Chem. 690 (2005) 1947-1958.
- [57] G.S. Mishra, E.C.B. Alegria, L.M.D.R.S. Martins, A.J.L. Pombeiro, J. Mol. Catal. A 285 (2008) 92-100.
- [58] E.C.B. Alegria, L.M.D.R.S. Martins, M. Haukka, A.J.L. Pombeiro, Dalton Trans. 41 (2006) 4954-4961
- [59] G. Rouschias, G. Wilkinson, J. Chem. Soc. A 3 (1968) 489-496.
- [60] R. Rouschias, G. Wilkinson, J. Chem. Soc. A 6 (1967) 993-1000.
- [61] J. Chatt, J.R. Dilworth, G.J. Leigh, J. Chem. Soc., Dalton Trans. 6 (1973) 612-618.
- G.W. Parshall, Inorg. Synth. 17 (1977) 110. [62]
- [63] J. Chatt, A.G. Row, J. Chem. Soc. (1962) 4019.
- [64] B.P. Lever, Inorg. Chem. 30 (1991) 1980-1985.
- [65] http://www.chem.yorku.ca/profs/lever/elparam98.htm.
- [66] M.F.N.N. Carvalho, M.T. Duarte, A.M. Galvão, A.J.L. Pombeiro, J. Organomet. Chem. 469 (1994) 79-87.
- J. Chatt, C.T. Kan, G.J. Leigh, H. Neukomm, C.J. Pickett, D.R. Stanley, J. Chem. Soc., [67] Dalton Trans. 10 (1980) 2032-2041.
- [68] A.J.L. Pombeir, in: F. Scholz, C.J. Pickett, A.J. Bard, M. Stratmann (Eds.), Encyclopedia of Electrochemistry, Vol. 7 (Inorganic Chemistry), Wiley-VCH, 2006, pp. . 77–108.
- [69] A.J.L. Pombeiro, J. Organomet. Chem. 690 (2005) 6021-6040.
- [70] A.J.L. Pombeiro, Eur. J. Inorg. Chem. 11 (2007) 1473-1482.
- [71] T. Nicholson, J. Zubieta, Inorg. Chim. Acta 134 (1987) 191-193.
- [72] W.A. Herrmann, J.D.G. Correia, F.E. Kühn, G.R.J. Artus, C.C. Romão, Chem. Eur. J. 2 (1996) 168-173.
- [73] W.A. Herrmann, R.W. Fischer, W. Scherer, M.U. Rauch, Angew. Chem. Int. Ed. 105 (1993) 1209-1212.
- [74] W. Adam, W.A. Herrmann, J. Lin, C.R. Saha-Möller, R.W. Fischer, J.D.G. Correia, Angew. Chem. Int. Ed. 106 (1994) 2545-2546.
- [75] A.R. Olson, J.L. Hyde, J. Am. Chem. Soc. 63 (1941) 2459-2461.
- [76] D.E. Wurster, A. Aburub, J. Pharm. Sci. 95 (2006) 1540-1548.