

DOI:10.1002/ejic.201300213

Cobalt-Catalyzed Oxidation of Methane to Methyl Trifluoroacetate by Dioxygen

Thomas Strassner,*^[a] Sebastian Ahrens,^[a] Michael Muehlhofer,^[b] Dominik Munz,^[a] and Alexander Zeller^[b]

Keywords: Alkanes / Oxidation / Cobalt / Oxygen / C-H activation

The cobalt-catalyzed oxidation of methane to methyl trifluoroacetate by molecular oxygen in trifluoroacetic acid has been studied in detail. Yields of up to 50% based on methane were obtained. The catalytic activities were highly dependent on the anions of the cobalt salts (Co^{II}, Co^{III}) under investigation. Deactivation by precipitation of the cobalt catalyst could be prevented by the addition of trifluoroacetic anhydride.

Introduction

The activation and functionalization of C-H bonds in alkanes is a challenge for chemists worldwide.^[1] In particular, the selective oxidation of methane to methanol, which is difficult to achieve due to the highly inert nature of C-H bonds, is of interest to the chemical industry. However, some important progress has been made: After the early work of Shilov and co-workers in 1972,^[2] the "Catalytica" system^[3] in oleum set a new milestone in 1998. Our group has contributed to this field through the functionalization of methane to methyl trifluoroacetate (Scheme 1) by using Pd^{II} and Pt^{II} complexes with chelating bis(NHC) ligands in trifluoroacetic acid (TFA).^[4,5] Methyl trifluoroacetate (b.p. 43 °C), which is stable under the reaction conditions, can be removed from the reaction mixture by distillation (TFA b.p. 72 °C) and then hydrolyzed to give methanol and trifluoroacetic acid.^[6] The latter could then be reprocessed.

 $CH_4 + \frac{1}{2}O_2 + CF_3COOH \xrightarrow{cat.} CF_3COOCH_3 + H_2O$ $CF_3COOCH_3 + H_2O \longrightarrow CH_3OH + CF_3COOH$

Scheme 1. Partial oxidation of methane to methanol in TFA.

The highly stable bis(NHC) catalysts (Figure 1) allow for more than 40 turnovers under relatively mild conditions (T = 90 °C).

ONI INF LIBRARY



Figure 1. Ligands based on the bis(NHC) and bis(pyrimidine) ligand motifs.

We combined the "Catalytica" bis-pyrimidine ligand with the bis(NHC) ligand motif to synthesize the corresponding palladium(II) and platinum(II) complexes (Figure 1).^[5] All these palladium- and platinum-based systems rely on well-defined molecular catalysts, which operate by nonradical mechanisms.

Compared with oleum, which is used in the "Catalytica" process, the main drawback of the Pd^{II} – and Pt^{II} –NHC-based systems is the need for an external oxidant like $K_2S_2O_8$.^[7] From an economic viewpoint, it would be advantageous to use benign oxidants like dioxygen or air. Dioxygen has been shown to work together with reductive coreagents like $CO^{[8]}$ or dihydrogen.^[9] However, with the palladium(II) and platinum(II) systems, we have not yet been able to implement efficient redox cycles for the oxidation step, as have been reported in the literature.^[8b,9b,10] We therefore decided to investigate the partial oxidation of methane in the presence of molecular oxygen and cobalt salts.

It has been reported that cobalt,^[7g,11] copper,^[7a,9a,12] rare-earth-metal,^[13] manganese,^[14] and vanadium^[7d,7i,9a,15] salts as well as heteropolyanions^[15d,16] are capable of oxid-

 [[]a] Physikalische Organische Chemie, Technische Universität Dresden,
 Bergstrasse 66, 01062 Dresden, Germany
 Fax: +49-351-46339679
 E-mail: thomas.strassner@chemie.tu-dresden.de
 Homepage: www.chm.tu-dresden.de/oc3
 [b] Densettment Chemie Lehrstuhl für Anorganische Chemie

[[]b] Department Chemie, Lehrstuhl für Anorganische Chemie, Technische Universität München, Lichtenbergstrasse 4, 85747 Garching bei München, Germany



izing methane in trifluoroacetic acid by radical pathways. Although some^[11a,11b,11e,11f,14] of these systems have been shown to work with the oxidant dioxygen without the addition of a co-reductant, the reported chemoselectivities are very modest as significant over-oxidation occurs. To the best of our knowledge, the highest yield (only 37% based on methane) has been reported for an Mn_2O_3 -based system.^[14]

Cobalt catalysts in combination with dioxygen are well known in oxidation catalysis and have, for example, been used to oxidize aromatic compounds, aldehydes, and alcohols.^[17] Cobalt(III) trifluoroacetate is capable of stoichiometrically oxidizing alkanes in trifluoroacetic acid at ambient temperatures.^[18] It is interesting to note that high-spin Co^{III} oxides and complexes have also been shown to be promising candidates for the selective activation of methane.^[19] Moiseev and co-workers showed that the reaction of cobalt precatalysts with methane and longer alkane homologues could be rendered catalytic by the addition of molecular oxygen.^[11a,11b,11f] However, reports on the homogeneous aerobic oxidation of alkanes by cobalt salts are scarce, and the related chemistry is not very well understood.^[20] Herein, we report a detailed study of a catalytic system that relies on molecular oxygen as the terminal oxidant and converts methane to methyl trifluoroacetate in remarkably high yields of up to 50%.

Results and Discussion

Several cobalt salts were tested as precatalysts for the oxidation of methane (Table 1). A solution of trifluoroacetic acid with catalyst loadings of 3.8 mol-% (relative to methane) of the cobalt salts $Co(OAc)_2$, $CoCl_2$, Co_2O_3 , and $Co(acac)_3$ yielded 6–9% of methyl trifluoroacetate (Entries 1–4). The very similar catalytic activities of the Co^{II} $[Co(OAc)_2$ und $CoCl_2]$ and Co^{III} salts $[Co_2O_3$ und $Co(acac)_3]$ indicate that under the reaction conditions Co^{II} is oxidized to Co^{III} . As no conversion to methyl trifluoroacetate was obtained without the addition of oxygen (Entry 11), we have reason to believe that the "activation" of methane is mediated by a Co^{III} compound.

Control experiments performed without the addition of catalyst (Entry 9) or methane (Entry 10) showed no conversion of methane into methyl trifluoroacetate. Likewise co-balt(II) bromide, cobalt(II) fluoride, and cobalt(II) sulfate, which are not soluble in trifluoroacetic acid, were completely inactive (Entries 6–8). Mn(OAc)₃ was also tested and showed stoichiometric reactivity (Entry 12).

The highest yield (21%) was observed for $Co^{II}(NO_3)_2$. It is very interesting to note in this context that nitrate salts can be used as a redox co-catalyst for the aerobic palladium-catalyzed oxidation of hydrocarbons.^[21] The drawback of this catalyst is the very aggressive reaction mixture, which even attacked the gold-faced rupture disc of the autoclave at 180 °C. We therefore decided to refrain from using $Co(NO_3)_2$ for further optimization studies at 180 °C. The harsh reaction conditions complicate the investigation of

Table 1. Investigation of different cobalt and manganese salts in the oxidation of methane $^{\left[a\right] }$

Entry	Catalyst	mol-%	Yield [%]
1	Co(OAc) ₂ ·4H ₂ O	3.8	7
2	CoCl ₂ ·6H ₂ O	3.8	6
3	Co_2O_3	3.8	6
4	$Co(acac)_3$	3.8	9
5	$Co(NO_3)_2 \cdot 6H_2O$	3.8	21
6	CoBr ₂ ·6H ₂ O	3.8	0
7	CoF_2	3.8	0
8	CoSO ₄ ·7H ₂ O	3.8	0
9	_	_	0
10	$Co(OAc)_2 \cdot 4H_2O^{[b]}$	3.8	0
11	$Co(OAc)_2 \cdot 4H_2O^{[c]}$	3.8	0
12	Mn(OAc) ₃	3.8	4

[a] Reaction conditions: 20 bar CH₄, 10 bar O₂, T = 180 °C, 70 mL TFA, 3 h; mol-% and yields are given relative to methane. [b] 0 bar CH₄, 10 bar O₂. [c] 20 bar CH₄, 0 bar O₂.

the underlying reaction mechanism. However, as the addition of the radical scavenger benzophenone completely stops the reaction, a radical mechanism appears likely. We carefully monitored the pressure differences and the volume changes of the reaction mixture and analyzed the composition of the gas phase in detail for Co(OAc)₂. We did not see a considerable change in overall pressure of the gas phase during the course of the reaction, but observed that about half of the dioxygen was consumed and about 30% of the methane in the gas phase was replaced by CO₂. Because only a small part of the solvent (ca. 1 mL) decomposed to CO₂ during the reaction, we concluded that the formation of carbon dioxide is mainly due to over-oxidation of methane and not to the decomposition of TFA.

It has been suggested that the decomposition of trifluoroacetic acid leads to the formation of 'CF₃ radicals, which readily react with hydrocarbons^[1g,7d,22] and also slowly with methane.^[22c] The decomposition of trifluoroacetic acid does not seem to be coupled with the formation of the methyl ester in our case, as we found about the same degree of solvent decomposition in experiments in which no product was formed. Consequently, and also considering the relative speed of the reaction in comparison with 'CF₃mediated processes,^[22c] 'CF₃ radicals do not play an important role in the formation of the methyl trifluoroacetate.

The yield of methyl trifluoroacetate was determined with $Co(OAc)_2$ as precatalyst under our standard reaction conditions after 1, 3, 11, and 24 h (Table 2, Entries 1–4). Following an induction period of about 1 h, a significant amount of ester could be detected after 3 h. The increase in ester concentration slowed down significantly after 3–4 h, when the catalyst precipitates in the form of a catalytically inactive pink solid. According to an energy-dispersive X-ray analysis, this precipitate contained mainly cobalt fluorides (ca. 20 atom-% cobalt) (cf. CoF_2 , Table 1). UV/Vis analysis indicated that cobalt(II) species remained in solution at low concentrations.

An increase in the concentration of the catalyst (Table 2, Entries 5–10) and, in the case of $CoCl_2$, longer reaction times had a beneficial effect on the yield (Table 2, Entries 8



Table 2. Investigation of the oxidation of methane after different reaction times and catalyst loadings.^[a]

Entry	Catalyst	mol-%	Reaction time [h]	Yield [%]
1	Co(OAc) ₂ ·4H ₂ O	3.8	1	0
2	$Co(OAc)_2 \cdot 4H_2O$	3.8	3	7
3	$Co(OAc)_2 \cdot 4H_2O$	3.8	11	8
4	Co(OAc) ₂ ·4H ₂ O	3.8	24	8
5	Co(OAc) ₂ ·4H ₂ O	5.5	24	10
6	$Co(OAc)_2 \cdot 4H_2O$	10.0	24	14
7	$Co(acac)_3$	5.5	3	13
8	CoCl ₂ ·6H ₂ O	5.5	3	10
9	CoCl ₂ ·6H ₂ O	10.0	24	19
10	CoCl ₂ ·6H ₂ O	5.5	72	26

[a] Reaction conditions: 20 bar CH₄, 10 bar O₂, T = 180 °C, 70 mL TFA; mol-% and yields are given relative to methane.

and 9). Considering the induction period observed, we believe, in analogy to the proposal of others,^[11a,11e,23] that during the first hour of the reaction a cobalt catalyst in the oxidation state +III or higher is formed, which then reacts rapidly with methane. This interpretation is in agreement with the observation that no product at all was formed in the absence of molecular oxygen in the reaction mixture (Table 1, Entry 11).

For the functionalization of methane catalyzed by Pd^{II}– bis(NHC) catalysts we could significantly reduce the wear on the reaction vessel (without losing catalytic activity) by adding trifluoroacetic anhydride (TFAA) to the reaction mixture.^[4d] We therefore also investigated the effect of adding TFAA to the cobalt-based system. TFAA clearly prevents catalyst deactivation, as even after 24 h no precipitation of cobalt fluorides could be detected as long as anhydride remained in the reaction mixture (Table 3).

Table 3. Investigation of solvent effects on the oxidation of methane. $^{\left[a\right] }$

Entry	Catalyst	mol-%	TFA/TFAA [mL]	Yield [%]
1	Co(OAc) ₂ ·4H ₂ O	3.8	70:0	8
2	$Co(OAc)_2 \cdot 4H_2O$	3.8	60:10	13
3	$Co(OAc)_2 \cdot 4H_2O$	3.8	40:30	47
4	Co(OAc) ₂ ·4H ₂ O	3.8	30:40	49
5	$Co(OAc)_2 \cdot 4H_2O$	3.8	10:60	50
6	$Co(OAc)_2 \cdot 4H_2O$	3.8	0:70	47
7	_	_	40:30	0
8	Co(OAc) ₂ ·4H ₂ O	3.8	[b]	0

[a] Reaction conditions: 20 bar CH₄, 10 bar O₂, T = 180 °C, 24 h; mol-% and yields are given relative to methane. [b] 70 mL acetic acid.

Higher concentrations of anhydride in the solvent led to yields of up to 50% of methyl trifluoroacetate (Entries 1– 5). However, we observed thermal decomposition of TFAA together with a higher degree of over-oxidation. Up to 50% of the added anhydride was consumed, which we attribute to the reactivity of trifluoroacetic anhydride towards radicals.^[22c] Analysis of the gas phase after the reaction revealed a similar composition to that observed without the addition of anhydride, albeit with a higher consumption of oxygen (ca. 10% O₂, ca. 35% CO₂, ca. 55% CH₄). The control reaction without catalyst did not lead to the formation of products (Table 3, Entry 7). TFAA clearly fulfills two major tasks that might be connected: It removes water from the reaction mixture and prevents the precipitation of the catalyst in the form of cobalt fluorides, which in combination leads to a higher conversion of methane to methyl trifluoroacetate. The substitution of the solvent TFA by the less acidic and less corrosive acetic acid was also investigated (Entry 8). Indeed, we detected methyl acetate as the reaction product, but the formation of the methyl ester was not dependent on the presence of methane but rather due to the degradation of the acetic acid. The oxidative coupling of CO and methane to acetic acid, which presumably forms part of the reverse reaction of this process, is well known and has been investigated in detail by different groups.^[7b,7d,7g,8c–8e,8g,10b,24] The substitution of dioxygen by N₂O as the oxidant led to the formation of CO₂ only.

Table 4 shows the results of an optimization study that includes the use of the most active precatalyst cobalt(II) nitrate from Table 1 under less demanding reaction conditions (150 and 160 °C).

Table 4. Optimization of reaction temperature in the oxidation of methane. $^{\left[a\right] }$

Catalyst	<i>T</i> [°C]	TFA/TFAA [mL]	Yield [%]
$Co(NO_3)_2 \cdot 6H_2O$	160	70:0	8
$Co(NO_3)_2 \cdot 6H_2O$	160	40:30	32
Co(OAc) ₂ ·4H ₂ O	160	70:0	6
Co(OAc) ₂ ·4H ₂ O	160	40:30	28
$Co(NO_3)_2 \cdot 6H_2O$	150	70:0	6
$Co(NO_3)_2 \cdot 6H_2O$	150	70:0 ^[b]	5
	Catalyst Co(NO ₃) ₂ ·6H ₂ O Co(NO ₃) ₂ ·6H ₂ O Co(OAc) ₂ ·4H ₂ O Co(OAc) ₂ ·4H ₂ O Co(NO ₃) ₂ ·6H ₂ O Co(NO ₃) ₂ ·6H ₂ O	$\begin{array}{c c} Catalyst & T [^{\circ}C] \\ \hline Co(NO_3)_2 \cdot 6H_2O & 160 \\ Co(NO_3)_2 \cdot 6H_2O & 160 \\ Co(OAc)_2 \cdot 4H_2O & 160 \\ Co(OAc)_2 \cdot 4H_2O & 160 \\ Co(NO_3)_2 \cdot 6H_2O & 150 \\ Co(NO_3)_2 \cdot 6H_2O & 150 \\ \end{array}$	$\begin{array}{ c c c c c c }\hline Catalyst & T [^{\circ}C] & TFA/TFAA [mL] \\ \hline Co(NO_3)_2 \cdot 6H_2O & 160 & 70:0 \\ Co(NO_3)_2 \cdot 6H_2O & 160 & 40:30 \\ Co(OAc)_2 \cdot 4H_2O & 160 & 70:0 \\ Co(OAc)_2 \cdot 4H_2O & 160 & 40:30 \\ Co(NO_3)_2 \cdot 6H_2O & 150 & 70:0 \\ Co(NO_3)_2 \cdot 6H_2O & 150 & 70:0 [^{b]} \\ \hline \end{array}$

[a] Reaction conditions: 20 bar CH_4 , 10 bar O_2 , 3.8 mol-% catalyst, 24 h; mol-% and yields are given relative to methane. [b] Addition of 1 g of silica to the reaction mixture.

With the addition of TFAA we still obtained a yield of 32% with Co(NO₃)₂ [Co(OAc)₂: 28%] compared with 8% [Co(OAc)₂, 6%] in pure TFA (Entries 1, 2 vs. 3, 4). Cobalt nitrate still showed catalytic turnover at 150 °C (Entry 5). We tried to prevent the precipitation of cobalt fluorides by the addition of silica instead of trifluoroacetic anhydride, as has been suggested in the literature.^[14] However, we did not observe any beneficial effect on the yield (Entry 6).

Conclusions

We have reported a catalytic system for the direct conversion of methane into methyl trifluoroacetate in yields of up to 50% based on methane. Various cobalt salts have been tested [Co(OAc)₂, CoCl₂, Co(NO₃)₂, Co(acac)₃, Co₂O₃, CoBr₂, CoSO₄] as precatalysts, and cobalt nitrate was found to be the most active. The use of dioxygen as oxidant offers an opportunity for the development of an economically reasonable process for the direct oxidation of methane to methanol. The challenge of the precipitation and deactivation of the catalyst in the form of cobalt fluorides can be addressed by the addition of TFAA to the reaction mixture.

Experimental Section

General: All chemicals were reagent-grade and used as received from commercial suppliers without further purification.



Catalysis: All experiments were conducted in a 160 mL Hastelloy-C2000 autoclave. This reaction vessel was filled with the given amount of catalyst and solvent (TFA or TFA/TFAA). Then the autoclave was flushed three times with 10 bar of dioxygen to remove the remaining air. Next the autoclave was pressurized with 10 bar of dioxygen and 20 bar of methane. The reaction mixture was heated to the given temperature and stirred with a gas injection stirrer at 500 rpm for the given reaction time. After the reaction, the stirring was stopped, and the reaction vessel was cooled to room temperature. *CAUTION:* The dioxygen/methane mixtures are potentially explosive and special care has to be taken!^[25]

Liquid-Phase Analysis: The autoclave was depressurized and the reaction mixture analyzed by gas chromatography with an Agilent 6850 Series II Networked GC apparatus equipped with a flame ionization detector (FID) and a Macherey–Nagel Optima-210 0.25 μ m column (30 m×0.25 mm). The yield of the methyl ester was quantified by the addition of *p*-xylene (25 μ L) as standard to the reaction mixture (1.00 mL) after the reaction and injection of this mixture into the GC apparatus. All GC measurements were repeated four times, given values are averaged over all measurements. The yields based on methane were calculated according to the ideal gas law.

Gas-Phase Analysis: Gas-phase analysis was performed with an Agilent 6850 Series II Networked GC apparatus, equipped with a thermal conductivity detector (TCD) and a J&W Scientific GS-GasPro column ($60 \text{ m} \times 0.32 \text{ mm}$). Samples of gas were taken from the autoclave with a custom-built 1.5 mL high-pressure gas mouse during and after the reaction at pressures of up to 60 bar. The gas sample was then expanded into an open-ended 1 mL sample loop in the GC. After complete pressure equalization, the sample loop was inserted into the stream of carrier gas with a computer-triggered pneumatic valve. The detected gases were identified and quantified by comparing the retention times on the column and signal areas of the samples with previously measured gas mixtures of known composition.

Energy-Dispersive X-ray Spectroscopy (EDX): The EDX measurement was performed with a Zeiss DSM982 Gemini scanning electron microscope equipped with a Voyager 984A-1SUS Noran Instruments energy-dispersive X-ray detector.

UV/Vis Spectrophotometry: The UV/Vis measurements were performed with a Cary 3 Perkin–Elmer Lambda 25 UV/Vis spectrophotometer at a resolution of 2 nm.

Acknowledgments

We are grateful for financial support from the Deutsche Forschungsgemeinschaft (DFG) (STR 526/7-1 and STR 526/7-2) and the Fonds der Chemischen Industrie (FCI). S. A. thanks the Konrad-Adenauer-Stiftung (KAS) and D. M. the Studienstiftung des Deutschen Volkes for their support. We are grateful for a generous donation of TFA and TFAA by Solvay GmbH Hannover. R. H. Crabtree, J. Organomet. Chem. 2004, 689, 4083–4091; i) R. H. Crabtree, J. Chem. Soc., Dalton Trans. 2001, 2437–2450; j) R. H. Crabtree, Chem. Rev. 1995, 95, 987–1007; k) A. Sen, Acc. Chem. Res. 1998, 31, 550–557; l) J. Sommer, R. Jost, M. Hachoumy, Catal. Today 1997, 38, 309–319; m) J. A. Labinger, J. E. Bercaw, Nature 2002, 417, 507–514; n) S. S. Stahl, S. J. Lippard, Iron Metab. 1999, 303–321; o) Y. Wang, D. L. An, Q. H. Zhang, Sci. China: Chem. 2010, 53, 337–350; p) M. Ayala, E. Torres, Appl. Catal. A 2004, 272, 1–13; q) G. Caeiro, R. H. Carvalho, X. Wang, M. A. N. D. A. Lemos, F. Lemos, M. Guisnet, F. R. Ribeiro, J. Mol. Catal. A 2006, 255, 131– 158.

- [2] a) N. F. Gol'dshleger, M. B. Tyabin, A. E. Shilov, A. A. Shteinman, *Zh. Fiz. Khim.* **1969**, *43*, 2174–2175; b) N. F. Gol'dshleger, V. V. Es'kova, A. E. Shilov, A. A. Shteinman, *Zh. Fiz. Khim.* **1972**, *46*, 1353.
- [3] a) R. A. Periana, D. J. Taube, S. Gamble, H. Taube, T. Satoh, H. Fujii, *Science* **1998**, *280*, 560–564; b) R. A. Periana, D. J. Taube, E. R. Evitt, D. G. Loffler, P. R. Wentreek, G. Voss, T. Masuda, *Science* **1993**, *259*, 340–343; c) J. Kua, X. Xu, R. A. Periana, W. A. Goddard III, *Organometallics* **2002**, *21*, 511– 525.
- [4] a) S. Ahrens, T. Strassner, *Inorg. Chim. Acta* 2006, 359, 4789–4796; b) S. Ahrens, A. Zeller, M. Taige, T. Strassner, *Organometallics* 2006, 25, 5409–5415; c) M. Muehlhofer, T. Strassner, W. A. Herrmann, *Angew. Chem.* 2002, 114, 1817; *Angew. Chem. Int. Ed.* 2002, 41, 1745–1747; d) T. Strassner, M. Muehlhofer, A. Zeller, E. Herdtweck, W. A. Herrmann, *J. Organomet. Chem.* 2004, 689, 1418–1424.
- [5] a) D. Meyer, M. A. Taige, A. Zeller, K. Hohlfeld, S. Ahrens, T. Strassner, *Organometallics* 2009, 28, 2142–2149; b) D. Meyer, A. Zeller, T. Strassner, J. Organomet. Chem. 2012, 701, 56–61.
- [6] L. Amiet, Rhone-Poulenc Specialties Chimiques, France, U.S. Pat. 4730082, 1988.
- a) G. Yin, D.-G. Piao, T. Kitamura, Y. Fujiwara, Appl. Or-[7] ganomet. Chem. 2000, 14, 438-442; b) P. M. Reis, J. A. L. Silva, A. F. Palavra, J. J. R. Frausto da Silva, T. Kitamura, Y. Fujiwara, A. J. L. Pombeiro, Angew. Chem. 2003, 115, 845; Angew. Chem. Int. Ed. 2003, 42, 821-823; c) C. Jia, T. Kitamura, Y. Fujiwara, Acc. Chem. Res. 2001, 34, 633-639; d) M. Zerella, S. Mukhopadhyay, A. T. Bell, Org. Lett. 2003, 5, 3193-3196; e) L. J. Lobree, A. T. Bell, Ind. Eng. Chem. Res. 2001, 40, 736-742; f) N. Basickes, T. E. Hogan, A. Sen, J. Am. Chem. Soc. 1996, 118, 13111-13112; g) M. Asadullah, Y. Taniguchi, T. Kitamura, Y. Fujiwara, Appl. Catal. A 2000, 194-195, 443-452; h) M. V. Kirillova, A. M. Kirillov, D. Mandelli, W. A. Carvalho, A. J. L. Pombeiro, G. B. Shul'pin, J. Catal. 2010, 272, 9-17; i) M. V. Kirillova, M. L. Kuznetsov, P. M. Reis, J. A. da Silva, J. J. da Silva, A. J. Pombeiro, J. Am. Chem. Soc. 2007, 129, 10531-10545; j) M. V. Kirillova, A. M. Kirillov, A. J. L. Pombeiro, Chem. Eur. J. 2010, 16, 9485-9493; k) M. V. Kirillova, A. M. Kirillov, M. L. Kuznetsov, J. A. L. Silva, J. J. R. F. da Silva, A. J. L. Pombeiro, Chem. Commun. 2009, 2353-2355.
- [8] a) G. B. Shulpin, *Mini-Rev. Org. Chem.* 2009, *6*, 95–104; b) M. Lin, T. Hogan, A. Sen, *J. Am. Chem. Soc.* 1997, *119*, 6048–6053; c) E. G. Chepaikin, A. P. Bezruchenko, A. A. Leshcheva, G. N. Boyko, I. V. Kuzmenkov, E. H. Grigoryan, A. E. Shilov, *J. Mol. Catal. A* 2001, *169*, 89–98; d) E. G. Chepaikin, G. N. Boyko, A. P. Bezruchenko, A. A. Leshcheva, E. H. Grigoryan, *J. Mol. Catal. A* 1998, *129*, 15–18; e) M. Kurioka, K. Nakata, T. Jintoku, Y. Taniguchi, K. Takaki, Y. Fujiwara, *Chem. Lett.* 1995, 244–247; f) M. Zerella, A. T. Bell, *J. Mol. Catal. A* 2006, *259*, 296–301; g) M. Lin, A. Sen, *Nature* 1994, *368*, 613–615.
- [9] a) E. D. Park, Y.-S. Hwang, C. W. Lee, J. S. Lee, *Appl. Catal.* A 2003, 247, 269–281; b) N. I. Kuznetsova, L. I. Kuznetsova, *Kinet. Catal.* 2009, 50, 1–10; c) K. Otsuka, Y. Wang, *Appl. Catal.* A 2001, 222, 145–161.
- [10] a) E. D. Park, Y. S. Hwang, J. S. Lee, *Catal. Commun.* 2001, *2*, 187–190; b) M. Zerella, S. Mukhopadhyay, A. T. Bell, *Chem. Commun.* 2004, 1948–1949; c) Y. Fan, Z. An, X. Pan, X. Liu,

a) A. E. Shilov, G. B. Shul'pin, Chem. Rev. 1997, 97, 2879–2932; b) E. G. Chepaikin, Russ. Chem. Rev. 2011, 80, 363–396;
 c) J. A. Labinger, J. Mol. Catal. A 2004, 220, 27–35; d) A. Sen in Applied Homogeneous Catalysis with Organometallic Compounds (Eds.: B. Cornils, W. A. Herrmann), Wiley-VCH, Weinheim, 2002, vol. 3, pp. 1226–1240; e) B. G. Hashiguchi, S. M. Bischof, M. M. Konnick, R. A. Periana, Acc. Chem. Res. 2012, 45, 885–898; f) H. Schwarz, Angew. Chem. 2011, 123, 10276; Angew. Chem. Int. Ed. 2011, 50, 10096–10115; g) A. A. Fokin, P. R. Schreiner, Chem. Rev. 2002, 102, 1551–1594; h)



X. Bao, *Chem. Commun.* **2009**, 7488–7490; d) I. Bar-Nahum, A. M. Khenkin, R. Neumann, *J. Am. Chem. Soc.* **2004**, *126*, 10236–10237.

- [11] a) M. N. Vargaftik, I. P. Stolarov, I. I. Moiseev, J. Chem. Soc., Chem. Commun. 1990, 1049–1050; b) M. N. Vargaftik, I. P. Stolyarov, D. I. Shishkin, I. I. Moiseev, Teor. Eksp. Khim. 1991, 27, 301–307; c) A. E. Shilov, Activation of Saturated Hydrocarbons by Transistion Metal Complexes, Springer, Dordrecht, 1984; d) M. Asadullah, Y. Taniguchi, T. Kitamura, Y. Fujiwara, Tetrahedron Lett. 1999, 40, 8867–8871; e) H. Tang, C. Y. Shen, M. R. Lin, Y. Sen, Inorg. Chim. Acta 2000, 300, 1109– 1111; f) I. P. Stolarov, M. N. Vargaftik, D. I. Shishkin, I. I. Moiseev, J. Chem. Soc., Chem. Commun. 1991, 938–939.
- [12] G. Ingrosso, N. Midollini, J. Mol. Catal. A 2003, 204–205, 425– 431.
- [13] I. Yamanaka, M. Soma, K. Otsuka, *Res. Chem. Intermed.* 2000, 26, 129–135.
- [14] W. Chen, J. A. Kocal, T. A. Brandvold, M. L. Bricker, S. R. Bare, R. W. Broach, N. Greenlay, K. Popp, J. T. Walenga, S. S. Yang, J. J. Low, *Catal. Today* 2009, 140, 157–161.
- [15] a) M. Kirillova, A. Kirillov, P. Reis, J. Silva, J. Frausto da Silva, A. Pombeiro, J. Catal. 2007, 248, 130–136; b) M. V. Kirillova, J. A. L. da Silva, J. J. R. Frausto da Silva, A. F. Palavra, A. J. L. Pombeiro, Adv. Synth. Catal. 2007, 349, 1765–1774; c) L. Gonzalez Cuervo, Y. N. Kozlov, G. Suss-Fink, G. B. Shulpin, J. Mol. Catal. A 2004, 218, 171–177; d) M. V. Kirillova, J. A. L. da Silva, J. J. R. Frausto da Silva, A. J. L. Pombeiro, Appl. Catal. A 2007, 332, 159–165.
- [16] T. Kitamura, D.-G. Piao, Y. Taniguchi, Y. Fujiwara, *Stud. Surf. Sci. Catal.* **1998**, *119*, 301–305.
- [17] a) R. A. Sheldon, J. K. Kochi, Metal-Catalyzed Oxidations of Organic Compounds, Academic Press, New York, 1981; b)
 G. W. Parshall, Homogenous Catalysis. The Application of Catalysis by Soluble Transition Metal Complexes, Wiley, New

York, **1980**; c) R. A. Sheldon, G. Papadogianakis, "Oxidations" in *Aqueous-Phase Organometallic Catalysis* (Eds.: B. Cornils, W. A. Herrmann), Wiley-VCH, Weinheim, **2004**, pp. 473–480; d) G. L. Zhuo, X. Z. Jiang, *Catal. Lett.* **2003**, *87*, 225–227; e) W. J. Zhao, X. Z. Jiang, G. L. Zhuo, *J. Mol. Catal. A* **2005**, *225*, 131–135.

- [18] R. Tang, J. K. Kochi, J. Inorg. Nucl. Chem. 1973, 35, 3845– 3856.
- [19] a) M. F. Ryan, A. Fiedler, D. Schröder, H. Schwarz, Organometallics 1994, 13, 4072–4081; b) H. Schwarz, D. Schröder, Pure Appl. Chem. 2000, 72, 2319–2332; c) E. R. King, G. T. Sazama, T. A. Betley, J. Am. Chem. Soc. 2012, 134, 17858–17861.
- [20] L. Simandi, Catalytic Activation of Dioxygen by Metal Complexes, Kluwer Academic Publishers, Dordrecht, 1992.
- [21] K. J. Stowers, A. Kubota, M. S. Sanford, *Chem. Sci.* **2012**, *3*, 3192–3195.
- [22] a) E. M. Wilcox, G. W. Roberts, J. J. Spivey, *Appl. Catal. A* 2002, 226, 317–318; b) D. M. Camaioni, J. T. Bays, W. J. Shaw, J. C. Linehan, J. C. Birnbaum, *J. Org. Chem.* 2001, 66, 789–795; c) T. Hogan, A. Sen, *J. Am. Chem. Soc.* 1997, 119, 2642–2646.
- [23] P. B. Armentrout, L. F. Halle, J. L. Beauchamp, J. Chem. Phys. 1982, 76, 2449–2457.
- [24] a) R. A. Periana, O. Mironov, D. Taube, G. Bhalla, C. J. Jones, *Top. Catal.* **2005**, *32*, 169–174; b) E. G. Chepaikin, A. P. Bezruchenko, G. N. Boiko, A. E. Gekhman, I. I. Moiseev, *Kinet. Catal.* **2006**, *47*, 12–19; c) R. A. Periana, O. Mironov, D. Taube, G. Bhalla, C. J. Jones, *Science* **2003**, *301*, 814–818.
- [25] a) C. M. Cooper, P. J. Wiezevich, Ind. Eng. Chem. 1929, 21, 1210–1214; b) H. H. Storch, J. Am. Chem. Soc. 1935, 57, 685– 686.

Received: February 13, 2013 Published Online: July 2, 2013