## Catalysts

# A Cheap, Efficient, and Environmentally Benign Synthesis of the Versatile Catalyst Methyltrioxorhenium (MTO)**

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*Dedicated to the memory of Ernst Otto Fischer and to Süd-Chemie on the occasion of its 150th anniversary*

Organometallic oxides in high oxidation states play a key role as catalysts in oxygen-transfer reactions.[1] The catalytic potential of methyltrioxorhenium (MTO, **1**) is unrivalled in numerous reactions.[2] MTO was first synthesized in a quite time-consuming (weeks) and low-scale (milligrams) process.[3] Based on extensive studies in academia and industry, MTO has been recognized to be the most active available catalyst for olefin epoxidation. Aside from its application as an oxidation catalyst, MTO is also used to catalyze other reactions, for example, olefin metathesis and aldehyde olefination. However, its synthetic access suffers from severe drawbacks with respect to larger scale applications:[4]

a) Direct alkylation of dirhenium heptoxide ($Re_2O_7$) with the non-reducing alkyl-transfer reagent tetramethyltin[5] wastes half of the rhenium by concomitant formation of (catalytically inactive) trimethyltin perrhenate, $(CH_3)_3SnOReO_3$.

b) Alkylation of $Re_2O_7$ in the presence of trifluoroacetic anhydride ("anhydride route") results in nearly quantitative yields of MTO.[6] However, toxic methyltin reagents are required.

c) Preparation from inorganic perrhenates via the covalent trimethylsilyl perrhenate[7] once again requires the use of tetramethyltin.

$Re_2O_7$ is in principle the most straightforward starting material for the synthesis of MTO since both the pure metal and inorganic perrhenates are prepared from $Re_2O_7$. The disadvantage of the above methods is that good yields of MTO are obtained only if the volatile, highly toxic, and carcinogenic tetramethyltin or related, still quite toxic derivatives are applied. Thus, both the synthesis and purification of MTO is expensive, with complex safety precautions as well as cumbersome purifying procedures being mandatory. This prevented any reasonable industrial application of MTO (and any of its derivatives).

Alkylrhenium(VII) oxides are also available via dialkyl zinc precursors.[8] However, dimethylzinc entails significant reduction of $Re^{VII}$ when exposed to $Re_2O_7$ and related $Re^{VII}$ precursor compounds.[5,9] We have now discovered unexpectedly that clean methylation without any reduction occurs when methylzinc acetate[10] is allowed to react with perrhenylacetate [Eq. (1)]. The yields of methyltrioxorhenium

isolated are about 90%. Under nonoptimized conditions, a 50 g-scale synthesis yielded around 75% of the pure MTO catalyst. The new synthesis is not only efficient but also cheap. Methylzinc acetate is available from inexpensive readily available chemicals according to Equation (2). As the han-

$$Zn[OC(=O)CH_3]_2 + \tfrac{1}{3}\,Al(CH_3)_3 \longrightarrow$$
$$CH_3ZnOC(=O)CH_3 + \tfrac{1}{3}\,Al[OC(=O)CH_3]_3 \quad (2)$$

dling of trimethylaluminum is no significant obstacle for a synthetic chemist, the synthesis of methylzinc acetate according to Equation (2) is superior to that following the most common method given in Equation (3).

$$(CH_3)_2Zn + CH_3COOH \longrightarrow CH_3ZnOC(=O)CH_3 + CH_4 \quad (3)$$

The new synthesis proceeds conveniently as follows: First, $Re_2O_7$ is dissolved in acetonitrile to quantitatively form perrhenylacetate upon treatment with acetic anhydride. The

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methylating reagent $CH_3Zn[OC(=O)CH_3]$ is then added slowly at $-10°C$ [Eq. (1)]. For purification, the resulting solution is separated from the precipitated zinc acetate. After several washing steps, pure MTO is obtained in about 90% yield. Table 1 shows the results of various experiments in

**Table 1:** Synthesis of alkylrhenium(VII) oxides.

| Reactive Re$^{VII}$ precursor | Alkylating reagent | Yield [%][a] |
|---|---|---|
| $CH_3C(=O)OReO_3$ | $CH_3ZnOC(=O)CH_3$ | 90[b] (R = CH$_3$) |
| $CF_3C(=O)OReO_3$ | $CH_3ZnOC(=O)CH_3$ | 95[b] (R = CH$_3$) |
| $CH_3C(=O)OReO_3$ | $CH_3CH_2ZnOC(=O)CH_3$ | 60[c] (R = C$_2$H$_5$) |

[a] Yield of RReO$_3$. [b] Yield of isolated product. [c] Yield quantified by $^1$H NMR spectroscopy.

which different carboxylic acid anhydrides were applied for the activation of $Re_2O_7$ and alkylzinc acetates to prepare MTO and its derivative ethyltrioxorhenium(VII) (ETO).

For MTO, the overall preparation follows the net Equation (4). Zinc serves only as the alkyl mediator metal.

$$Re_2O_7 + 2[CH_3C(=O)]_2O + {}^2\!/_3\, Al(CH_3)_3 \longrightarrow$$
$$2\, CH_3ReO_3 + {}^2\!/_3\, Al[OC(=O)CH_3]_3 \tag{4}$$
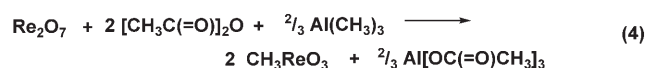
This novel procedure avoids the use of toxic organotin reagents and is much cheaper and easier to perform than all previously known routes. The synthesis of MTO according to Equation (4) should now facilitate wide industrial application of the catalyst MTO.

Nevertheless, another drawback for the synthesis of MTO in large quantities (and thus for the application of MTO in industrial processes) is the sensitivity of $Re_2O_7$ towards traces of water; all manipulations described above have to be performed under strict exclusion of moisture. In contrast, inorganic perrhenates are stable towards air and water, and can be stored without decomposition over long periods of time. In addition, they are readily available, also on a large scale, from rhenium metal. Therefore, it would be highly desirable to replace dirhenium heptoxide as the starting material by simple and more cost-efficient perrhenates. Along these lines, we found that the reaction of silver perrhenate with one equivalent of acetyl chloride delivers perrhenyl acetate in 98% yield which, after alkylation with methylzinc acetate, likewise delivers MTO in high yields [>90%, Eq. (5)].

$$AgReO_4 \xrightarrow[{-\, AgCl}]{CH_3C(=O)Cl} \cdots \xrightarrow{CH_3ZnOC(=O)CH_3} \cdots \tag{5}$$
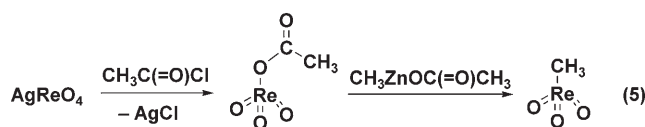
The reaction of silver perrhenate with acetyl chloride is fast and occurs with a quantitative precipitation of silver chloride. After filtration of the by-product, the reaction solution can directly be treated with methylzinc acetate without further purification. The silver chloride can be recovered quantitatively. Other perrhenates can also be

used, but to date silver perrhenate shows the best results. More work is now underway to optimize this route. The combination of the surprisingly efficient alkylating agent methylzinc acetate and the new rhenium source, based on perrhenates, elegantly eliminates two of the major "trouble makers" at the same time, namely the sensitive and less easy to handle dirhenium heptoxide, and the expensive, highly toxic tinalkyls. Both issues were a severe problem, which—up to now—hampered all efforts to bring MTO to industrial use beyond laboratory-scale reactions. We are now in a position to develop a pilot-plant synthesis of MTO. The ongoing fine-tuning of the methyl-transfer agent is well set to enable commercial synthesis of MTO on a multi-kilogram scale.

Our new approach not only provides a route for the production of the catalyst MTO, but also promises a general economic and simple high-yield access to alkylrhenium(VII) oxides by means of nontoxic, non-reducing, and robust alkylating reagents.

## Experimental Section

All experiments were carried out under an oxygen- and water-free argon atmosphere using standard Schlenk techniques. All solvents for use in an inert gas atmosphere were purified by a solvent purification system MB SPS (MBraun).

Methylzinc acetate, $CH_3ZnOC(=O)CH_3$: Powdered $Zn[OC(=O)CH_3]_2 \cdot 2H_2O$ (11.1 g, 60.6 mmol) was dried for 3 h at 70°C. The loss of water was gravimetrically determined. Anhydrous zinc acetate was suspended in toluene (50 mL). At $-10°C$, $Al(CH_3)_3$ (20 mmol) in toluene was added dropwise, and the reaction mixture was stirred for 5 h at $-10°C$. After removal of the solvent in vacuo, methylzinc acetate was obtained as a white solid. Yield: 80% (6.7 g); $^1$H NMR (400 MHz, CDCl$_3$, 25°C): $\delta = 2.14$ (s, 3H, C-CH$_3$), $-0.68$ ppm (s, 3H, Zn-CH$_3$); $^{13}$C NMR (400 MHz, CDCl$_3$, 25°C): $\delta = 180.4$ (s, C=O), $-15.2$ ppm (s, Zn-CH$_3$).

Methyltrioxorhenium(VII), $CH_3ReO_3$: $Re_2O_7$ (10 g, 22.0 mmol) was suspended in acetonitrile (50 mL), and then one equivalent of acetic anhydride was added. The reaction mixture was stirred for 30 min. Two equivalents of methylzinc acetate dissolved in acetonitrile were then added dropwise at $-10°C$ to the resulting clear solution. After a reaction time of 30 min, the solution was separated, and the solvent was removed in vacuo. The resulting solid was washed several times with small portions of cold ($-20°C$) n-pentane to obtain pure MTO. The analytical data are identical to the previously published data and confirm that the compound is pure.[5] Yield: 90% (10.9 g).

Ethylzinc acetate, $CH_3CH_2ZnOC(=O)CH_3$: Dimethylzinc (20 mmol) in n-hexane was added dropwise to a suspension of acetic acid (1.2 g, 20 mmol) in n-hexane (100 mL) at $-78°C$. The reaction mixture was allowed to warm up to ambient temperature. After removal of the solvent in vacuo, and a washing step with cold acetonitrile, a white solid was obtained. Yield: 93% (2.85 g).

Ethyltrioxorhenium(VII), $CH_3CH_2ReO_3$: $Re_2O_7$ (4.88 g (10 mmol) was suspended in acetonitrile (100 mL), and then acetic acid anhydride (1.03 g, 10 mmol) was added. After a reaction time of 20 min, ethylzinc acetate (2.09 g, 20 mmol) in acetonitrile was slowly added at $-10°C$. After removal of the solvent in vacuo, ethyltrioxorhenium(VII) was obtained. The analytical data correspond to those in literature.[8]

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