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Methylrhenium oxides

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Abstract—Reactions of the rhenium(VII) precursors Re_2O_7, acetyl perrhenate, trifluoroacetyl perrhenate, chlorotrioxorhenium and trimethylsilyl perrhenate are performed with various common tin free methylating agents. The yields of MTO and the products of partial reduction, bis[dimethyl(μ-oxo)oxo-rhenium(VI)] and (μ-oxo)bis[trimethyloxorhenium(VI)], are quantified by NMR spectroscopy. With aluminium- and copper-containing methylating agents none of the above mentioned compounds are formed, solely perrhenate and rhenium(VI) oxide are detected. The best result is achieved with trifluoroacetyl perrhenate and dimethylzinc, yielding >60% MTO.

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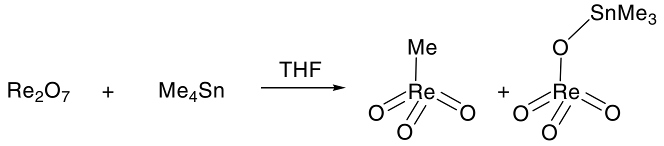
1. Introduction

MTO was first detected in trace amounts by the reaction of $(CH_3)_4$ ReO with air by Beattie and Jones in 1979.[1] The breakthrough towards larger-scale syntheses and possible applications came about 10 years later, when a much more efficient synthetic route was developed starting from Re_2O_7 and tetramethyltin (Eq. 1).[2] This synthetic procedure made it possible to prepare MTO within hours and in amounts of up to 10 g. However, the most evident drawback of this method is the formation of an equimolar amount of trimethyl tin perrhenate, thus wasting half of the comparatively expensive rhenium. This so called 'tin route' was further improved in 1992 when it became possible to obtain nearly quantitative yields of MTO by the addition of carboxylic



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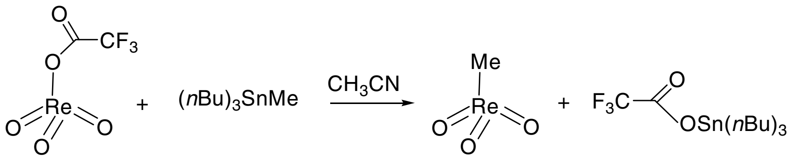

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Keywords: Methylation; Methyltrioxorhenium; Rhenium; Synthesis.

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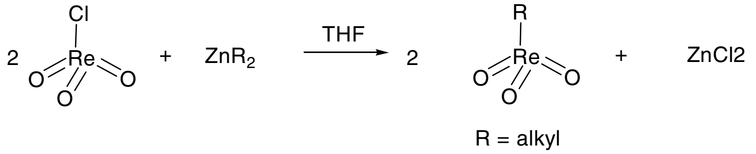
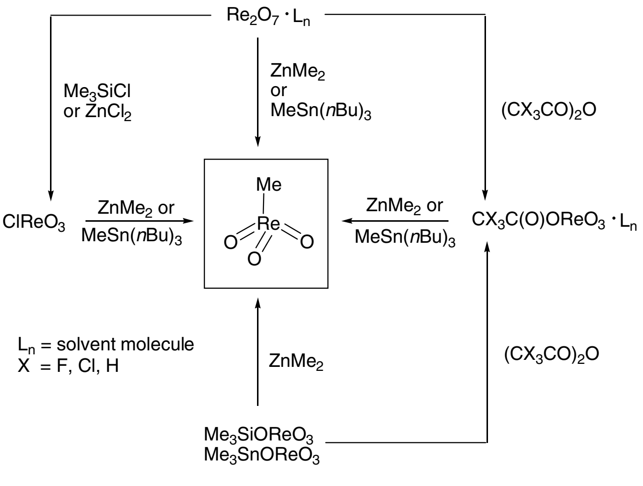


(3)

anhydrides to the reaction mixture. The in situ-generated perrhenyl carboxylates as well as solvent ligated chlorotrioxorhenium(VII) are more useful precursors for the $[ReO_3]^+$ ('perrhenyl') moiety than Re_2O_7.[3] Both compounds are easily and quantitatively available from Re_2O_7 and can be used in situ for the reaction with the organylating tin reagent without rhenium loss (Eqs. 2 and 3).

Covalent perrhenates such as $Me_3SiOReO_3$ and $Me_3SnOReO_3$ are also suitable precursor compounds for $R–ReO_3$ complexes, when applied together with organotin reagents.[4] However, the tin precursors, such as tetramethyl tin are highly toxic. The toxicity of these complexes and of some of the by-products of the synthesis of the rhenium complexes, such as trimethyl tin chloride prevented an industrial application of MTO or one of its derivatives to a large extent, regardless of its high catalytic activity in many organic reactions. It had been shown, however, that organozinc precursors are also useful organylating agents, particularly for the preparation of long-chain alkylrhenium oxides,[5] σ-arylrehnium oxides,[6] while methyl-, alkenyl-, alkynylrhenium(VII) oxides are solely available via organotin precursors.[7] The success of the synthesis depends on the transferability of the organic group, the redox potential of the precursors and the thermal stability of the product.[8] Organotin precursors need higher reaction temperatures in organylating reactions than their zinc counterparts. Organozinc compounds are reactive already at dry ice temperature in many cases, but at higher temperatures reduction to rhenium(VI) (or lower oxidation states) frequently occurs.[9,10] Scheme 1 summarizes the synthetic pathways to organorhenium(VII) oxides starting from Re(VII) precursors.



Scheme 1.

In this work we examine the reaction of different common methylating agents with several potential rhenium(VII) precursors with quantitative NMR techniques in order to compare the obtained MTO yields and the yields of the dimeric by-products bis[dimethyl(μ-oxo)oxo-rhenium(VI)] and (μ-oxo)bis-[trimethyloxorhenium(VI)], resulting from the partial reduction of the rhenium(VII) starting material.

2. Results and discussion

Reactions of various common methylating agents with rhenium(VII) precursors of different activity have been performed in order to determine the product distribution by quantitative NMR spectroscopy.[11,12] As rhenium(VII) starting materials Re_2O_7, acetyl perrhenate, trifluoroacetyl perrhenate, chlorotrioxorhenium and trimethylsilyl perrhenate, were applied, being prepared according to the literature procedures.[3b,4,13] The perrhenyl carboxylates and chlorotrioxorhenium were synthesized prior to use and reacted in situ with the methylating agent. Trimethylsilyl perrhenate was obtained as a white solid and the observed analytical data confirm that the substance is pure and the experimental data are in accord with the published literature.[13] MeLi, MeMgCl, Me_2Zn, Me_3Al and $MeAlCl_2$ were used as commercial available solutions. Me_2CuLi,[14] MeCu,[14] MeZnCl[15] and $MeTi(OiPr)_3$[16] were prepared prior to use according to the literature. The synthesis of $MeAl(OC(O)CH_3)_2$ and $Me_2Al(OC(O)CH_3)$ were carried out analogous to the preparation of $MeZn(O(C)OCH_3)$ developed by Coates et al.[17] The results of the methylating reactions are summarized in Table 1.

The formation of the by-products bis[dimethyl-(μ-oxo)oxo-rhenium(VI)] and (μ-oxo)bis[trimethyloxo-rhenium(VI)] resulting from partial reduction is observed in nearly all performed experiments, even when no MTO can be detected, especially in the case of methylating agents containing aluminium in combination with a monomeric rhenium precursor. In these experiments only traces of dimeric methylrhenium(VI) oxides are found. The loss of about two thirds of the applied rhenium as perrhenate and rhenium(VI) oxide is observed during the preparation. The latter compounds can be easily identified by their distinctive IR spectra. Therefore, all employed aluminium containing methylating agents are not suitable for the transfer of the methyl group to a monomeric rhenium precursor. When Re_2O_7 reacts with Me_3Al and $MeAlCl_2$ only tiny amounts of MTO can be obtained. The results of the experiments with copper compounds as methylating agents are also unsatisfactory, because only

Table 1. Results of the methylating experiments (Me = CH_3, OAc = acetate, *i*Pr = $CH(CH_3)_2$)

Rhenium precursor	Methylating reagent	MTO[a] (%)	Bis[dimethyl(μ-oxo-)oxo-rhenium] (%)	(μ–Oxo)bis-[trimethyloxorhenium] (%)
$CH_3C(O)O–ReO_3$	MeLi	9	—	<1
	Me_2CuLi	—	—	—
	MeMgCl	5	<1	<1
	Me_3Al	—	<1	—
	$MeAlCl_2$	—	<1	<1
	$Me_2Al(OAc)$	—	<1	—
	$MeAl(OAc)_2$	—	<1	—
	$MeTi(OiPr)_3$	34	<1	<1
	Me_2Cu	6	—	—
	Me_2Zn	39	<1	—
	MeZnCl	13	<1	—
$CF_3C(O)O–ReO_3$	MeLi	14	<1	<1
	Me_2CuLi	<1	—	<1
	MeMgCl	12	<1	4
	Me_3Al	—	<1	<1
	$MeAlCl_2$	—	<1	—
	$Me_2Al(OAc)$	—	<1	—
	$MeAl(OAc)_2$	—	—	<1
	$MeTi(OiPr)_3$	7	<1	<1
	Me_2Cu	<1	—	—
	Me_2Zn	61	<1	3
	MeZnCl	18	<1	—
Re_2O_7	MeLi	7	4	—
	Me_2CuLi	<1	—	—
	MeMgCl	18	6	—
	Me_3Al	8	1	—
	$MeAlCl_2$	2	1	—
	$Me_2Al(OAc)$	—	<1	—
	$MeAl(OAc)_2$	—	<1	—
	$MeTi(OiPr)_3$	21	5	—
	Me_2Cu	<1	<1	—
	Me_2Zn	9	1	—
	MeZnCl	27	<1	—
$Cl–ReO_3$	MeLi	18	<1	<1
	Me_2CuLi	<1	—	<1
	MeMgCl	12	<1	—
	Me_3Al	—	<1	<1
	$MeAlCl_2$	—	—	<1
	$Me_2Al(OAc)$	—	<1	<1
	$MeAl(OAc)_2$	—	<1	—
	$MeTi(OiPr)_3$	8	15	—
	Me_2Cu	<1	<1	—
	Me_2Zn	29	—	<1
	MeZnCl	28	<1	—
$TMSO–ReO_3$	MeLi	<1	<1	—
	Me_2CuLi	<1	—	—
	MeMgCl	28	7	—
	Me_3Al	—	<1	—
	$MeAlCl_2$	<1	<1	—
	$Me_2Al(OAc)$	—	4	—
	$MeAl(OAc)_2$	—	<1	—
	$MeTi(OiPr)_3$	13	37	—
	Me_2Cu	<1	—	—
	Me_2Zn	3	2	—
	MeZnCl	15	1	—

[a] The isolated yield of MTO is about 5% lower.

traces of MTO are detected. Applying MeLi, with rhenium precursors of increasing reactivity ($Re_2O_7 <$ $TMSO–ReO_3 < CH_3C(O)O–ReO_3 < CF_3C(O)O–ReO_3 <$ $Cl–ReO_3$) leads to a rise in the yield of MTO from 7% to 18%, with the exception of $TMSO–ReO_3$ where only traces of the desired product can be found. Besides MTO, the Re(VI) reduction products are always detected when MeLi is utilized as methylating agent. Comparable results can be obtained when applying the Grignard compound MeMgCl as the transfer agent for the methyl group with $CH_3C(O)O–ReO_3$, $CF_3C(O)O–ReO_3$ and $Cl–ReO_3$, being the most reactive rhenium precursors. However, the less reactive TMSO–$\mathrm{ReO_3}$ and $\mathrm{Re_2O_7}$ reach significant better yields of MTO when applied together with the Grignard reagent MeMgCl. However, higher amounts of bis[dimethyl-(μ-oxo)oxo-rhenium(VI)] (up to 7%) are detected in these cases as well. The reaction of TMSO–$\mathrm{ReO_3}$ with MeMgCl yields 28% MTO. When $\mathrm{MeTi(O}i\mathrm{Pr)_3}$ is used, the less reactive rhenium precursors show the best performance. With acetyl perrhenate 34% MTO are obtained. Nevertheless, in almost all reactions of Re(VII) precursors with $\mathrm{MeTi(O}i\mathrm{Pr)_3}$ higher amounts of bis[dimethyl(μ-oxo)oxo-rhenium(VI) are found than with all other methylating agents. When using chlorotrioxorhemiun and trimethylsilyl perrhenate, significantly higher amounts of the dimeric rhenium(VI) compounds than of MTO are obtained, particularly when applying TMSO–$\mathrm{ReO_3}$. This is not surprising, however, when considering that this combination of a rhenium(VII) precursor and a methylating agent is the most commonly applied synthetic route to bis-[dimethyl(μ-oxo)oxo-rhenium.[9a] Dialkylzinc compounds are useful for the preparation of long-chain alkylrhenium oxides,[5] but can also be used for the transfer of the methyl group to the $[\mathrm{ReO_3}]^+$ moiety. Unfortunately, significant amounts of reduction products are formed during this reaction, especially when the reaction temperature is not carefully controlled.[9] The MTO yield increases with the reactivity of the rhenium precursors when dimethylzinc is applied as the methylating agent. The highest amount of MTO (ca. 60%) is reached with trifluoroacetyl perrhenate, but the yield decreases to ca. 30% when the more reactive chlorotrioxorhenium is used. In every experiment applying dimethylzinc the dimeric by-products bis[dimethyl(μ-oxo)oxo-rhenium(VI)] and (μ-oxo)bis[trimethyloxorhenium(VI)], resulting from partial reduction, are obtained. Compared to all other examined methyl group transfer agents dimethylzinc shows the best performance under the conditions applied. The reactivity of dialkylzinc compounds can be reduced when one methyl group is replaced by a halogen.[6b] However, when utilizing MeZnCl, the yields of MTO are lower (up to ca. 30%) than with the more reactive $\mathrm{Me_2Zn}$.

In summary, in nearly all experiments executed to obtain MTO by a tin free route, the dimeric rhenium(VI) complexes bis[dimethyl(μ-oxo)oxo-rhenium(VI)] and (μ-oxo)bis[trimethyloxorhenium(VI)] resulting from partial reduction are detected as by-products. MTO is indeed found in most cases, except when aluminium and copper methylating agents are applied. As proven by IR spectroscopy, the applied rhenium is lost under these circumstances as perrhenate and rhenium(VI) oxide. The most suitable methylating agents are based on titanium and zinc. The highest yield of MTO is obtained when trifluoroacetyl perrhenate reacts with dimethylzinc (61% MTO).

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References and notes

1. Beattie, R. I.; Jones, P. J. *Inorg. Chem.* **1979**, *18*, 2318.
2. Herrmann, W. A.; Kuchler, J. G.; Felixberger, J. K.; Herdtweck, E.; Wagner, W. *Angew. Chem.* **1988**, *100*, 420; *Angew. Chem., Int. Ed. Engl.* **1988**, *27*, 394.
3. (a) Herrmann, W. A.; Thiel, W. R.; Kühn, F. E.; Fischer, R. W.; Kleine, M.; Herdtweck, E.; Scherer, W.; Mink, J. *Inorg. Chem.* **1993**, *32*, 5188; (b) Herrmann, W. A.; Kühn, F. E.; Romão, C. C.; Kleine, M.; Mink, J. *Chem. Ber.* **1994**, *127*, 47.
4. Herrmann, W. A.; Kühn, F. E.; Fischer, R. W.; Romão, C. C. *Inorg. Chem.* **1992**, *31*, 4431.
5. (a) Herrmann, W. A.; Kühn, F. E.; Romao, C. C.; Tran Huy, H.; Wang, M.; Fischer, R. W.; Scherer, W.; Kiprof, P. *Chem. Ber.* **1993**, *126*, 24; (b) Herrmann, W. A.; Romao, C. C.; Fischer, R. W.; Kiprof, P.; de Méric de Bellefon, C. *Angew. Chem.* **1991**, *103*, 183; *Angew. Chem., Int. Ed. Engl.* **1991**, *30*, 185.
6. (a) Herrmann, W. A.; Ladwig, M.; Kiprof, P.; Riede, J. *J. Organomet. Chem.* **1989**, *371*, C13; de Méric de (b) Bellefon, C.; Herrmann, W. A.; Kiprof, P.; Whitaker, C. R. *Organometallics* **1992**, *11*, 1072; (c) Herrmann, W. A.; Taillefer, M.; de Méric de Bellefon, C.; Behm, J. *Inorg. Chem.* **1991**, *30*, 3247.
7. (a) Herrmann, W. A.; Kühn, F. E.; Romão, C. C.; Tran Huy, H. *J. Organomet. Chem.* **1994**, *481*, 227; (b) Herrmann, W. A.; Kühn, F. E.; Romão, C. C. *J. Organomet. Chem.* **1995**, *489*, C56; (c) Herrmann, W. A.; Kühn, F. E.; Romão, C. C. *J. Organomet. Chem.* **1995**, *489*, 209.
8. (a) Kühn, F. E.; Herrmann, W. A.; Hahn, R.; Elison, M.; Blümel, J.; Herdtweck, E. *Organometallics* **1994**, *13*, 1601; (b) Kühn, F. E. Ph.D. Thesis, TU München, 1994.
9. (a) Herrmann, W. A.; Romão, C. C.; Kiprof, P.; Behm, J.; Cook, M. R.; Taillefer, M. *J. Organomet. Chem.* **1991**, *413*, 11; (b) Rost, A. M. J.; Scherbaum, A.; Kühn, F. E.; Herrmann, W. A. *New J. Chem.* **2006**, *30*, 1599.
10. (a) Herrmann, W. A.; Kühn, F. E. *Acc. Chem. Res.* **1997**, *30*, 169; (b) Romão, C. C.; Kühn, F. E.; Herrmann, W. A. *Chem. Rev.* **1997**, *97*, 3197; (c) Kühn, F. E.; Santos, A. M. *Mini-Rev. Org. Chem.* **2004**, *1*, 55; (d) Santos, A. M.; Pedro, F. M.; Yogalekar, A. A.; Lucas, I. S.; Romão, C. C.; Kühn, F. E. *Chem. Eur. J.* **2004**, *10*, 6313; (e) Pedro, F. M.; Hirner, S.; Kühn, F. E. *Tetrahedron Lett.* **2005**, *46*, 7777; (f) Kühn, F. E.; Zhao, J.; Herrmann, W. A. *Tetrahedron: Asymmetry* **2005**, *16*, 3469; (g) Kühn, F. E.; Scherbaum, A.; Herrmann, W. A. *J. Organomet. Chem.* **2004**, *689*, 4149; (h) Kühn, F. E. In *Homogeneous Multiphase Catalysis*; Cornils, B., Herrmann, W. A., Horváth, I. T., Leitner, W., Mecking, S., Olivier-Bourbigou, H., Vogt, D., Eds.; Wiley-VCH: Weinheim, 2005; Vol. 1, pp 210–217; (i) Santos, A. M.; Kühn, F. E. In *Homogeneous Multiphase Catalysis*; Cornils, B., Herrmann, W. A., Horváth, I. T., Leitner, W., Mecking, S., Olivier-Bourbigou, H., Vogt, D., Eds.; Wiley-VCH: Weinheim, 2005; Vol. 2, pp 807–818; (j) Kühn, F. E.; Fischer, R. W.; Herrmann, W. A., 2nd ed. In *Transition Metals for Organic Synthesis*; Beller, M., Bolm, C., Eds.; Wiley-VCH: Weinheim, 2004; Vol. 2, pp 357–367; (k) Kühn, F. E.; Herrmann, W. A. In *Aqueous-Phase Organometallic Catalysis Concepts and Applications*; Cornils, B., Herrmann, W. A., Eds., 2nd completely revised and enlarged edition; Wiley-VCH: Weinheim, 2004; pp 488–500.
11. *Typical procedure*: To a solution of a rhenium precursor (1 mmol) in 20 mL THF at −78 °C a solution of a methylating reagent (1 transferable methyl group per equiv Re) was added dropwise. The reaction mixture was stirred for 1 h at −78 °C before quenching with a drop of

isopropanol. Then it was allowed to warm up to room temperature and the solvent was removed under vacuum. The resulting solid was extracted with *n*-hexane. The solution was filtered and the solvent was removed under vacuum. Then 137 μL (1 mmol) mesitylene as internal standard and 0.7 mL $CDCl_3$ were added. The resulting solution was filtered and used for quantitative ^1H NMR measurements (400 MHz, $CDCl_3$, 298 K).

12. (a) Malz, F.; Jancke, H. *J. Pharm. Biomed. Anal.* **2005**, *38*, 813; (b) Rizzo, V.; Pinciroli, V. *J. Pharm. Biomed. Anal.* **2005**, *38*, 851.
13. Schmidt, M.; Schmidbaur, H. *Chem. Ber.* **1959**, *92*, 2667.
14. (a)in *Organocopper Reagents: A Practical Approach*; Taylor, J. K., Ed.; Oxford University Press: Oxford, 1994; (b)in *Modern Organocopper Chemistry*; Krause, N., Ed.; Wiley-VCH: Weinheim, 2002.
15. Matsushita, H.; Negishi, E. *J. Org. Chem.* **1982**, *47*, 4161.
16. Reetz, M. T.; Westermann, J.; Steibach, R.; Wenderoth, B.; Peter, R.; Ostarek, R.; Maus, S. *Chem. Ber.* **1985**, *118*, 1421.
17. Coates, G. E.; Ridley, D. *J. Chem. Soc.* **1965**, 1870.