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Insights into a Nontoxic and High-Yielding Synthesis of Methyltrioxorhenium (MTO)

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Dedicated to Wolfgang A. Herrmann on the occasion of his 60th birthday

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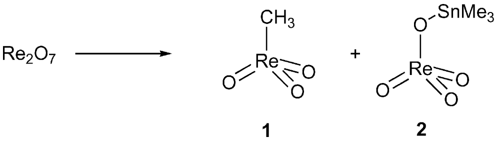
The versatile catalyst methyltrioxorhenium(VII) (MTO) is now available in high yields by utilizing easily accessible nontoxic starting materials. The new synthetic pathway allows an inexpensive, large-scale production of MTO, paving the way for industrial applications. A variety of starting materials is compared with respect to their applicability, availability and ease of handling. The reaction times and the byproducts formed are compared under different reaction conditions. It was seen that silver perrhenate in combination with methylzinc acetate, which was derived from trimethylaluminum and zinc acetate, are the best starting materials for a high-yielding large-scale synthesis of MTO.

Introduction

High oxidation state organometallic oxides have been established as important catalysts in many organic transformations.[1] This is especially true for catalytic oxidation reactions.[2] One of the best studied pre-catalysts in this field is methyltrioxorhenium (MTO).[3] It was first mentioned in the literature – almost 30 years ago – by Beattie and Jones in 1979 who isolated tiny amounts of MTO from the decay of trimethyldioxorhenium(VII) exposed to air.[4] Because this method of access was time consuming (weeks) and restricted to low scale (milligrams), MTO was originally regarded as another mere lab curiosity. This situation remained unchanged until 1988, when Herrmann et al. found a much better synthetic procedure for the preparation of MTO. The alkylation of dirhenium heptoxide (Re_2O_7) with the nonreducing alkylating agent tetramethyltin gave MTO (**1**) in almost quantitative yield on scales of up to ca. 10 g (Scheme 1).[5] This discovery was the starting point for the exploration of the catalytic potential of MTO, which has shown to be considerable. MTO is particularly stable and therefore easy to handle, and it has been proven to be an extremely versatile and powerful catalyst.[3] MTO can be used in the epoxidation of olefins and in the oxidation of aromatics, ethers, alcohols or amines.[3,6–10] Moreover, MTO is a highly active catalyst for olefin metathesis as well as for the olefination of aldehydes and has even found entry into the field of material science.[11–13]



Scheme 1. The first literature reported multigram-scale synthesis of methyltrioxorhenium.[5]

The multitude of applications led to a steady increase in the interest in MTO, and it was soon revealed that the synthetic pathway established in 1988 was not satisfactory, as half the employed rhenium was converted into a catalytically inactive compound – trimethylstannyl perrhenate (**2**). The reason for the formation of this byproduct was ascribed to the heterolytic cleavage of the Re–O–Re moiety in dirhenium heptoxide.[14]

It is known that dirhenium heptoxide, being the anhydride of perrhenic acid, reacts with carboxylic anhydrides to form mixed anhydrides of type **3** (Scheme 2). In this reaction, the heterolytic cleavage of dirhenium heptoxide into a "perrhenyl perrhenate" is avoided. The preparation of complexes of type **3** is quite generally applicable and the corresponding carboxyl perrhenates are usually obtained in very high yields.[15] The subsequent treatment of carbonyl perrhenates with methyl tin reagents gives MTO in moderate to excellent yields,[16] and the outcome of the reaction is strongly dependent on the nature of the employed carbox-

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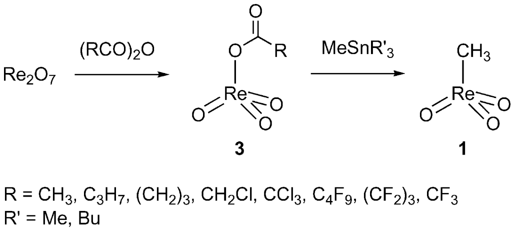
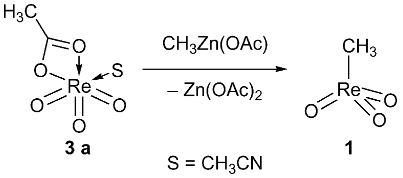
ylic acid derivative. The carboxylate ligands in such complexes are either mono- or bidentate. Electron-rich alkyl substituents in **3** lead to an η^2-coordination geometry, whereas the electron-withdrawing character of halogenated substituents results in monodentate (η^1) coordination.[15] Concomitantly with the change of the coordination mode a significant change in the reactivity can be observed. When acetyl perrhenate is allowed to react with tetramethyltin, MTO is obtained in only moderate yields of about 50%. In contrast, the reactions of trifluoroacetyl perrhenate with methyltin reagents give MTO in yields of up to 90%.[15,16] Following this methodology, even the considerably less-reactive trimethylstannyl perrhenate can be activated and transformed into MTO with good yields.[15,16]



Scheme 2. Synthesis of MTO with mixed anhydrides of perrhenic acid.[15]

In spite of further synthetic progress made since 1992,[17,18] one major drawback of all the established synthetic procedures towards MTO remained: volatile, highly toxic, carcinogenic tin reagents must be utilized. Thus, both the synthesis and the purification of MTO require high safety precautions. Alternative alkylating agents like dialkylzinc, Grignard, organolithium or organocopper reagents lead to poor yields of the desired product as a result of the partial reduction of the rhenium species and the formation of inorganic perrhenates.[19]

Recently, we reported on a new and efficient synthesis of MTO by utilizing the stable and easy to prepare methylzinc acetate as the alkylating agent (Scheme 3). The alkylation of the less-reactive acetyl perrhenate proceeds cleanly without any reduction of the Re^{VII} species and gives MTO in up to 90% isolated yield.[20]



Scheme 3. Synthesis of MTO with the use of acetyl perrhenate and methylzinc acetate.[20]

The findings described above indicate that the choice of the combination of the reactive rhenium intermediate and the alkylating agent is crucial for the success of the quantitative formation of MTO. In order to further optimize the current synthetic procedure of MTO, the reactions of various nonactivated carboxyl perrhenates with methylzinc acetate were studied in detail and the results are presented below.

Results and Discussion

Preparation of Methylzinc Acetate

The methylating agent methylzinc acetate, which is used for the transformation of the carboxyl perrhenates into MTO, can be prepared by three different routes: (i) The reaction of dimethylzinc with acetic acid[21] [Equation (1)]. (ii) The comproportionation of equimolar amounts of dimethylzinc and zinc acetate [Equation (2)]. (iii) The reaction of trimethylaluminum with zinc acetate [Equation (3)].

$$Me_2Zn + HOAc \rightarrow MeZn(OAc) + CH_4\uparrow \qquad (1)$$

$$Me_2Zn + Zn(OAc)_2 \rightarrow 2\ MeZn(OAc) \qquad (2)$$

$$2\ Me_3Al + 3\ Zn(OAc)_2 \rightarrow 3\ MeZn(OAc) + 2\ Al(OAc)_3\downarrow \qquad (3)$$

For the preparation of methylzinc acetate according to Equation (1), dimethylzinc is added slowly to a precooled suspension (–78 °C) of acetic acid in toluene. When kept at this temperature, no reaction can be observed. Therefore, the reaction mixture must be warmed slowly to room temperature. During this period, vivid evolution of stoichiometric amounts of methane can be observed. After evolution of the gas stops, the solvent is removed in vacuo to afford methylzinc acetate in an excellent yield of 95%. However, due to formation of large quantities of gas, which might become a considerable safety issue, and because the loss of “active” methyl groups is not economical, the reaction is not very well suited for scale up.

The comproportionation of dimethylzinc and dehydrated zinc acetate [Equation (2)] proceeds smoothly at room temperature. After removal of the solvent, methylzinc acetate is obtained in near quantitative yield. Nevertheless, dimethylzinc is pyrophoric and expensive, and therefore, it is desirable to replace dimethylzinc by more cost effective methyl sources.

The reaction of dehydrated zinc acetate with trimethylaluminum (which is considerably less expensive than the above-described methylating agents) likewise delivers methylzinc acetate in high yields (up to 90%) and of very good quality at room temperature. The reaction can be performed on any scale without loss of yield. To study the reaction in more detail, its pathway was followed by in situ IR spectroscopy (Figure 1).

Upon addition of trimethylaluminum to a suspension of zinc acetate in toluene, the ν(CO) vibrations seen at 1458 and 1543 cm^{-1} immediately diminish. After a short induction period, a set of two new bands is formed at 1477 and 1589 cm^{-1} (Figure 1). The data are consistent with those obtained from an authentic sample of methylzinc acetate. After 3 h at room temperature the reaction reaches completion and no further change in the intensities can be observed. Precipitated aluminum acetate cannot be observed in the spectra due to the extremely poor solubility of this compound. Therefore, byproduct formation (e.g., aluminates) due to reactions with MeZnOAc does not occur.

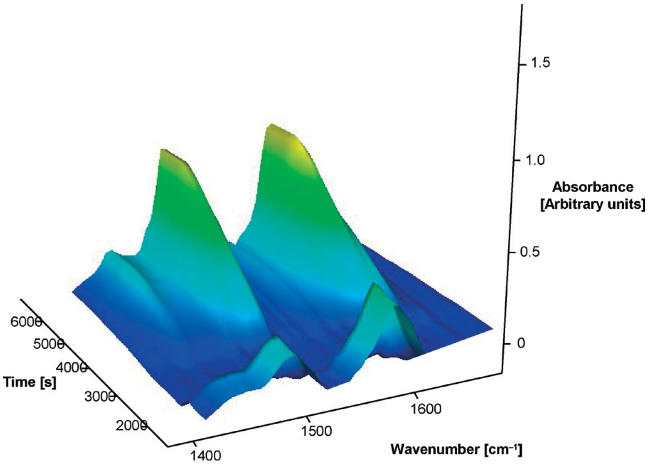


Figure 1. In situ IR spectra for the synthesis of methylzinc acetate from the reaction of zinc acetate with trimethylaluminum.

When the reaction is monitored by ^{1}H NMR spectroscopy only the starting compounds and the product can be observed during the course of the reaction.

Synthesis of MTO

The synthetic procedure for the preparation of MTO is as follows: In a first step, carboxyl perrhenate is prepared. Following the established method, dirhenium heptoxide is dissolved in a donor solvent like THF or acetonitrile and allowed to react with a carboxylic anhydride. The progress of the reaction can be monitored by in situ IR spectroscopy. The time needed to obtain complete conversion ranges between seconds and hours, according to the electronic and steric requirements of the carboxylic anhydrides. In general, aliphatic carboxylic anhydrides react smoothly to give mixed anhydrides in quantitative yields. In contrast, the reaction of Re_2O_7 with 2-naphthalene carboxylic anhydride remains incomplete even after 24 h at ambient temperature. The reaction at elevated temperatures (40 °C) leads to the rapid decomposition of the desired product, which is unfortunately thermally labile. Because polymerization of THF occurs after prolonged reaction times, acetonitrile proved to be the solvent of choice for such reactions.

However, another severe problem for the large-scale synthesis of MTO is the pronounced sensitivity of dirhenium heptoxide towards water. Even trace amounts of moisture readily react with dirhenium heptoxide to yield perrhenic acid. Inorganic perrhenates, however, are readily available in large quantities directly from rhenium metal, are stable towards air and water and can be stored over long periods of time without any signs of decomposition. The reaction of silver perrhenate with acetic chloride also delivers acetyl perrhenate in quantitative yield (Figure 2). The reaction is fast and occurs with a quantitative precipitation of silver chloride. A selected set of other synthesized carboxyl perrhenates is displayed in Scheme 4.

The spectroscopic data of carboxyl perrhenates **3a**–**i** are in good accordance with those previously reported in the literature.[15] The ν(CO) vibration mode at rather low energies confirms the η^2-coordination geometry of all tested perrhenates (Table 1). The ν(CO) vibration mode of the carboxylic ligands with η^1-coordination is usually found at a considerably higher wavenumber (1792 cm^{-1} for $CF_3COOReO_3$). Although, perrhenyl carboxylates are known to be significantly moisture and temperature sensitive, they are stable in solution for several hours when kept under an inert atmosphere (IR evidence), (Figure 2). As isolation of the pure perrhenyl carboxylates proved to be difficult due to their sensitivity, selected examples were isolated as bipyridine adducts [$RCOORe(bipy)O_3$; R = Me (**4a**), Et (**4b**), *n*Pr (**4c**), *t*Bu (**4d**), Ph (**4e**)] and were characterized by elemental analysis and spectroscopic methods (see Experimental Section).

For the conversion into MTO, the perrhenyl carboxylates are treated with one equivalent of solid methylzinc acetate, added in small portions at ambient temperature. Upon addition of the alkylating agent the clear reaction solution immediately darkens from red to violet and $Zn(OAc)_2$ is

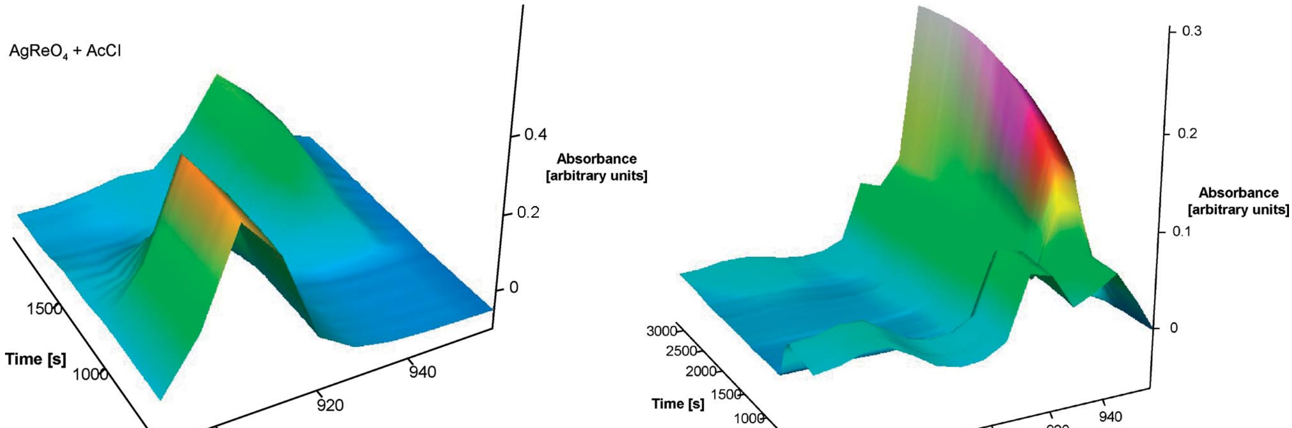
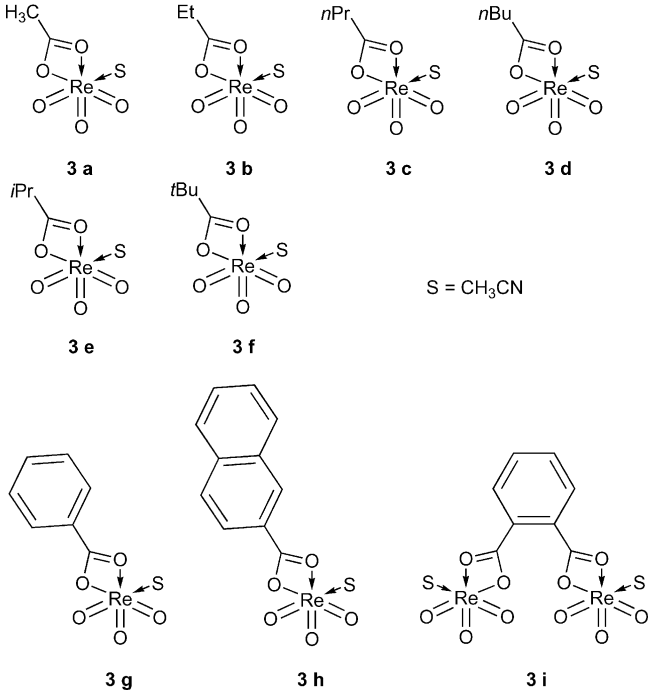


Figure 2. Series of IR spectra obtained from the reaction of silver perrhenate with acetic chloride (left) and Re_2O_7 with acetic anhydride (right), indicating the formation of acetyl perrhenate. Both spectra show the product at 940 cm^{-1}.



Scheme 4. Selected set of perrhenyl carboxylates **3a**–**i**.

Table 1. ν(CO) Vibration of perrhenyl carboxylates **3a**–**i** in acetonitrile at room temperature.

Compound	$\nu_{asymm.}$(CO) [cm^{-1}]	$\nu_{asymm.}$(CO) [cm^{-1}]
$CH_3(C{=}O)OReO_3$ (**3a**)	1493	1448
$C_2H_5(C{=}O)OReO_3$ (**3b**)	1490	1440
$C_3H_7(C{=}O)OReO_3$ (**3c**)	1487	1435
$C_4H_9(C{=}O)OReO_3$ (**3d**)	1487	1435
$(CH_3)_2CH(C{=}O)OReO_3$ (**3e**)	1495	1452
$(CH_3)C(C{=}O)OReO_3$ (**3f**)	1499	1456
$C_6H_5(C{=}O)OReO_3$ (**3g**)	1509	1487
$C_{10}H_7(C{=}O)OReO_3$ (**3h**)	1512	1489
o-$C_6H_4[(C{=}O)OReO_3]_2$ (**3i**)	1501	1456

precipitated. Again, the progress of the reaction is followed by in situ-IR spectroscopy. As can be seen from the spectra, acetyl perrhenate is smoothly converted into MTO. Only trace amounts of zinc perrhenate and ReO_3 are formed during the reaction as byproducts. The waterfall plot obtained from a typical reaction is displayed in Figure 3. Unfortunately, kinetic data could not be obtained with this method, as the conversion to MTO happens virtually immediately with the addition of the methylating agent.

For purification, the resulting suspension can be filtered from the precipitated $Zn(OAc)_2$. After removal of the solvent, pure MTO can easily be obtained by recrystallization or sublimation. The employed rhenium precursors gave generally good yields ranging from 66–92% and are, by far, superior to dirhenium heptoxide (**5**), chloro trioxorhenium[22] (**6**) or trimethylsilyl perrhenate[23] (**7**) as more reactive rhenium sources (Table 2). The best results were obtained with acetic and isobutyric acid derivatives. The differences in the reactivities and product yields observed for and obtained from the different perrhenates cannot be explained in all detail yet, but it is assumed that the steric hindrance as well as the varying solubility of the resulting zinc salts (precipitation of the byproduct as one of the driving forces of the reaction) play a role. However, for economic reasons, acetic chloride or anhydride are clearly preferred. It is noteworthy that the yields obtained from silver perrhenate as starting materials are always higher (about 2–5%) than those obtained with dirhenium heptoxide as a rhenium source.

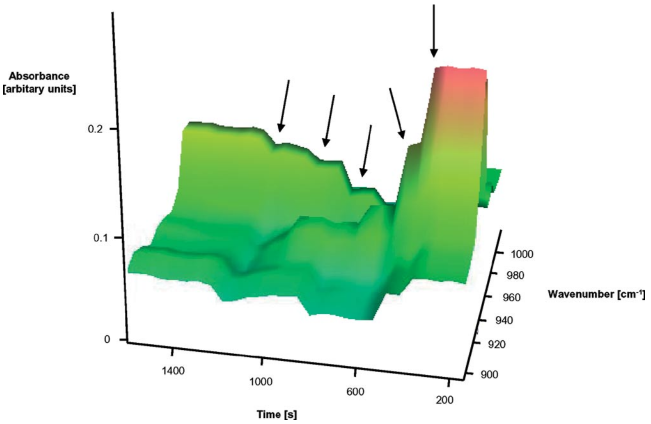


Figure 3. Series of IR spectra obtained from the reaction of acetyl perrhenate with methylzinc acetate (successive addition of small portions of methylzinc acetate is indicated by black arrows). MTO shows a pronounced vibration at 961 cm^{-1}.

Table 2. Synthesis of MTO from carboxyl perrhenates **3a**–**g**, **3i**, Re_2O_7 (**5**), $ClReO_3$ (**6**) and $(CH_3)_3SiOReO_3$ (**7**) with methylzinc acetate as alkylating agent.

Reactive rhenium(VII) precursor	Isolated yield [%]
$CH_3(C{=}O)OReO_3$ (**3a**)	90
$C_2H_5(C{=}O)OReO_3$ (**3b**)	66
$C_3H_7(C{=}O)OReO_3$ (**3c**)	76
$C_4H_9(C{=}O)OReO_3$ (**3d**)	69
$(CH_3)_2CH(C{=}O)OReO_3$ (**3e**)	92
$(CH_3)C(C{=}O)OReO_3$ (**3f**)	75
$C_6H_5(C{=}O)OReO_3$ (**3g**)	73
o-$C_6H_4[(C{=}O)OReO_3]_2$ (**3i**)	73
Re_2O_7 (**5**)	26 (52 % of theory)
$ClReO_3$ (**6**)	55
$(CH_3)_3SiOReO_3$ (**7**)	48

The formation of the bis[dimethyl(μ-oxo)oxorhenium(VI)] and (μ-oxo)bis[trimethyloxorhenium(VI)] byproducts due to the partial reduction and higher alkylation of the rhenium entity has already been described in the literature.[11] This side reaction was reported as dominant for stronger alkylating agents like aluminum reagents or MeTi(O*i*Pr)$_3$ (**8q**). In fact, bis[dimethyl(μ-oxo)oxorhenium(VI)] can be prepared in high yields by reaction of dirhenium heptoxide with MeTi(O*i*Pr)$_3$ (**8q**). In order to investigate the selectivity of the alkylating agent methylzinc acetate, the

Table 3. Product distribution for the synthesis of MTO from carboxyl perrhenates **3a** and **3e**–**g** with methylzinc acetate as alkylating agent.

Reactive rhenium(VII) precursor	MTO [%]	Bis[dimethyl(μ-oxo)oxorhenium(VI)] [%]	(μ-Oxo)bis[trimethyloxorhenium(VI)] [%]
$CH_3(C{=}O)OReO_3$ (**3a**)[a]	90	<1	0
$CH_3(C{=}O)OReO_3$ (**3a**)[b]	84	5	2
$(CH_3)_2CH(C{=}O)OReO_3$ (**3e**)[a]	92	2	0
$(CH_3)C(C{=}O)OReO_3$ (**3f**)[a]	75	4	0
$C_6H_5(C{=}O)OReO_3$ (**3g**)[a]	73	4	0

[a] Obtained by the reaction of silver perrhenate with acetyl chloride. [b] Obtained by the reaction of dirhenium heptoxide with acetic anhydride.

product distribution was determined by quantitative GC and ^{1}H NMR spectroscopy. The results are summarized in Table 3.

Conclusions

After many years of research, an industrially applicable preparation of MTO has finally been found. The combination of the efficient alkylating agent methylzinc acetate with carboxyl perrhenates as reactive rhenium intermediates is highly efficient and elegantly eliminates the two major drawbacks for the large-scale preparation of MTO, namely, the sensitivity of dirhenium heptoxide and the expensive and highly toxic methyltin reagents. Furthermore, easily accessible rhenium sources can now be relied upon, such as silver perrhenates, which can be synthesized in a simple way from rhenium metal or as a product of catalyst recycling. Perrhenates are – in contrast to rhenium heptoxide – stable towards moisture. The sensitivity of rhenium heptaoxide to hydrolysis does not pose a significant problem at the laboratory scale, but it is of critical importance in an industrial context. The acyl perrhenates, which are at least in part sensitive to elevated temperatures, need not be isolated. In situ they are – as reaction intermediates – easy to handle.

In this context, IR spectroscopic methods proved to be a very useful tool for monitoring the reactions quickly and directly, whereas "traditional" methods, which require the preparation of separate samples, are in comparison quite cumbersome due to the considerable sensitivity of some of the species under examination.

Experimental Section

General: All experiments were performed under an atmosphere of argon or nitrogen purified over molecular sieves and BTS catalyst in flame-dried standard Schlenk-type glassware. Dry solvents were obtained from an MBraun SPS system. Chemicals were purchased from Merck, Acros Organics and Aldrich, and in case of liquids, distilled under an inert gas prior to use. NMR spectra were recorded with a JEOL JMX-GX 400 (400 MHz). Chemicals shifts are reported in ppm, referenced to the residual solvent signal. IR spectra were recorded with a JASCO FT/IR-460 spectrometer. For ex situ liquid IR, KBr cells were used. Solids were prepared as nujol mulls. GC analyses were performed with a Varian CP-3800 equipped with a VF-5ms column and an FID and with mesitylene as an internal standard. In situ IR spectroscopy was performed with a Bruker-Optics Matrix-M "IR-Cube" FT-NIR spectrometer couple with a diamond ATR-probe IN350.

Preparation of MeZnOAc: Finely ground zinc acetate dihydrate (11.1 g, 60.06 mmol) was dried at 70 °C for 3 h. The loss of water was determined gravimetrically. The obtained anhydrous zinc acetate was then suspended in dry toluene (50 mL) and a stoichiometric amount of $Al(CH_3)_3$ was added at –10 °C. After stirring for 5 h, the resulting reaction mixture was separated from the precipitated $Al(OAc)_3$, and the solvent of the filtrate was evaporated in vacuo. MeZnOAc was obtained as a colourless powder (7.5 g, 90%). ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 2.14 (s, 3 H, C-CH_3), –0.68 (Zn-CH_3) ppm. ^{13}C NMR (400 MHz, $CDCl_3$, 25 °C): δ = 180.4 (C=O), 25.0 (C-CH$_3$), –15.2 (Zn-CH$_3$) ppm.

Preparation of Perrhenyl Carboxylates from Re_2O_7: Dirhenium heptoxide (Re_2O_7; 1 g, 2.06 mmol) was suspended in acetonitrile (10 mL). Then, one equivalent of the corresponding carboxylic anhydride was slowly added. The end of the reaction was indicated by the complete dissolution of dirhenium heptoxide.

Preparation of Perrhenyl Carboxylates from $AgReO_4$: $AgReO_4$ (1 g, 2.79 mmol) was dissolved in acetonitrile (10 mL) and on equivalent of the corresponding carboxylic chloride was added. AgCl precipitated immediately. After 10 min of stirring, the solution was filtered.

NMR Spectroscopic Data for Selected Perrhenyl Carboxylates

$MeCOOReO_3$: ^{1}H NMR (400 MHz, CD_3CN, 25 °C): δ = 2.16 [s, 3 H, C(=O)-CH_3] ppm.

$EtCOOReO_3$: ^{1}H NMR (400 MHz, CD_3CN, 25 °C): δ = 2.52 [q, 2 H, C(=O)-CH_2-], 1.16 (t, 3 H, -CH_3) ppm.

***n*$PrCOOReO_3$:** ^{1}H NMR (400 MHz, CD_3CN, 25 °C): δ = 2.47 [m, 2 H, C(=O)-CH_2-], 1.67 [m, 2 H, C(=O)-CH$_2$-CH_2-], 0.97 (t, 3 H, -CH_3) ppm.

***t*$BuCOOReO_3$:** ^{1}H NMR (400 MHz, CD_3CN, 25 °C): δ = 2.66 (s, 9 H, CH$_3$) ppm.

$PhCOOReO_3$: ^{1}H NMR (400 MHz, CD_3CN, 25 °C): δ = 8.12 (d, 2 H, *o*-H), 7.77 (t, 1 H, *p*-H), 7.58 (dd, 2 H, *m*-H) ppm.

Typical Procedure for the Synthesis of MTO from Acyl Perrhenates: To a previously stirred solution of the appropriate acyl perrhenate in acetonitrile, solid MeZnOAc (1 equiv.) was added in small portions. The solution immediately turned turbid and its colour changed from light yellow to dark red. After complete addition of the methylating agent, stirring was continued for a further 30 min. The reaction mixture was then filtered, and the solvent was removed in vacuo from the filtrate. The remaining solid was sublimed (10^{-1} mbar, 40 °C). MTO was obtained as a colourless crystalline solid. The analytical data correspond with those reported in the literature.[2]

Preparation of Bipyridine Adducts 4a–e: A solution of freshly prepared perrhenyl carboxylate (1 mmol) was treated with 2,2′-bipyridine (1 equiv.) with vigorous stirring. The product was immediately formed as a voluminous precipitate. After filtration, the remaining solid was washed with benzene (2×) and dried in vacuo. NMR spectroscopic data cannot be provided due to the poor solubility of the bipyridine adducts.

MeCOOReO$_3$·bipy (4a): Yield: 0.35 g (0.78 mmol; 78%). IR (nujol): $\tilde{\nu}$ = 3105 (s), 3080 (w), 3071 (m), 3029 (w), 2989 (w), 1781 (vs), 1598 (vs), 1560 (m), 1551 (w), 1497 (m), 1473 (m), 1449 (s), 1272 (w), 1176 (m), 1110 (m), 1032 (m), 1024 (w), 987 (w), 961 (w), 918 (vs), 660 (w), 544 (w), 420 (m) cm^{-1}. $C_{12}H_{11}N_2O_5Re$ (449.43): calcd. C 32.07, H 2.47, N 6.23; found C 31.98, H 2.54, N 6.51.

EtCOOReO$_3$·bipy (4b): Yield: 0.37 g (0.79 mmol; 79%). IR (nujol): $\tilde{\nu}$ = 3110 (w), 3065 (w), 2724 (w), 1651 (s), 1601 (m), 1496 (m), 1317 (m), 1286 (s), 1233 (m), 1172 (w), 1152 (w), 1118 (w), 1103 (w), 1079 (w), 1065 (m), 1035 (w), 1024 (w), 999 (w), 943 (s), 922 (s), 908 (vs), 893 (s), 804 (w), 773 (s), 731 (m), 658 (w) cm^{-1}. $C_{13}H_{13}N_2O_5Re$ (463.46): calcd. C 33.69, H 2.83, N 6.04; found C 33.57, H 2.64, N 5.91.

***n*PrCOOReO$_3$·bipy (4c):** Yield: 0.39 g (0.81 mmol; 81%). IR (nujol): $\tilde{\nu}$ = 1649 (m), 1600 (m), 1315 (m), 1260 (m), 1213 (w), 1171 (w), 1101 (m), 1034 (m), 944 (s), 921 (s), 890 (s), 798 (m), 773 (m), 721 (m) cm^{-1}. $C_{14}H_{15}N_2O_5Re$ (477.49): calcd. C 35.22, H 3.17, N 5.87; found C 35.22, H 2.94, N 5.82.

***t*BuCOOReO$_3$·bipy (4d):** Yield: 0.38 g (0.78 mmol; 78%). IR (nujol): $\tilde{\nu}$ = 3112 (w), 1646 (m), 1601 (m), 1315 (w), 1302 (m), 1196 (m), 1169 (w), 1155 (w), 1102 (m), 1061 (m), 1033 (m), 942 (s), 922 (s), 893 (s), 776 (m), 732 (m) cm^{-1}. $C_{15}H_{17}N_2O_5Re$ (491.51): calcd. C 36.65, H 3.49, N 5.70; found C 36.87, H 3.33, N 5.51.

PhCOOReO$_3$·bipy (4e): Yield: 0.39 g (0.77 mmol; 77%). IR (nujol): $\tilde{\nu}$ = 3113 (s), 2359 (m), 1660 (vs), 1601 (s), 1580 (m), 1497 (m), 1445 (s), 1311 (vs), 1295 (s), 1171 (w), 1158 (w), 1124 (m), 1106 (m), 1079 (w), 1067 (w), 1035 (w), 1023 (m), 943 (s), 914 (s), 903 (s), 765 (s), 717 (s), 689 (w), 669 (w) cm^{-1}. $C_{17}H_{13}N_2O_5Re$ (511.50): calcd. C 39.92, H 2.56, N 5.48; found C 39.56, H 2.23, N 5.40.

Acknowledgments

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