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Simple and Efficient Synthesis of Methyltrioxorhenium(VII): A General Method[1]

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Introduction

The title compound CH_3ReO_3 (**1a**) has been shown to be an efficient catalyst for olefin metathesis,[2] olefin oxidation,[3] and aldehyde olefination.[4] Beyond that, this compound represents the best studied key example of organic metal oxides.[5] Numerous derivatives[6] and osmium congeners[7] have recently entered the literature.

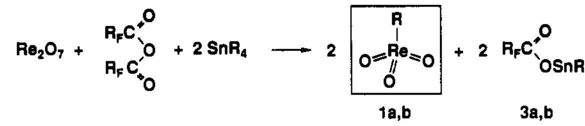
Treatment of dirhenium heptoxide with tetramethyltin according to eq 1 marked a breakthrough in this chemistry,[8] because

$$Re_2O_7 + Sn(CH_3)_4 \longrightarrow \underset{\mathbf{1a}}{CH_3ReO_3} + \underset{\mathbf{2a}}{(CH_3)_3SnOReO_3} \qquad (1)$$

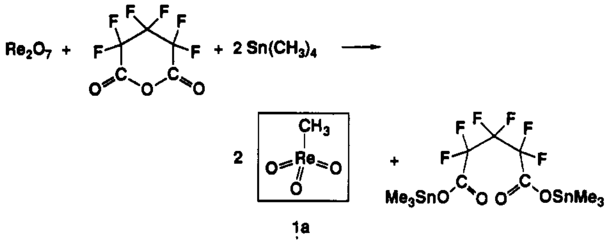
it made the title compound **1a** easily available. On the other hand, concomitant formation of the rather unreactive stannyl perrhenate **2a** has remained a drawback of this otherwise very convenient preparation: the equimolar appearance of **2a** limits the yield of **1a** to 50% based on total rhenium.

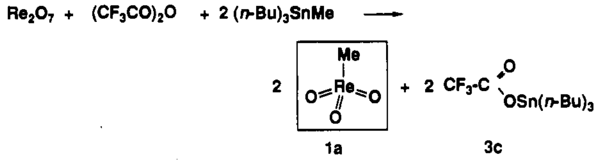
Results and Discussion

Parts a and b of eq 2 represent the new synthesis described in the present note: If dirhenium heptoxide in a solution of tetrahydrofuran or acetonitrile is first treated with an anhydride $(R_FCO)_2O$ of a perfluorinated carboxylic acid (e.g. trifluoroacetic anhydride) and afterwards with the 2-fold molar amount of a tetraalkyltin SnR_4 (e.g. tetramethyltin), the expected organic rhenium(VII) oxide of formula $R{-}ReO_3$ is formed *in almost quantitative yield.*


(2a)

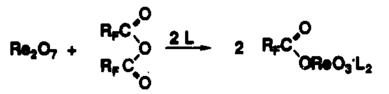
1,3	a	b
R	CH_3	C_2H_5


(2b)


(2c)

The driving force of this reaction is to be assigned to the strength of the tin–oxygen bond in the stannyl ester **3a** of eq 2a. However, separation of the two products **1a** and **3a** proved difficult because of their similar solubilities and volatility (sublimation of CH_3ReO_3, mp 111 °C, at ca. 60 °C/10^{-3} mmHg together with the ester $CF_3C({=}O)OSn(CH_3)_3$). To overcome this problem, we used long-chained, functionalized, or cyclic anhydrides such as commercial perfluoroglutaric (eq 2b). *Cyclic* perfluorinated anhydrides such as perfluoroglutaric anhydrides are particularly useful because they form ω,ω'-dicarboxylic acid esters which are much less volatile than the respective ester of a monocarboxylic acid. By variation of the organotin component, we found that the easily accessible tris(*n*-butyl)organotin compounds[9] transfer selectively the organic substituent R and not a *n*-butyl group to the rhenium fragment. This is not surprising, as it is known that the tin–butyl bond is normally stronger than other Sn–R bonds.

The new, one-pot synthesis is easy to carry out on any scale. No reduction of the heptavalent rhenium occurs. The method relies on the intermediate formation of the mixed anhydride $R_FC({=}O)OReO_3$ (**4**) from dirhenium heptoxide and the carboxylic anhydride used (eq 3).[10] The simplest derivative $CF_3C({=}O)OReO_3$ (**4a**) was independently synthesized as a THF-adduct **4a**·2THF by simply mixing the metal oxide and the anhydride in a THF solution at room temperature. **4a** forms colorless, water-sensitive needles that can be purified by recrystallization from acetonitrile forming the acetonitrile adduct **4a**·2CH_3CN. Stirring **4a**·2THF in THF over a period of few hours causes polymerization of the solvent, while **4a**·2CH_3CN is stable in CH_3CN. These compounds react quickly with tetramethyltin and similar alkylating reagents to form title compound **1a** and its congeners, respectively. Thermogravimetry coupled with simultaneous mass spectrometry of **4a** shows elimination of CO_2 at 61 °C. The synthesis following eq 2a,b works at room temperature.


(3)

4a ($R_F = CF_3$; L = THF or CH_3CN)

According to the old preparation following eq 1, we had accumulated a big supply of the stannylperrhenate **2a**. This compound can now be utilized for the synthesis of CH_3ReO_3, too: A transesterification takes place upon treatment of **2a** with the

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† Alexander von Humboldt Fellow (1992).

[1] Part 113 of the series Multiple Bonds between Main-Group Elements and Transition Metals. Preceding paper: Herrmann, W. A.; Fischer, R. W.; Scherer, W. *Angew. Chem.*, in press; *Angew. Chem., Int. Ed. Engl.*, in press.

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[5] Reviews: (a) Bottomley, F.; Sutin, L. *Adv. Organomet. Chem.* **1988**, *28*, 339. (b) Herrmann, W. A. *Angew. Chem., Int. Ed. Engl.* **1988**, *27*, 1297; *Angew. Chem.* **1988**, *100*, 1269.

[6] Examples: (a) Herrmann, W. A.; Ladwig, M.; Kiprof, P.; Riede, J. *J. Organomet. Chem.* **1988**, *371*, C13. (b) Herrmann, W. A.; Romao, C. C.; Fischer, R. W.; Kiprof, P.; de Mèric de Bellefon, C. *Angew. Chem.* **1991**, *103*, 185; *Angew. Chem., Int. Ed. Engl.* **1991**, *30*, 185. (c) Herrmann, W. A.; Kiprof, P.; Rypdal, K.; Tremmel, J.; Blom, R.; Alberto, R.; Behm, J.; Albach, R. W.; Bock, H.; Solouki, B.; Mink, J.; Lichtenberger, D.; Gruhn, N. E. *J. Am. Chem. Soc.* **1991**, *113*, 6527. (d) Herrmann, W. A.; Taillefer, M.; de Mèric de Bellefon, C.; Behm, J. *Inorg. Chem.* **1991**, *30*, 3247.

[7] (a) Herrmann, W. A.; Eder, S. J.; Kiprof, P.; Rypdal, K.; Watzlowik, P. *Angew. Chem., Int. Ed. Engl.* **1990**, *29*, 1445; *Angew. Chem.* **1990**, *102*, 1460. (b) Rypdal, K.; Herrmann, W. A.; Eder, S. J.; Albach, R. W.; Watzlowik, P.; Solouki, B. *Organometallics* **1991**, *10*, 1331.

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[9] (a) Jones, W. J.; Evans, D. P.; Gulwell, T.; Griffiths, D. C. *J. Chem. Soc.* **1935**, 39. (b) Neumann, W. P. *Die organische Chemie des Zinns*; Ferdinand Enke Verlag: Stuttgart, Germany, 1967.

[10] Edwards, P.; Wilkinson, G. *J. Chem. Soc., Dalton Trans.* **1984**, 2695.

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anhydride of a perfluorinated carboxylic acid or with trichloroacetic anhydride. If we add tetramethyltin to such a mixture, eq 4 is established, and the yields of CH_3ReO are >85% after sublimation and recrystallization.

$$\underset{\mathbf{2a}}{(CH_3)_3SnOReO_3} \xrightarrow[b)\ Sn(CH_3)_4]{a)\ (R_FCO)_2O} \underset{\mathbf{1a}}{CH_3ReO_3} + 2\ \underset{\mathbf{3a}}{R_FCO_2Sn(CH_3)_3} \qquad (4)$$

The success of these new synthetic methods for organic rheniumoxides—and, probably, similar compounds of other metals—clearly depends on the right choice of the anhydride. Thus, no advantage over the old preparation (eq 1) is seen if nonfluorinated anhydrides such as maleic, 3-nitrophthalic, succinic, or acetic anhydride are used. Albeit they form the corresponding esters of perrhenic acid, almost no CH_3ReO_3 (**1a**) results when Re_2O_7 is treated with one of these anhydrides in the presence of tetraalkyltin compounds.

Yet another way of making compounds $R{-}ReO_3$ is represented by eq 5a,b: if Re_2O_7 is first treated with $(CH_3)_3SiCl$ in acetonitrile solution at room temperature (eq 5a) and then with SnR_4 (eq 5b), high yields of $R{-}ReO_3$ are also achieved (e.g. 75% for CH_3ReO_3 (**1a**)) via the solvated intermediate $ClReO_3$.[11]

$$Re_2O_7 + 2\,(CH_3)_3SiCl \rightleftharpoons 2\,ClReO_3 + (CH_3)_3Si{-}O{-}Si(CH_3)_3 \qquad (5a)$$

$$ClReO_3 + (CH_3)_4Sn \longrightarrow \underset{\mathbf{1a}}{CH_3ReO_3} + (CH_3)_3SnCl \qquad (5b)$$

Work to exploit this new, efficient access of other organic metal oxides is underway.

Experimental Section

Materials and General Procedures. The following reagents were obtained from commercial sources and used without further purification: Re_2O_7 (Degussa), trifluoroacetic anhydride (Aldrich, 10,623-2), perfluoroglutaric anhydride (Aldrich, 29,051-3), tetramethyltin (Aldrich, 22922-9), and tetraethyltin (Aldrich, 14,647-1). All operations were carried out under an atmosphere of purified nitrogen by applying Schlenk techniques. Solvents were dried and distilled before use by standard methods. Infrared spectra were recorded with a Nicolet FT-5DX and a Perkin-Elmer 1650 Series FT-IR spectrometer, and NMR spectra, with a JEOL-JNM-GX 400 (^1H, ^{13}C) and with a Bruker AM-360 (^{19}F) instrument.

Methyltrioxorhenium (1a). Method A. A typical preparation for laboratory use (eq 2b) is as follows: A solution of Re_2O_7 (5.00 g, 10.30 mmol) in 60 mL of acetonitrile is treated with 2.45 g of perfluoroglutaric anhydride (10.30 mmol) at room temperature. After a few minutes, 3.85 g of $Sn(CH_3)_4$ (20.60 mmol) is added and the mixture is stirred for 2.5 h at room temperature. Acetonitrile is then carefully removed in an oil-pump vacuum at room temperature, and **1a** is consecutively sublimed as colorless crystals at 65 °C/10^{-3} mmHg; isolated yield 4.26 g (83%). Analytical data are as follows.[8] The correct elemental analysis was obtained. The melting point of very pure samples is 111 °C (previously reported: 106 °C[8]).

Method B (eq 2c) uses trifluoroacetic anhydride and tri-*n*-butylmethyltin instead of perfluoroglutaric anhydride and tetramethyltin. The workup is as described in method A. Isolated yield: 4.30 g (85%).

(Trifluoroacetyl)perrhenate(VII) (4a·2THF). A solution of 1.00 g (2.06 mmol) Re_2O_7 in 15 mL of THF is treated with 0.30 mL of trifluoroacetic anhydride (0.50 g, 2.06 mmol). The mixture is stirred for 1 h at room temperature. After that time, THF is removed in an oil-pump vacuum at 0 °C and the residue is washed twice with 20 ml of cold *n*-pentane. Isolated yield: 1.93 g (95%) as a white powder. ^{19}F NMR (235.34 MHz, THF, 20 °C, external standard CF_3COOH): $\delta = 2.24$ ppm. Anal. Calcd for $C_{10}H_{16}F_3O_7Re$: C, 24.43; H, 3.28; F, 11.60; Re, 37.91. Found: C, 24.22; H, 3.30; F, 11.59; Re, 38.15.

(Trifluoroacetyl)perrhenate(VII) (4a·2CH₃CN). A solution of 1.00 g (2.06 mmol) of Re_2O_7 in 15 mL of acetonitrile is treated with 0.30 mL of trifluoroacetic anhydride (0.50 g, 2.06 mmol). The mixture is stirred for 1 h at room temperature. After that time, acetonitrile is removed in an oil-pump vacuum at 10 °C, and the residue is washed twice with 20 mL of cold *n*-pentane and recrystallized from acetonitrile. Isolated yield: 1.70 g (96%) as white crystals. ^{19}F NMR (235.34 MHz, CH_3CN, 20 °C, external standard CF_3COOH): $\delta = 2.52$ ppm. Anal. Calcd for $C_6H_6F_3N_2O_5Re$: C, 16.74; H, 1.40; F, 13.28; N, 6.51; Re, 43.57. Found: C, 16.06; H, 1.38; F, 13.61; N, 5.95; Re, 45.37.

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(11) The isolated compound has been made by a different, less convenient route (Re_2O_7/Cl_2O, sealed bomb): Dehnicke, K.; Liese, W. *Chem. Ber.* **1977**, *110*, 3959. Pyridine and bipyridine complexes of $ClReO_3$ have also been made according to eq 5a: (a) Herrmann, W. A.; Thiel, W. R.; Herdtweck, E. *Chem. Ber.* **1990**, *123*, 271. (b) Kühn, F. E. Diploma Thesis, Technische Universität München, 1992.