Inorg. Chem. 1993, 32, 5188-5194

Multiple Bonds between Transition Metals and Main-Group Elements. 124.[1] Structures and Reactivity of Acylperrhenates[†]

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Received February 24, 1993[•]

Two structural types of perrhenic anhydrides result from treatment of Re_2O_7 with carboxylic anhydrides $(RCO)_2O$ in acetonitrile or tetrahydrofuran solution. Strongly electron-withdrawing groups, *cf.* R = CF_3, thus lead to complexes of type $RC(O)–O–ReO_3{\cdot}2L$ (L = CH_3CN, thf) exhibiting η^1-coordinated carboxylato groups and octahedral coordination at rhenium(VII), both in solution (IR, ^{17}O NMR) and in the solid state (X-ray crystal structure of $CF_3C(O)–O–ReO_3{\cdot}2CH_3CN$ (crystal data: space group $P2_1/n$ (No. 14), a = 10.522(3) Å, b = 8.193(1) Å, c = 13.094(4) Å, β = 90.59(1)°, Z = 4)). Analogous coordination is observed in the X-ray crystal structure of $Re_2O_7{\cdot}2CH_3CN$ (space group $P2_1/m$ (No. 11), a = 5.363(1) Å, b = 11.763(2) Å, c = 8.273(2) Å, β = 94.395(9)°, Z = 2)). By way of contrast, anhydrides of weak carboxylic acids, *cf.* R = CH_3, yield mixed anhydrides of general formula $RC(O)–OReO_3{\cdot}L$ (L = CH_3CN, thf), the structures of which compounds display octahedral rhenium(VII) and η^2-coordinated carboxylato groups. These structures are again observed in solution and in the solid state (X-ray crystal structure of $CH_3C(O)–OReO_3{\cdot}CH_3CN$ (space group $C2/m$ (No. 12), a = 14.818(8) Å, b = 6.976(2) Å, c = 7.390(4) Å, β = 94.64(2)°, Z = 4)). As a result of these structural features, only mixed anhydrides containing strongly electron-withdrawing substituents react cleanly with alkyltin compounds to yield the alkylrhenium(VII) oxides of the type alkyl–ReO_3.

Introduction

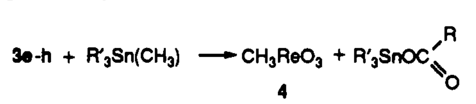
Dirheniumheptoxide (**1**)—the anhydride of perrhenic acid—reacts with carboxylic anhydrides **2** to form the *mixed* anhydrides (solvated; n = 1, 2) of type **3** in almost quantitative yields. They undergo alkylation following eq 2 by means of tetramethyltin ($R' = CH_3$) or tri(n-butyl)methyltin ($R' = n\text{-}C_4H_9$) *only* if anhydrides of *strong* carboxylic acids (e.g., R = CCl_3, CF_3) are used in eq 1.[2] This new synthesis of methyltrioxorhenium(VII) (MTO, **4**) does not limit the rhenium-based yield to 50%, which was the case for the previous route shown in eq 3.[3]

$$\underset{\mathbf{1}}{Re_2O_7} + \underset{\mathbf{3a\text{-}h}}{(RCO)_2O} \xrightarrow{\text{solv}} \underset{\mathbf{3a\text{-}h}}{2(\text{solv})_nO_3ReO\text{-}C(O)R} \qquad (1)$$

2,3	a	b	c	d	e	f	g*	h
R	CH_3	C_3H_7	$-(CH_2)_3-$	CH_2Cl	CCl_3	C_4F_9	$-(CF_2)_3-$	CF_3
n	1	1	1	1	2	2	2	2

solv = CH_3CN, thf

*perfluoroglutaric anhydride



$$\mathbf{3e\text{-}h} + R'_3Sn(CH_3) \longrightarrow \underset{\mathbf{4}}{CH_3ReO_3} + R'_3SnOC(O)R \qquad (2)$$

$$\underset{\mathbf{1}}{Re_2O_7} + Sn(CH_3)_4 \longrightarrow \underset{\mathbf{4}}{CH_3ReO_3} + \underset{\mathbf{5}}{(CH_3)_3SnOReO_3} \qquad (3)$$

The byproduct **5** of eq 3 can be considered to be an ester of perrhenic acid and trimethylstannol and thus gives, *via* transesterification, mixed anhydrides of type **3** when an anhydride of a strong carboxylic acid is added to a solution of **5** in thf or acetonitrile.[2] Since MTO (**4**) is an efficient catalyst of olefin epoxidation,[4] olefin metathesis,[5] and olefination of aldehydes,[6] the general synthesis of alkylrhenium oxides, with groups R′ other than methyl,[7] according to eq 2 initiated a systematic investigation of perrhenic anhydrides. This class of compounds was previously mentioned by *Wilkinson* et al.[8] The present paper describes two different kinds of rhenium(VII) complexes that can result when

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[†] Dedicated to Professor M. F. Lappert on the occasion of his 65th birthday and in recognition of his outstanding contributions to inorganic and organometallic chemistry.

[•] Abstract published in *Advance ACS Abstracts*, October 1, 1993.

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Re_2O_7 (**1**) reacts with carboxylic anhydrides $(RCO)_2O$ (**2a**-**h**) depending on the electronic character of the group R. We also show that **1** forms asymmetric complexes of the type O_3ReO–$ReO_3(L)_2$ in coordinating solvents L.

Experimental Section

All compounds were synthesized in an atmosphere of dry nitrogen using strictly dried solvents (thf, Na and molecular sieves; CH_3CN, $CaCl_2$, P_2O_5, CaH_2, and molecular sieves). Solutions (0.17 M) of the mixed anhydrides for IR and NMR investigations were obtained by reacting 242 mg (0.50 mmol) of Re_2O_7 (**1**) in 3 mL of acetonitrile with 1 equiv of a carboxylic anhydride **2a**-**h**. These solutions are stable at room temperature for several hours, at 0 °C for several days, and at –25 °C for months. The carboxylic anhydrides **2a**-**h** were purchased from Aldrich, Re_2O_7 was a gift of Degussa AG. Elemental analyses were performed in the Mikroanalytisches Laboratorium of our institute (M. Barth). IR spectra were recorded with a Perkin-Elmer 1600 Series FTIR spectrometer (resolution 4 cm^{-1}).

$^{17}O\{^1H\}$ NMR spectra were recorded on a JEOL-JMX-GX 400 spectrometer at 25 °C (Spectrometer frequency 54.21 MHz, window 172 414 Hz, chemical shift range +1840 to –1340 ppm). With an aquisition time of *ca.* 0.095 s and a pulse delay of *ca.* 0.005 s, it was possible to accumulate *ca.* 10 pulses per second. Thus spectra of *ca.* 300 000 pulses were obtained after 8–9 h. Fourier transformation was carried out with both an exponential (broadening factor 10 Hz) and a trapezoid window function (T1, 0%; T2, 0.2–1%; T3, 70%; T4, 100%), without zero-filling. For the preparation of the samples, 3 mL of the 0.17 M solutions of **3a**-**h** in CH_3CN (see above) were transferred under nitrogen into a NMR tube of 10 mm diameter. As we used CH_3CN as solvent, it was necessary to transfer a sealed NMR tube (5 mm diameter) into the 10-mm-tube, which contained the lock solvent (CD_3CN), and another sealed 1-mm tube with the internal standard (H_2O).

Samples for thermogravimetric analyses were heated in a dynamic helium atmosphere (45 sccm, 5.0 He) on a Perkin Elmer TGA-7 instrument at a heating rate of 10 $K{\cdot}min^{-1}$ unless otherwise stated. Volatile decomposition products were transferred into a mass spectrometer (Balzers QMG 420) coupled to the TGA instrument by a heated capillary (280 °C, l = 30 cm).

Single crystals of compounds **3a**, **3h**, and **1**·$2CH_3CN$ suitable for X-ray analysis were grown in a glovebox at –30 °C from acetonitrile solutions. Preliminary examination and data collection were carried out with Mo Kα radiation on an Enraf-Nonius CAD-4 diffractometer. Final cell constants were obtained by least-squares refinement of 25 automatically centered high-angle reflections ($40.0° < 2\theta < 48.7°$, $40.0° < 2\theta < 46.6°$, and $39.8° < 2\theta < 49.7°$, respectively). Data were collected in the ω-scan mode. Orientation control reflections were monitored every 100th reflection, and the intensity of three reflections were checked every 60 min. Changes in intensities for **3h** and **1**·$2CH_3CN$ were corrected. Absorption corrections were applied (T_{max}/T_{min}: **3a**, 1.00/0.69; **3h**, 1.00/0.60; **1**·$2CH_3CN$, 1.75/0.83). No extinction correction was made for **3a**; strong extinction effects were corrected for **3h** and **1**·$2CH_3CN$. Crystal data, intensity collection parameters, and details of refinement procedures are summarized in Table I.

All structures were solved by Patterson methods and subsequent difference Fourier maps. Full-matrix least-squares refinement was carried out by minimizing $\sum w(|F_o| - |F_c|)^2$. Final positional parameters are given in Tables II–IV. Hydrogen atoms were calculated in their ideal positions (d_{C-H} = 0.95 Å, $B_H = 1.3B_C$) and included in the data set, but they were not refined. Scattering factors and anomalous dispersion corrections were taken from ref 9a,b. The refinements stopped at shift/err < 0.001, and final difference Fourier maps showed no significant features. All calculations were performed on a MicroVAX 3100 computer with STRUX-IV[10a] including the programs ORTEP,[10b] PLATON,[10c] PLUTON,[10c] SCHAKAL,[10d] SDP,[10e] SHELX-86,[10f] and CRYSTALS.[10g] Additional details, including a full representation of data collection parameters and refinement procedure, bond distances and angles, and least-squares planes, are available as supplementary material.

The syntheses of **1**·$2CH_3CN$, **3a**·CH_3CN, and **3h**·$2CH_3CN$ were performed as follows. Compounds **3b**-**d**·CH_3CN and **3e**-**g**·$2CH_3CN$ were obtained by the same procedure. All compounds are extremely sensitive to moisture.

Table I. Crystallographic Data[a]

(a) $(CH_3CO_2)ReO_3{\cdot}CH_3CN$ (**3a**)	
formula: $C_4H_6NO_5Re$	fw = 334.3
a = 14.818(8) Å	Space group: $C2/m$ (No. 12)
b = 6.976(2) Å	T = –80 °C
c = 7.390(4) Å	λ = 0.7107 Å
β = 94.64(2)°	ρ_{calcd} = 2.916 $g{\cdot}cm^{-3}$
V = 761.4 $Å^3$	R = 0.028
Z = 4	R_w = 0.030
μ = 161.5 cm^{-1}	
(b) $(CF_3CO_2)ReO_3{\cdot}2CH_3CN$ (**3h**)	
formula: $C_6H_6F_3N_2O_5Re$	fw = 429.3
a = 10.522(3) Å	space group: $P2_1/n$ (No. 14)
b = 8.193(1) Å	T = –50 °C
c = 13.094(4) Å	λ = 0.7107 Å
β = 90.59(1)°	ρ_{calcd} = 2.526 $g{\cdot}cm^{-3}$
V = 1128.6 $Å^3$	R = 0.097
Z = 4	R_w = 0.077
μ = 109.6 cm^{-1}	
(c) $(O_3ReO)ReO_3{\cdot}2CH_3CN$ (**1**·$2CH_3CN$)	
formula: $C_4H_6N_2O_7Re_2$	fw = 566.5
a = 5.363(1) Å	space group: $P2_1/m$ (No. 11)
b = 11.763(2) Å	T = –80 °C
c = 8.273(2) Å	λ = 0.7107 Å
β = 94.395(9)°	ρ_{calcd} = 3.615 $g{\cdot}cm^{-3}$
V = 520.4 $Å^3$	R = 0.037
Z = 2	R_w = 0.035
μ = 235.8 cm^{-1}	

[a] $R = \sum||F_o| - |F_c||/\sum|F_o|$. $R_w = [\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2}$.

Table II. Final Fractional Atomic Coordinates and Equivalent Temperature Factors of (η^2-CH_3CO_2)$ReO_3{\cdot}CH_3CN$ (**3a**) with Estimated Standard Deviations in Parentheses

atom	x	y	z	B_{eq},[a] $Å^2$
Re	0.10265(3)	0	0.22314(7)	0.656(8)
O(1)	–0.0055(5)	0	0.2867(11)	2.1(2)
O(2)	0.1059(4)	–0.1951(11)	0.0865(7)	1.5(1)
O(3)	0.1526(4)	0.1535(10)	0.4643(7)	1.0(1)
N	0.2596(7)	0	0.2162(13)	1.2(2)
C(1)	0.3348(7)	0	0.2252(15)	0.9(2)*
C(2)	0.4322(8)	0	0.2458(18)	1.6(3)
C(3)	0.1727(7)	0	0.5522(13)	0.4(2)*
C(4)	0.2171(8)	0	0.7366(16)	1.3(3)

[a] Equivalent isotropic $B_{eq} = (4/3)[a^2\beta(1,1) + b^2\beta(2,2) + c^2\beta(3,3) + ac(\cos\beta)\beta(1,3)]$. An asterisk denotes isotropic refinement.

Table III. Final Fractional Atomic Coordinates and Equivalent Temperature Factors for (η^1-CF_3CO_2)$ReO_3{\cdot}2CH_3CN$ (**3h**) with Estimated Standard Deviations in Parentheses

atom	x	y	z	U_{eq},[a] $Å^2$
Re	0.3860(1)	0.1580(1)	0.2435(1)	0.0248(6)
F(1)	0.879(3)	0.016(4)	0.295(2)	0.124(9)*
F(2)	0.808(3)	–0.026(4)	0.162(2)	0.14(1)*
F(3)	0.843(2)	0.188(3)	0.211(1)	0.068(5)*
O(1)	0.231(1)	0.118(2)	0.250(1)	0.0330(9)
O(2)	0.397(2)	0.280(3)	0.140(1)	0.0414(11)
O(3)	0.414(1)	0.274(3)	0.342(1)	0.0392(10)
O(4)	0.583(2)	0.099(3)	0.227(1)	0.0409(12)
O(5)	0.662(2)	0.082(3)	0.383(1)	0.0586(15)
N(1)	0.410(2)	–0.061(4)	0.344(2)	0.0416(15)
N(2)	0.395(2)	–0.060(3)	0.134(1)	0.0339(14)
C(1)	0.410(2)	–0.171(5)	0.392(2)	0.0483(18)
C(2)	0.408(3)	–0.318(4)	0.455(2)	0.0587(18)
C(3)	0.385(2)	–0.175(4)	0.086(2)	0.0324(16)
C(4)	0.377(3)	–0.327(4)	0.028(2)	0.0603(22)
C(5)	0.672(3)	0.089(4)	0.290(2)	0.047(7)*
C(6)	0.775(3)	0.089(4)	0.237(2)	0.050(7)*

[a] Equivalent isotropic U_{eq} defined as one-third of the trace of the orthogonalized U_{ij} tensor. An asterisk denotes isotropic refinement.

1·2CH₃CN. A 0.46-g (1.00-mmol) sample of **1** was suspended in 5 mL of dry acetonitrile. The solution was warmed up (*ca.* 40 °C) until all solid material had dissolved. Then 0.51 g (94 %) of **1**·$2CH_3CN$ was obtained after the solution was cooled to 4 °C overnight. Anal. Calcd

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Table IV. Final Fractional Atomic Coordinates and Equivalent Temperature Factors for (η^1-O_3ReO)$ReO_3 \cdot 2CH_3CN$ (**1**·$2CH_3CN$) with Estimated Standard Deviations in Parentheses

atom	x	y	z	B_{eq},[a] Å^2
Re(1)	0.49953(6)	1/4	0.48487(5)	1.028(8)
Re(2)	0.48787(6)	1/4	0.03217(5)	0.862(8)
O(1)	0.3914(13)	1/4	0.2748(8)	1.3(1)
O(2)	0.3898(8)	0.3698(5)	0.5760(5)	1.7(1)
O(3)	0.8155(13)	1/4	0.5025(9)	1.7(1)
O(4)	0.2976(8)	0.3647(4)	−0.0096(6)	1.7(1)
O(5)	0.6787(14)	1/4	−0.1226(10)	2.1(2)
N(1)	0.7642(10)	0.3710(5)	0.1558(7)	1.4(1)
C(1)	0.9061(13)	0.4360(6)	0.2049(9)	1.4(1)
C(2)	1.0909(16)	0.5187(6)	0.2690(10)	1.8(1)

[a] See Table I.

Table V. pK_a Values for the Carboxylic Acids **2a**′-**h**′ [11a,b] and $HReO_4$ (**1**′) [11c]

		pK_a
acetic acid	**2a**′	4.75
butyric acid	**2b**′	4.81
glutaric acid	**2c**′	4.31
chloroacetic acid	**2d**′	2.85
trichloroacetic acid	**2e**′	0.70
perfluorobutyric acid	**2f**′	0.63
hexafluoroglutaric acid	**2g**′	≈0.6
trifluoroacetic acid	**2h**′	0.53
perrhenic acid	**1**′	−1.25

Table VI. IR Data [ν(COO), cm^{-1}] for the Mixed Anhydrides **3a-h** in Acetonitrile Solution

anhydr	complex	ν_a(COO)	ν_s(COO)	ν(C=O)
2a	**3a**	1493 vs	1448 m	
2b	**3b**	1487 vs	1435 m	
2c	**3c**	1488 vs	1438 m	
2d	**3d**	1509 m	1452 s	
2e	**3e**			1786 s
2f	**3f**			1785 s
2g	**3g**			1770 s
2h	**3h**			1792 s

for $C_4H_6N_2O_7Re_2$: C, 8.48; H, 1.06; N, 4.95; Re, 66.00. Found: C, 8.44; H, 1.09; N, 4.93; Re, 66.60.

3a·CH_3CN. A solution of 1.00 g (2.06 mmol) of **1** in 15 mL of acetonitrile was treated with 0.21 mL (0.21 g, 2.06 mmol) of acetic anhydride. The mixture was stirred for 1 h at room temperature and then slowly cooled to 4 °C. Then 1.22 g (92 %) of **3a**·CH_3CN was obtained as colorless needles. Anal. Calcd for $C_4H_6NO_5Re$: C, 14.36; H, 1.81; N, 4.19; Re, 55.70. Found: C, 14.31; H, 1.82; N, 4.29; Re, 55.62.

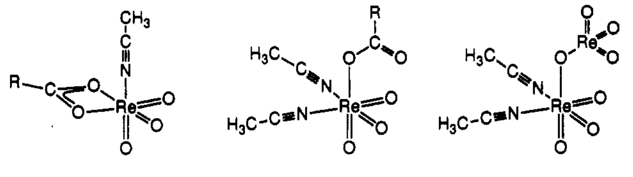
3h·$2CH_3CN$. A solution of 1.00 g (2.06 mmol) of **1** in 15 mL of acetonitrile was treated with 0.30 mL (0.50 g, 2.06 mmol) of trifluoroacetic anhydride. The mixture was stirred for 0.5 h at room temperature and then slowly cooled to −30 °C. Then 1.70 g (96%) of **3h**·$2CH_3CN$ was obtained as colorless needles. Anal. Calcd for $C_6H_6F_3N_2O_5Re$: C, 16.74; H, 1.40; F, 13.28; N, 6.51; Re, 43.37. Found: C, 16.60; H, 1.38; F, 13.61; N, 5.95; Re, 45.37.

Results and Discussion

Different α-substituents in carboxylic compounds strongly effect the pK_a value of the corresponding acids. We thus selected a representative set of carboxylic anhydrides: acetic anhydride (**2a**), butyric anhydride (**2b**), glutaric anhydride (**2c**), chloroacetic anhydride (**2d**), trichloroacetic anhydride (**2e**), perfluorobutyric anhydride (**2f**), hexafluoroglutaric anhydride (**2g**), and trifluoroacetic anhydride (**2h**). The pK_a values of the acids **2a-h**′, Table V, were taken from the literature.[11] As chloroacetic acid (**2d**′) is of moderate acidity, it was not predictable whether **2d** would form a reactive mixed anhydride with **2** or not. A comparison of perrhenic acid (**1**′; pK_a = −1.25) with the carboxylic acids of Table V suggests that dirheniumheptoxide (**1**) should show a reactivity similar to **3e-h**, whose compounds also derive from *strong* acids.

Vibrational Spectroscopy. The C≡N stretching modes of the acetonitrile ligands are shifted to higher wavenumbers with respect to free acetonitrile (2249 cm^{-1}). The local symmetry of the coordinated solvent molecules L influences the number and intensities of the bands. Three examples show that two different coordination patterns are verified in **3a-h** and **1**·$2CH_3CN$, just depending on the pK_a of the corresponding acids **1**′ and **2a-h**′. **3a** shows two C≡N absorptions, one at 2319 cm^{-1}, which we assign to a strongly coordinated acetonitrile ligand, the other at 2264 cm^{-1} assigned to a weakly coordinated acetonitrile. **3b-d** show the same pattern. The IR spectrum of **3h** shows two C≡N absorptions, at 2319 (A-type) and 2299 cm^{-1} (B-type), which effect can be explained in terms of vibrational coupling of two acetonitrile ligands coordinated to rhenium resulting from facial coordination of the three oxo ligands. The B-type mode is surprisingly close to the strong feature observed in acetonitrile (at 2232 cm^{-1}). Analogous absorptions are found in acetonitrile solutions of **1** and **3e-g**. This supports the theory that **1** forms a complex of the type O_3ReO–$ReO_3 \cdot 2CH_3CN$, which can be formulated as a perrhenate coordinated to a $[ReO_3(CH_3CN)_2]^+$ moiety. This complex shows the same coordination geometry (tetrahedral and octahedral at Re) in the solid state[12a] as found for the structures of Re_2O_7 (**1**),[12b,c] $Re_2O_7 \cdot 2$thf,[12d] and $Re_2O_7 \cdot$DME.[12d]

Chart I



3a-d **3e-h** **1**·$(CH_3CN)_2$

Carboxylate ligands are either mono- or bidentate. A change from η^1- to η^2-coordination shifts the ν(COO) absorptions from approximately 1750 to 1450 cm^{-1} Table VI.

Two groups of compounds are again seen within the series **3a-h**. The electron-rich alkyl substituents in **3a-d** lead to a *bidentate* coordination geometry of the carboxylate ligands (*two* ν(COO) bands), while the electron-withdrawing character of the halogenated substituents of **3e-h** entails *monodentate* coordination (*one* ν(C=O) mode). Counting a bidentate carboxylate as a 4-electron donor makes **3e-h** 18-electron complexes (Chart I).

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Table VII. IR Data [ν(Re=O), cm^{-1}] for the Mixed Anhydrides **3a**, **3h**, and $Re_2O_7 \cdot 2CH_3CN$ in Acetonitrile Solution

type	**3a**	**3h**	$Re_2O_7 \cdot 2CH_3CN$	assignt
A	976 w	972 w	965 w	$\nu_s(ReO_3)$
	940 vs	937 vs	937 s	$\nu_a(ReO_3)$
B	965 w			$\nu_s(ReO_3)$
	928 m, sh			$\nu_a(ReO_3)$
C	953 vw	952 w		$\nu_s(ReO_3)$
	913 w	926 vw		$\nu_a(ReO_3)$
D			910 vs	$\nu_a(ReO_4)$

Table VIII. ^{17}O NMR Data for the Mixed Anhydrides **3a-h**[a]

complex	δ(CO)	$Lw_{1/2}$	δ(ReO)	$Lw_{1/2}$
3a	262	100	790	80
3b	258	100	788	50
3c	260	270	789	430
3d	261	150	793	150
3e	252	330	841	100
			804	650
3f	274	570	841	70
			812	170
3g	270	570	841	110
			811	160
3h	262	800	841	80
			813	830

[a] Solvent CH_3CN, δ in ppm, line widths $Lw_{1/2}$ given in Hz, resolution 10 Hz.

While the CO stretching modes of **3a-h** change with the electron-withdrawing character of the substituents,[13] there is almost no variation in the ν(Re=O) modes; *cf.* Table VII.

The dominating strong band at 940 cm^{-1} is the degenerate asymmetric ReO_3 stretching mode. The average splitting between ReO_3 symmetric and asymmetric stretching modes is approx. 35 cm^{-1}.[14] This means that the strong band at 940 cm^{-1} should have a (weaker) satellite at about 975 cm^{-1}. In addition to strong absorptions at 940/970 cm^{-1} (A), weak bands of types B and C indicate that a small amount of the ReO_3 species has a different coordination than the major species. It is not clear as yet what kind of compounds are responsible for these bands. The strong band of $Re_2O_7 \cdot 2CH_3CN$ at 910 cm^{-1} is likely to belong to the (anionic) ReO_4 fragment. Its symmetric counterpart is not observable in the IR spectra since the ReO_4 fragment has a local tetrahedral symmetry. It is surprising that, in spite of the different coordination geometry of **3a** no significant shift of the ReO_3 bands occurs for **3h** and $Re_2O_7 \cdot 2CH_3CN$. This can be explained by assuming preservation of the ReO_3-symmetry in solution (which is C_{3v}, total symmetry C_s) of **3a** as well as **3h** and $Re_2O_7(CH_3CN)_2$ **3a** has one nitrogen and two oxygen donor ligands; **3h** and $Re_2O_7 \cdot 2CH_3CN$ have one oxygen and two nitrogen donor ligands (Chart I). The electronic effects of these ligand patterns are seemingly identical.

^{17}O NMR Spectroscopy. The ^{17}O NMR spectra, taken in acetonitrile, prove the existence of two different types of mixed anhydrides **3a-h** *in solution* (Table VIII).

Two signals occur in case of **3a-d**, one at ≈260 ppm for the C*O*$_2$ moiety, one at ≈790 ppm for the Re*O*$_3$ fragment. By way of contrast, carboxylic anhydrides $(RCO)_2O$ show signals at 440–400 ppm (C=*O*) and at 240–200 ppm (C*O*C). **3a-d** thus do not exhibit a free carbonyl group but rather a ***bidentate carboxylate***, consistent with the IR data.

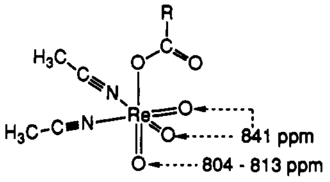
The relatively small line widths of both signals (70–150 Hz) of **3a**, **3b**, and **3d** indicate rigid geometries with regard to η^1/η^2-shifts of the carboxylic groups. The only exception is **3c**, with half-widths of 430 and 270 Hz. We assume that the increased line widths are due to the fluxionality of the $-CH_2CH_2CH_2-$ bridge that connects the two $O_3ReO-C(O)$ fragments.

The X-ray crystal structure of **3a**, the infrared data of **3a-d**, and elemental analyses of complexes with electron-rich carboxylate ligands unequivocally prove that only *one molecule of acetonitrile* is coordinated to the rhenium atom in the solid state and in solution. An **18e** configuration is thus attained by the strongly Lewis acidic heptavalent rhenium. The moderate low-field shifts of the Re*O* resonances should not be compared with that of $[ReO_4]^-$ (570 ppm; H_2O)[15a] or (η^5-C_5Me_5)ReO_3 (646 ppm; $CDCl_3$),[15b] but rather with those of other formal **18e** oxo complexes containing σ-donor ligands.[15c]

According to structural features (see below), **3a** should show two ^{17}O resonances for the ReO_3 moiety. As we observe only *one* Re=*O* resonance, the octahedral coordination geometry must be fluxional. This seems to be caused by the small bidentate carboxylato ligand. It is spectroscopically proven that **3d** belongs to the family of **3a-c** (η^2-coordination) and not to that of **3e-h** (η^1-coordination).

The ^{17}O NMR spectra of **3e-h** exhibit resonances at ≈810 and ≈840 ppm due to *two different ReO moieties*. The carboxylate resonances are found in the same region as the C*O* resonances of **3a-d**, but the oxygen atoms are clearly less electron-rich than in **3a-d** (electron-withdrawing substituents R_x). However, **3e-h** crystallize with *two solvent molecules* thus attaining hexacoordination of rhenium. In the solid state, the carboxylate ligands are monodentate, leading to **18e** compounds of octahedral geometry. This observation is consistent with the IR solution data. The electron density of the carboxyl fragments of **3e-h** is obviously (much) lower as compared to **3a-d**. The rigid octahedral coordination, with a facial arrangement of the three oxo ligands, causes *two* ^{17}O resonances to occur: oxo *trans* to acetonitrile and *trans* to carboxylate.

Comparison of the trichloroacetyl complex **3e** with the fluorinated derivatives **3f-h** allows an assignment of the Re*O* resonances. While a resonance at 841 ppm is found in the ^{17}O NMR spectra of **3e** and **3f**, the second signal shifts from 804 ppm (**3e**) to 813 ppm (**3h**). The latter one is assigned to the oxo ligand *trans* to the carboxylate, the resonance at 841 ppm is assigned to the oxo ligand *trans* to the coordinated acetonitrile (different *trans* influence of carboxylates and acetonitrile!).



3e-h

Only *one* broad resonance occurs for the carboxylate ligands of **3e-h**. The oxo ligands in *trans* positions with respect to the carboxylate ligands have broad signals, too, while the oxo ligands *trans* to acetonitrile show normal line widths. We believe that this observation results from fluxionality of the carboxylate ligands, which would furnish a **20e** species upon bidentate coordination. An equilibrium of species with a *monodentate* and an ion-paired carboxylate with $[(CH_3CN)_2ReO_3]^+$ as counterion is likely to occur Scheme I. This type of ion-pair could well

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(13) Slight changes in COO streching modes can also be explained by the different mass effects of the substituents R of **3a-h**.

(14) 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.

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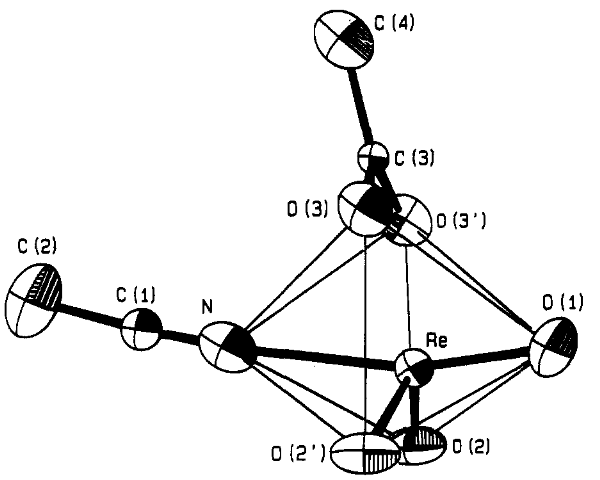


Figure 1. ORTEP drawing of the crystal structure of $(\eta^2\text{-}H_3CCO_2)ReO_3{\cdot}CH_3CN$ (**3a**). Thermal ellipsoids are at a 90% probability level. Symmetry-related atoms at $[x, -y, z]$ are primed.

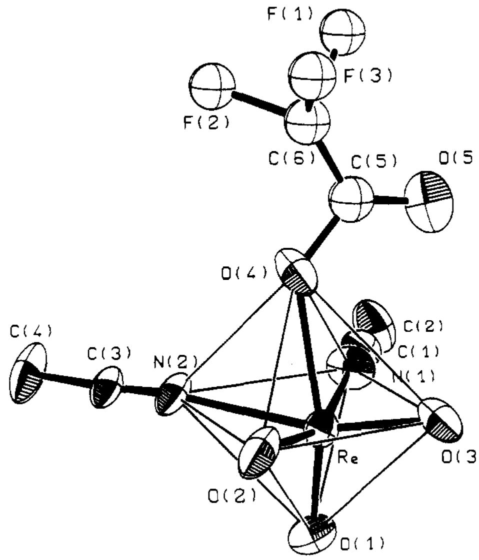
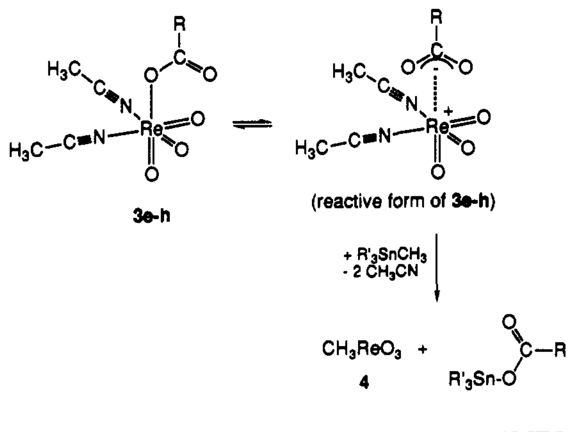


Figure 2. ORTEP drawing of the crystal structure of $(\eta^1\text{-}F_3CCO_2)ReO_3{\cdot}(CH_3CN)_2$ (**3h**). Thermal ellipsoids are at a 50% probability level. Isotropically refined atoms are drawn with arbitrary radii.

Scheme I



represent the reactive intermediate in the formation of MTO (**4**) according to eq 2.

Solid-State Structures. The crystal and molecular structures of complexes **3a,h** and **1**·2CH$_3$CN are depicted in Figures 1–3. The crystallographic results are in full agreement with the conclusion drawn from solution data.

Compounds of type **3a-d** with just one N-donor ligand L (n = 1) prefer pathway A–B–A′ Scheme II, with an energy minimum at B resulting in a **18e** rhenium moiety. In the transition state A (or A′), a pentacoordinated **16e** system forms. As shown by *Berry*[17] a ML$_5$ system is fluxional in solution. It is therefore impossible to distinguish between apical and equatorial positions. From theoretical considerations[18] we expect either a *trans* configuration of the carboxylate and the acetonitrile ligands or the *cis* isomer with a distorted octahedral coordination sphere of C_s symmetry. The latter is observed in the solid state for **3a**. The carboxylate ligand acts as a bidentate 4-electron ligand. All atoms except O(2), O(3), and H(2) are located in a mirror plane. The related compound CH$_3$ReO$_3$·H$_2$NC$_6$H$_5$ has literally the same structural features.[15c] Bond distances and angles are listed in Table IX.

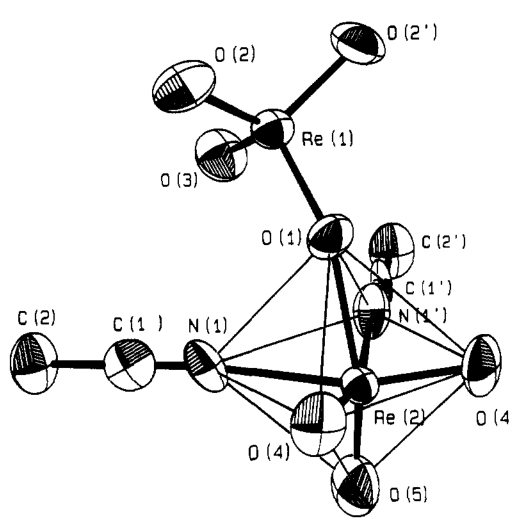
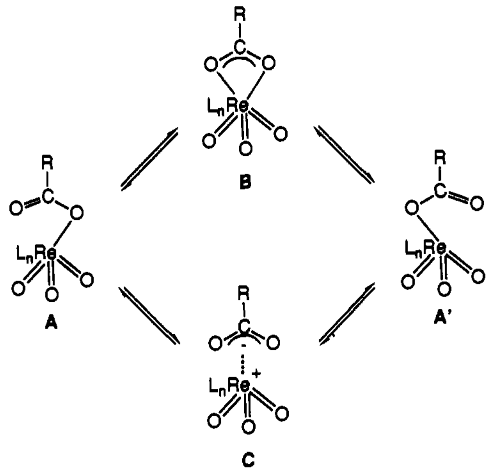


Figure 3. ORTEP drawing of the crystal structure of $(O_3ReO)ReO_3{\cdot}(CH_3CN)_2$ (**1**·2CH$_3$CN). Thermal ellipsoids are at a 90% probability level. Symmetry-related atoms at $[x, {}^1/_2 - y, z]$ are primed.

Scheme II



In contrast to **3a-d**, the energy minimum of the isomerism path of carboxylate complexes **3e-h** (electron-withdrawing substituent R) is shifted to A/A′, and the isomerization follows the new pathway A–C–A′. As shown by the IR and ^{17}O NMR (solution) data, complexes of type **3h** form octahedral structures around the rhenium centers (monodentate carboxylato ligands). This geometry is indeed observed in the solid state (Figure 2). Three facial oxo ligands, a monodentate trifluoroacetate ion, and two solvent molecules (L = acetonitrile) define the core geometry.

Stacking effects seem to prevent the system to build up a principally possible crystallographic intramolecular mirror plane.

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Table IX. Selected Structural Data for (η^2-CH_3CO_2)ReO_3·CH_3CN (**3a**)[a]

Distances (Å)			
Re–O(1)	1.705(4)	Re–O(3)	2.158(3)
Re–O(2)	1.698(4)	O(3)–C(3)	1.276(4)
Re–O(2′)	1.698(4)	N–C(1)	1.111(8)
Re–C_m	2.099(5)	C(1)–C(2)	1.439(9)
Re–N	2.331(5)	C(3)–C(4)	1.464(9)
Angles (deg)			
O(1)–Re–O(2)	103.7(1)	O(3)–Re–O(3′)	59.5(2)
O(1)–Re–O(2′)	103.7(1)	O(1)–Re–O(3)	92.3(1)
O(1)–Re–C_m	92.8(2)	O(2)–Re–O(3)	149.8(1)
O(1)–Re–N	165.3(2)	O(2)–Re–O(3′)	94.0(1)
O(2)–Re–O(2′)	106.6(2)	O(3)–Re–N	75.0(1)
O(2)–Re–C_m	122.5(2)	Re–O(3)–C(3)	93.1(3)
O(2′)–Re–C_m	122.5(2)	Re–N–C(1)	175.3(5)
O(2)–Re–N	84.9(1)	N–C(1)–C(2)	177.4(7)
O(2′)–Re–N	84.9(1)	O(3)–C(3)–O(3′)	114.2(5)
C_m–Re–N	72.5(1)	O(3)–C(3)–C(4)	122.9(2)

[a] C_m denotes the midpoint of the carboxylato group. Symmetry-related atoms at [*x*, –*y*, *z*] are primed.

Table X. Selected Structural Data for (η^1-CF_3CO_2)ReO_3·2CH_3CN (**3h**)

Distances (Å)			
Re–O(1)	1.66(2)	N(1)–C(1)	1.09(4)
Re–O(2)	1.69(2)	N(2)–C(3)	1.14(4)
Re–O(3)	1.62(2)	O(4)–C(5)	1.25(3)
Re–O(4)	2.14(2)	O(5)–C(5)	1.23(3)
Re–N(1)	2.24(2)	C(1)–C(2)	1.46(5)
Re–N(2)	2.29(2)	C(3)–C(4)	1.46(4)
		C(5)–C(6)	1.29(4)
Angles (deg)			
O(2)–Re–O(1)	103.2(8)	N(2)–Re–O(3)	160.5(9)
O(3)–Re–O(1)	104.1(8)	N(2)–Re–O(4)	73.4(7)
O(3)–Re–O(2)	106.1(9)	N(2)–Re–N(1)	74.8(9)
O(4)–Re–O(1)	155.4(8)	C(5)–O(4)–Re	132.1(17)
O(4)–Re–O(2)	88.8(7)	C(1)–N(1)–Re	173.3(23)
O(4)–Re–O(3)	92.7(7)	C(3)–N(2)–Re	171.0(19)
N(1)–Re–O(1)	85.3(8)	C(2)–C(1)–N(1)	178.8(29)
N(1)–Re–O(2)	160.0(9)	C(4)–C(3)–N(2)	176.2(30)
N(1)–Re–O(3)	88.9(9)	O(5)–C(5)–O(4)	126.0(27)
N(1)–Re–O(4)	77.2(7)	C(6)–C(5)–O(4)	105.9(24)
N(2)–Re–O(1)	85.6(8)	C(6)–C(5)–O(5)	128.1(27)
N(2)–Re–O(2)	87.6(8)		

Table XI. Selected Structural Data of (η^1-O_3ReO)ReO_3·2CH_3CN (**1**·2CH_3CN)[a]

Distances (Å)			
Re(1)–O(1)	1.789(6)	Re(2)–O(5)	1.699(9)
Re(1)–O(2)	1.723(5)	Re(2)–N(1)	2.244(6)
Re(1)–O(3)	1.689(7)	N(1)–C(1)	1.132(9)
Re(2)–O(1)	2.111(7)	C(1)–C(2)	1.460(12)
Re(2)–O(4)	1.711(4)		
Angles (deg)			
O(1)–Re(1)–O(2)	109.2(2)	O(4)–Re(2)–O(5)	103.4(2)
O(1)–Re(1)–O(3)	109.4(4)	O(4)–Re(2)–N(1)	87.4(2)
O(2)–Re(1)–O(2′)	109.7(3)	O(4)–Re(2)–N(1′)	162.8(2)
O(2)–Re(1)–O(3)	109.7(2)	O(5)–Re(2)–N(1)	85.9(3)
O(1)–Re(2)–O(4)	90.4(2)	N(1)–Re(2)–N(1′)	78.7(3)
O(1)–Re(2)–O(5)	157.2(3)	Re(1)–O(1)–Re(2)	147.0(4)
O(1)–Re(2)–N(1)	76.6(2)	Re(2)–N(1)–C(1)	173.9(6)
O(4)–Re(2)–O(4′)	104.1(4)	N(1)–C(1)–C(2)	179.3(7)

[a] Symmetry-related atoms at [*x*, $^1/_2 - y$, *z*] are primed.

It has often been observed that trifluoromethyl groups do not properly locate in X-ray data refinements. Bond distances and angles are listed in Table X.

Roesky et al. reported the structure of **1**·2CH_3CN.[12a] We redetermined this structure at low temperature to get more precise data (Figure 3). Bond distances and angles are listed in Table XI. The molecule shows a crystallographic mirror plane passing through O(1), Re(1), Re(2), O(3), and O(4). *We again emphasize the highly asymmetrical oxo bridge O(1)* which, in our opinion, predetermines a perrhenate species in reactions of Re_2O_7 carried out in solvents such as acetonitrile.

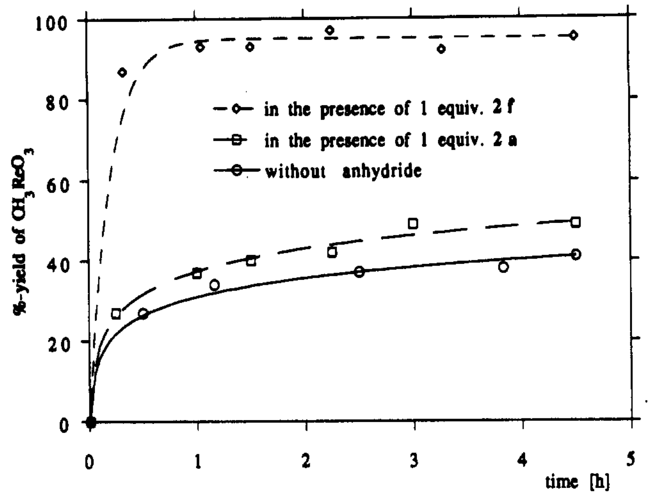

Figure 4. Formation of MTO (**4**) from dirheniumheptoxide (**1**) and tetramethyltin with and without carboxylic anhydrides. Conditions: 1.00 g (2.064 mmol) of **2** in 10.00 mL of thf; GC-MS detection; peak area calibration with a standard solution of **4** in thf. Temperature: (○) 65 °C; (□, ◇) 20 °C.

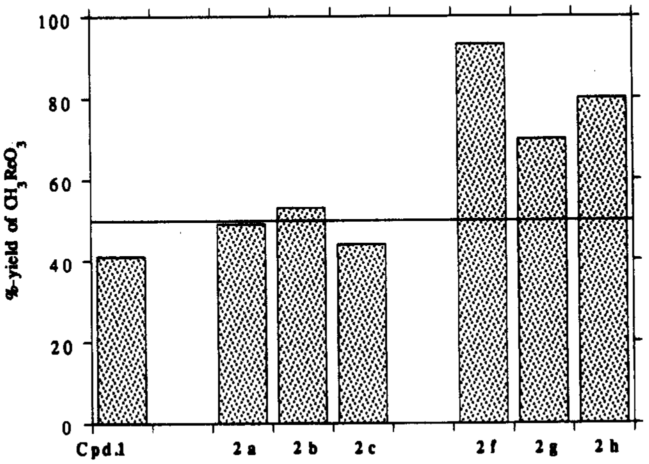

Figure 5. Yield (%) of MTO (**4**) in the presence and in the abscence of carboxylic anhydrides, respectively. Conditions: Re_2O_7 (**1**) alone (yield after 4.5 h at 65 °C); nonfluorinated acids **2a-c** (yield after 4.5 h at 20 °C); fluorinated acids **2f-h** (yield after 0.5 h at 20 °C).

The facial arrangement of the oxo ligands, with an average ReO distance of 1.69 ± 0.02 Å and O–Re–O angles of 106 ± 1°, is common to all structures. According to *Marz*,[19] the Re–N distances around 2.25 Å in length exhibit medium to strong ligand–metal interactions. The distances between rhenium(VII) and the carboxylato ligands are within the expected range of covalent bonding.

Reactivity. To correlate spectroscopic and structural results with the reactivity of the intermediates, the formation of **4** was followed by gas chromatography as a function of time. Figures 4 and 5provide convincing proof of the high reactivity of **1** toward tetramethyltin if *fluorinated* carboxylic anhydrides are present. Other carboxylic anhydrides do not improve the reaction according to eq 2 as compared to simple Re_2O_7 (without anhydride).

The formation of **4** is strongly accelerated upon prior addition of chlorinated and fluorinated carboxylic anhydrides to Re_2O_7. Fluorinated and chlorinated carboxylato ligands of **3e-h** are more weakly coordinated to the heptavalent rhenium (and thus are better leaving groups) than the simple alkylcarboxylates of **3a-d**. **1** belongs to the *first* group of complexes, as judged from the

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(19) Marz, D. W. Ph. D. Thesis, Technische Universität München, 1990.

spectroscopic and structural data (*vide infra*). The leaving group $[ReO_4]^-$ limits the rhenium yield of **4** to 50% (eq 3).

Thermogravimetry. Thermogravimetry was expected to show whether compounds **3** degrade along defined pathways, e.g. loss of CO_2, to form organorhenium oxides (eq 4).

$$\underset{\mathbf{3a\text{-}h}}{RC(O)O{-}ReO_3(CH_3CN)_n} \xrightarrow[-CO_2]{\Delta T} RReO_3 + \underset{n=1,2}{nCH_3CN} \tag{4}$$

3a·CH_3CN eliminates the acetonitrile (11% loss of mass at 190 °C). From room temperature up to 240 °C small amounts of water and carbon dioxide are lost. Only at 340–500 °C is 1 equiv of carbon dioxide eliminated. The nonvolatile residue, equal to 62 mass % of the applied material, is ReO_3 (theory, 66%). **3h**·2thf loses both thf ligands up to 160 °C (29% loss of mass; theory, 30%). Only traces of carbon dioxide are formed at the same time while the majority of CO_2 is only lost >325 °C (6% loss of mass; theory, 9%); 46 mass % of nonvolatile residue is equivalent to ReO_3 (theory, 49%). **3h**·$2CH_3CN$ behaves similarly: elimination of both acetonitrile ligands is complete at 130 °C (19 mass %; theory, 21%). Carbon dioxide and water are also lost. No plateau is observed up to 400 °C so it is impossible to discuss the nature of the nonvolatile residue which amounts to 57 mass % of the applied material. The expected formation of CH_3ReO_3 (**4**) and CF_3ReO_3, respectively, was not observed so eq 4 can not be considered an alternative synthesis of these compounds.

A 3.506-mg example of **1**·$2CH_3CN$ was heated from 50 to 700 °C at a rate of 20 K·min^{-1}. The decomposition of the sample and the mass spectroscopic characterization of volatile decomposition products are shown in parts a and b of Figure 6, respectively.

The first decomposition step (extrapolated onset 130 °C, 7.4%) implies loss of one molecule of CH_3CN (theoretical, 7.25%); *cf.* mass spectrometry (m/z = 41, 39, 38). Re_2O_7·$2CH_3CN$ is thermally as stable as Re_2O_7·dme.[12d] Starting with the first decomposition, a stepwise declining oxygen content (m/z = 32) in the atmosphere, associated with an increase in carbon dioxide (m/z = 44), suggests combustion of CH_3CN. The oxygen in the combustion products is likely to originate from traces of this element in the atmosphere and from Re_2O_7·$2CH_3CN$ or Re_2O_7·CH_3CN. The reduction of the heptoxide and its adducts yields ReO_3 (theoretical, 82.7%). The observed higher loss of mass (residue, 68.9%) is probably due to sublimation of some Re_2O_7 (onset 241 °C) immediately after its formation. This behavior is known from TG-MS studies of related compounds.[12d] A decomposition step at 520 °C may be due to loss of an equivalent of oxygen (theoretical, 2.8%; $Re_2O_7 \rightarrow 2\,ReO_3 + O_2$). It is not yet clear whether the reduction of Re_2O_7 takes place at 520 °C or at lower temperatures.

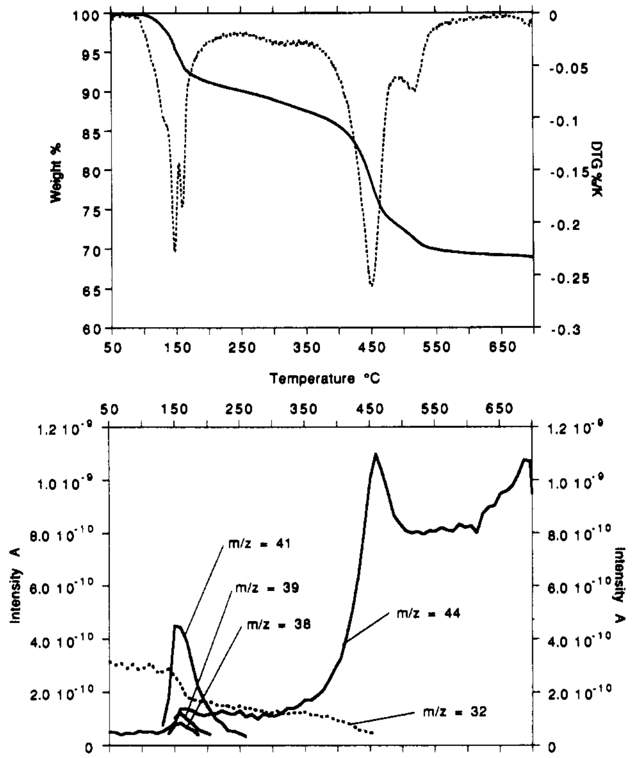

Figure 6. 6a and 6b. (a) Top: Decomposition of **1**·$2CH_3CN$ vs temperature (—) and the first derivative of the observed curve (· · ·). (b) Bottom: Mass spectrometric characterization of volatile decomposition products.

Conclusion

The conversion of dirheniumheptoxide into mixed anhydrides of carboxylic acids greatly enhances the reactivity of these compounds. It has unambiguously been shown in the present paper that the correct adjustment of electronic effects is an additional prerequisite of this simple concept: only strong electron-withdrawing groups R_x in compounds (η^1-R_xCO_2)ReO_3·2L (L = donor ligand, *e.g.* acetonitrile) make the carboxylate good enough a leaving group upon reactions with alkylating reagents such as tetraalkyltin compounds SnR_4. As to whether the coordination mode of the carboxylate (η^1 vs η^2) results from the number of ligands L (n = 1, 2) or from the nature of the substituents R_x in compounds (R_xCO_2)ReO_3·nL is not easy to establish but is not relevant for the problem. Our results rather should help to establish a general route to other high-valent organometal oxides. Perfluorocarboxylato complexes of titanium,[16a] vanadium,[16b,c] chromium,[16d] and uranium oxides[16e] have been known for some time. They should exhibit a similar reactivity as that encountered for Re_2O_7/$(CF_3CO)_2O$. The results of our thermogravimetric experiments correspond with the thermogravimetry and thermolysis data of Re_2O_7·2thf, Re_2O_7·dme, and Re_2O_7·$2CH_3CN$ where almost quantitative formation of ReO_3 was observed.[12c]

Acknowledgment. This work was supported by the European Community through a grant to J.M. and by the Hermann-Schlosser-Stiftung, e.V. (Frankfurt), through a graduate fellowship to F.E.K. The Deutsche Forschungsgemeinschaft is acknowledged for supporting our research on organometallic oxides. We are indebted to Degussa AG (Prof. Offermanns and Dr. Gerhartz) for a generous gift of Re_2O_7 as well as to Hoechst AG (Prof. Kühlein) for support of this work.

Supplementary Material Available: Tables of complete crystallographic data, positional parameters, anisotropic displacement coefficients, bond lengths, bond angles, and least-squares planes for **3a**, **3h**, and **1**·$2CH_3CN$ (29 pages). Ordering information is given on any current masthead page.