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Multiple bonds between main-group elements and transition metals

CXXXI. * Allyl-, vinyl- and related rhenium(VII) trioxides: synthesis and degradation

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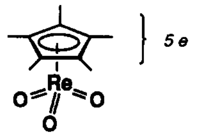
Abstract

The preparations are described of the unstable allyl-, pseudo-allyl- and benzyl- complexes of formula $RReO_3$ ($R = C_3H_5$–, $CH_2CMe{=}CH_2$–, $CH_2{=}CHCH{=}CHCH_2$–, $C_2H_5OC(O)CH_2$–, $PhCH_2$–) from Re_2O_7 and the tin reagents $RSn(n\text{-}Bu)_3$. *In situ*-NMR studies show that the allylic species exhibit η^1-coordination. The vinyl analogue $(CH_2{=}CMe)ReO_3$ is prepared from Re_2O_7 and $Zn(CMe{=}CH_2)_2$. Quinuclidine adducts of type $RReO_3 \cdot$ Quin are also reported. Decomposition studies of the allyl and 1-methallyl derivatives show concentration-dependent radical pathways in anhydrous solution (1,5-hexadiene and propene evolution) and facile hydrolysis (propene evolution) at low temperature. Allyltrioxorhenium(VII) does not react with oxygen, while peroxides predominantly yield 2-propen-1-ol.

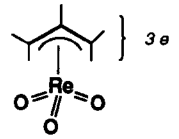
Key words: Rhenium; Vinyl; Allyl; Thermochemistry; Synthesis

1. Introduction

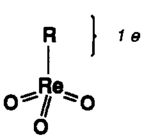
In a series of recent studies we have prepared a variety of organic derivatives of the high oxidation-state fragment "$[ReO_3]^+$" and, just as predicted at the beginning of these studies [2], some of these compounds proved to be efficient catalysts or catalyst precursors [3]. Compounds of the general formula $RReO_3$ can be placed in two main families: (i) coordinatively saturated, formally 18-electron complexes **Ia** with pentahapto-coordinated cyclopentadienyl ligands, $(\eta^5$-Cp')ReO_3 (*e.g.* $Cp' = C_5Me_5$, C_5H_5) [1,4]; (ii) coordinatively unsaturated complexes $(\eta^1$-R)ReO_3 **IIIa** with monohapto σ-alkyl [5] and σ-aryl [6] ligands. Although EHMO studies have shown that CH_3ReO_3 may be



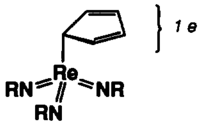
Ia



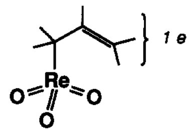
IIa



IIIa



Ib



IIb

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considered an 18e complex due to reinforced oxygen π-bonding [7a], the (η^1-R)ReO$_3$ complexes (in contrast to (η^5-Cp)ReO$_3$[1]) still possess high Lewis acidity at the metal, promptly coordinating ligands (*e.g.*, *N*-bases) [5,7b]. Spectroscopic studies of both these families of complexes suggest that Lewis acidity can be controlled through the nature of the R substituent which, of course, suggests the possibility of achieving a tunable reactivity control over these compounds [8].

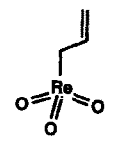
Still absent from this picture is a putative third branch of this family, namely the formally 16-electron trihapto complex (η^3-allyl)ReO$_3$ **IIa** and its derivatives. This kind of oxo complex has been proposed as intermediates in the SOHIO process of propene ammoxidation [9]. The first example, W(O)(η^3-C$_3$H$_5$)Cl(PMe$_3$)$_2$, was reported only recently [10], though it does not exhibit the metal in its highest possible oxidation state as would be required for ammoxidation [9,11]. In the present case, preliminary EHMO calculations predict the preferential formation of (as yet unknown) (η^1-allyl)ReO$_3$ **IIb** just as observed for the closely related complexes of type RRe(NR)$_3$ where the allylic derivative was identified as the monohapto species (η^1-allyl) Re(NR)$_3$ [12]. This was attributed to the very strong π-donation effect of the imido (NR) ligands which also force (C$_5$H$_5$)Re(NR)$_3$ **Ib** to adopt a η^1-coordination of the cyclopentadienyl ligand [13].

To answer some of these questions we prepared several examples of this important sub-class of organometallic oxides and now report on the preparation of allyl-, pseudo-allyl- and vinyl derivatives of the "[ReO$_3$]$^+$" fragment as well as the decomposition studies of the parent compound (η^1-allyl)ReO$_3$.

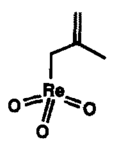
2. Results and discussion

2.1. Chemical studies

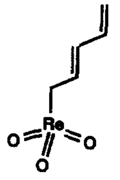
The typical preparation of (alkyl)ReO$_3$ complexes [5] cannot be extended to the allyl derivatives. Indeed, reaction of Zn(C$_3$H$_5$)$_2$ with Re$_2$O$_7$ in thf even at −78°C leads to instant decomposition (dark-brown to black colour), a behaviour like that observed for the system Re$_2$O$_7$/ZnR$_2$ (R = ^{i}Pr, ^{t}Bu, CH$_2^t$Bu, CH$_2$Ph). This result initially suggested an intrinsic instability of an intermediate {(C$_3$H$_5$)ReO$_3$} towards decomposition since the allyl radical, like the above mentioned α-substituted alkyl radical, is very stable. A thermal radical-type decomposition is known for R-ReO$_3$ complexes [1,5a,b,14]. However, addition of Sn(C$_3$H$_5$)$_4$ to a solution of Re$_2$O$_7$ in thf at −40°C gave an immediate reaction recognizable by the appearance of a yellow-orange colour. Upon warming the solution to around 0°C, decomposition became significant (black precipitate). When (C$_3$H$_5$)Sn(^{n}Bu$_3$) was substituted for Sn(C$_3$H$_5$)$_4$, a similar reaction was observed, leading to the conclusion that (C$_3$H$_5$)ReO$_3$ (**1a**) is formed in both reactions (eqn. 1).



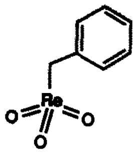
1a



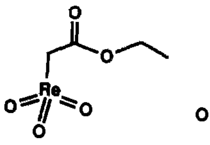
1b



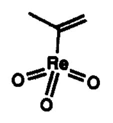
1c



1d

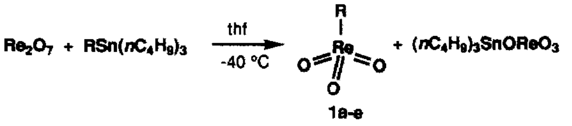


1e

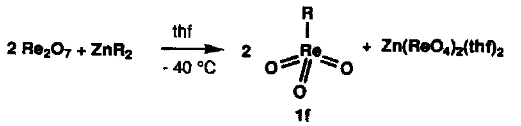


1f

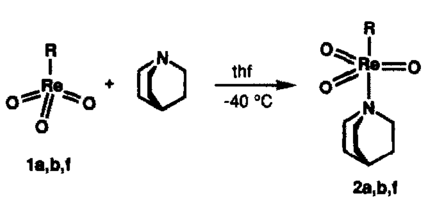
Using the approach developed for other temperature-sensitive (alkyl)ReO$_3$ complexes [5a,b], quinuclidine was added to the reaction solution at −40°C to give a deep orange solution. After low temperature evaporation (−50°C) and extraction of the residue with *n*-pentane at *ca.* −10°C, the complex [(allyl)ReO$_3$ · quin] (**2a**) was obtained as a bright-orange solid upon concentration and further cooling (eqn. 3).



(1)



(2)



(3)

Starting from RSn(^{n}Bu$_3$) and Re$_2$O$_7$ (eqn. 1), a series of related complexes—all containing allylic or other double bonds in β-position—was prepared: (methallyl)ReO$_3$ (**1b**), (2,4-pentadienyl)ReO$_3$ (**1c**), (benzyl)ReO$_3$ (**1d**) and (ethylacetyl)ReO$_3$ (**1e**). Due to thermolability, these compounds except for **1d** (MS) were characterized by *in situ* NMR (see NMR section) and through their more stable quinuclidine adducts **2a, b, f** of eqn. 3.

The stability of the allyl complexes **1a, b** is similar, in contrast to the well-documented increased stability of a η^3-methallyl- *vs.* η^3-allyl complex of low oxidation-state metals [15].

The 2,4-pentadienyl derivative **1c** is an unstable complex which partially decomposes at −40°C. This seems to follow the reported trend in that longer-chain alkyl groups R make the complexes in R-ReO_3 less stable [5b].

$Sn(CH_2Ph)_4$ does not react with Re_2O_7, even at room temperature. Steric hindrance is a possible explanation. However, $(PhCH_2)Sn(^nBu)_3$ reacts promptly but rapid decomposition occurs at −45°C in thf solution, immediately after the formation of **1d**. A CI mass spectrum of the black residue obtained after evaporating the reaction mixture to dryness at *ca.* −80°C gave the expected peaks for **1d**, namely the parent ion peak at $m/z = 326$. Analysis of the reaction mixture by GC-MS revealed the formation of several dibenzyl isomers, indicating a radical type decomposition of **1d**. These degradation products are also present in the mixtures resulting from $Zn(CH_2Ph)_2$ and Re_2O_7 (thf) that turns black above −80°C.

The presence of a β-keto group in **1e** (from $[CH_2C(O)(OC_2H_5)]Sn(^nBu)_3$ and Re_2O_7 in thf at −40°C) does not make its stability differ significantly from that of **1a, b**.

(Methylvinyl)$Sn(^nBu)_3$—isomeric with (allyl)Sn ($^nBu_3$)—does not react with Re_2O_7. However, the zinc derivative yields $[CH_2{=}C(CH_3)]ReO_3$ (**1f**) in good yield (eqn. 2). Nevertheless, **1f** is a labile species and could therefore only be characterized as the quinuclidine adduct **2f**. **1f** is the first example of a vinylmetaloxide, *i.e.* with an α-double bond to Re, and is much less stable than the phenyl (aryl) congeners also bearing bonds between Re^{VII} and a sp^2-hybridized carbon [6].

The quinuclidine adducts **2a, b, f** (eqn. 3) are clearly less stable than their alkyl analogues [5]. Indeed, they quickly decompose at room temperature to give black masses of high rhenium content and the dimer of the organic ligand as main products. This result once again agrees with a radical decomposition pathway (see below). In moist air, **2a, b** quickly hydrolyse to quinuclidinium perrhenate $[Quin]^+[ReO_4]^-$. However, in a solid KBr matrix or in dilute solutions of hydrophobic solvents (room temp.), **2a, b** decompose much move slowly. The growth of the typical infrared $\nu(Re{=}O)$ band of $[ReO_4]^-$ at 909 cm^{-1} gradually appears when IR spectra of **2a** in a KBr pellet are recorded at intervals of several minutes [$\nu_{as}(Re{=}O)$ at 920 cm^{-1}, **2a**].

2.2. NMR studies

Complexes **1a–c, e** were identified by *in situ*-NMR spectroscopy. The (alkenyl)$Sn(^nBu)_3$ reagent was added to a 0.2 *M* solution of Re_2O_7 in d_8-thf at −50°C. The ^1H- and ^{13}C NMR spectra of **1a–c, e** and **2a, b, f** prove that all alkenyl ligands are η^1-coordinated to the $[Re^{VII}O_3]$ fragment. In the simple cases **1b** and **2b**, η^3-coordination of the methallyl ligand would yield two ^1H and three ^{13}C signals, while η^1-coordination yields the observed three ^1H and four ^{13}C signals, respectively (−80... +50°C). A typical "η^1 pattern" is also present in the NMR spectra of **1a**, quite similar to the one of the isoelectronic complex $(\eta^1\text{-}C_3H_5)Re(NR)_3$ [12].

TABLE 1. NMR Data of $(R'CH_2)ReO_3$ (**1**) and $(R'CH_2)ReO_3 \cdot Quin$ [a] (**2**) in d_8-*thf*

R′	1		2
	$\delta(^1H)$	$\delta(^{13}C)$	$\delta(^1H)$
$-H$	2.14	19.26	1.23
$-CH_3$	3.10	36.56	–
$-CH{=}CH_2$	3.65	46.96	2.73
$-(CH_3)C{=}CH_2$	3.63	50.50	2.90
$-CH{=}CHCH{=}CH_2$	3.74	46.36	–
$-C({=}O)OCH_2CH_3$	3.23	41.22	–

[a] Quin = $C_7H_{13}N$ (quinuclidine)

The 2,4-pentadienyl derivative **1c** also has a η^1-hapticity although it could attain either η^3- or η^5-coordination as seen in the structurally characterized complexes $(C_5H_5)Cr(\eta^3\text{-}C_5H_7)(CO)_2$ [16a] and $Mn(\eta^5\text{-}C_5H_7)(CO)_3$, respectively [16b]. **1e, 1f** present the simple spectra expected for monohapticity, similar to the respective organotin starting materials.

Table 1 quotes the chemical shifts (^{13}C and ^1H) of the metal-attached (α-)CH_2 groups. The significant low-field shift of the CH_2 group attached to the Re^{VII} centre is characteristic of all known $RReO_3$ compounds [5].

2.3. Decomposition studies

It has been observed for organylrhenium(VII) trioxides that their stability increases upon dilution. The allyl complexes **1a, b** cannot be isolated pure because, even below −40°C, evaporation of the solvent yields a rapidly decomposing residue. It was shown by the NMR spectra, however, that the *in situ*-generated complexes survive for long times, even at higher temperatures. For example, a ^1H NMR spectrum of **1a** can be recorded at +50°C in d_8-thf (*ca.* 10 min). The more dilute the solution, the higher the onset temperature of decomposition. We define this "onset" by the time when a black or brown-black shade in the solution becomes visibly detected (Fig. 1). A marked dependence of the decomposition rate and of the nature of the decomposition products on the initial concentration of **1a** is inferred. The only organic decomposition products found were 1,5-hexadiene and propene (solu-

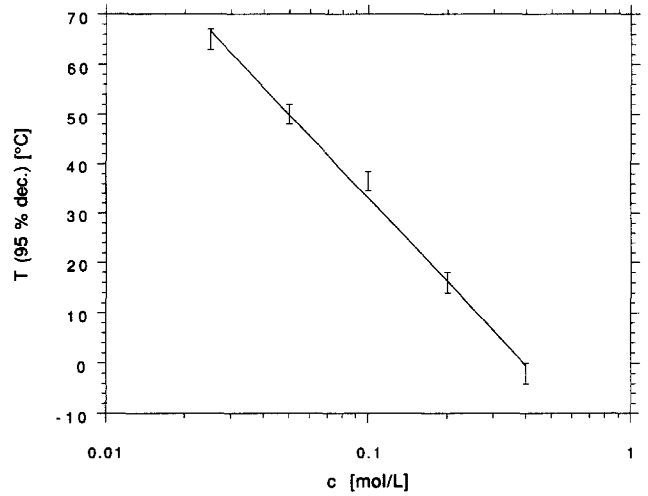


Fig. 1. Concentration-dependent decomposition temperatures of (η^1-allyl)trioxorhenium (**1a**). The experiments were carried out under rigorous anhydrous conditions. "Black colour" corresponds to the formation of 95% of the final propene concentration (detected in the gas phase).

tion GC-MS (AS 60) and gas-phase GC). An increase of initial concentration of **1a** lowers the decomposition onset temperature; at the same time a higher fraction of 1,5-hexadiene is among the decomposition products (Figs. 2 and 3). At any concentration, more equivalents of allyl are transformed into 1,5-hexadiene than into propene. When the solution becomes black, *ca.* 90–95% of the final concentrations of 1,5-hexadiene and propene are already reached (solution GC-MS; gas-phase GC).

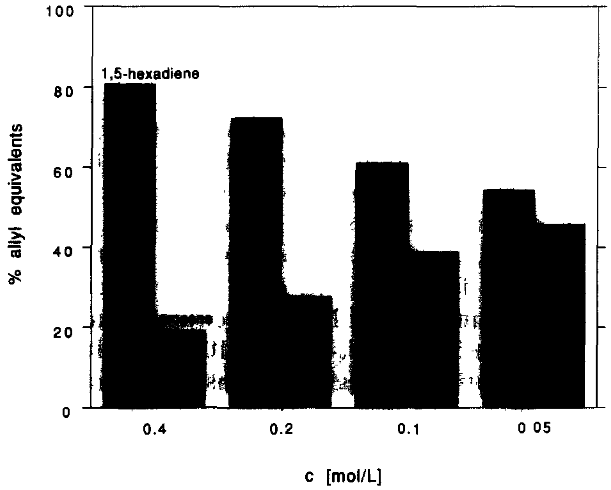


Fig. 2. Concentration-dependent formation of 1,5-hexadiene and propene (one molecule of 1,5-hexadiene contains two allyl equivalents). The experiments were performed under rigorous anhydrous conditions.

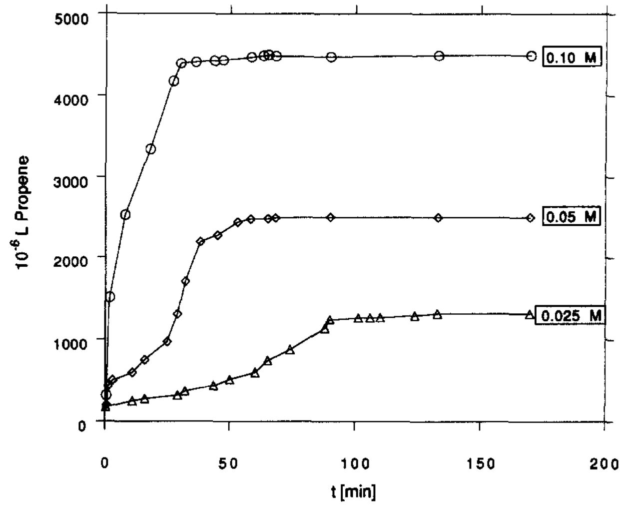


Fig. 3. Time-dependent formation of propene during the decomposition of solutions of (η^1-allyl)trioxorhenium (**1a**), same conditions as indicated in Figs. 1 and 2.

After a few hours at room temperature, under totally anaerobic conditions, polymerization of the solvent (thf) is only observed with the more concentrated solutions. If these decomposition occur in d_8-thf, d_1-propene is formed selectively (GC-MS). The decomposition of the 1-methallyl derivative **1b** proceeds in an analogous manner (Fig. 4).

The radical decomposition pathway according to eqn. 4b accommodates the above observations: homolytic cleavage of the Re–C bond forms allyl radicals that may recombine, dimerize (1,5-hexadiene) or abstract H(D) (from the solvent) to give propene (or

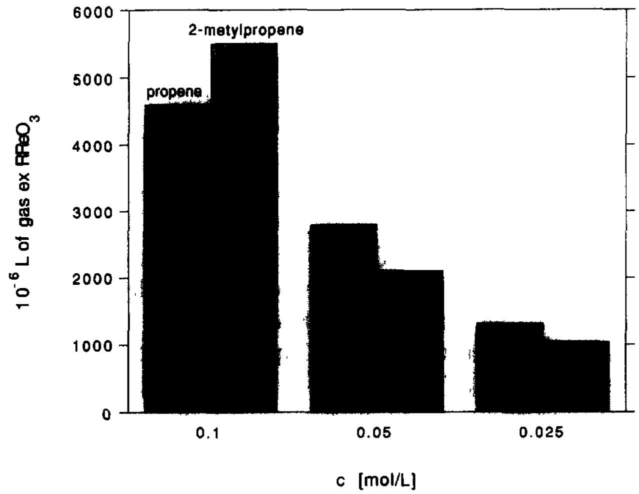
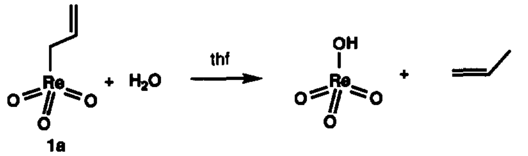


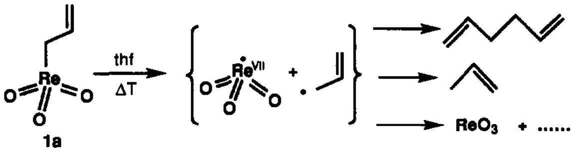
Fig. 4. Final concentrations of propene (*ex* (η^1-C_3H_5)ReO_3 (**1a**)) *vs.* methylpropene (*ex.* (η^1-$CH(CH_3)CH{=}CH_2$)ReO_3 (**1b**)) as a function of the starting concentrations of **1a** and **1b**, respectively.

d_1-propene). This second pathway is less favoured as shown by the increased thermal stability of the more dilute solutions. The darkening of the decomposing solution is attributed to the formation of rhenium oxides, in particular ReO_3 which is black in colloidal and finely divided form [14].

The formation of propene could also result from hydrolytic cleavage of the Re–allyl bond by traces of water. In order to check this possibility, excess water was added to a fresh *in situ*-preparation of **1a**. The initially yellow solution loses colour within a few minutes at −40°C, with quantitative formation of propene upon warming to room temperature (solution GC–MS; gas-phase GC). No polymerization of thf takes place even in concentrated solutions. No other allyl-containing or -derived products such as allylalcohol, propanal or propenal could be detected. Therefore, the formation of perrhenic acid is assumed to occur in the reaction represented by eqn. 4a. This observation is surprising since other complexes of type $R\text{-}ReO_3$ are relatively stable to hydrolysis in neutral or acidic media, particularly CH_3ReO_3 [17].



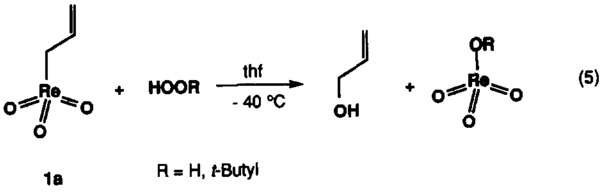
(4a)



(4b)

The reaction of **1a** with oxygen was examined. The "SOHIO product" $CH_2{=}CH\text{–}CHO$ does not form. **1a** is formed under a dry oxygen atmosphere in the same way as under a nitrogen atmosphere. Warming **1a** in thf under bubbling O_2 shows the formation of propene and 1,5-hexadiene. No significant influence of O_2 can be observed.

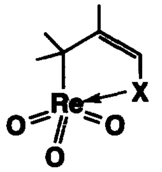
1a reacts at −40°C with stoichiometric amounts of H_2O_2 in Et_2O and ^{t}butylhydroperoxide with formation of 2-propen-1-ol. The yellow solution of **1a** nearly loses its colour within *ca.* 1 h. Again perrhenic acid (reaction with H_2O_2) and $(^tBuO)ReO_3$ [18] (reaction with ^tBuOOH) are formed (eqn. 5). The latter complex slowly decomposes at room temperature (*ca.* 15 h) with formation of *t*-butanol (GC–MS). **1a** does not react with $^tBuOO^tBu$ at low temperatures, while at 25°C the usual decomposition products propene and 1,5-hexadiene occur.



(5)

3. Conclusions

It has become clear from the present study that alkenyl groups R form well-defined organorhenium(VII) oxides of formula $R\text{-}ReO_3$ with allyltrioxorhenium $(\eta^1\text{-}C_3H_5)ReO_3$ being a typical example. However, the very low thermal stability may preclude further studies, and in this case, the stability of the quinuclidine adducts is barely improved. Nevertheless we propose to attempt the synthesis of functionalized derivatives of type IV that could well enjoy a much improved stability than the simple CC-unsaturated congeners **1a–c**. A theoretical study of $(C_3H_5)ReO_3$ is under way [19].



IV

X = heteroatom group
e.g., OR, NR_2

4. Experimental section

All reactions were performed with standard Schlenk techniques in an oxygen-free and water-free nitrogen atmosphere. Solvents were dried with standard methods and distilled under N_2. IR spectra were recorded on a Perkin-Elmer 1600 series FTIR spectrometer (resolution 4 cm^{-1}), the ^1H- and ^{13}C spectra at 399.78 and 100.5 MHz, respectively, on a FT-JEOL GX 400 instrument. The ^{17}O NMR spectrum of **1a** was recorded at 54.21 MHz. All NMR solvents were "freeze pump–thaw" degassed and stored over molecular sieves before use. Elemental analyses were performed in the Microanalytical Laboratory of our Institute. Mass spectra were obtained with Finnigan MAT 311A- and MAT 90 spectrometers. Re_2O_7 (Degussa), quinuclidine (Aldrich) and $Sn(allyl)_4$ (Aldrich) were used as received. Other tin compounds were prepared according to literature procedures or similar methods: $(^nBu)_3Sn(C_3H_5)$ [20], $(^nBu)_3Sn(CH_2CMe{=}CH_2)$ [21], $(^nBu)_3Sn(2,4\text{-pentadienyl})$ [22], $(^nBu)_3Sn(CH_2C(O)OC_2H_5)$ [23], $Sn(CH_2Ph)_4$ [24], $(^nBu)_3Sn(CH_2Ph)$ [25].

4.1. *Bis(1-methylvinyl)zinc*

To a solution of 200 ml of (1-methylvinyl)potassium (50 mmol) in 200 ml of diethylether (−20°C), was added dropwise 25 ml of a 1 M solution of $ZnCl_2$ (25 mmol) in diethylether. The reaction mixture was stirred for 2 h at 25°C. The solution was then filtered and washed with ether to give a 150 ml solution of bis(1-methylvinyl)zinc $Zn[C(CH_3)=CH_2]_2$ (0.1 M).

4.2. *In situ-preparation of R-ReO$_3$ (1a–3)*

A solution of Re_2O_7 (500 mg; 1.03 mmol) in d_8-thf (5 ml) in a Schlenk tube is cooled to −50°C. At this temperature, partial precipitation of white $Re_2O_7 \cdot 2$thf [26] is observed. The stoichiometric amount of the (alkenyl)$SnBu_3$ reagent is added to the solution which immediately turns yellow. After stirring for 5–10 min, a clear solution is obtained which is further stirred for 30 min at −35°C and then again cooled to −50°C. Part of this solution is transferred into a NMR tube (kept inside a Schlenk cooled to −80°C in a dry-ice/isopropanol bath) by means of a stainless-steel needle externally cooled with dry ice. The NMR spectra are immediately recorded at −40°C. The formation of **1a–d** is practically quantitative since no peaks due to the organotin starting compounds (or only traces of them) are observed in the NMR spectra. For comparison, the NMR spectra (^{1}H, ^{13}C) of all organotin compounds were recorded (d_8-thf at −50°C).

4.2.1. *Allyltrioxorhenium(VII) (1a)*

^{1}H-NMR (d_8-thf, −40°C): $\delta = 3.65$ (d, 2H, Re-CH_2), 4.84 (dd, 2H, CH_2-CH=CH_2), 5.93 (m, 1H, Re-CH_2-). $^{13}C\{^1H\}$-NMR (d_8-thf, −45°C): $\delta = 46.96$ (Re-CH_2), 119.40 (=CH_2), 138.77 (-CH=). ^{13}C-NMR (d_8-thf, −40°C): $\delta = 46.7$ (t, Re-CH_2), 119.5 (t, =CH2), 138.69 (d, -CH=). ^{17}O NMR (d_8-thf, −50°C): $\delta = 894$ ppm.

4.2.2. *Methylallyltrioxorhenium(VII) (1b)*

^{1}H-NMR (d_8-thf, −40°C): $\delta = 1.53$ (s, 3H, -C(CH_3)), 3.63 (s, 2H, Re-CH_2), 4.64 (d, 2H, =CH_2). $^{13}C\{^1H\}$-NMR (d_8-thf, −40°C): $\delta = 20.65$ (-C(CH_3)), 50.50 (Re-CH_2), 119.30 (=CH_2), 144.32 (=C(CH_3)-). ^{13}C (d_8-thf, −45°C): $\delta = 20.6$ (q, -C(CH_3)), 50.5 (t, ReCH_2), 117.8 (t, =CH_2), 145.0 (s, =C(CH_3)-).

4.2.3. *2,4-Pentadienyltrioxorhenium(VII) (1c)*

^{1}H-NMR (d_8-thf, −45°C): $\delta = 3.74$ (d, 2H, Re-CH_2-), 4.89 (d, 1H, =CH_2) 4.97 (d, 1H, =CH_2), 5.82 (dd, 1H, Re-CH_2-CH=CH-), 6.42 (dt, 1H, Re-CH_3-CH=), 6.64 (dt, 1H, H_2C=CH-), $^{13}C\{^1H\}$-NMR (d_8-thf, −45°C): $\delta = 46.36$ (Re-CH_2), 117.92 (=CH_2), 134.68 (Re-CH_2-CH=), 135.46, 136.66 (H_2C=CH- and H_2C=CH-CH=).

4.2.4. *Benzyltrioxorhenium(VII) (1d)*

CI-MS (isobutene for chemical ionization): $m/z = 326$ (3%) [M^+], 235 (100°C) [$M^+ - C_7H_7$]. GC-MS: $CH_3C_6H_5$ ($m/z = 92$) and dimethylbiphenyl ($m/z = 182$) in ratio of *ca.* 1/10.

4.2.5. *Ethylacetyltrioxorhenium(VII) (1e)*

^{1}H-NMR (d_8-thf, −60°C): $\delta = 1.20$ (t, 3H, (-O-CH_2CH_3)), 3.23 (s, 2H, (Re-CH_2-)), 4.06 (q, 2H, -O-CH_2-). $^{13}C\{^1H\}$-NMR (d_8-thf, −60°C): 14.30 (-O-CH_2CH_3), 41.22 (Re-CH_2-), 61.50 (-O-CH_2-), 171.73 (-C(O)O-).

4.3. *(η^1-Allyl)(quinuclidine)trioxorhenium(VII) (2a)*

A solution of 484 mg (1.00 mmol) of Re_2O_7 in thf (10 ml) was cooled to −40°C and then treated with the stoichiometric amount (1.00 mmol) of $(C_3H_5)Sn(^nBu)_3$ or $Sn(C_3H_5)_4$. The solution immediately became yellow and was further stirred at −40°C for 1 h. Dropwise addition of quinuclidine (20 ml of a 0.1 M solution of $C_7H_{13}N$ in *n*-pentane) resulted in a clear but deeper yellow-orange solution which was further stirred at −40°C for 10 min and then evaporated to dryness at −50°C (high vacuum). The yellow residue was extracted with cold (−15°C) pentane (5 × 10 ml) and the extract concentrated to *ca.* 5 ml and cooled to −78°C. The mother liquor was decanted. The remaining yellow powder was dried at −40°C under high vacuum. Yield 239 mg (61%) from $(C_3H_5)Sn(^nBu)_3$ and 220 mg (57% from $Sn(C_3H_5)_4$.

^{1}H NMR (d_8-thf, −40°C): $\delta = 1.52$ (m, 6H, $CH_2(CH_2)_3$, 1.67 (m, 1H, $CH(CH_2)_3$), 2.46 (m, 6H, $N(CH_2)_3$), 2.73 (d, 2H, ReCH_2), 4.44 (dd, 2H, CH_2=CH), 5.77 (m, 1H, CH_2=$CH$$CH_2$). CI-MS (^{187}Re), [$m/z$ (rel. int. %)]: 277 ([$M - NC_7H_{13}]^+$, 60), 111 ($[NC_7H_{13}]^+$, 100). IR (KBr, cm^{-1}): 3080w (CH=CH_2), 920vst (Re=O). IR (CS_2, cm^{-1}): 3075w, 926vst. UV(*n*-pentane, nm): $\lambda = 226$, 269, 275, 281, 353. Anal. Calcd. for $C_{10}H_{18}NO_3Re$ (386.36), C, 31.00; H, 4.70; N, 3.61; Re, 48.18; Found: C, 30.29; H, 5.05; N, 3.50; Re, 47.46%.

4.4. *(η^1-Methylallyl)(quinuclidine)trioxorhenium(VII) (2b)*

Preparation as described above for **2a** (from 1 mmol of Re_2O_7 and 1 mmol of $(C_4H_7)Sn(^nBu)_3$: Yield 253 mg (63%) .

^{1}H-NMR (d_8-thf, −40°C): $\delta = 1.50$ (m, 9H, $CH_2(CH_2)_3$ and $ReCH_2C(CH_3)$=) 1.65 (m, 1H, $CH(CH_2)_3$), 2.41 (m, 6H, $N(CH_2)_3$), 2.90 (s, 2H, ReCH_2), 4.38 (d, 2H, CH_2=C(CH_3)-). EI-MS (70 eV, ^{187}Re), [m/z (rel. int. %)]: 293 ($[M - NC_7H_{13}]^+$, 6), 111 ($[NC_7H_{13}]^+$, 100). IR (KBr, cm^{-1}): 3077w (=CH_2), 2863m (-CH_3), 921vst, (Re=O). Anal. Calcd. for

$C_{11}H_{20}NO_3Re$ (400.39): C, 33.00; H 5.04; N 3.49. Found: C, 33.11; H, 5.41; N, 3.46%.

4.5. (η^1-Methylvinyl)(quinuclidin)trioxorhenium(VII) (2f)

A cooled (−50°C) stirred solution of Re_2O_7 (1 g; 2.06 mmol) in thf (30 ml) was treated with 10 ml of 0.1 *M* di(methylvinyl)zinc in diethylether (1 mmol), see 4.1. After the dropwise addition, the solution was stirred at −50°C for 30 min. The solvent was then removed at −40°C under reduced pressure. The residue was extracted with cold *n*-pentane (5×5 ml) and 20 ml of a 0.1 M solution of quinuclidine in ^{n}pentane was added. The reaction mixture was stirred for 0.5 h at room temperature. The volatiles were removed *in vacuo* before materials were removed and 5 ml of cooled CH_2Cl_2 was added. The filtered solution was cooled overnight on dry ice, leading to yellow crystals (340 mg, yield 45%).

IR (KBr, cm^{-1}): $\nu = 3054$w (=CH), 2931st (CH_3), 2866m (CH_3), 986w (ReO), 917vst(ReO); EI-MS (70 eV, ^{187}Re): m/z (%) = 276 (22) [$M^+ - NC_7H_{13}$], 111 (100) [NC_7H_{13}]$^+$. ^{1}H-NMR (d_8-thf, −40°C): d = 1.54 (6H, m, $CH_2(CH_2)_3$), 2.09 (3H, s, $-CH_3$), 2.48 (6H, m, ($N(CH_2)_3$)), 1.65 (m, 1H, $CH(CH_3)$), 5.54, 6.70 (2H, m, $=CH_2$); $^{13}C\{^1H\}$-NMR (d_8-thf, −20°C): $\delta = 21.61$ (CH, $CH(CH_2)_3$), 26.51 (CH_3), 32.84 ($CH(CH_2)_3$), 49.13 (NCH_2), 135.27 ($=CH_2$), 178.73 ($Re-C(CH_3)CH_2$).

Anal. Calcd. for $C_{10}H_{18}NO_3Re$ (386.36): C, 31.09; H, 4.66, N, 3.62, 46.18. Found: C, 29.98; H, 5.19; N, 3.62; Re, 46.25%.

4.6. GC-and GC–MS studies

The composition of the gaseous phase was analyzed with a Hewlett Packard capillary gas-chromatograph (HP 5890) with a flame ionization detector and a HP 3394-A integrator. The liquid phase and the labelling experiments were analyzed in a gas chromatograph HP 5890-A with a mass detector HP 5970 using a HP, BP5, Scientific Glass Engineering GmbH column (95% methylpolysiloxane/5% phenyl-polysiloxane; length = 25 m, $\phi = 0.22$ mm, thickness 25 mm).

4.6.1. Calibration

Known amounts of propene and 1,5-hexadiene were added to probes with identical amounts of solvent and propane (internal standard). The amount of added propene corresponds to the amounts of propene actually produced in the decomposition reactions. These probes were stirred at constant temperature for 20 min. Several samples were then withdrawn and GC-analyzed. These analyses were repeated several times to minimize systematic errors. The calibration curves were plotted from the peak areas; they encompass solubility and response factors. For **1b** the same procedure was used with 2,5-dimethylhexadiene(1,5) and 2-methylpropene.

4.6.2. Concentration-dependent decomposition studies

Solutions of Re_2O_7 (240 mg; 0.5 mmol) were made up in thf (20, 10, 5, 2.5, 1.25 ml) and cooled to −45°C, Precipitation of some $Re_2O_7 \cdot 2thf$ was observed in the more concentrated solutions. After treatment with the stoichiometric amount of $(C_3H_5)Sn(^nBu)_3$ (or (C_4H_7)-$Sn(^nBu)_3$ stirring was continued until a constant concentration of propene (2-methylpropene) was reached. The solutions were then stirred in a waterbath at room temperature; the changes in the concentration of propene and 1,5-hexadiene (2-methylpropene and 2,5-dimethylhexadiene(1.5)) were followed by GC and GC–MS. Control experiments were made with $(C_3H_5)Sn(^nBu)_3$ $(C_4H_7)Sn(^nBu)_3$ where no signs of decomposition could be observed under these conditions in the absence of Re_2O_7. Decomposition reactions performed by addition of $(C_3H_5)Sn(^nBu)_3$ to Re_2O_7 in thf solutions at room temperature showed only slightly faster decomposition with identical (within experimental error) final yields of propene and 1,5-hexadiene. The decomposition of **1a, b** with water was performed as above, except that excess water (1 mmol) was added to the solutions (thf) after initial propene build-up was attained.

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