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On the formation of $(CH_3)_4Re_2O_4$ from methyl trioxorhenium complex CH_3ReO_3 under non-alkylating conditions

Henri Rudler *, Jose Ribeiro Gregorio, Bernard Denise, Jacqueline Vaissermann

Laboratoire de Chimie Organique, URA 408 and Laboratoire de Chimie des Métaux de Transition, URA 604, Université Pierre et Marie Curie, Tour 44-45, 4 Place Jussieu, Paris Cedex 5, 75252, France

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Abstract

Attempts to deprotonate and alkylate at oxygen methyltrioxorhenium complex (MTO) by means of nitrogen ylides $PhC(O)CH^-N^+R_1R_2R_3$ led unexpectedly to the known dinuclear Re(VI) complex $Me_4Re_2O_4$ in 30% ($R_1 = R_2 = R_3 = Et$) and 72% ($R_1 = Me$, $R_2R_3 = (CH_2)_5$) yield, and to the corresponding ammonium perrhenates $ReO_4^-PhC(O)CH_2N^+R_1R_2R_3$. Both complexes could be fully characterized by their spectroscopic data and by X-ray crystallography. © 1997 Elsevier Science S.A.

Keywords: Methyl trioxorhenium complex; Dinuclear Re(VI) complex; Ammonium perrhenates

1. Introduction

It has been shown by Herrmann et al. [1–3] that MTO is a versatile catalyst or catalyst precursor for several transformations. On the one hand, it has been found as one of the most active catalyst for the epoxidation of olefins [4,5]. On the other hand, it is also known as a very active catalyst for the olefin metathesis reaction in the presence of a cocatalyst [2,6].

Whereas the mechanism of the epoxidation of alkenes could be firmly established on the grounds of the isolation and structure determination of a crucial intermediate, a diperoxo complex [4], the transformation of MTO into a metathesis catalyst, is less well understood. Although it has been shown that for some catalytic systems, the methyl group of MTO is not directly involved in the reaction [7,8], its transformation upon hydride abstraction into a carbene moiety could not be fully excluded [9].

A last property that has recently been depicted by the same authors is the polymerizability of MTO in aqueous medium to give polyMTO [10]. This polymer is deficient in methyl groups with respect to the monomer MTO.

The purpose of this paper is to describe experiments directed towards the detection of an elusive carbene complex derived from MTO and which shows finally that under non-alkylating conditions, methyl migration along with reduction can take place leading inter alia to a dimeric complex.

2. Results

The behavior of MTO can be compared in some of its aspects to that of an organic carbonyl compound, the carbonyl–carbon being replaced by a rhenium atom.

Indeed, in the same sense as carbonyl compounds lead to dialkyl dioxiranes A upon treatment with peroxo derivatives [11], MTO leads, upon treatment with hydrogen peroxide to a mono and a di-peroxo complex B and C [4]. A, B and C react with olefins to give epoxides (Scheme 1) with regeneration of the starting compounds. Similarly, like ketones, MTO reacts with diols to give E [12], which are analogs of ketals D (Scheme 2).

We reasoned, therefore, that the formation of a carbene complex from MTO could be understood along the same lines: since enolization of a ketone, followed by alkylation or acylation leads either to enol ethers or to enol esters, the same reaction performed on MTO might lead to an alkoxy or an acyloxy carbene complex, although no evidence for the presence of a carbene type contribution in the structure of MTO could be established by NMR spectroscopy (Scheme 3).

* Corresponding author.

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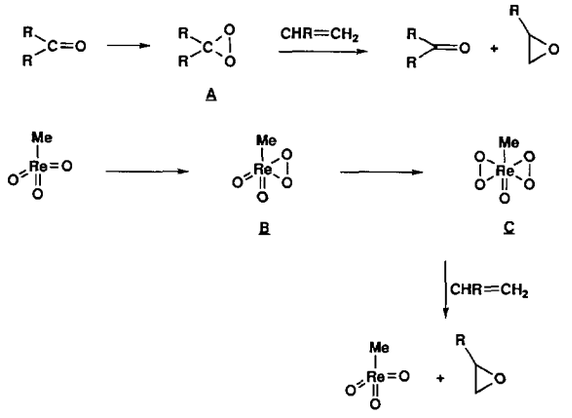
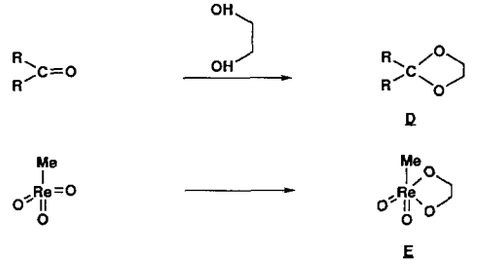


Scheme 1.



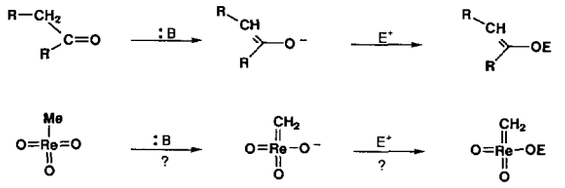
Scheme 2.

Attempts were thus undertaken to deprotonate MTO by strong bases such as NaH, KH, LDA and further to alkylate the hypothetical enolate. However, only the decomposition of the starting MTO was observed. [1]

Similarly, the analogs of enol ethers or enol esters did not form upon use of classical reaction conditions that convert ketones into such derivatives (methylorthoformate, acid anhydrides, etc.).

We finally decided to use as deprotonation/alkylation agent, a series of nitrogen ylides of the general structure $PhC(O)CH^{-}N^{+}R_1R_2R_3$ which are easily protonated and which can be considered as alkylating agents, since one alkyl group on nitrogen can be transferred, upon thermolysis, to the adjacent carbon atom [13]. Thus, they might deprotonate the methyl group of MTO and deliver an alkyl group from nitrogen either to oxygen or to carbon. This was, however, not the case (Scheme 4). Thus, addition of a solution of the ylide **2a** in CH_2Cl_2, to a solution of MTO in the same solvent, at 0°C, led to a fast reaction. A deep purple solution developed after a few minutes. After a further 8 h of reaction, at room temperature, the solution had turned pale yellow.

According to TLC, all MTO had reacted and a new less polar complex had formed. Evaporation of the solvent followed by silica gel chromatography of the



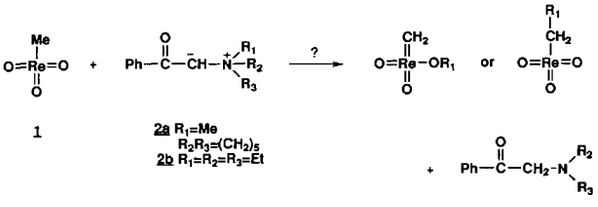
Scheme 3.

residue allowed the separation of the reaction mixture into a fast-moving, yellow complex, the physical properties and spectroscopic data of which were in full agreement with those of the known Re(VI) dinuclear complex $Me_4Re_2O_4$ **3** [14]. The ^1H NMR spectrum disclosed a signal at 2.8 ppm as a singlet, whereas the ^{13}C NMR spectrum confirmed the presence of a methyl group with a signal at 30.57 ppm, which appeared as a quartet in the off-resonance mode. To ascertain the structure of this complex, an X-ray analysis was carried out confirming the reduction–rearrangement of MTO into the dinuclear complex **3**.

A second very polar compound **4a** could also be isolated, as white crystals, m.p. 125°C. Its ^1H NMR spectrum confirmed the presence of an organic moiety, the structure of which agreed with the protonated form of the starting ylide: signals in the ^1H NMR spectrum at δ 8.15 (d, 2H), 7.80 (t, 1H), and 7.63 (t, 2H) for the five aromatic protons, at δ 5.48 (s, 2H) for the NCH_2CO methylene group, at δ 4.03 and 3.92 for the two NCH_2 group at δ 3.64 for the N–Me group and at δ 2.15 and 1.83 for the remaining six protons of the six-membered ring agreed with this hypothesis.

To establish the nature of the anion associated with the ammonium group, crystals suitable for an X-ray analysis were grown from CH_2Cl_2/MeOH. The ORTEP projection of complex **4a** is shown in Fig. 1: it confirms the presence of the ammonium group associated with the perrhenate ReO_4^- group. Surprisingly, the same complex could be isolated in high yield upon treatment of dirhenium heptoxide with the ylide *2a*, in CH_2Cl_2.

That the extra methyl groups of the tetramethylated dinuclear complex **3** did not originate from the NMe group of ylide **2a** was confirmed by the following experiment: when a similar reaction was carried out between MTO and the ylide **2b** ($R_1 = R_2 = R_3 = Et$) thus lacking methyl groups on nitrogen, the same dinuclear complex **3** together with the corresponding ammo-



Scheme 4.

[1] Unpublished results from this laboratory.

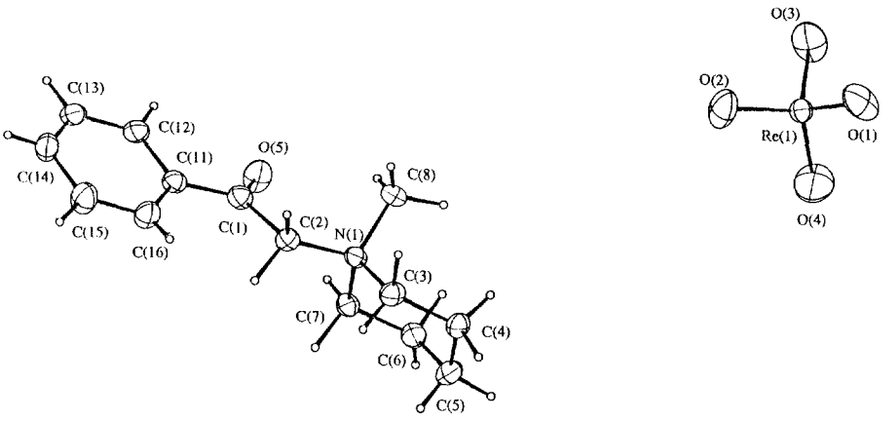


Fig. 1. Perspective view and numbering scheme for complex **4**.

nium perrhenate **4b** could be isolated. The ^{1}H NMR spectrum of this complex showed again the presence of the protonated form of the starting *N*-ylide **2b**, with a signal for the NCH_2CO methylene group at δ 5.29 ppm.

3. Discussion

The dinuclear complex $Me_4Re_2O_4$ can be prepared either from Re_2O_7 or from MTO by using as alkylating agents either $ZnMe_2$ or $CH_3Ti(OiPr)_3$ [14]. The interaction of Re_2O_7 with $ZnEt_2$ is known to lead to $Et_4Re_2O_4$. Thus, it clearly appears that ZnR_2 transfers its alkyl groups during the interaction with Re_2O_7. The transfer of a methyl group from $ZnMe_2$ to MTO to give the dinuclear complex **3** seems to be logical since $ZnEt_2$ reacts with MTO to give, by the transfer of two ethyl groups, the mixed dinuclear complex $Me_2Et_2Re_2O_4$ [15]. The formation of the dinuclear complex **3** have also been observed during the interaction of MTO with H_2O, yet in very small amounts, under non-alkylating conditions [10]. Since methyl radicals could be detected during the polymerization of MTO, it is likely that the formation of complex **3**, bearing two extra methyl groups with respect to MTO, might be due to a similar methyl radical transfer reaction followed or preceded by an oxido–reduction reaction. Although no oxidation products of the ylides such as, for example, phenylglyoxal could be detected (phenylglyoxal itself reacts with MTO) during this reaction, it is obvious that the reducing agents in these transformations are the *N*-ylides.

The role of water during these oligomerization/polymerization reactions of MTO is crucial. The following observation is striking in this respect: the *N*-ylides which were used to carry out the dimerization reactions are known for being very hygroscopic but could nevertheless be obtained free of water by heating under vacuum. Whereas the reaction carried out with anhydrous reagents only gave low yields of the dinuclear complex, we found that the yield of the reaction could be considerably increased by the use of their hydrated form. Moreover, the transformation of dirhenium heptoxide into ammonium perrhenate **4a,b** can only be explained by the presence of water in the starting *N*-ylides. It thus appears difficult to establish the exact stoichiometry of the reaction and the yield of the dinuclear complex: if one assumes that the ylide deoxygenates MTO, and since MTO reacts with phenylglyoxal, a reasonable product of this deoxygenation reaction, then six moles of MTO are required together with four moles of ylide and two moles of water to generate one mole of complex **3**.

4. Conclusion

Although no evidence for the formation of carbene complexes from MTO could be provided, its transformation into the dinuclear complex **3** with migration of methyl groups constitutes a surprising and interesting observation, and seems to be directly related to the oligomerization/polymerization reactions of MTO in aqueous medium.

5. Experimental

5.1. General methods

^{1}H NMR and ^{13}C NMR spectra were recorded on a AC 200 or ARX 400 Bruker spectrometer. IR spectra were recorded on a Perkin-Elmer 1420 spectrophotometer. Mass spectra were recorded on a ZAB HSQ (Fisons) instrument. Column chromatography was performed with Merck silica gel (70–230 mesh) using various ratios of ethyl acetate/light petroleum ether or dichloromethane/light petroleum ether as eluent. All reagents were obtained from commercial suppliers and used as received. Reactions were performed under an

argon atmosphere in carefully dried glassware. Benzene, tetrahydrofuran (THF), and diethyl ether were distilled from sodium/benzophenone ketyl under a nitrogen atmosphere. Dichloromethane (CH_2Cl_2) and acetonitrile were distilled from phosphorous pentoxide under a nitrogen atmosphere.

5.2. Synthesis of MTO

MTO was obtained from Re_2O_7 according to the method of reference [3]. A modification was introduced for its purification. Thus, simple silica gel chromatography of the residue of the reaction between Re_2O_7, $SnMe_4$ and perfluoroglutaric anhydride, gave, first with CH_2Cl_2, MTO (> 70%) and with ethylacetate, the stannyl ester.

The *N*-ylides were synthesized according to the literature [13] from the corresponding ammonium bromides.$PhC(O)CH_2N(Et)_3Br$: ^1H NMR (200 MHz, $CDCl_3$) δ 8.35 (m, 2H, Ar), 7.60 (m, 1H, Ar), 7.55 (m, 2H, Ar), 5.53 (s, 2H, NCH_2CO), 3.85 (q, 6H, $3CH_2$), 1.40 (t, 9H, $3CH_3$).$PhC(O)CHN(Et)_3$: ^1H NMR (200 MHz, $CDCl_3$) δ 7.65 (m, 2H, Ar), 7.13 (m, 3H, Ar), 5.15 (s, 0.7H, NCHCO), 4.50 (s, 0.3H, NCHCO), 3.49 (q, 6H, $3NCH_2$), 1.09 (t, 9H, $3CH_3$).$PhC(O)CHN(CH_2)_5(CH_3)Br$: ^1H NMR (200 MHz, $CDCl_3$) δ 8.07 (m, 2H, Ar), 7.52 (m, 1H, Ar), 7.40 (m, 2H, Ar), 5.60 (s, 2H, NCH_2CO), 4.19 (m, 2H, NCH_2), 3.51 (s, 3H, NCH_3), 2.93 (m, 2H, NCH_2), 1.77 (m, 6H, $3CH_2$).$PhC(O)CHN(CH_2)_5(CH_3)$: ^1H NMR (200 MHz, $CDCl_3$) δ 7.64 (m, 2H, Ar), 7.23 (m, 3H, Ar), 5.06 (s, 1H, NCHCO), 4.28 (m, 2H, NCH_2), 3.45 (s, 3H, NCH_3), 2.93 (m, 2H, NCH_2), 2.01 (m, 2H), 1.71–1.40 (m, 4H, $2CH_2$).

Table 1
Crystal data for $(C_{14}H_{20}ON)(ReO_2)$ **4**

Fw	468.5
a (Å)	8.725(3)
b (Å)	9.426(2)
c (Å)	10.532(3)
α (°)	86.30(3)
β (°)	81.35(4)
γ (°)	66.59(3)
V (Å^3)	785.8
Z	2
Crystal system	Triclinic
Space group	$P\bar{1}$
Linear absorption coefficient μ (cm^{-1})	78.5
Density ρ (g cm^{-3})	1.98
Diffractometer	Philips PW1100
Radiation	Mo–K α (λ = 0.71069 Å)
Scan type	$\omega/2\theta$
Scan range (°)	$1.20 + 0.345 \tan\theta$
θ Limits (°)	2–28.5
Temperature of measurement	Room temperature
Octants collected	h −11, 11; k −12, 12; l 0, 14
No. of data collected	4200
No. of unique data collected	3989
No. of unique data used for refinement	3539 (F_o)^2 > 3σ(F_o)^2
R(int)	0.029
$R = \Sigma\|\|F_o\| - \|F_c\|\|/\Sigma\|F_o\|$	0.037
$R_w = \Sigma w(\|F_o\| - \|F_c\|)^2/\Sigma wF_o^2$	0.042 w = 1.0
Absorption correction	DIFABS (min = 0.76, max = 1.43)
Extinction parameter ($\times 10^{-6}$)	143
Goodness of fit s	0.85
No. of variables	252
$\Delta\rho_{min}$ (e Å^{-3})	−1.98
$\Delta\rho_{max}$ (e Å^{-3})	1.53

Table 2
Interatomic distances (Å) for $(C_{14}H_{20}ON)(ReO_4)$ **4**

Re(1)–O(1)	1.716(6)
Re(1)–O(3)	1.724(6)
O(5)–C(1)	1.226(9)
N(1)–C(3)	1.529(9)
N(1)–C(8)	1.499(9)
C(1)–C(11)	1.47(1)
C(4)–C(5)	1.51(1)
C(6)–C(7)	1.51(1)
C(11)–C(16)	1.39(1)
C(13)–C(14)	1.38(1)
C(15)–C(16)	1.39(1)
Re(1)–O(2)	1.696(6)
Re(1)–O(4)	1.691(8)
N(1)–C(2)	1.513(8)
N(1)–C(7)	1.521(9)
C(1)–C(2)	1.521(9)
C(3)–C(4)	1.52(1)
C(5)–C(6)	1.53(1)
C(11)–C(12)	1.397(9)
C(12)–C(13)	1.38(1)
C(14)–C(15)	1.39(1)

5.3. Reaction of MTO with $PhC(O)CH^-N^+(CH_2)_5(CH_3)$ **2a**

MTO (0.5 g, 2 mmol) in CH_2Cl_2 (10 ml) was added to the *N*-ylide **2a** (0.43 g, 2 mmol) in CH_2Cl_2 (10 ml), at room temperature. After stirring for 12 h, the solvent was evaporated under vacuum, and the residue chromatographed on silica gel. Elution with petroleum ether/ethyl acetate (93/7) gave complex **3** as a yellow powder (0.180 g, 72%) which was recrystallized from pentane: CH_2Cl_2 to give yellow crystals ; m.p. 120°C (litt. m.p. 120°C). ^1H NMR (200 MHz, $CDCl_3$) δ 2.81 (s) ppm. ^{13}C NMR (50 MHz, $CDCl_3$) δ 30.57 ppm. MS Found: 498 (M^+), 249 (base peak, 1/2 M^+). Elution with MeOH gave the perrhenate $PhC(O)CH_2N^+(CH_3)(CH_2)_5ReO_4^-$ **4a** (0.4 g) as white crystals which were recrystallized from methanol/CH_2Cl_2 ; m.p. 125°C. ^1H NMR (400 MHz, $(CD_3)_2CO$) δ 8.15 (d, 2H, Ar), 7.80 (t, 1H, Ar), 7.63 (t, 2H, Ar), 5.48 (s, 2H, NCH_2CO), 4.03 (m, 2H, NCH_2),

Table 3
Bond angles (°) for $(C_{14}H_{20}ON)(ReO_4)$ **4**

O(1)–Re(1)–O(2)	110.5(4)
O(2)–Re(1)–O(3)	108.1(4)
O(2)–Re(1)–O(4)	110.5(5)
C(2)–N(1)–C(3)	104.8(5)
C(3)–N(1)–C(7)	109.6(5)
C(3)–N(1)–C(8)	110.1(6)
O(5)–C(1)–C(2)	121.9(7)
C(2)–C(1)–C(11)	116.1(6)
N(1)–C(3)–C(4)	113.4(6)
C(4)–C(5)–C(6)	110.5(6)
N(1)–C(7)–C(6)	111.7(5)
C(1)–C(11)–C(16)	124.2(6)
C(11)–C(12)–C(13)	121.3(7)
C(13)–C(14)–C(15)	119.6(8)
C(11)–C(16)–C(15)	121.3(8)
O(1)–Re(1)–O(3)	106.3(4)
O(1)–Re(1)–O(4)	108.8(5)
O(3)–Re(1)–O(4)	112.5(5)
C(2)–N(1)–C(7)	109.6(5)
C(2)–N(1)–C(8)	111.7(5)
C(7)–N(1)–C(8)	111.0(6)
O(5)–C(1)–C(11)	122.0(6)
N(1)–C(2)–C(1)	117.6(5)
C(3)–C(4)–C(5)	111.1(6)
C(5)–C(6)–C(7)	111.9(6)
C(1)–C(11)–C(12)	118.0(7)
C(12)–C(11)–C(16)	117.8(7)
C(12)–C(13)–C(14)	120.2(7)
C(14)–C(15)–C(16)	119.8(8)

3.92 (m, 2H, NCH_2), 3. 63 (s, 3H, NCH_3), 2.15 (m, 4H, $2CH_2$), 1.83 (m, 2H, CH_2). ^{13}C NMR (100 MHz, $(CD_3)_2CO$) δ 191.26 (CO), 135.22, 135.07, 129.37, 128.55 (Ar), 65.17 (NCH_2CO), 63.03 (NCH_2), 48.77 (NCH_3), 21.35 (CH_2), 20.20 ($2CH_2$). Anal. Found: C, 36.01; H, 4.30; N, 3.03. $C_{14}H_{20}NO_5Me$ Calc.: C, 35.90; H, 4.21; N, 2.99.

Under the same conditions, a second experiment with MTO (1.03 mmol) and the same *N*-ylide gave complex **3** (0.128 g, 66%).

5.4. Reaction of MTO with $PhC(O)CH^-N^+(Et)_3$

Under the same conditions as above, the *N*-ylide **2b** gave complex **3** in 30% yield together with the perrhenate **4b** (40% yield) as white crystals, m.p. 133°C. ^1H NMR (200 MHz, $CDCl_3$) δ 8.08 (m, 2H, Ar), 7.45 (t, 1H, Ar), 7.15 (t, 2H, Ar), 5.29 (s, 2H, NCH_2CO), 3.89 (q, 6H, NCH_2), 1.44 (t, 9H, NCH_2CH_3).

6. X-ray study of complex 4a

Intensity data were collected at room temperature on a Philips PW 1100 diffractometer using Mo–K α radiation. Accurate cell dimensions and orientation matrix were obtained from least-squares refinement of the setting angles of 25 well-defined reflections. No decay in the intensities of two standard reflections was observed during the course of data collection. Complete crystal data, collection parameters and other significant details are listed in Tables 1–3. The usual corrections for Lorentz and polarization effects were applied. Computations were performed by using the PC version of CRYSTALS [14]. Scattering factors and corrections for anomalous dispersion were taken from Ref. [15]. The structure was resolved by standard Patterson-Fourier techniques and refined by least-squares with anisotropic thermal parameters for all non-hydrogen atoms. Hydrogen atoms were located on a Fourier difference map, and their coordinates were refined with an overall refinable isotropic thermal parameter. The structure was refined to $R = 0.037$ with the use of 3539 reflections for 252 least-squares parameters.

Complex **3** was well characterized by its cristallographic cell : monoclinic, $a = 9.200(2)$ Å, $b = 8{,}531(2)$ Å, $c = 6{,}021(2)$ Å, $\beta = 95{,}10(3)$ Å.

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