Reductive Aggregation of an Organorhenium Oxide: an Unusual Metal Chain Structure

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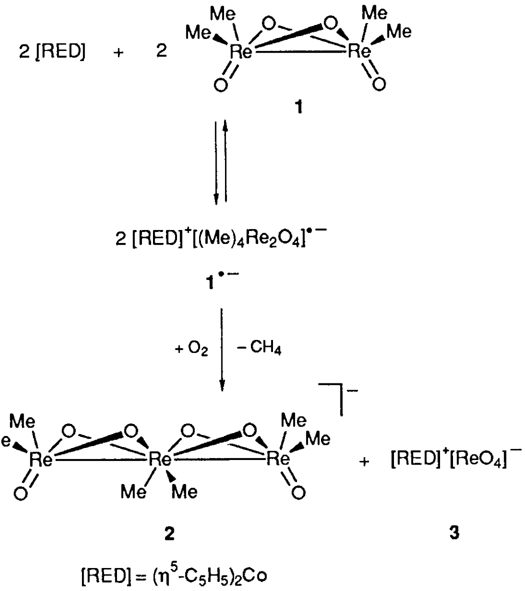
Electrochemical reduction of the dinuclear d^1–d^1 organorhenium oxide $Me_4Re_2O_4$ **1** or chemical reduction by cobaltocene cleanly yields the radical anion $\mathbf{1}^{\cdot -}$ which, upon controlled exposure to oxygen, disproportionates into hydrocarbons and the novel trinuclear complex $[(C_5H_5)_2Co][(Me)_6Re_3O_6]$ **2**; this compound represents the first example of an acyclic organometallic oxide framework with metal–metal bonding.

The little explored class of organometallic oxides has the potential for use in homogeneous and heterogeneous catalysis, but the structure and reactivity[1–3] of these compounds needs further investigation. Systematic access to only a few well-characterised compounds is available, while the majority of known examples have resulted from serendipity. In the present communication, we draw attention to a reductive coupling process which could prove a general route to organometallic oxides having extended structures, *e.g.* chains, rings or cluster frameworks.

The rhenium(VI) complex $Me_4Re_2O_4$ **1**, most conveniently accessible from dirhenium heptaoxide and dimethylzinc or methyltris(isopropoxy)titanium,[4] undergoes reversible electrochemical reduction to a monoanion $\mathbf{1}^{\cdot -}$ at $E_{1/2} = -0.64$ V



Scheme 1

(*vs.* Ag/AgCl; MeCN, 28 °C).[†] Oxidation is not possible at reasonable potentials. At −2.0 V the radical anion is further reduced in an irreversible wave.[‡] When cobaltocene, $(\eta^5\text{-}C_5H_5)_2Co$, ($E_{1/2}$ = −0.82 V *vs.* Ag/AgCl in MeCN) is used as a chemical reducing agent, it is possible to obtain *selectively* and *quantitatively* the product of the first reduction wave, the green radical anion $\mathbf{1}^{\bullet-}$. This extraordinarily air-sensitive compound shows an ESR spectrum consistent with a dinuclear radical complex. However, the material is so sensitive that full analytical characterisation was not possible. Oxidation of $\mathbf{1}^{\bullet-}$ with ferricinium hexafluorophosphate, $[(\eta^5\text{-}C_5H_5)_2Fe]^+$-$[PF_6]^-$ gives **1** in quantitative yield. Using oxygen to oxidize the radical anion $\mathbf{1}^{-\bullet}$ [average oxidation number (ON) +5½], no starting compound **1** (ON +6) is formed at all. The solution of $\mathbf{1}^{\bullet-}$ changes colour to red with concomitant formation of an unprecedented compound **2**, when a stoichiometric amount of oxygen is added (Scheme 1).[§] Disproportionation occurs with formation of the trinuclear complex **2** (ON +5⅔) and the perrhenate **3** (ON +7) with concomitant elimination of methane, ethane and traces of ethylene. Compound **2** is obtained in high yield (86%) and is in solution air-sensitive but water-stable. The ionic character results from conductivity data (Λ = 172 S mol^{-1} cm^2; MeCN, 3 × 10^{-4} mol l^{-1}, 20 °C) and from an X-ray crystal structure determination.[¶] A cobalticinium cation acts as counterion to the trinuclear anion $[Me_6Re_3O_6]^-$ which, in contrast to the isoelectronic[||] cation $[(\eta^5\text{-}C_5Me_5)_3Re_3O_6]^{2+}$,[5][¶][**] does not have a cyclic metal core but a strictly linear sequence of three rhenium atoms. Metal–metal bonds are clearly present as proven by both the short distances (*ca.* 265 pm) and the small Re–O–Re′ angles (*ca.* 86°). The sets of metal atoms are additionally linked by two bent oxo bridges each. The central metal is surrounded by four oxygen and two methyl groups. While the coordination geometry of the outer metal atoms Re(1) and Re(3) is square-pyramidal, as in the precursor complex **1**,[4a] the inner atom has a trigonal-prismatic ligand arrangement (Fig. 1). All terminal and bridging Re–O– and the Re–Me bond lengths are unexceptional.

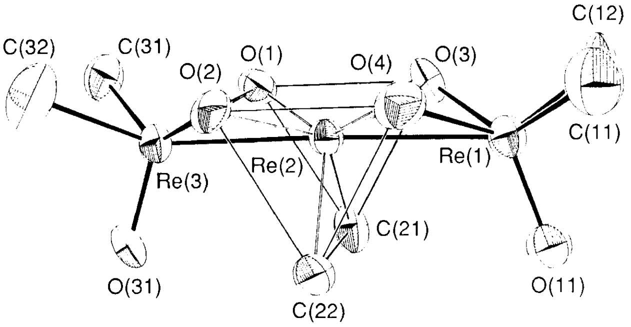


Fig. 1 Crystal and molecular structure (ORTEP representation) of the anion $[Me_6Re_3O_6]^-$ in compound **2**. Thermal ellipsoids are drawn at the 50% probability level. Hydrogen atoms are omitted for clarity. Selected bond lengths (pm) and angles (°): Re(1)–Re(2) 264.70(6), Re(1)–C(11) 207(1), Re(1)–C(12) 213(1), Re(1)–O(11) 167.6(6), Re(1)–O(3) 192.6(6), Re(1)–O(4) 193.2(6), Re(2)–C(21) 217.6(9), Re(2)–C(22) 216.2(8), Re(2)–O(3) 195.2(6); Re(1)–Re(2)–Re(3) 177.83(2), Re(1)–O(3)–Re(2) 86.1(2), C(11)–Re(1)–C(12) 83.0(4), C(21)–Re(2)–C(22) 75.2(4).

[†] Ferrocene has a potential of $E_{\frac{1}{2}}$ = +0.54 V under the same conditions.

[‡] *For comparison:* $[Me_3CCH_2]_4Re_2O_4$ is reduced at $E^1_{\frac{1}{2}}$ = −0.64 V *vs.* standard calomel electrode (SCE) in MeCN, $E^2_{\frac{1}{2}}$ is not given. Only the mononuclear anion $[\{Me_3CCH_2\}_2ReO_2]^-$ is obtained by use of Na/Hg and was isolated as the sodium salt, *cf.* S. Cai, D. Hoffmann, J. C. Huffman, D. A. Wierda and H.-G. Woo, *Inorg. Chem.*, 1987, **26**, 3693.

[§] *Procedure:* To a solution of **1** (200 mg, 0.40 mmol) in n-pentane (10 ml), at ambient temperature a solution of 75 mg $(\eta^5\text{-}C_5H_5)_2Co$ in n-pentane (10 ml) was added. The green ionic product $[(\eta^5\text{-}C_5H_5)_2Co]^+[(Me)_4Re_2O_4]^-$ precipitated immediately. After stirring for another 30 min it was washed twice with diethyl ether (5 ml each) and dried *in vacuo* (10^{-3} bar). The isolated yield was 240 mg (88%): IR (KBr, νRe=O): 974, 954 cm^{-1}. *g*-Value 1.81 (THF, 4 K). Upon addition of 20 ml of air to a green solution of 120 mg (0.18 mmol) of $\mathbf{1}^{\bullet-}$ in thf, this solution turned red (further addition of air led to the formation of **1** and **3**). The solvent was evaporated off and the residue washed with diethyl ether and extracted with small portions of tetrahydrofuran (thf) until the solution was only pale-red. From the thf washings, compound **2** (105 mg, 0.13 mmol) was precipitated with n-pentane. The residue contained 15 mg (0.034 mmol) of $[(\eta^5\text{-}C_5H_5)_2Co]^+[ReO_4]^-$ **3**. Data for **2**: ^{1}H NMR ([^{2}H$_8$]thf): δ 6.00 (s, 10H), 1.97 (s, 12H) and 1.81 (s, 6H); IR (KBr, νRe=O): 998 and 910 cm^{-1}; FDMS: *m/z* 691/689/687 and 251/249; cyclic voltammetry (MeCN, 0.1 mol dm^{-3} Bu$^n_4$NPF$_6$): *E*/V −1.91 (quasi-reversible, one-electron), −0.82 (reversible, $[(\eta^5\text{-}C_5H_5)_2Co]^{+/0}$), −0.62 V (quasi-reversible, $\mathbf{1}^{0/-}$ from decomposition of **2**), and +0.94 (irreversible).

[¶] *Crystal data* for $C_{16}H_{28}O_6Re_3Co$: *M* = 933.9, monoclinic, space group $P2_1/n$ (No. 14); lattice constants least squares-refined from 25 reflections at high diffraction angles: *a* = 933.8(3), *b* = 1174.0(1), *c* = 2020.3(4) pm, β = 91.38(1)°; *V* = 2214 × 10^6 pm^3; *Z* = 4; *F*(000) = 1696; D_c = 2.801 g cm^{-3}; Enraf-Nonius CAD-4, Mo-Kα irradiation (λ = 71.073 pm), graphite mono-chromator; *T* = 23 ± 1 °C; scan range 1.0° < θ < 25.0°; ω-scan; scan width (1.20 + 0.30tanΘ)° ± 25% before and after each reflection for zero-line correction; *t*(max) = 90 s; 3772 recorded reflections (±11, +13, +24), 3002 unique reflections of which 2999 were used for refinement (3 reflections because of insufficient absorption correction discarded): 225 parameters full-matrix least-squares-refined, all non-hydrogen atoms anisotropically except O(11) and C(52) which were refined isotropically because of inaccuracy of empirical absorption correction. *R* = 0.051; R_w = 0.035; GOF = 2.525. The structure was solved by the Patterson method and refined by difference-Fourier techniques; the empirical absorption correction, μ = 173.4 cm^{-1}; transmission factors 0.133–1.000. Extinction was not corrected. Hydrogen positions were calculated for an ideal geometry [*d*(CH) = 95 pm] but not refined. Anomalous dispersion was considered. Shift/err: <0.001 in the last cycle. Residual electron density: +2.17 e Å^{-3} 1.3 Å from Re(3), −1.83 e Å^{-3} 1.0 Å from Re(1). Further details of the crystal structure determination can be obtained from the Fachinformationszentrum Karlsruhe, Gesellschaft für wissenschaftlich-technische Information mbH, D-7514 Eggenstein-Leopoldshafen 2 (Germany), by quoting the depository number CSD 54901, the name of the authors and the journal citation. Atomic coordinates, bond lengths, bond angles and thermal parameters have also been deposited at the Cambridge Crystallographic Centre. See Notice to Authors, Issue No. 1.

[||] Me and C_5Me_5 counted as mono-anionic ligands.

[**] Synthesis of $[(\eta^5\text{-}C_5Me_5)_3Re_3O_6][BF_4]_2$ in quantitative yields from $(\eta^5\text{-}C_5Me_5)_2Re_2O_4$ and Ag[BF$_4$] is somewhat reminiscent of the reaction shown in Scheme 1: W. A. Herrmann and U. Küsthardt, unpublished results 1986/87; results reported in the Ph.D. thesis of U. Küsthardt, p. 52, Technische Universität München 1986.

In both $[Me_6Re_3O_6]^-$ and $[(\eta^5\text{-}C_5Me_5)_3Re_3O_6]^{2+}$ the metals are in the formal oxidation state $+5\frac{2}{3}$. In the dication the π-donating aromatic ligands counteract the charge deficiency at the Re_3 core structure while in the monoanion no such ligands are required. From a formal point of view, **2** represents a chain-extended derivative of the precursor compound **1**, induced by a net reductive step. During the formation of **2**, the stereochemistry changes from a *cis*-geometry **1** to a *trans*-disposition of the $ReMe_2$ moieties.

Related tri- and higher-nuclear complexes have recently been reported by Bottomley *et al.*, *e.g.*, $(\eta^5\text{-}C_5Me_5)_3V_3O_6$ and $(\eta^5\text{-}C_5H_5)_5V_6O_9$;[6] they all exhibit cyclic structures. Compound **2** is the first example of a linear chain-type oligomeric organometallic oxide. Reactivity studies, *e.g.*, alkylation, to find out the prerequisites of cyclizations are under investigation.

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