

Towards Carbohydrate Derivatives of the $\text{Re}^{\text{I}}(\text{CO})_3$ Fragment**Matthias Hinrichs, Florian R. Hofbauer, and Peter Klüfers*^[a]

Abstract: With the $[\text{Re}(\text{CO})_3\text{Br}_3]^{2-}$ ion as a precursor for the $\text{Re}^{\text{I}}(\text{CO})_3$ fragment, the diols (1*R*,2*R*)-cyclohexane-1,2-diol [(1*R*,2*R*)-Chxd], anhydroerythritol (AnEryt), and (1*S*,2*S*)-cyclopentane-1,2-diol [(1*S*,2*S*)-Cptd] form dinuclear monoanions in the salts $(\text{NBU}_4)[\text{Re}_2(\text{CO})_6\{\mu-(1*R*,2*R*)\text{-ChxdH}_{-1}\}_3]$ (**1**), $[\text{K}([18]\text{crown-6})][\text{Re}_2(\text{CO})_6(\mu\text{-OMe})_2(\mu\text{-AnErytH}_{-1})]$ (**2**) and $(\text{NBU}_4)[\text{Re}_2(\text{CO})_6\{\mu-(1*S*,2*S*)\text{-CptdH}_{-1}\}_3]$ (**3**). The monoanionic diolato ligands in these triply bridged dirhenates(*i*) are

monodentate. Bridging triolato ligation in the trirhenates(*i*) is supported by the anions of glycerol (Glyc) and methyl β -D-ribose (Me- β -D-Ribp), the latter binding in its ${}^1\text{C}_4$ conformation, in $(\text{DBUH})_2[\text{Re}_3(\text{CO})_9(\mu_3\text{-O})(\mu_3\text{-GlycH}_{-3})] \cdot 0.5 \text{ MeCN}$ (**4a**), $(\text{NET}_4)[\text{Re}_3(\text{CO})_9(\mu_3\text{-OMe})(\mu_3\text{-GlycH}_{-3})]$ (**4b**)

and $(\text{DBUH})[\text{Re}_3(\text{CO})_9(\mu_3\text{-OMe})(\mu_3\text{-}^1\text{C}_4\text{-Me-}\beta\text{-D-Ribp}_{2,3,4}\text{H}_{-3})]$ (**5**). The chiral sugar alcohols L-threitol (L-Thre) and D-arabitol (D-Arab) act as tetra- and pentadentate ligands, respectively, in $(\text{NET}_4)[\text{Re}_2(\text{CO})_6(\text{L-ThreH}_{-3})] \cdot \text{MeCN}$ (**6**) and $(\text{NET}_4)_2(\text{DBUH})_2[\text{Re}_6(\text{CO})_{18}(\text{D-ArabH}_{-5})_2]$ (**7**). Complexes **6** and **7** are free of supporting oxo or methoxo ligands and use solely the O-atom pattern of the polyol for the connection of the $\text{Re}^{\text{I}}(\text{CO})_3$ moieties.

Keywords: bioinorganic chemistry • carbohydrates • carbonyl ligands • polyols • rhenium

Introduction

The *fac*-configured $\text{Re}^{\text{I}}(\text{CO})_3$ fragment is particularly suited to bind to a variety of ligands including biomolecules and mimics thereof and is thus a prominent building block in that area of rhenium chemistry devoted to the preparation of tumour diagnostics and therapeutics.^[1] Hydrolytic stability of the $\text{Re}^{\text{I}}(\text{CO})_3$ -biomolecule links appears to be a prerequisite in this field of interest. Among biomolecules, both amino acids and their oligomers appear to be reliably binding chelators, and nucleobase coordination has also been investigated.^[2] Direct carbohydrate ligation to the $\text{Re}^{\text{I}}(\text{CO})_3$ centre has not been reported,^[3] though these polyols are generally powerful chelators of metal centres sufficiently Lewis acidic to stabilise the deprotonated forms of a carbohydrate. Carbohydrate complexes of high thermodynamic stability are thus expected, perhaps even in neutral aqueous

solution, if the ligand provides an O-atom pattern so suitable that its deprotonated state is supported by the corresponding metal-atom assembly. This work is a first attempt to unravel the rules of carbohydrate- $\text{Re}^{\text{I}}(\text{CO})_3$ binding, to clarify whether there are such well suited central metal/O-atom pattern combinations in the carbohydrate- $\text{Re}^{\text{I}}(\text{CO})_3$ area.

Both the bioinorganic orientation of this work and the solution behaviour of the more complex carbohydrates place the focus of this research on aqueous environments. The aqueous chemistry of the $\text{Re}^{\text{I}}(\text{CO})_3$ fragment may be derived from the mononuclear aqua complex $[\text{Re}^{\text{I}}(\text{CO})_3(\text{H}_2\text{O})_3]^+$, which is the main species at pH values of about five or less in the absence of strong ligands.^[4] At higher pH values, deprotonation produces hydroxo ligands, which, as a result of their pronounced tendency to act as μ_2 and μ_3 bridging ligands, give rise to the formation of oxorhenium clusters. The main species of aqueous solutions are thus $[\text{Re}_3(\text{CO})_9(\mu_3\text{-OH})(\mu\text{-OH})_3]^-$ in about neutral solution, and $[\text{Re}_2(\text{CO})_6(\mu\text{-OH})_3]^-$ at higher pH values,^[4] and analogous species are predominant in methanol as solvent. The binuclear $[\text{Re}_2(\text{CO})_6(\mu\text{-OMe})_3]^-$ has thus been used as a precursor for the preparation of related compounds including alkoxides other than methoxide.^[5] The formation tendency of the $[\text{Re}_2(\text{CO})_6(\mu\text{-OR})_3]^-$ motif is underlined by the finding that ethane-1,2-diol does not act as a bidentate ligand towards a $\text{Re}^{\text{I}}(\text{CO})_3$ centre but forms a binuclear $(\mu_2\text{-alkoxo})_3$

[a] Dipl.-Chem. M. Hinrichs, F. R. Hofbauer, Prof. Dr. P. Klüfers
Department of Chemistry and Biochemistry of the Ludwig Maximilian University
Butenandtstrasse 5–13, 81377 Munich (Germany)
Fax: (+49) 89-2180-77407
E-mail: kluef@cup.uni-muenchen.de

[**] Polyol Metal Complexes, Part 52; for Part 51 see: X. Kästele, P. Klüfers, F. Kopp, J. Schuhmacher, M. Vogt, *Chem. Eur. J.* **2005**, *11*, 6326–6346.

bridged compound, leaving one hydroxy function of each $\text{HOCH}_2\text{CH}_2\text{O}^-$ ligand un-coordinated.^[5b] This finding illustrates the main problem to be solved: μ -hydroxo and μ -alkoxo ligands are difficult to displace from the bridged $\text{Re}^{\text{I}}(\text{CO})_3$ cores in favour of a chelator. The question is thus focussed on whether or not carbohydrate-based diol, triol or higher polyol bonding patterns are able to force chelation of $\text{Re}^{\text{I}}(\text{CO})_3$ centres rather than simply reacting as monovalent alkoxides.

In this first approach, we thus investigated the coordination of sterically restricted diols such as cyclopentane- and cyclohexanediol to the rhenium fragment. Subsequently, ligands closely resembling the carbohydrates or truly belonging to the class of carbohydrates were used.

Results and Discussion

Carbohydrate-mimicking diols form the binuclear $[\text{Re}_2(\text{CO})_6(\mu\text{-OR})_3]^-$ motif: The diol moiety is the basic functional group that enables a carbohydrate to act as a chelate ligand. The steric requirements for the chelation of quite a large central metal such as rhenium(I) should be met by *cis*- and *trans*-pyranose diol functions and by *cis*-furanose functions, but not by *trans*-furanose diols, due to the unsuitably large O-C-C-O torsion angle in this case.^[6] In terms of furanose- and pyranose-mimicking diols, *cis*- and *trans*-cyclohexane-1,2-diol, *cis*-cyclopentane-1,2-diol and anhydroerythritol (*cis*-oxolane-3,4-diol), but not *trans*-cyclopentane-1,2-diol, would appear to be candidates for rhenium chelation.

A first attempt to synthesise a tricarbonylrhenium(I) chelate was made with the two isomers of cyclohexane-1,2-diol (Chxd). Because of the synthetic restrictions described above, acetonitrile was chosen as the solvent when $(\text{NBu}_4)[\text{Re}_2(\text{CO})_6(\mu\text{-OMe})_3]$ was treated with a threefold amount of diol. ^{13}C NMR spectra indicated not chelation, but the formation of the same $[\text{Re}_2(\text{CO})_6(\mu\text{-DioIH}_{-1})_3]^-$ ion that had been synthesised with the sterically unrestricted ethanediol by Klausmeyer and Beckles.^[5b] Attempts to substantiate this result by crystal-structure analysis revealed an obviously general methodological restriction for this class of compounds. If two $\text{Re}(\text{CO})_3$ fragments are bridged by three monodentate diolato ligands, one of the two hydroxy functions of each diol is left hanging. Which of the two oxygen atoms binds the rhenium centre and which leaves it unbound is arbitrary, and the result—unless a C_2 -symmetric diol is chosen—is heavy disorder of the crystalline packing. All attempts to prepare well ordered crystals of the *cis*-cyclohexanediol derivative thus failed, but crystals of $(\text{NBu}_4)[(\text{Re}_2(\text{CO})_6\{\mu\text{-(1R,2R)-ChxdH}_{-1}\}_3)]$ (**1**) of suitable quality, containing the *trans* isomer of the ligand, could be grown. Crystal-structure analysis (Figure 1) corresponded to the NMR spectroscopic results (Table 1; note the “coordination-induced shifts” (CISs), the typical downfield shifts of the signals of those carbon atoms that bear a metal-binding oxygen substituent). The three diolato ligands are monoanionic and monodentate and do not bind in a chelate-like fashion.

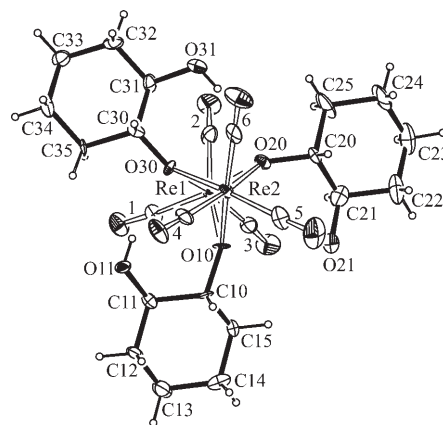


Figure 1. Structure of the $[\text{Re}_2(\text{CO})_6\{\mu\text{-(1R,2R)-ChxdH}_{-1}\}_3]^-$ ion in **1** (40 % probability ellipsoids; the number n at the carbonyl ligands should be read as C_n and O_n). Distances [Å] and angles [°]: Re1–O10 2.194(8), Re1–O20 2.142(9), Re1–O30 2.167(8), Re2–O10 2.140(9), Re2–O20 2.164(9), Re2–O30 2.147(8), mean Re–C_{CO} 1.906, mean C–O_{CO} 1.130; nonbonded Re–Re distance 3.163(1); donor–acceptor distances in intramolecular hydrogen bonds: O11...O30 3.004(14), O21...O10 2.986(16), O31...O20 3.151(15); mean Re–O–Re 94.2.

Table 1. ^{13}C NMR chemical shifts (in ppm) in CH_2Cl_2 solutions of: **1** (free (1R,2R)-Chxd: C1/2 74.8, C3/6 32.0, C4/5 23.4) and **3** (free (1S,2S)-Cptd: C1/2 78.6, C3/5 30.9, C4 19.3). Bold: $\Delta\delta$ values of carbon atoms bearing a rhenium-binding oxygen atom.

		C1	C2	C3	C4	C5	C6
1	δ	86.9	76.2	31.5	23.6	24.0	33.3
	$\Delta\delta$	12.1	1.4	–0.5	0.2	0.6	1.3
3	δ	90.1	79.7	29.8	18.2	32.3	
	$\Delta\delta$	11.5	1.1	–1.1	–1.1	1.4	

Generally, the dianion of anhydroerythritol (*cis*-oxolane-3,4-diol; AnEryt) is a much better chelating ligand than the cyclohexanediols towards a variety of central metals and in special cases has even been found to be a better ligand than a glucose itself. Some 20 metal and semimetal chelate complexes of anhydroerythritol are known.^[6] Usually a bidentate κ^2O,O' -AnErytH₂ ligand forms five-membered chelate rings in these compounds, the central atoms spanning a size range from silicon(IV) to lead(II). The unusual versatility of the AnErytH₂ ligand is the result of the variability of a furanoidic ligand's bite, AnEryt being the prototype of this kind of ligand. In terms of size, rhenium(I) centres appear well suited for chelation by a furanoidic diol. Treatment of AnEryt and base with $(\text{NEt}_4)_2[\text{Re}(\text{CO})_3\text{Br}_3]$ in methanol, however, yielded mixtures of hexacarbonyl-dirhenates(I) of the general formula $[\text{Re}_2(\text{CO})_6(\mu\text{-OMe})_{3-n}(\kappa O\text{-}\mu\text{-AnErytH}_{-1})_n]^-$ in terms of ^{13}C NMR spectra. In accordance with the apparent C_s -symmetry of AnEryt, attempts to crystallise any of the constituents of these mixtures were unsuccessful. Eventually, a few crystals of the $\text{K}([\text{18}]\text{crown-6})$ salt of the anion with $n = 1$ — $[\text{K}([\text{18}]\text{crown-6})][\text{Re}_2(\text{CO})_6(\mu\text{-OMe})_2(\kappa O\text{-}\mu\text{-AnErytH}_{-1})]^-$ (**2**)—were obtained from a low-conversion batch obtained with use of short reaction times and low temperatures. Structure analysis revealed the same

result as before, even for such a reliable chelator as AnEryt. Sharing the same bonding mode with the diols above, a single monodentate $\kappa\text{O}-\mu\text{-AnErytH}_{-1}$ ligand takes one of the three alkoxo positions in the usual hexacarbonyl-trialkoxo-dirhenate(i) anion, leaving the other two for methoxo groups (Figure 2).

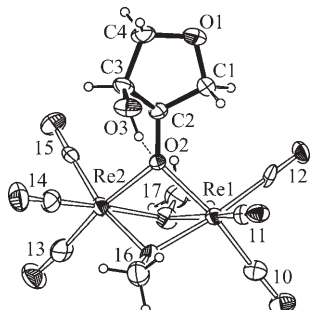


Figure 2. Structure of the $[\text{Re}_2(\text{CO})_6(\mu\text{-OMe})_2(\mu\text{-AnErytH}_{-1})]^-$ ion in **2** (30% probability ellipsoids; the number n at the carbonyl ligands should be read as C_n and O_n). Distances [Å] and angles [°]: Re1–O2 2.156(8), Re1–O16 2.101(8), Re1–O17 2.130(8), Re2–O2 2.174(8), Re2–O16 2.117(7), Re2–O17 2.105(9), mean Re–C_{CO} 1.894, mean C–O_{CO} 1.155; Re1–O2–Re2 92.1(3), Re1–O16–Re2 95.4(3), Re1–O17–Re2 94.8(3); non-bonded Re–Re distance: 3.118(2); intramolecular hydrogen bond O3–H...O2: O3–H 0.84, H...O2 2.21, O3...O2 2.691(13); O3–H...O2 116; diol torsion angle O2–C2–C3–O3 42.6(15).

Since no chelation at all was observed with carbohydrate-mimicking diols, no distinction needed to be made between the usually chelating members of this substance class and the furanoidic *trans*-diols, which usually give nonchelated reaction products.^[6] Thus, in the case of the $\text{Re}^{\text{I}}(\text{CO})_3$ moiety, *trans*-cyclopentane-1,2-diol resembled the other diols. Consistently with the rule of thumb regarding crystallisation, well ordered crystals of these C_2 -symmetric diols could be prepared. With *trans*-cyclopentane-1,2-diol, crystals of $(\text{NBu}_4)[\text{Re}_2(\text{CO})_6\{\mu\text{-}(1\text{S},2\text{S})\text{-CptdH}_{-1}\}_3]$ (**3**) showed the triply bridged pattern (Figure 3). The ^{13}C NMR data corresponded to the solid-state species (Table 1).

1,2,3-Triols support a truncated heterocubane assembly: The predominance of the $\kappa\text{O}-\mu$ -binding in the case of a diol may be associated with a mismatch of these potentially bidentate chelators and the *fac*-pattern of three coordination sites at the rhenium(i) central atom. Triols thus appear to be candidates promising a better match of binding sites. However, treatment of the parent triol, glycerol, with the Re precursor and base under various conditions did not result in NMR spectra of pure compounds in aprotic environments. Eventually, after checking the effect of hydrolytic conditions, a procedure including the addition of small amounts of water was developed. A small quantity of water (typically 0.03 mL per 2 mL of acetonitrile) greatly improved the ^{13}C NMR spectra of the reaction products. Application of this recipe to solutions of a 1:1:1.4 ratio of Re/Glyc/DBU (DBU = 1,8-diazabicyclo[5.4.0]undec-7-ene) resulted in spectra indicating two signals of unreacted glycerol and two signals of rhenium-bonded glycerol, the larger signal of the methylene-C atoms being downfield-shifted by almost 20 ppm (Table 2). Though this shift pattern was consistent with a mononuclear,

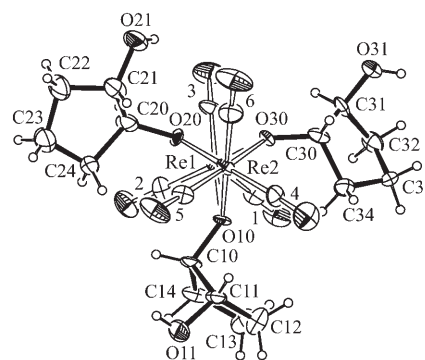


Figure 3. Structure of the $[\text{Re}_2(\text{CO})_6\{\mu\text{-}(1\text{S},2\text{S})\text{-CptdH}_{-1}\}_3]^-$ ion in **3** (30% probability ellipsoids; the number n at the carbonyl ligands should be read as C_n and O_n). Distances [Å] and angles [°]: Re1–O10 2.152(8), Re1–O20 2.102(8), Re1–O30 2.160(8), Re2–O10 2.143(8), Re2–O20 2.130(9), Re2–O30 2.131(8); mean Re–C_{CO} 1.867, mean C–O_{CO} 1.181; mean Re–O–Re 93.7°; nonbonded Re–Re distance: 3.117(1); donor-acceptor distances in intermolecular hydrogen bonds: O11...O11ⁱ 2.837(16), O21...O31ⁱⁱ 2.790(17), O31...O21ⁱⁱ 2.790(17). Symmetry codes: ⁱ: $-x, y, 1-z$; ⁱⁱ: $1-x, y, 1-z$.

nium-bonded glycerol, the larger signal of the methylene-C atoms being downfield-shifted by almost 20 ppm (Table 2). Though this shift pattern was consistent with a mononuclear,

Table 2. ^{13}C NMR chemical shifts (ppm) in acetonitrile solutions (free MeOH: 50.1) of: **4** (free Glyc: CH = 73.7, CH₂ = 64.1), the tentative trinuclear $[\text{Re}_3(\text{CO})_9(\mu_3\text{-OMe})(\text{L-Thre}1,2,3\text{H}_3)]$ complex (free Thre: CH = 72.9, CH₂ = 64.3), and **5** (free Me- β -D-Ribp: C1 = 102.9, C2 = 72.0, C3 = 70.4, C4 = 67.1, C5 = 64.3, O1–Me = 55.7). Bold: $\Delta\delta$ values of carbon atoms bearing a rhenium-binding oxygen atom.

		C1	C2	C3	C4	C5	O1-CH ₃	μ_3 -OCH ₃
4a	δ	82.7	76.9	82.7				
	$\Delta\delta$	18.6	3.2	18.6				
4b	δ	82.7	76.5	82.7				80.4
	$\Delta\delta$	18.6	2.8	18.6				30.3
$\kappa^3\text{O},\text{O}',\text{O}''\text{-Thre}$	δ	85.0	77.4	90.6	67.0			80.8
	$\Delta\delta$	20.7	4.5	17.7	2.7			30.7
5	δ	102.5	79.3	72.0	78.6	63.4	55.3	81.2
	$\Delta\delta$	-0.4	7.3	1.6	11.5	-0.9	-0.4	31.1

C_3 -symmetric $[\text{Re}(\text{CO})_3(\kappa^3\text{O},\text{O}',\text{O}''\text{-GlycH}_{-n})]^{1-n}$ species, the large amount of unreacted glycerol indicated a higher Re/Glyc molar ratio in the product. Finally, a ^{13}C NMR spectrum free of unreacted glycerol was obtained at a 3:1 Re/Glyc ratio, whilst the maximum yield of crystalline product was obtained at a 3:1:5 ratio of Re/Glyc/DBU. The result of the structure analysis is shown in Figure 4. In accordance with the NMR spectra, the complex dianion in $(\text{DBUH})_2\text{-}[\text{Re}_3(\text{CO})_9(\mu_3\text{-O})(\mu_3\text{-GlycH}_{-3})]\cdot 0.5\text{MeCN}$ (**4a**) has (noncrystallographic) C_3 symmetry, the mirror plane containing O2, C2, O4 and Re3. The glycerol ligand is trianionic and triply bridging as a whole, each O atom bridging two rhenium(i) centres. The need for the addition of water in the course of the preparation is obvious from the structure: a water-derived μ_3 -oxo ligand opposite the GlycH₋₃ ligand completes the trinuclear rhenate(i). The structure is closely related to

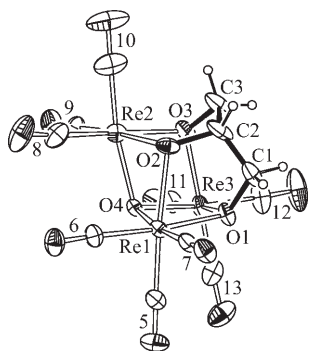


Figure 4. Structure of the $[\text{Re}_3(\text{CO})_9(\mu_3\text{-O})(\mu_3\text{-GlycH}_{-3})]^{2-}$ ion in **4a** (30% probability ellipsoids; the number n at the carbonyl ligands should be read as C_n and O_n). Distances [\AA] and angles [$^\circ$]: Re1–O1 2.130(5), Re1–O2 2.220(5), Re1–O4 2.117(4), Re2–O2 2.168(5), Re2–O3 2.127(5), Re2–O4 2.111(5), Re3–O1 2.174(5), Re3–O3 2.168(5), Re3–O4 2.137(4), Re1–O1–Re3 101.4(2), Re1–O2–Re2 96.3(2), Re2–O3–Re3 103.4(2), Re2–O4–Re1 101.3(2), Re2–O4–Re3 105.1(2), Re1–O4–Re3 103.1(2); mean Re–C_{CO} 1.898, mean C–O_{CO} 1.161, mean nonbonded Re–Re distance 3.324 \AA .

one of the predominant rhenate(i) species of an aqueous solution of the $[\text{Re}(\text{CO})_3(\text{H}_2\text{O})_3]^+$ parent complex. On raising the pH value of such solutions, Alberto et al. identified the $[\text{Re}_3(\text{CO})_9(\mu_3\text{-OH})(\mu_2\text{-OH})_3]^-$ ion, which, due to its μ_3 -hydroxo ligand instead of an oxo bridge, appears as the parent conjugate acid of the glycerol complex.^[10] A closer look at the individual distances and angles makes it necessary critically to scrutinize the finding that there is a μ_3 -oxo bridge in **4a** (mean values: Re–O 2.122 \AA , Re–O–Re 103.2 $^\circ$) rather than a μ_3 -hydroxo ligand as in Alberto's compound (mean values: Re–O 2.167 \AA , Re–O–Re 104.3 $^\circ$). It is the unexpectedly small Re–O–Re angle in **4a** that needs an explanation. In the crystal structure, the μ_3 -oxo atom O4 is within hydrogen-bonding distance of the enimine N of a DBU molecule (O \cdots N 2.718 \AA). In a difference Fourier synthesis, residual electron density corresponding to a hydrogen atom is between the O and N atoms at about 1.16 \AA from the N atom. Refinement of H(x,y,z) left the atom in this position (N–H 1.1, H \cdots O 1.6 \AA , N–H \cdots O 163 $^\circ$). Refinement of other kinds of H distribution (close to O or statistical) always resulted in the N–H \cdots O hydrogen bridge (i.e., the formulation of a μ_3 -oxo rather than a μ_3 -hydroxo bridge appears to be ensured). Accordingly, the preparation of crystalline **4a** needed the 3:1:5 Re/Glyc/DBU ratio but was hampered at a lower base content. Attempts to isolate the related conjugate acid $[\text{Re}_3(\text{CO})_9(\mu_3\text{-OH})(\mu_3\text{-GlycH}_{-3})]^-$ failed. When one equivalent of base was kept back, the ^{13}C NMR spectra remained unchanged, but crystallisation did not occur.

Replacement of water, the source of the μ_3 -oxo ligand, with methanol results in the synthesis of a μ_3 -methoxo complex as an analogue of the missing hydroxo species. On application of the same procedure as above, except that a drop of methanol was added instead of water, the same two-signal pattern was observed in the ^{13}C NMR spectra (Table 2). In addition to the signals observed for **4a**, a methanol-derived signal turned up downfield-shifted by about

30 ppm, which is indicative of a μ_3 -methoxo ligand. Crystals were grown by cooling the solutions. The structure of the methoxo-bridged trirhenate(i) ion in $(\text{NET}_4)[\text{Re}_3(\text{CO})_9(\mu_3\text{-OMe})(\mu_3\text{-GlycH}_{-3})]^-$ (**4b**) corresponds to the structure of **4a** (see Figure 5 for distances and angles), as well as to the me-

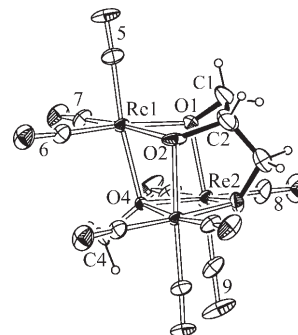


Figure 5. Structure of the C_3 -symmetric $[\text{Re}_3(\text{CO})_9(\mu_3\text{-OMe})(\mu_3\text{-GlycH}_{-3})]^-$ ion in **4b** (25% probability ellipsoids; the number n at the carbonyl ligands should be read as C_n and O_n). Distances [\AA] and angles [$^\circ$]: Re1–O1 2.131(7), Re1–O2 2.141(6), Re1–O4 2.198(5), Re2–O1 2.157(7), Re2–O4 2.178(8); Re1–O1–Re2 104.7(3), Re1–O2–Re1 103.8(4); mean Re–O4–Re 101.2; mean Re–C_{CO} 1.899, mean C–O_{CO} 1.152, mean nonbonded Re–Re distance 3.386 \AA . Symmetry code: $\bar{1}: x, y, 0.5-z$.

thoxo analogue of the hydroxo-bridged $[\text{Re}_3(\text{CO})_9(\mu_3\text{-OH})(\mu_2\text{-OH})_3]^-$ ion, the $[\text{Re}_3(\text{CO})_9(\mu_3\text{-OMe})(\mu_2\text{-OMe})_3]^-$ ion.^[11] The largest differences between the rhenate(i) parts of the structures of **4a** and **4b** were observed, as expected, for the bonding parameters about the μ_3 -O atom (mean values for the oxo ligand in **4a**: see above; for the methoxo ligand in **4b**: Re–O 2.191 \AA , Re–O–Re 101.2 $^\circ$).

The μ_3 -methoxo ligand of **4b** may be replaced by a diol. Attempts to prepare diol-linked trirhenates such as $[\{\text{Re}_3(\text{CO})_9(\mu_3\text{-GlycH}_{-3})\}_2(\mu_3,\mu_3\text{-EthgH}_{-2})]^{2-}$ did not result in the formation of crystals but the mass spectra contained the expected signals of hexanuclear species. This point should be kept in mind when carbohydrates with terminal hydroxy functions are used as ligands. In particular, the pentofuranoses and the hexopyranoses feature such functionalities in their terminal hydroxy groups attached to C5 and C6, respectively.

Methyl β -D-ribose (Me- β -D-Ribp) was used to check whether the triolate moiety of **4** can also be provided as part of a carbohydrate molecule. Crystals of suitable quality were obtained by the acetonitrile-plus-one-drop-of-methanol route, after crystallisation was initiated by the addition of water. The crystal structure of $(\text{DBUH})[\text{Re}_3(\text{CO})_9(\mu_3\text{-OMe})(\mu_3\text{-}^1\text{C}_4\text{-Me-}\beta\text{-D-Ribp}2,3,4\text{H}_{-3})]^-$ (**5**) revealed the O2/3/4 part of the riboside as the attempted tridentate chelator (Figure 6). The carbohydrate ligand has adopted the $^1\text{C}_4$ conformation instead of the $^4\text{C}_1$ conformation of its pyranose ring (cf. Scheme 1), a situation that is energetically less suited to the free riboside. This structural peculiarity should be kept in mind when the ^{13}C NMR data are inspected for typical shift differences, the "coordination-induced

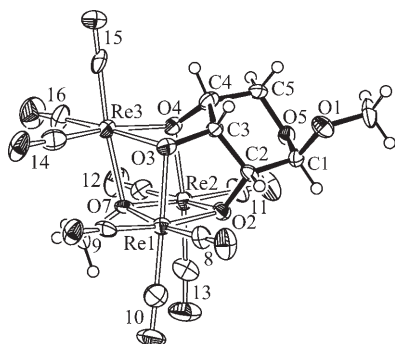
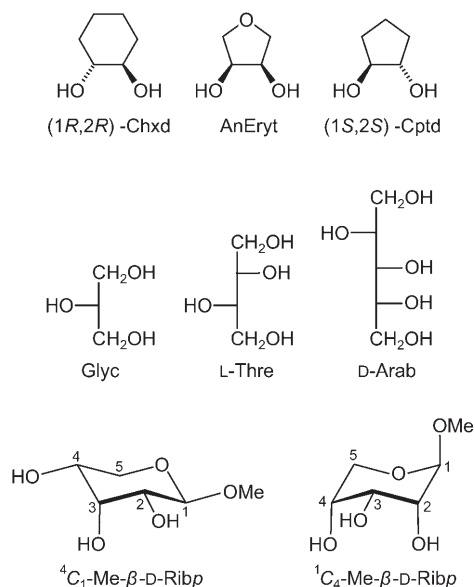


Figure 6. Structure of the $[\text{Re}_3(\text{CO})_9(\mu_3\text{-OMe})(\mu_3\text{-}^1\text{C}_4\text{-Me-}\beta\text{-D-Ribp2,3,4H-}_3)]^-$ ion in **5** (50% probability ellipsoids; the number n at the carbonyl ligands should be read as Cn and On). Distances [\AA] and angles [$^\circ$]: Re1–O2 2.171(7), Re1–O3 2.158(7), Re1–O7 2.187(7), Re2–O2 2.200(7), Re2–O4 2.158(7), Re2–O7 2.169(7), Re3–O3 2.160(7), Re3–O4 2.133(7), Re3–O7 2.193(6); Re1–O2–Re2 103.8(3), Re1–O3–Re3 101.9(3), Re2–O4–Re3 104.5(3); mean Re–O7–Re 102.2; mean Re–C_{CO} 1.901, mean C–O_{CO} = 1.156, mean nonbonded Re–Re distance 3.396 \AA ; pyranose torsion angles: O2–C2–C3–O3 42.4(11), O3–C3–C4–O4 $-38.7(10)$.



Scheme 1. Polyols used in this work.

shifts" (CISs). Since the shift values of free Me- β -D-Ribp refer to solutions that are enriched with the $^4\text{C}_1$ -conformer of the glycoside, the differences between a bonded and a free ligand may be biased. In fact, the values in Table 2 differ markedly from the corresponding glycerol values though they repeat the general pattern of larger CISs for the triolate's terminal carbon atoms and a smaller CIS for the carbon in the middle.

The crystallisation procedures for the triolate complexes show that the trinuclear triolato rhenates(I) are not sensitive to rapid hydrolysis. Attempts to prepare **4** or **5** directly from alkaline aqueous solutions as the only products, however, failed. Instead, the precipitation of the hydroxorhenate species interfered with the attempted reactions.

The glycerol partial structure is common to both glycosides and sugar alcohols. Accordingly, the typical ^{13}C NMR shift-difference pattern of the trinuclear triolato-rhenate(I) was observed with some polyols. The tetraol L-threitol was examined as an example (Table 2). Figure 7 top shows a typ-

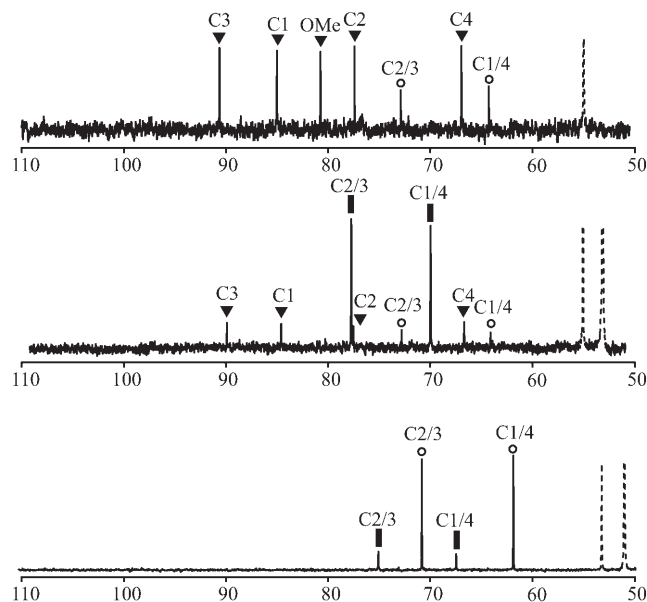


Figure 7. DEPT-assigned ^{13}C NMR spectra of various threitol complexes (triangles and rectangles denote the trinuclear and dinuclear species, respectively, described in the text; free Thre is marked by open circles). Top: Re/Thre/DBU molar ratio 3:1:4, MeOH added, MeCN solvent; the trinuclear complex is the main species; the DBU signal is drawn as a dashed line; no NET_4 signal is recorded due to the use of $[\text{Re}(\text{CO})_3\text{Br}]$ as the rhenium educt. Middle: Re/Thre/DBU 2:1:4, no MeOH or H_2O added, MeCN solvent; the dinuclear complex is the main species; the DBU (left) and the NET_4 (right) signals are drawn as dashed lines. Bottom: Re/Thre/DBU 2:1:4, H_2O solvent; the dinuclear complex is the only Thre-containing species; the DBU (left) and the NET_4 (right) signals are drawn as dashed lines. See Table 2 for shift differences for the trinuclear complex; for the dinuclear complex: $\Delta\delta = 5.8$ (C1/4), 4.9 (C2/3).

ical ^{13}C NMR spectrum of the tetraol-derived triolato complex. At this point, however, we experienced another practical restriction regarding crystallisation. In all the cases studied, the presence of pendant hydroxy functions have until now thwarted all attempts to crystallize any further trinuclear polyolatorhenate(I).

The threitol partial structure dinucleates the $\text{Re}^I(\text{CO})_3$ moiety:

In accordance with the findings described above, ^{13}C NMR spectra of reaction mixtures of a 3:1:4 stoichiometry of Re precursor, Thre and base, plus a drop of methanol, pointed to the trinuclear anion as the only species in an acetonitrile solution (Figure 7, top). On keeping back of one third of the Re, at 2:1:4 reactant molar ratio, and, more significantly, avoiding the addition of methanol, the typical four-signal pattern of the Re3 anion was superimposed on by a component that showed two signals for the four threitol carbons, thus indicating a new, C_2 -symmetric threitolatorhe-

niun complex (middle part of Figure 7). Crystallisation occurred only if added DBU base was withheld, but at the same time the corresponding ^{13}C NMR spectra became low in quality. Crystals suitable for structure determination were obtained at a 2:1:3 stoichiometry of Re precursor, Thre and base, though the resulting molecular structure is consistent with the two-signal threitol part of the ^{13}C NMR spectrum. Figure 8 shows the structure of the binuclear anion of

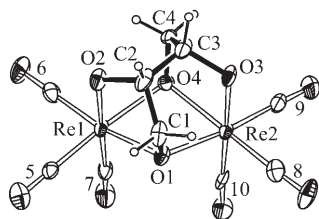


Figure 8. Structure of the $[\text{Re}_2(\text{CO})_6(\kappa^4\text{-O-L-ThreH}_{-3})]^-$ ion in **6** (40% probability ellipsoids; H^+ from intermolecular hydrogen bond omitted; the number n at the carbonyl ligands should be read as C_n and O_n). Distances [Å] and angles [°]: Re1–O1 2.164(5), Re1–O2 2.123(5), Re1–O4 2.178(6), Re2–O1 2.162(5), Re2–O3 2.114(5), Re2–O4 2.154(5); Re1–O1–Re2 102.3(2), Re1–O4–Re2 102.0(2); mean Re–C_{CO} 1.891, mean C–O_{CO} 1.157, nonbonded Re–Re distance 3.357(1); threitol torsion angles: O1–C1–C2–O2 56.4(8), O2–C2–C3–O3 –133.4(6), O3–C3–C4–O4 55.9(9).

$(\text{NEt}_4)[\text{Re}_2(\text{CO})_6(\kappa^4\text{-O-L-ThreH}_{-3})]\cdot\text{MeCN}$ (**6**). Deprotonated threitol is the only alkoxide component in a binuclear anion, the two $\text{Re}(\text{CO})_3$ parts of which are bridged in a different way from the $(\mu\text{-OR})_3$ motif of the mono-alkoxide class of binuclear compounds. With four O atoms instead of three for the bridge, the more basic terminal alkoxo functions are in the μ_2 mode, whereas the O atoms of the secondary alcohol functions bind to one central atom only. The O_4 set provided by the threitolato ligand resembles the O atom pattern in related binuclear compounds containing the $\text{Re}(\text{CO})_3$ fragment. Firstly, there is Alberto and Hegetschweiler's tentative $[\text{Re}_2(\text{CO})_6(\mu\text{-OH})_2(\text{H}_2\text{O})_2]$ species, the $(\mu\text{-OH})_2(\text{H}_2\text{O})_2$ part of which is replaced in **6** by the tetradentate threitolato ligand.^[4] Substitution of the two aqua ligands by a $\kappa^2\text{O,O'}$ -binding carboxylate yields the second group of related complexes, recently described by Klausmeyer and Beckles. In this class of compounds, the μ -hydroxo ligands could be substituted by methoxo or κO -carboxylato ligands.^[5a]

The crystal structure of **6** is remarkable in terms of its hydrogen bonds. The binuclear anions form hydrogen-bridged columns along [100], which are arranged into a hexagonal column packing. The individual columns are made up of anions that show contacts indicative of strong hydrogen bonding between the non-Re-bridging O2 and O3 atoms of the threitolato ligands. The O–O distance of 2.364 Å in these hydrogen bonds is exceptionally short (cf. the values of about 2.5 Å for the related hydrated hydroxide ion, $\text{H}_3\text{O}_2^{[7]}$). To the best of our knowledge, no shorter hydrogen bond has ever been observed in an alkoxide structure.

Intermolecular hydrogen bonding, the apparent trigger of crystallisation, adds one proton per threitolato ligand to the formula of the solid compound, the net formula of which thus contains ThreH_3 instead of the tetradeprotonated ligands that appear to be the constituents of the more basic solutions giving the clearer ^{13}C NMR spectra.

The more elaborate tetradentate pattern in the binuclear compound **6** lends this species a particularly high stability. Whereas, perhaps for kinetic reasons, the trinuclear structural motif is not hydrolytically sensitive, the thermodynamic stability of **6** is high enough to allow the preparation of this anion in an aqueous solution. The bottom part of Figure 7 shows the ^{13}C NMR spectrum of an aqueous solution of the rhenium precursor, Thre and DBU at a molar ratio of 2:1:4. As usual, a substantial amount of the Re precursor has been transformed into hydroxorhenate precipitate, but the dinuclear threitolatorhenate is clearly detectable in the spectrum of the remaining solution. The $\text{Re}_2\text{-Thre}$ pattern has thus emerged, for the first time, as a promising starting point for the search for even more elaborate ligands that might pave the way towards aqueous carbohydrate chemistry of the carbonylrhenium(I) core.

The higher polyol D-arabitol supports an oxorhenium cluster architecture:

Pentitols show more complex NMR spectra, which are not discussed in this work since their interpretation is still obscured by too many ambiguities. However, there is evidence that a higher polyol acts with its specific O atom pattern: 1) as a polydentate ligand in its own right, 2) as a triolato ligand with one of its triol partial structures, and 3) as a tetraolato ligand with a Thre partial structure. (There is promising carbonylrhenium chemistry of the tetraol erythritol as well, but due to the lack of structural information from crystals it is not considered in this work). The most interesting question of whether such ligands are able to provide extended O atom patterns and thus support new cluster architectures has been answered for the chiral pentitol D-arabitol (D-Arab, cf. Scheme 1). On attempts to prepare $\text{Arab-Re}^{\text{I}}(\text{CO})_3$ complexes, precipitates were usually formed. Mass spectra indicated hexanuclear species, but no reliable crystallisation routine could be developed. Finally, crystallisation was successful at least once and the crystals proved to be of suitable quality for an X-ray investigation. Structure analysis of crystalline $(\text{NEt}_4)_2(\text{DBUH})_2\text{-}[\text{Re}_6(\text{CO})_{18}(\text{D-ArabH}_{-5})_2]$ (**7**) revealed a hexanuclear complex in which the $\text{Re}^{\text{I}}(\text{CO})_3$ centres are connected solely by the entirely deprotonated pentitol (Figure 9). An apparent mirror plane, the trace of which runs perpendicular to the figure should be noted. All the atoms except the C_5 chain of the Arab ligands approximately match this symmetry element, so it was expected that an analogous xylitol complex (the right half of the rhenate plus its mirror image), as well as an analogous ribitol complex (the left half of the rhenate plus its mirror image) should form as more symmetrical derivatives of the anion of **7**. At present, however, there are no hints that such complexes of the two *meso*-pentitols exist.

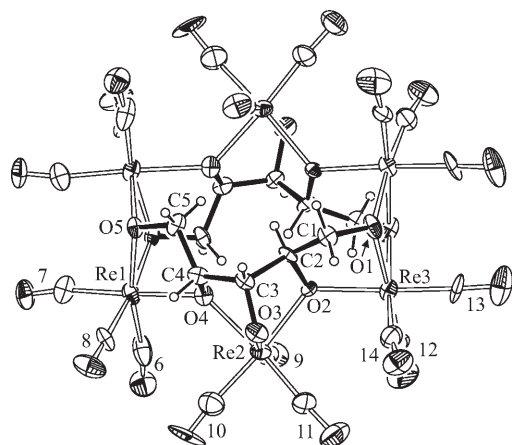


Figure 9. Structure of the $[\text{Re}_6(\text{CO})_{18}(\text{D-ArabH-5})_2]^{4+}$ ion in **7** (30% probability ellipsoids; the number n at the carbonyl ligands should be read as C_n and O_n). Distances [Å] and angles [°]: Re1–O4 2.158(10), Re1–O5 2.159(11), Re1–O5' 2.195(11), Re2–O2 2.170(10), Re2–O3 2.092(8), Re2–O4 2.176(12), Re3–O1 2.112(12), Re3–O1' 2.147(12), Re3–O2 2.159(9); Re3–O1–Re3' 104.4(4), Re2–O2–Re3 126.1(5), Re1–O4–Re2 131.5(6), Re1–O5–Re1' 101.3(4); mean Re–C_{CO} 1.898, mean C–O_{CO} 1.159, mean nonbonded distance in doubly bridged Re–Re pairs 3.367; arabitol torsion angles: O1–C1–C2–O2 41.7(15), O2–C2–C3–O3 29.1(14), O3–C3–C4–O4 –60.7(13), O4–C4–C5–O5 47.6(15). Symmetry codes: i : $1-x, y, 1-z$.

Conclusion

According to the pK_A value of the $[\text{Re}(\text{CO})_3(\text{H}_2\text{O})_3]^+$ ion (about 7.5^[4]), the metal centre is of moderate Lewis acidity. The synthesis of complexes of the $\text{Re}^{\text{I}}(\text{CO})_3$ fragment containing a carbohydrate anion as the ligand thus requires, in an aqueous solution, a pH value in the basic region. Metal centres of similar acidity, such as lead(II), prefer carbohydrate- to hydroxo-ligand binding, due to the chelate effect. In $\text{Re}^{\text{I}}(\text{CO})_3$ chemistry, however, di- and trinuclear hydroxo species are of particularly high stability. With strong ligands such as amino acid anions, on the one hand, complex formation is not hampered by the hydroxo species.^[8] Carbohydrate anions, on the other hand, obviously cannot compete with hydroxo ligands unless they exhibit multidentate O-atom patterns. The requirements for a carbohydrate-provided O-atom pattern to act as a powerful ligand to the $\text{Re}^{\text{I}}(\text{CO})_3$ core are unexpectedly high. The $[\text{Re}_3(\text{CO})_9(\mu_3\text{-OH})(\mu_2\text{-OH})_3]^-$ ion appears to be an instructive example. On substitution of the three μ_2 -hydroxo ligands by a sterically well-fitting tridentate triolato ligand a complex of so high a stability was expected that its synthesis in an aqueous environment appeared as possible. However, the hydroxo-rhenate formed. Even the tetradentate threitolato(4–) ligand merely begins to compete with its hydroxo counterpart in an aqueous solution. Nevertheless, a strategy is emerging from the gains in stability in the series of diols, triols and *threo*-tetraols. Well matching multidentate O-atom patterns thus seem to open a way to aqueous carbohydrate chemistry of the $\text{Re}^{\text{I}}(\text{CO})_3$ fragment.

These problems do not arise outside of medicinal chemistry. In a nonaqueous environment, carbohydrate ligands support interesting and new assemblies of $\text{Re}^{\text{I}}(\text{CO})_3$ moieties. In particular, the hexanuclear anion of **7**, to the best of our knowledge the largest assembly of $\text{Re}^{\text{I}}(\text{CO})_3$ fragments, impressively shows the synthetic potentiality of a multidentate ligand derived from a carbohydrate backbone.

Experimental Section

Tetrabutylammonium bromide, (1*R*,2*R*)-cyclohexane-1,2-diol, (1*S*,2*S*)-cyclopentane-1,2-diol, glycerol, and 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) were used as supplied by Fluka, *D*-arabitol (Slovak Academy of Sciences, Institute of Chemistry), diethyleneglycol dimethyl ether (diglyme, Aldrich), decacarbonylrhenium (Strem) and tetraethylammonium bromide (Merck) were also used as supplied. Solvents were dried (molecular sieve) and deoxygenated: acetonitrile was supplied by Fisher Scientific, whilst tetrahydrofuran (THF), toluene, and dichloromethane were purchased from Fluka. Bromo-pentacarbonyl-rhenium(I) was prepared by standard procedures.^[9] Standard Schlenk techniques (nitrogen as the inert gas) were used.

(NEt₄)₂[Re(CO)₅Br]: The general route given in reference [10] was used. $[\text{Re}(\text{CO})_5\text{Br}]$ (4.90 g, 12.1 mmol) was suspended in diglyme (80 mL) and heated to 50 °C. NEt₄Br (5.47 g, 26.0 mmol) was suspended in diglyme (250 mL) and heated to 70 °C. The suspensions were combined and heated to 115 °C with stirring. A colourless precipitate formed over the course of 5 h. The precipitate was filtered off, washed three times with diglyme and diethyl ether, and dried in vacuo. Excess NEt₄Br was removed by suspension of the solid in ethanol (40 mL) and drying in vacuo again. The product was obtained as a colourless powder (7.36 g, 9.55 mmol, 79.3% yield). IR carbonyl valence absorptions (KBr): $\tilde{\nu}$ = 2000 (s), 1866 (s) cm^{-1} ; elemental analysis (%) calcd for C₁₉H₄₀Br₃N₂O₃Re: C 29.6, H 5.2, N 3.6, Br 31.1; found: C 29.7, H 5.2, N 3.6, Br 30.9.

(NBu₄)₂[Re₂(CO)₆(μ -OMe)₃]: The general route given in reference [11] was used. $[\text{Re}(\text{CO})_5\text{Br}]$ (406 mg, 1.00 mmol) was suspended in a mixture of THF (10 mL) and methanol (5 mL). A clear solution formed on addition of a solution of NaOMe in methanol (6 mL 0.5 M NaOMe solution, 3 mmol NaOMe). The solution was stirred for 1 h at room temperature under reduced pressure. Stirring was continued for 12 h under nitrogen. The solvent was removed, the colourless residue was dried in vacuo and redissolved in methanol (25 mL), and the solution was filtered. A solution of NBu₄Br (3.22 g, 10 mmol) in water (25 mL) was added. The colourless precipitate was washed with a small amount of water and dried in vacuo (358 mg, 0.41 mmol, 81.7% yield). Selected IR bands (KBr): $\tilde{\nu}$ = 1986 (s), 1888 (s), 1854 (s), 1837 (s) cm^{-1} ; elemental analysis (%) calcd for C₂₅H₄₅NO₉Re₂: C 34.3, H 5.2, N 1.6; found: C 34.3, H 5.2, N 1.6.

(NBu₄)₂[Re₂(CO)₆(μ -(*1R,2R*)-ChxdH-₁)] (**1**): (NBu₄)₂[Re₂(CO)₆(μ -OMe)₃] (175 mg, 0.200 mmol) and (1*R*,2*R*)-cyclohexane-1,2-diol (61 mg, 0.60 mmol) were dissolved in acetonitrile (70 mL) and the mixture was heated to 100 °C in a distillation apparatus. On completion of the distillation, more acetonitrile (70 mL) was added and the distillation was repeated. This procedure was repeated again. Residual solvent was removed in vacuo. The obtained colourless solid was dissolved in dichloromethane (3 mL), the solution was filtered, and toluene (7 mL) was added. Colourless crystals of **1** formed over the course of one day at a temperature of 4 °C. The yield was improved by addition of more toluene (2 mL) (119 mg, 0.1 mmol, 50.0% yield). ¹³C NMR (67.93 MHz, CH₂Cl₂, 25 °C): δ = 86.9 (C1), 76.2 (C2), 33.3 (C6), 31.5 (C3), 24.0 (C5), 23.6 (C4) ppm; selected IR bands (KBr): $\tilde{\nu}$ = 2000 (s), 1877 (s) cm^{-1} ; MS-FAB: m/z calcd for C₂₄H₃₃O₁₂Re₂ = [(CO)₅Re(μ -(*1R,2R*)-*trans*-ChxdH-₁)₂Re(CO)₃]⁻: 885.9; found 884.9 with a typical Re₂ pattern; elemental analysis (%) calcd for C₄₀H₆₉NO₁₂Re₂: C 42.6, H 6.2, N 1.2; found: C 42.5, H 6.1, N 1.3.

Table 3. Crystallographic data.

	1	2	3	4a	4b	5	6	7
empirical formula	C ₄₀ H ₆₉ NO ₁₂ Re ₂	C ₂₄ H ₃₆ KO ₁₇ Re ₂	C ₃₇ H ₆₃ NO ₁₂ Re ₂	C ₃₁ H _{40.50} N _{4.50} O ₁₃ Re ₃	C ₂₁ H ₂₈ NO ₁₃ Re ₃	C ₂₅ H ₂₉ N ₂ O ₁₅ Re ₃	C ₂₀ H ₂₉ N ₂ O ₁₀ Re ₂	C ₆₂ H ₈₈ N ₆ O ₂₈ Re ₆
<i>M_r</i> [g mol ⁻¹]	1128.389	1008.045	1086.310	1242.797	1031.067	1156.123	829.866	2482.628
crystal size [mm]	0.25 × 0.22 × 0.14	0.28 × 0.08 × 0.07	0.36 × 0.20 × 0.10	0.18 × 0.17 × 0.11	0.08 × 0.05 × 0.04	0.15 × 0.1 × 0.08	0.18 × 0.08 × 0.05	0.15 × 0.10 × 0.04
<i>T</i> [K]	200(2)	200(2)	200(2)	200(2)	200(2)	200(2)	200(2)	200(2)
diffractometer	Stoe IPDS	Stoe IPDS	Stoe IPDS	KappaCCD	KappaCCD	KappaCCD	KappaCCD	KappaCCD
crystal system	monoclinic	monoclinic	monoclinic	monoclinic	orthorhombic	monoclinic	orthorhombic	monoclinic
space group	<i>P</i> 2 ₁	<i>C</i> 2/ <i>c</i>	<i>C</i> 2	<i>P</i> 2 ₁ / <i>n</i>	<i>Pbcm</i>	<i>P</i> 2 ₁	<i>P</i> 2 ₁ 2 ₁ 2 ₁	<i>C</i> 2
<i>a</i> [Å]	13.1068(16)	23.100(14)	16.7594(14)	19.0360(3)	13.4042(2)	12.8610(2)	10.83200(10)	17.3800(4)
<i>b</i> [Å]	13.3313(11)	13.876(3)	22.5613(16)	9.23400(10)	9.3686(2)	12.5560(2)	18.6490(2)	24.7230(5)
<i>c</i> [Å]	13.3885(16)	22.997(8)	11.2651(12)	21.0590(4)	21.8892(5)	19.3160(4)	24.9750(3)	9.6980(2)
β [°]	89.281(15)	113.45(5)	91.619(11)	98.5010(10)	90	90.2930(9)	90	116.2970(9)
<i>V</i> [Å ³]	2339.2(4)	6763(5)	4257.8(7)	3661.05(10)	2748.81(10)	3119.16(9)	5045.10(9)	3735.84(14)
<i>Z</i>	2	8	4	4	4	4	8	2
ρ [g cm ⁻³]	1.6021(3)	1.9801(15)	1.6947(3)	2.25481(6)	2.56397(9)	2.46196(7)	2.18516(4)	2.20703(8)
μ [mm ⁻¹]	5.225	7.346	5.738	9.964	13.242	11.687	9.643	9.765
absorption correction	numerical	none	numerical	numerical	numerical	numerical	numerical	none
transmission	0.2928–0.5091	–	0.2290–0.5533	0.2157–0.3789	0.4938–0.6275	0.2389–0.4295	0.3738–0.6349	–
factor range	13 430	19 230	15 039	37 365	28 335	38 773	45 449	25 375
refls. measured	13 430	19 230	15 039	37 365	28 335	38 773	45 449	25 375
<i>R</i> _{int}	0.0792	0.1211	0.0776	0.0787	0.0755	0.0704	0.0701	0.1301
mean σ(<i>I</i>)/ <i>I</i>	0.1263	0.1540	0.0975	0.0498	0.0379	0.0774	0.0522	0.0910
θ range	1.55–24.15	1.75–24.02	1.81–25.84	3.14–27.46	3.24–27.46	3.16–27.44	3.27–27.57	3.25–27.59
observed refls.	4984	2858	5651	6513	2433	11 374	9154	6746
<i>x</i> , <i>y</i> (weighting scheme)	0.0300, 0	0.0196, 0	0.0482, 0	0.0491, 9.2294	0.0309, 36.9014	0.0418, 0	0.0111, 12.8528	0.0521, 23.1749
Flack parameter	0.026(16)	–	–0.029(18)	–	–	–0.014(11)	–0.006(12)	0.08(2)
refls in refinement	7126	5302	7237	8327	3220	14 149	11 543	8547
parameters	497	397	471	455	165	812	618	377
restraints	7	18	7	2	6	1	0	23
<i>R</i> (<i>F</i> _{obs})	0.0422	0.0483	0.0470	0.0411	0.0422	0.0430	0.0347	0.0510
<i>R</i> _w (<i>F</i> ²)	0.0890	0.0876	0.1015	0.1037	0.0982	0.0977	0.0775	0.1394
<i>S</i>	0.831	0.783	0.929	1.030	1.065	1.007	1.029	1.032
shift/error _{max}	0.005	0.001	0.001	0.002	0.001	0.002	0.002	0.001
max electron density [e Å ⁻³]	1.411	2.156	2.012	1.864	1.890	2.210	1.961	2.259
min electron density [e Å ⁻³]	–1.861	–0.968	–2.181	–2.024	2.027	–1.393	–1.279	–2.219

[K([18]crown-6)][Re₂(CO)₆(μ-Ome)₂(μ-AnErytH₁)] (2): Anhydroerythritol (0.400 mL, 1 M solution in methanol, 0.400 mmol) was added to (NEt₄)₂[Re(CO)₃Br₃] (154 mg, 0.200 mmol) in methanol (1.2 mL). [18]crown-6 (53 mg, 0.20 mmol) and subsequently KOMe (0.4 mL, 1 M solution in methanol) were added. The mixture was stirred at room temperature for 2 h and was then cooled to 4 °C, and diethyl ether vapour was allowed to diffuse into it. After 5 d the solution was separated from colourless crystals of NEt₄Br. Hexane vapour was now allowed to diffuse into the solution at 4 °C. In the course of one day, a few small crystalline needles formed.

(NBu₄)[Re₂(CO)₆(μ-(1S,2S)-CptdH₁)] (3): A colourless powder of **3** was prepared by the procedure described for **1**. After drying in vacuo, the solid was dissolved in dichloromethane (3 mL). Toluene (1 mL) was added to 0.5 mL of the filtered solution, small amounts of precipitate being dissolved with a few drops of dichloromethane. Keeping the solution at 4 °C made colourless crystals grow within 30 minutes (97.7 mg, 0.09 mmol, 45.0% yield). ¹³C NMR (67.93 MHz, CH₂Cl₂, 25 °C): δ = 90.1 (C1), 79.7 (C2), 32.3 (C5), 29.8 (C3), 18.2 (C4) ppm; selected IR bands (KBr): ν̄ = 1995 cm⁻¹(s), 1865(s); MS-FAB⁺: *m/z* calcd. for C₂₁H₂₇O₁₂Re₂ = [(CO)₃Re{μ-(1S,2S)-CptdH₁}]₂Re(CO)₃: 843.9; found

842.5 with a typical Re₂ pattern; elemental analysis (%) calcd for C₃₇H₆₃NO₁₂Re₂: C 40.9, H 5.9, N 1.3; found: C 40.4, H 5.9, N 1.3.

(DBUH)₂[Re₃(CO)₉(μ₃-O)(μ₃-GlycH₃)]·0.5 MeCN (4a): (NEt₄)₂[Re(CO)₃Br₃] (154 mg, 0.200 mmol) and glycerol (6 mg, 0.07 mmol) were dissolved in acetonitrile (2 mL). After the addition of DBU (53 mg, 0.35 mmol) and one drop of water (0.03 mL) the solution was heated (6 h, 85 °C). The reaction mixture was filtered after cooling to room temperature. Water was added to the point at which a transient precipitate redissolved (ca. 1 mL). In the course of one day, pale yellow crystals formed on keeping of the solution at 4 °C (39 mg, 0.0313 mmol, 47% yield). The measured crystal grew from an anhydrous 1:1:3 batch of Re/Glyc/base, which did not give the typical NMR spectra of the pure trinuclear complex but contained free glycerol as well as uninterpreted signals; a few crystals grew after the addition of water just to the point where a transient precipitate redissolved. ¹³C NMR (67.93 MHz, MeCN, 25 °C): δ = 82.7 (CH₂), 76.9 (CH) ppm; selected IR bands (KBr): ν̄ = 2010(m), 1983(s), 1868(s), 1845(s) cm⁻¹; MS-FAB⁺: *m/z* calcd. for C₁₂H₅O₁₃Re₃ = [Re₃(CO)₉(μ₃-O)(GlycH₃)]²⁺: 915.8; found 916.8 with a typical Re₃ pattern; elemental analysis (%) calcd for C₃₁H_{40.5}N_{4.5}O₁₃Re₃: C 30.0, H 3.3, N 5.1; found: C 29.6, H 3.3, N 4.8.

(NEt₄)[Re₃(CO)₉(μ₃-OMe)(μ₃-GlycH₋₃)] (4b): (NEt₄)₂[Re(CO)₃Br₃] (154 mg, 0.200 mmol) and glycerol (6 mg, 0.07 mmol) were dissolved in acetonitrile (2 mL). DBU (43 mg, 0.28 mmol) and one drop of methanol (0.1 mL) were added. The solution was heated to 85 °C for 5 h. After filtration, colourless crystals formed on cooling overnight (29 mg, 0.027 mmol, 39% yield). ¹³C NMR (67.93 MHz, MeCN, 25 °C): δ = 82.7 (CH₂), 80.4 (CH₃), 76.5 (CH) ppm; selected IR bands (KBr): $\tilde{\nu}$ = 2026 (s), 2004 (s), 1897 (s), 1861 (s) cm⁻¹; MS-FAB⁻: *m/z* calcd. for C₁₃H₈O₁₃Re₃ = [Re₃(CO)₉(μ₃-OMe)(GlycH₋₃)]⁻: 930.8; found 930.9 with a typical Re₃ pattern; elemental analysis (%) calcd for C₂₁H₂₈NO₁₃Re₃: C 23.8, H 2.7, N 1.3; found: C 24.0, H 2.8, N 1.5.

(DBUH)[Re₃(CO)₉(μ₃-OMe)(μ₃-C₄-Me-β-D-Ribp2,3,4H₋₃)] (5): (NEt₄)₂[Re(CO)₃Br₃] (154 mg, 0.2 mmol) and Me-β-D-ribofuranoside (11 mg, 0.07 mmol) were dissolved in acetonitrile (2 mL). DBU (43 mg, 0.28 mmol) and one drop of methanol (0.1 mL) were added. The solution was heated to 85 °C for 3 h, cooled and filtered. Water was added dropwise just to the point where a transient precipitate redissolved. Colourless crystals of **5** formed over the course of 1 h (35 mg, 0.031 mmol, 45% yield). ¹³C NMR (100.63 MHz, MeCN, 25 °C): δ = 102.5 (C1), 81.2 (μ₃-OMe), 79.3 (C2), 78.6 (C4), 72.0 (C3), 63.4 (C5), 55.3 (OMe) ppm; selected IR bands (KBr): $\tilde{\nu}$ = 2028 (m), 2005 (s), 1896 (s), 1883 (s) cm⁻¹; MS-FAB⁻: *m/z* calcd. for C₁₆H₁₂O₁₅Re₃ = [Re₃(CO)₉(μ₃-OMe)(Me-β-D-RibpH₋₃)]⁻: 1002.9; found 1002.3 with a typical Re₃ pattern; elemental analysis (%) calcd for C₂₅H₂₉N₂O₁₅Re₃: C 26.0, H 2.5, N 2.4; found: C 26.4, H 2.8, N 2.3.

(NEt₄)[Re₂(CO)₆(L-ThreH₋₃)]·MeCN (6): (NEt₄)₂[Re(CO)₃Br₃] (154 mg, 0.200 mmol) and L-threitol (12 mg, 0.10 mmol) were dissolved in acetonitrile (2 mL), and DBU (45 mg, 0.30 mmol) was added. The solution was heated to 85 °C for 3.5 h. A colourless precipitate formed after some minutes and redissolved on continued heating. The solution was cooled to room temperature and filtered. Water was added dropwise just to the point where a transient precipitate redissolved. On standing overnight, a few colourless crystals grew.—A solution that contained **6** as the main species in terms of NMR spectra was obtained by using more DBU (61 mg, 0.40 mmol). ¹³C NMR (100.52 MHz, MeCN, 25 °C): δ = 77.7 (C2/3), 69.9 (C1/4) ppm.

(NEt₄)₂(DBUH)₂[Re₆(CO)₁₈(D-ArabH₋₅)₂] (7): (NEt₄)₂[Re(CO)₃Br₃] (154 mg, 0.2 mmol) and D-arabitol (11 mg, 0.07 mmol) were dissolved in acetonitrile (2 mL). DBU (43 mg, 0.28 mmol) and 1 drop of methanol (0.1 mL) were added. The solution was heated to 85 °C for 3.5 h, cooled and filtered. Colourless crystals of **7** formed overnight. Selected IR bands (KBr): $\tilde{\nu}$ = 2001 (s), 1837 (s), 1644 (m) cm⁻¹; MS-FIB⁻: *m/z* calcd. for C₂₈H₁₄O₂₈Re₆ = [Re₆(CO)₁₈(ArabH₋₅)₂]⁴⁺: 1915.6; found: 1917.4 with a typical Re₆ pattern = [Re₆(CO)₁₈(ArabH₋₅)₂]⁴⁺+2H⁺ and 2047.5 with a typical Re₆ pattern = [Re₆(CO)₁₈(ArabH₋₅)₂]⁴⁺+2H⁺+NEt₄⁺; elemental analysis (%) calcd for C₆₂H₈₈N₆O₂₈Re₆: C 30.0, H 3.6, N 3.4; found: C 30.2, H 3.5, N 3.8.

Spectroscopy: ¹³C{¹H} spectra were recorded with 1 mL of filtered reaction mixture in a 5 mm tube. Equipment used: ¹³C NMR: Jeol EX-400, GSX 270, 400 e; mass spectra: Jeol JMS-700 (ionisation method: FAB⁻); IR: Jasco FT/IR-460plus. NMR shift differences are given according to Δδ = δ(complex)–δ(free polyol). Only NMR signals of the anionic parts of the compounds are considered throughout the Experimental Section and Table 1 and Table 2.

Crystal structure determination and refinement: Crystals suitable for X-ray crystallography were selected with the aid of a polarization microscope, mounted on the tip of a glass fibre and investigated either on a Nonius KappaCCD diffractometer with graphite-monochromated Mo_{Kα} radiation (λ = 0.71073 Å) or a Stoe IPDS diffractometer with the same radiation. The structures were solved by Direct Methods (SIR 97, SHELXS) and refined by full-matrix, least-squares calculations on F² (SHELXL-97). Anisotropic displacement parameters were refined for all non-hydrogen atoms. The numbers of restraints given refer to ISOR and DFIX restraints. Crystallographic data are listed in Table 3.

CCDC-292785 (**1**), CCDC-292786 (**2**), CCDC-292787 (**3**), CCDC-292788 (**4a**), CCDC-292789 (**4b**), CCDC-292790 (**5**), CCDC-292791 (**6**) and CCDC-292792 (**7**), contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Center via www.ccdc.cam.ac.uk/data_request/cif.

Acknowledgements

We acknowledge Mihael Suhanji's support in the course of an advanced practical training.

- [1] a) R. Alberto, R. Schibli, R. Waibel, U. Abram, A. P. Schubiger, *Coord. Chem. Rev.* **1999**, 190–192, 901–919; b) R. Schibli, P. A. Schubiger, *Eur. J. Nucl. Med.* **2002**, 29, 1529–1542.
- [2] a) T. A. Oriskovich, P. S. White, H. H. Thorp, *Inorg. Chem.* **1995**, 34, 1629–1631; b) F. Zobi, B. Spingler, T. Fox, R. Alberto, *Inorg. Chem.* **2003**, 42, 2818–2820.
- [3] T. Storr, M. Obata, C. L. Fisher, S. R. Bayly, D. E. Green, I. Brudzińska, Y. Mikata, B. O. Patrick, M. J. Adam, S. Yano, C. Orvig, *Chem. Eur. J.* **2005**, 11, 195–203.
- [4] A. Egli, K. Hegetschweiler, R. Alberto, U. Abram, R. Schibli, R. Hedinger, V. Gramlich, R. Kissner, P. A. Schubiger, *Organometallics* **1997**, 16, 1833–1840.
- [5] a) K. K. Klausmeyer, F. R. Beckles, *Inorg. Chim. Acta* **2005**, 358, 1041–1049; b) K. K. Klausmeyer, F. R. Beckles, *Inorg. Chim. Acta* **2005**, 358, 1050–1060.
- [6] X. Kästele, P. Klüfers, F. Kopp, J. Schuhmacher, M. Vogt, *Chem. Eur. J.* **2005**, 11, 6326–6346.
- [7] G. Weck, A. Milet, R. Moszynski, E. Kochanski, *J. Phys. Chem. A* **2002**, 106, 12084–12094.
- [8] J. Petrig, R. Schibli, C. Dumas, R. Alberto, P. A. Schubiger, *Chem. Eur. J.* **2001**, 7, 1868–1873.
- [9] G. Brauer, *Handbuch der Präparativen Anorganischen Chemie Bd. 3*, Ferdinand Enke Verlag Stuttgart, **1981**.
- [10] R. Alberto, A. Egli, U. Abram, K. Hegetschweiler, V. Gramlich, P. A. Schubiger, *J. Chem. Soc. Dalton Trans.* **1994**, 2815–2820.
- [11] C.-H. Jiang, Y.-S. Wen, L.-K. Liu, T. S. A. Hor, Y. K. Yan, *Organometallics* **1998**, 17, 173–181.

Received: December 14, 2005

Published online: March 28, 2006