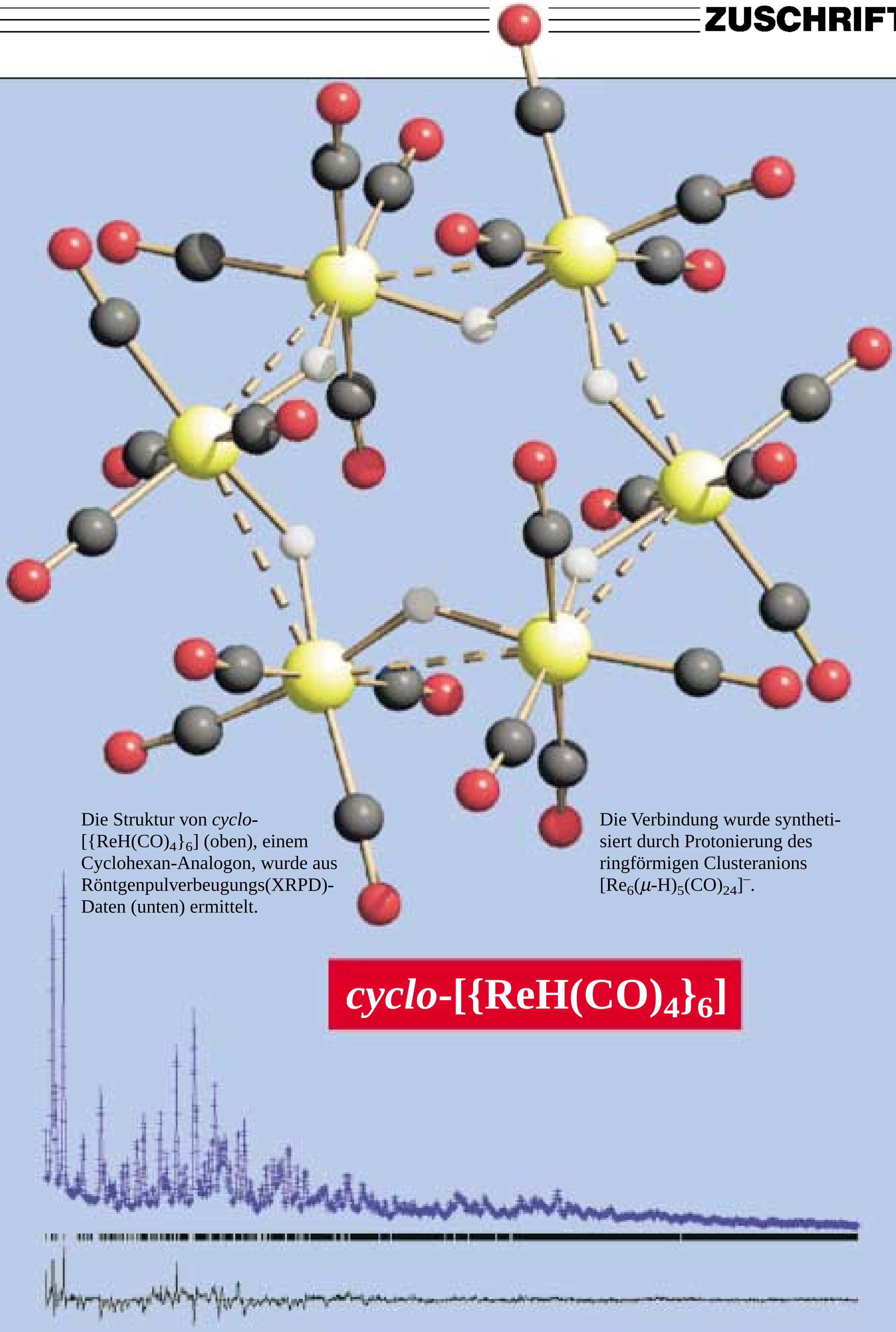

Die Struktur von *cyclo*-[{ReH(CO)$_4$}$_6$] (oben), einem Cyclohexan-Analogon, wurde aus Röntgenpulverbeugungs(XRPD)-Daten (unten) ermittelt.

Die Verbindung wurde synthetisiert durch Protonierung des ringförmigen Clusteranions [Re$_6$(μ-H)$_5$(CO)$_{24}$]$^-$.

cyclo-[{ReH(CO)$_4$}$_6$]

Mehr dazu auf den folgenden Seiten.

Complete Structural Characterization by Ab Initio X-Ray Powder Diffraction of [{Re(μ-H)(CO)$_4$}$_n$] and [{Re(μ-H)(CO)$_4$}$_6$], Inorganic Analogues of Polyethylene and Cyclohexane**

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We have recently shown that anionic "initiators", $X^- = Re(CO)_5^-$ or Cl^-, can promote the oligomerization of the unsaturated ("ethylene-like") complex $[Re_2(\mu\text{-}H)_2(CO)_8]$ (**1**).[1] This process is unprecedented in organometallic chemistry and mimics the polymerization of olefins, even if only relatively short chains (up to ca. 10 metal atoms) have been obtained so far by this approach.[2] These $X[ReH(CO)_4]_{2n}^-$ oligomers can be viewed as isolobal analogues of linear alkanes, thanks to the established[3] isolobal relationship[4] between (singlet) methylene and the $ReH(CO)_4$ fragment. We report here the characterization of a truly isolobal analogue of polyethylene, that is the $[\{ReH(CO)_4\}_n]$ polymer (**2**), obtained by polymerization of $[Re_2(\mu\text{-}H)_2(CO)_8]$. This process occurs spontaneously, affording a white, highly insoluble precipitate, when the concentration of **1** in a donor solvent like THF exceeds 10^{-2} M, at, or below, room temperature. At lower concentrations, **1** is still unstable, but the main reaction process is the cyclodimerization to the square cluster $[Re_4(\mu\text{-}H)_4(CO)_{16}]$, whose synthesis and structure have been reported previously.[5]

The last species is a member of the series of cyclic oligomers of formula $[\{ReH(CO)_4\}_n]$ ($n = 3-5$),[3, 5] which provide isolobal analogues of $(CH_2)_n$ cycloalkanes. We have now obtained the highest member of this series, namely the neutral $[Re_6(\mu\text{-}H)_6(CO)_{24}]$ cluster (**3**), an analogue of cyclohexane. It has been synthesized by protonation of the hexametallic ring cluster anion $[Re_6(\mu\text{-}H)_5(CO)_{24}]^-$,[6] which was obtained recently through a [4+2] cycloaddition between $[Re_4H_2(\mu\text{-}H)_3(CO)_{16}]^-$ and the $[Re_2(CO)_8]$ fragment (generated from the labile $[Re_2(CO)_8(THF)_2]$ complex).[7]

Unfortunately, both **2** and **3** were obtained as fine powders that were insoluble in all common solvents,[8] thus hampering their characterization in solution and the formation of suitable single crystals for standard X-ray diffraction. Nowadays, however, this problem can be circumvented in some cases by attempting an ab initio X-ray powder diffraction (XRPD) structure determination,[9] a methodology pioneered by us in the field of coordination chemistry, by using conventional laboratory equipment.[10] Herein we report the full structural characterization of **2** and **3** by this approach.

$[Re_6(\mu\text{-}H)_6(CO)_{24}]$ (**3**) crystallizes in the monoclinic space group $P2_1/n$; according to the Patterson map, the metal skeleton consists of a ring of six rhenium atoms lying about a crystallographic inversion center. However, due to the intrinsic limitation of XRPD, we were unable to complete this starting model by Fourier methods; thus we had to rely on molecular mechanics and some previous stereochemical knowledge to obtain the whole structure. It is of particular interest that the preliminary information afforded by powder diffraction (i.e., lattice constants, space group symmetry, and "good" heavy atom locations) *uniquely determine the shape of the "cavity"* containing the molecule, and hence the molecular stereochemistry. For this reason even a rough force field can afford a "good" molecular geometry.[11] Practically, molecular graphics (SMILE[12]), using the known stereochemistry of $[Re_6(\mu\text{-}H)_5(CO)_{24}]^-$,[6] allowed the ligand envelope to be built; lattice-constrained molecular mechanics (PACKMM/MM3[13]) fitted the model structure into the crystal; and, eventually, a sagacious usage of constraints in the final Rietveld refinements (Figure 1) led to the ultimate stereochemistry (Figure 2), which fully confirmed the isolobal analogy with cyclohexane.

Even in the easiest cases, owing to the lack of a well-defined sequential strategy, ab initio XRPD is never trivial. This is particularly true when phase contamination and/or "uncertainties" in chemical formulation complicate the early steps of structure analysis. Indeed, the characterization of the $[\{ReH(CO)_4\}_n]$ polymer was only possible when we recognized that decomposition of **1** in THF affords two polymorphs (α and β) of **2**, and when we became able to selectively produce each of them, by controlling the reaction temperature (see Experimental Section). The α-phase, which has much narrower peaks than the β-phase, was successfully indexed and eventually fully characterized by following the steps described in the Experimental Section. The resulting crystal structure confirms the polymeric nature of **2**; it crystallizes in the trigonal $P3_1$ space group and consists of homochiral 3_1 helixes (parallel to c) hexagonally packed in the ab plane (Figure 3). Even though the poor crystallinity of the β-phase hampered its structural characterization, its negligible solubility, the IR spectrum (similar to that of the α phase and less structured than those of all known cyclic oligomers), and the (relative) paucity of low-angle peaks of its XRPD pattern (somewhat "similar" to that of the α-phase, Figure 4) suggest its polymeric nature, hence the above stated polymorphism. Polymer **2** is the second structurally characterized linear-chain metal carbonyl polymer, and, at variance from its predecessor *trans*-D_{4h}-$Ru(CO)_4$,[14] is constructed from *cis*-C_{2v}-$[M(CO)_4]$ units.

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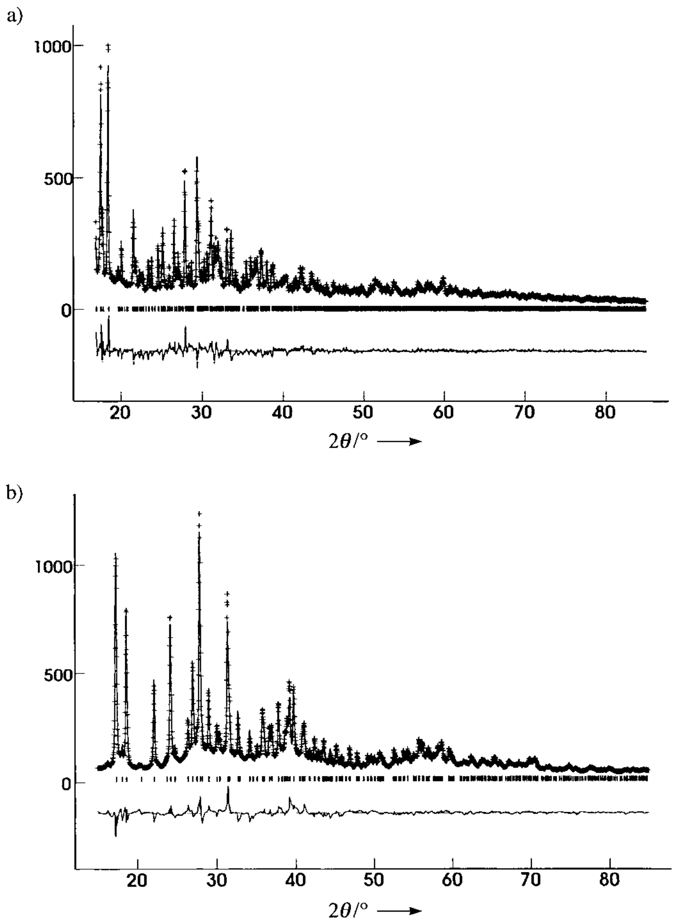

Figure 1. Rietveld refinement plots with peak markers and difference plots (bottom): a) [{ReH(CO)$_4$}$_6$] (**3**) and b) α-[{ReH(CO)$_4$}$_n$] (**2**). Low-angle data have been omitted to avoid beam overflow and axial divergence effects. Intensity values are in arbitrary units.

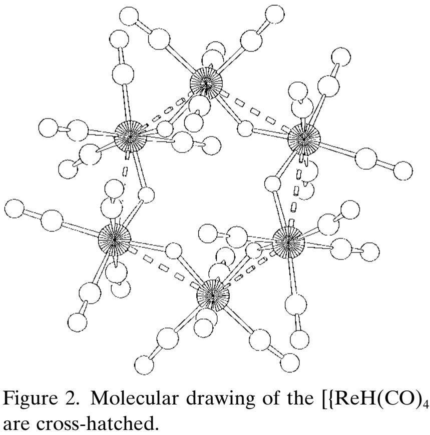

Figure 2. Molecular drawing of the [{ReH(CO)$_4$}$_6$] (**3**) species; Re atoms are cross-hatched.

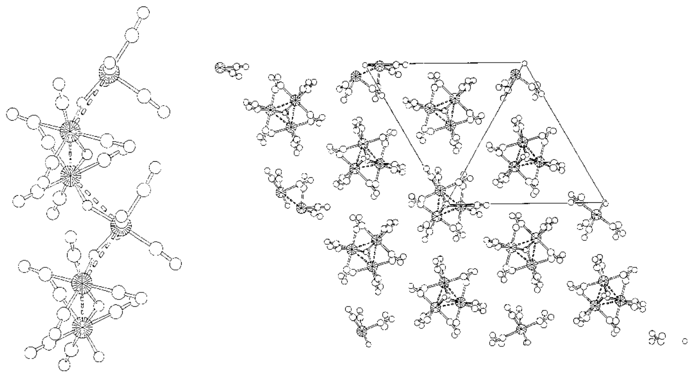

Figure 3. Sketches of the α-[{ReH(CO)$_4$}$_n$] (**2**) polymer; Re atoms are cross-hatched. Left) A fragment of the 3_1 helix; right) crystal packing viewed down *c*.

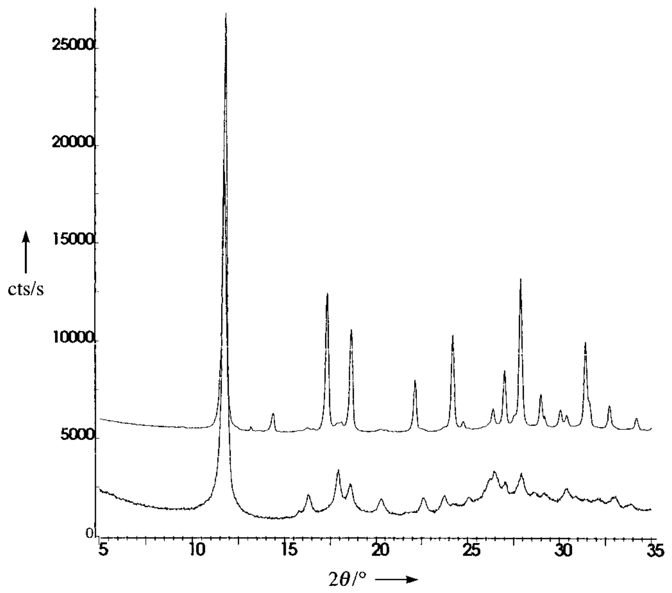

Figure 4. Raw diffraction data for the α- (top) and β- (bottom) [{ReH(CO)$_4$}$_n$] (**2**) phases.

In spite of their different backbones, **2** and **3** share a common structural feature, both having an "open" metal core which accommodates the hydrides. As shown by CPK models (see Supporting Information), these hydrides are not only inside the metal core, but also definitely buried within the carbonyl ligands cage, no space being left outside. Thus, it is the competition for space that pushes the less bulky (bridging) hydrogen atoms inside the "open" metal core. It might be considered odd to speak about hydrogen locations when we barely see the metal centers. However, it is well known that we can derive, at the molecular level, the location of the hydrides knowing that of the other atoms.[15] What we suggest here is that, at the crystal level (i.e. using the proper symmetry information), this is possible even starting from the metal atom positions alone. More than that, in the final stages of the refinement, carbonyl ligands contribute substantially to the fitting, and their location is no longer estimated by matching the diffraction experiment, but is actually determined from it.

A mechanistic problem still has to be solved: is the polymerization of **1** related to its anionic oligomerization,[1] in which the donor solvent replaces the X^- ion as initiator of the process? Preliminary experiments have shown that neutral donor molecules, such as PMe_2Ph, Me_2S, NC_5H_5, in a nondonor solvent like cyclohexane (in which **1** is quite stable), initiate the polymerization. The process, however, is much slower than in THF or acetone (days, instead of hours). Therefore the role of the donor solvents probably goes beyond that of a simple initiator and further studies of this are in progress.

Experimental Section

Synthesis of the polymer $[\{ReH(CO)_4\}_n]$ (**2**, α- and β-phases): A typical procedure for obtaining the α-phase of $[\{ReH(CO)_4\}_n]$ is as follows: A sample of $[Re_2(\mu\text{-}H)_2(CO)_8]$ (24.4 mg, 0.041 mmol) was added under N_2 to THF (2.0 mL) thermostated at 288 K. The solution (0.020 M) was maintained at this temperature for 24 h, affording a white precipitate that was isolated by centrifugation, washed with diethyl ether (5 × 5 mL), and dried under vacuum (10.9 mg, yield 44.6 %). IR: see Figure S1 in Supporting Information. Elemental analysis (%): calcd for $ReH(CO)_4$: C 16.0, H 0.33; found: C 15.8, H 0.38. The same phase was obtained by using different concentrations in the range $(1.5-2.5)\times 10^{-2}$ M at 288 K. The β-phase of $[\{ReH(CO)_4\}_n]$ was obtained in the same way at 298 K (40.7 % yield was obtained after 24 h from a 2.0×10^{-2} M solution). IR: see Figure S1; elemental analysis (%): C: 16.7, H: 0.47.

Synthesis of $[ReH(CO)_4]_6$ (**3**): A slight excess of CF_3SO_3H was added directly to the mixture formed in the reaction between $[Re_4H_2(\mu\text{-}H)_3(CO)_{16}]^-$ and $[Re_2(CO)_8(THF)_2]$[6] in CH_2Cl_2, affording a white precipitate that was isolated and washed with CH_2Cl_2. IR (KBr): $\tilde{\nu} = 2112$ m, 2101 mw, 2045 sh, 2016 vs, 2002 vs, 1975 m, 1951 s, 1936 m, 1921 m, 1892 m.

X-ray powder diffraction studies: For both **2** and **3**, the white powders were cautiously deposited with the aid of a diethyl ether slurry on the surface of a zero background plate (Si(511), supplied by The Gem Dugout, State College, PA). Diffraction data were collected on a Philips PW1820 vertical scan diffractometer ($Cu_{K\alpha}$, $\lambda = 1.5418$ Å), equipped with parallel Soller slits in the incident beam and a secondary beam graphite monochromator. The generator was operated at 40 kV and 40 mA. Stationary sample, DS: 1.0°, RS: 0.2 mm. DS = Divergence slit, RS = receiving slit. Step scan, $\Delta 2\theta = 0.02°$, $5° < 2\theta < 85°$, $t = 20$ s step^{-1}. Indexing, refinement, and molecular plots were performed with TREOR,[16] GSAS,[17] and Schakal,[18] respectively.

According to TREOR, **3** has a monoclinic cell of approximate dimensions $a = 13.14$, $b = 12.43$, and $c = 12.56$ Å, $\beta = 96.4°$ [M(20) = 14; F(20)[19] = 33(0.012, 52)]. The ab initio structure solution is fully described in the text.

For **2** TREOR suggested a trigonal/hexagonal primitive cell of approximate dimensions $a = 14.93$ and $c = 6.98$ Å [M(12) = 71; F(12) = 96(0.007,17)]. Volume considerations led to a Z value of 9, for a monomeric formula of $[ReH(CO)_4]$. Since many different compatible Laue groups ($6/mmm$, $6/m$, $-3m1$, $-31m$ or -3) exist, the structure solution required several independent assumptions to be made with regard to the choice of the correct space group and the determination of the starting model. The odd Z value clearly suggests, in conjunction with the observation that *cis*-$[Re(CO)_4]$ fragments cannot lie on inversion centers, a noncentrosymmetric space group. The small value for the c axis, together with the reduced "molar" volume (V/Z 151 versus 169 Å^3 for nine and twelve $[HRe(CO)_4]$ formula units in **2** and **3**, respectively) rules out the presence of cyclic oligomers and supports the polymeric nature of "molecules" of **2**, hence the presence of a 3_1 (or 3_2) screw axis (also confirmed by the most prominent peak in the Patterson map). Summarizing, the possible space groups are $P3_1$, $P3_121$, $P3_112$, and their enantiomorphs. Since $P3_121$ and $P3_112$ share the common subgroup $P3_1$, we decided to employ it as starting space group and to later verify the need of a higher symmetry descriptor. When run in $P3_1$, EXPO[20] located three crystallographically independent rhenium atoms, each of which generated slightly misoriented (*ab* projection) polymers, with Re···Re distances in the 3.2–3.3 Å range. Raising the space group symmetry (by forcing one rhenium on a twofold axis) dramatically worsened the overall pattern matching, particularly at high angles, where lighter atoms do not substantially contribute to the scattered intensity. Finally the full molecular model was derived from the locations of the metal atoms alone by following the very same methodology described for **3**. The final structural model was then optimized by a full, although restrained,[21] Rietveld refinement (Figure 1). Table 1 contains a summary of crystal data and final structural parameters for **2** and **3**. Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-145922 and CCDC-145923. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB21EZ, UK (fax: (+44) 1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

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Table 1. Summary of crystal data and structure refinement parameters for α-$[\{ReH(CO)_4\}_n]$ (**2**) and $[\{ReH(CO)_4\}_6]$ (**3**).

	C_4HO_4Re (**2**)	$C_{24}H_6O_{24}Re_6$ (**3**)
formula weight	299.3	1795.5
crystal system	trigonal	monoclinic
space group	$P3_1$	$P2_1/n$
a [Å]	14.9733(7)	13.1182(8)
b [Å]	14.9733(7)	12.4078(8)
c [Å]	6.9984(4)	12.5694(8)
α [°]	90	90
β [°]	90	96.328(3)
γ [°]	120	90
V [Å]^3	1358.8(1)	2033.4(2)
Z	9	2
2θ range [°]	15 to 85	17 to 85
steps	3500	3400
no. of independent atoms	30	30
min FWHM [°]	0.18	0.13
R_p, wR_p	0.055, 0.071	0.063, 0.079
R_F	0.054	0.069

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