Rhenium–Carbon Bonding in Er$_2$ReC$_2$, an Organometallic Polymer in the Solid State

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In the recently synthesized rare earth transition metal carbide Er$_2$ReC$_2$ one finds one-dimensional organometallic [ReC$_2$]$^{6-}$ polymers embedded in an Er$^{3+}$ ionic matrix. The electronic structure of the polymeric [ReC$_2$]$^{6-}$ chain was investigated with extended Hückel calculations. As the observed distances already indicated, the calculations show extensive Re–C interactions. Surprisingly, the states at and below the Fermi level are significantly Re–C antibonding. Some alternative structures which would reduce this antibonding are considered. It is predicted that the Fermi level of Er$_2$ReC$_2$ have a great deal of ReC antibonding character, which points to the possible existence of more stable compounds with reduced electron counts. The structural distortions within the polymeric chain and other possible structural alternatives of the same stoichiometry are also examined.

Er$_2$ReC$_2$ Crystal Structure

The ternary carbides R$_2$ReC$_2$ (R = Y, Ce–Nd, Sm, Gd–Tm, Lu) crystallize in the orthorhombic space group Pnma with four formula units per cell. The metal positions correspond to the atomic positions of Co$_2$Si (a distorted cubic body-centered structure), with some octahedral sites filled with carbon atoms. A single-crystal structure was determined for Er$_2$ReC$_2$, whose unit cell is shown in 1. Quasi-one-dimensional polymers of stoichiometry ReC$_2$ are well separated in the lattice. One of these, extended a little, is drawn in 2.

The polymeric structure consists of a -Re–C-Re–C- zigzag chain with an extra terminal carbon atom attached to each Re. All the atoms are in the same plane, and there is a 2, screw axis...
May formally assign a 6- charge to the ReC₂ unit. If the carbons experimental geometries. Calculations are performed the angles observed (108, 109, 143°) are far from equal. We may be approximated by a trigonal planar geometry, even though planar geometry, in the Appendix.

Confidence in the one-dimensionality of the polymer and the formal charge assignment of Er³⁺ and [ReC₂]⁶⁻. The calculation we present here are approximate molecular orbital calculations of the extended Hückel type; the relevant parameters are given along the chain. The middle carbon to Re distances are 2.03 and 1.97 Å, respectively, while the terminal carbon to Re distance is 1.93 Å. These separations are comparable to an estimated distance for a Re=C double bond. The Re atom in the ternary compound is in a distorted trigonal planar coordination geometry, with three C–Re–C angles of 108, 109, and 143°. The Re–C–Re angle is nearly linear (172°).

Each Re has in addition ten Er neighbors at separations ranging from 3.05 to 3.59 Å. The terminal carbon atoms have five Er neighbors, while the middle carbon atoms have four Er neighbors, at distances between 2.46 and 2.62 Å. Although the Re–Er and C–Er interactions at these distances are not negligible, the Re–C interactions are certainly most significant.

With the rare earth elements considered as 3+ cations, we may formally assign a 6– charge to the ReC₂ unit. If the carbons are taken as 4+, really an extreme, the oxidation state of Re may then be assigned as 2+, or a d⁴ configuration.

Given the observed isolation of the ReC₂ chains, our calculations are performed on single [ReC₂]⁶⁻ chains, with idealized and experimental geometries. Calculations on the entire three-dimensional Re₇C₁₅ sublattice in Er₇ReC₁₅ and on the whole crystal lattice of Er₇ReC₁₅ result in similar DOS curves. This gives us confidence in the one-dimensionality of the polymer and the formal charge assignment of Er³⁺ and [ReC₂]⁶⁻. The calculation we present here are approximate molecular orbital calculations of the extended Hückel type; the relevant parameters are given in the Appendix.

### A Molecular Model

The coordination environment of Re atoms in the solid state may be approximated by a trigonal planar geometry, even though the angles observed (108, 109, 143°) are far from equal. We first consider a molecular model, [ReC₂]¹⁰⁻, in an ideal trigonal planar geometry. A T-shaped geometry, another extreme approximation to the observed polymer geometry, is also studied.

![Figure 1](https://example.com/figure1.png)

**Figure 1.** Block diagram of orbital interactions between Re 5d and C 2p orbitals.

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![Figure 1](https://example.com/figure1.png)

**Figure 1 shows schematically how the orbitals on Re atoms**


### Band Structure of Polymeric [ReC₂]¹⁰⁻

Now we calculate the band structure for the organometallic polymer [ReC₂]¹⁰⁻. We begin with an idealized, locally trigonal geometry, keeping all the Re–C bond distances at 2.0 Å, all the C–Re–C angles (θ, φ, and φ') at 120°, and the Re–C–Re angles at 180° (5).

![Figure 5](https://example.com/figure5.png)

Although the angular distortions around Re atoms seem rather large on going from the idealized 5 to 2, the band structures, Fermi levels, and DOS and COOP curves of the two polymers are nearly the same. We will use 5 for subsequent discussions; later we will return to examine the structural distortions which
relate 5 to the experimental structure 2. Figure 3 shows the band structure for 5, with selected crystal orbitals drawn out at $\Gamma' = 0$. Since the unit cell contains two Re and four C atoms, there are a total of 22 bands in the energy window between -15 and -7 eV. Ten of these are from 5d orbitals of two Re atoms, and twelve from 2p orbitals of four carbon atoms. The bands due to Re 6s, 6p and carbon 2s orbitals lie outside of this energy window. All the bands at the zone boundary are doubly degenerate, due to the $2_i$ screw axis along the chain. The bands are numbered and also labeled according to their symmetry with respect to the $xy$ plane ($S$ or $A$) and the $2_i$ screw axis (+ or −). The bands involving Re 5d$_{xz}$, 5d$_{yz}$, and carbon 2p orbitals are antisymmetric ($A$) and those involving Re 5d$_{x^2-y^2}$, 5d$_{xy}$, 5d$_{yz}$, and carbon 2p, 2p$_z$ orbitals are symmetric ($S$).

We notice immediately the similarity of the ordering of the bands to the molecular orbitals of the model compound $[\text{ReC}_3]^{10-}$. Three Re orbitals interact with carbon 2p orbitals of appropriate symmetry to form ten Re–C bonding bands ($1$–$9$ and $11$) located between -14.5 and -12 eV (actually one of them, $9(A^+)$, is made up of only Re 5d$_{xz}$ orbitals, as no carbon 2p orbital combination has the right symmetry to match it). As in the molecular case, the mixing of the Re 6s orbitals lowers the energy of the two bands ($10$ and $12$) with Re 5d$_{z^2}$ character (just below -12 eV). Three bands, $13$, $14$, and $15$, are essentially centered on the carbon atoms. Bands $16$–$22$ are Re–C antibonding. The Fermi level is at $-9.72$ eV, cutting through the bands $18(A^+)$ and $16(S^+)$. One of the degenerate crystal orbitals at $\Gamma' = 0.5$ for each of these two bands is also shown; the two bands are Re–C antibonding across the first Brillouin zone.

The contributions of Re, terminal carbon, and middle carbon atoms to the total DOS are shown in Figure 4. They are spread out over the whole energy range, indicating extensive Re–C bonding interactions. The terminal carbon interacts less with the Re, and this is reflected in a smaller dispersion (second moment) of its contribution to the DOS. The Mulliken population analyses give net atomic charges of Re -2.6, terminal C -2.3, and middle C -1.1, substantially different from their formal oxidation states.

The COOP curve shows clearly the transition from the Re–C bonding region to antibonding at -11 eV. The Fermi level comes...
The structure of Er2ReC2 is unusual.20

The conducting and magnetic properties of the materials
synthesized have not been studied in detail. Our calculations
on the single [ReC2]6- chain and on the whole Er3ReC2 crystal
lattice indicate that the R2ReC2 compounds should be good conductors.
The polymeric [ReC2]6- chains are possibly Pauli-paramagnetic.
The magnetic properties of the materials should be determined
by both the [ReC2]6- chains and the intrinsic magnetism of the
lanthanide ions.

Structural Distortions

In this section we examine the angular distortions around Re atoms. First we vary the \( \theta \) angle in 5 from 180° (fully extended \(-\mathrm{Re}-\mathrm{C}-\mathrm{Re}-\mathrm{C}-\) chain) to 80° (compressed chain) while keeping the terminal carbons "vertical" [i.e., \( \phi = \phi' = (360° - \theta)/2 \)] and the angles at the middle carbons 180°. The energy minimum is located at \( \theta = 110° \) (Figure 5a), in good agreement with the experimental structure.

With the \( \theta \) angle set to 110°, we move the terminal carbon atoms away from "vertical" positions. There are two systematic ways to do this. One could move all terminal carbon atoms in one direction, as observed in the crystal structure of Er2ReC2 (distortion A). Alternatively one could move the terminal carbon atoms on one side of the chain in one direction, while moving those on the other side of the chain in the reverse direction (distortion B). The total energy as a function of \( \phi \) is shown in Figure 5b. Both distortions cost energy, although distortion A is less costly. A tilt of the terminal carbon atoms by about 15° from the vertical positions only incurs a penalty of 0.1 eV, or about 2 kcal/mol. By examining the crystal structure of Er2ReC2 (I), it becomes clear that the terminal carbon would be too close to one of the Er atoms if the \( \phi \) angle were 125° (i.e., the terminal carbon were vertical). The distortion observed in the solid state is likely to be caused by crystal packing forces. A distortion of the Re–C–Re angle from 180 to 172°, also studied by us, has no effect on the band structure of 5.

The basic information we obtained from the calculations on the single [ReC2]6- chain (5) remains valid as we consider the ReC2\(^{6-}\) sublattice and go on to the whole Er3ReC2 crystal lattice. Calculations on the latter indicate that the Re–Er and C–Er interactions are much weaker than the Re–C ones. Only 5% of the Er states were found below the Fermi level. Is the strong Re–C antibonding in the states just below the Fermi level, our most startling finding, changed by inclusion of the rare earth? No, this feature remains.

(20) At first we thought that the atypical behavior might arise from the choice of the ionization potential of the Re 5d orbitals in our calculations. But if one varies the \( N_p \) value of the Re 5d orbital from \(-12.66 \) eV up to \(-10.66 \) eV, the characteristics of the DOS and COOP curves at the Fermi level remain the same.

(21) (a) Richard Dronskowski and Jürgen Köhler, private communications.
(b) Jeitschko, W. Private communication.
Rhenium–Carbon Bonding in $\text{Er}_2\text{ReC}_2$


Figure 4. Contribution of the individual atoms to DOS of 5: (a) Re; (b) terminal carbon; (c) middle carbon; (d) COOP curves for Re–C(terminal) (—) and Re–C(middle) (—) bonds.

Structural Variations

Keeping the $\text{ReC}_2$ stoichiometry, other one-dimensional structures are possible. We examine some of these alternatives as a function of electron count, in particular one-dimensional structures based on trigonal planar, square planar, and tetrahedral Re coordinations shown in 7–9.

Some extended iron and cobalt disulfide anions exist in the form of the tetrahedral edge-sharing chain of 9, and some palladium and platinum disulfide anions in the form of the square-planar edge-sharing ribbon of 8.22 As far as we know there are no simple metal-containing one-dimensional chains of type 7, but the geometry is a plausible alternative based on trigonal planar coordination; a chain of type 7 containing all boron atoms was found in $\text{Ru}_{11}\text{B}_8$.23 The relative total energy of each structure (energy referenced to a hypothetical lattice of noninteracting C–Re–C linear molecules, i.e., relative total energy $= E(\text{C–Re–C}) - E_{\text{isol}}(i)$; a positive energy means the extended structure is more stable than the isolated linear C–Re–C molecule) is plotted as a function of electron counts between 18 and 26 in Figure 6. Between electron counts of 20–24, 5 is the most stable structure; specifically, at an electron count of 21 for $[\text{ReC}_2]^{16}$, 5 is more stable than all the other structures by at least 0.8 eV. As electrons are added, our calculations predict that isolated Re$_2$C$_2$ units should be preferred, at 25 or 26 electrons. Although such high electron

Figure 5. (a) Total energy as the function of $\theta$ in 5. (b) Total energy as the function of $\phi$, $\theta$ set at 110°.

Figure 6. Relative total energy $[=E(\text{C–Re–C}) - E_{\text{isol}}(i)]$ as a function of electron count per Re$_2$C$_2$ unit.

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(23) Asellus, J. Acta Chem. Scand. 1960, 14, 2169. We thank Dr. Jean-François Halet for bringing this reference to our attention.
Table I. Extended Hückel Parameters

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counts are not realistic for ReC2, ternary compounds with the U3IrC2 structure type do contain isolated linear MC2 units. They include Th2NiC2 and U2MC2 ($M = Pt, Rh, Ir, Ru, Os$), and they formally have 26–24 valence electrons, assuming tetravalent Th and U. With an electron count of 18, 9 seems to be more stable; here metal-metal bonding may be important. Relative total energies were also recalculated with the parameters of late transition metals Os and Pt; the graphs obtained were essentially the same as in Figure 6. Of course, our discussions are restricted to the above-mentioned structures; other possible structural types exist in two or three dimensions.

Conclusion

The electronic structure of the one-dimensional organometallic polymer [ReC2]4+ in Er2ReC2 is characterized by substantial Re–C antibonding character at the Fermi level. We predict that reduced valence electron counts might lead to other stable R2MC2 compounds. The energetics of several alternative one-dimensional structures as well as a linear triatomic C–M–C unit are examined as a function of the valence electron count. The only two known structural types with the R2MC2 stoichiometry, Er2ReC2 and U2IrC2, are the most stable with their respective electron counts. Further syntheses of new compounds in this family are encouraged.

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Appendix

Tight-binding extended Hückel calculations, with a weighted $H_{ij}$ approximation, have been applied throughout this paper. The extended Hückel parameters $H_{ij}$ for all atoms were taken from earlier work24,25 and are listed in Table I. All the Re–C bonds are set to 2 Å. Ideal trigonal planar, square planar, and tetrahedral geometries are used for Re coordination for structures 7–9, respectively.