Rhenium–Carbon Bonding in Er_2ReC_2, an Organometallic Polymer in the Solid State

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Received October 9, 1992

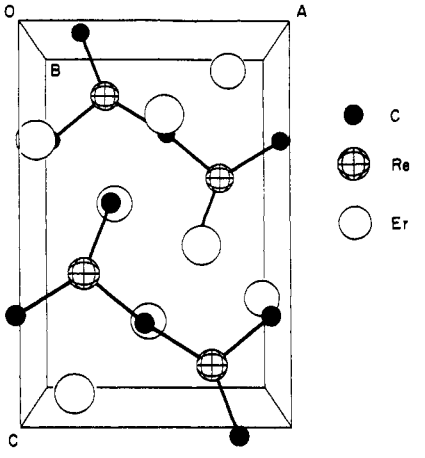
In the recently synthesized rare earth transition metal carbide Er_2ReC_2 one finds one-dimensional organometallic $[ReC_2]^{6-}$ polymers embedded in an Er^{3+} ionic matrix. The electronic structure of the polymeric $[ReC_2]^{6-}$ chain was investigated with extended Hückel calculations. As the observed 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 lower electron counts for the R_2ReC_2 (R = rare earth) stoichiometry would yield one-dimensional structures with still stronger Re–C bonds. Relative stabilities of several alternative structure types are examined as a function of the electron count. With 21 electrons for $[ReC_2]^{6-}$, the observed structural type was most stable. With 25–26 electron counts, the linear triatomic C–M–C unit, as found in the known U_2IrC_2 and Th_2NiC_2, was more favorable.

Organometallic compounds are characterized by single and multiple chemical bonds between metals and carbons. Their structure and reactivity have enriched modern chemistry. Recently, a variety of extended ternary transition metal carbides have been synthesized.[1-9] The third elements in these ternary systems are lanthanides, group 3 metals, or actinides, formally in the 3+ or 4+ oxidation state. Judging by the interatomic distances in these materials, the transition metals and carbon atoms are very strongly bonded to each other, frequently forming organometallic nets. One could think of these compounds as charged organometallic polymers embedded in an ionic matrix. These polymers may possess interesting conducting and magnetic properties. That useful guideline of molecular organometallic chemistry, the 18-electron rule, does not help us understand their electron counts and electronic structures. The solid-state language of band structures, density of states, and Fermi levels is necessary to describe these fascinating materials.

Previously we have studied the electronic structures of YCoC,[10] a simple one-dimensional polymer, as well as $DyCoC_2$ and $UCoC_2$,[11] two-dimensional polymers containing C_2 units. Within the RMC_2 stoichiometry (R = lanthanide, actinide; M = transition metal), there are now six structural types known, five of which contain C_2 units.[1,12,13] In this paper, we turn our attention to a new one-dimensional organometallic polymer in the ternary compound Er_2ReC_2 synthesized by the Jeitschko group.[2] For the stoichiometry R_2MC_2 the only other structural type known is U_2IrC_2, which contains instead linear triatomic C–M–C units.[6,14,15] As will emerge in the discussion, the states at the Fermi level of Er_2ReC_2 have a great deal of Re–C 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_2ReC_2 Crystal Structure

The ternary carbides R_2ReC_2 (R = Y, Ce–Nd, Sm, Gd–Tm, Lu) crystallize in the orthorhombic space group *Pnma* with four formula units per cell.[2] The metal positions correspond to the atomic positions of Co_2Si (a distorted cubic body-centered structure), with some octahedral sites filled with carbon atoms. A single-crystal structure was determined for Er_2ReC_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**.



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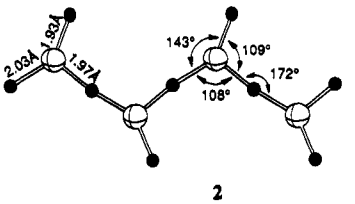

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The polymeric structure consists of a –Re–C–Re–C– zigzag chain with an extra terminal carbon atom attached to each Re. All the atoms are in the same plane, and there is a 2_1 screw axis

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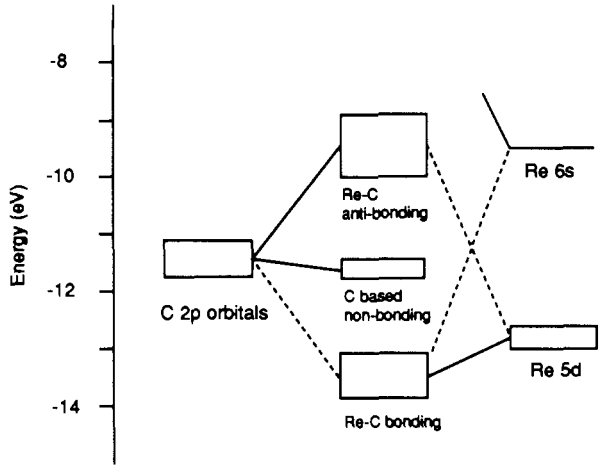

Figure 1. Block diagram of orbital interactions between Re 5d and C 2p orbitals.

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.[2] 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 ReC_2 unit. If the carbons are taken as 4–, really an extreme, the oxidation state of Re may then be assigned as 2+, or a d^5 configuration.

Given the observed isolation of the ReC_2 chains, our calculations are performed on single $[ReC_2]^{6-}$ chains, with idealized and experimental geometries. Calculations on the entire three-dimensional ReC_2 sublattice in Er_2ReC_2 and on the whole crystal lattice of Er_2ReC_2 result in similar DOS curves. This gives us confidence in the one-dimensionality of the polymer and the formal charge assignment of Er^{3+} and $[ReC_2]^{6-}$. The calculation we present here are approximate molecular orbital calculations of the extended Hückel type;[16-19] 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, $[ReC_3]^{10-}$, in an ideal trigonal planar geometry, **3**. A T-shaped geometry, **4**, another extreme approximation to the observed polymer geometry, is also studied.

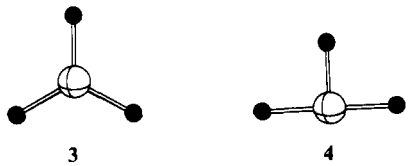

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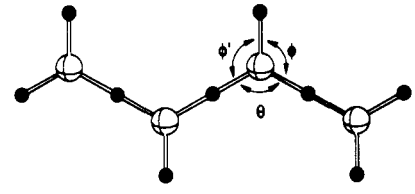
Figure 1 shows schematically how the orbitals on Re atoms interact with those on carbon ligands. Since carbon 2s orbitals are very low in energy, and Re 6p orbitals are high up in energy, both contribute little to Re–C bonding. Our parameters place the Re 5d orbitals just below the carbon 2p orbitals and the Re 5s orbital above the carbon 2p orbitals. The major bonding interactions are between carbon 2p symmetry-adapted fragment orbitals (9 orbitals) and Re 5d orbitals. Starting from the bottom of the diagram, we have Re–C bonding orbitals, mainly carbon-based 2p Re–C nonbonding combinations, and Re–C antibonding orbitals. The metal–carbon bonding orbitals have more Re 5d than carbon 2p character, whereas the antibonding ones are weighted more on the carbon atoms. This is the reverse of what one usually encounters in transition metal complexes, due to low metal d orbital and high ligand p orbital energy.[11]

The Walsh diagram between T-shaped and trigonal planar ReC_3 is shown in Figure 2, along with the orbital drawings. (For these molecular orbitals and later for the crystal orbitals, p_x, p_y, $d_{x^2-y^2}$, d_{xy}, and d_{z^2} are drawn in the xy plane; for p_z, d_{xz}, and d_{yz} orbitals, only the lobes above the xy plane are shown and these orbitals are labeled.) At the bottom of the diagram five Re 5d orbitals find symmetry-adapted combintions from the carbon ligands to form five Re–C bonding orbitals. There should be five Re–C antibonding orbitals at the top of the diagram. We only find four of them. The missing one should involve the Re $5d_{z^2}$ orbital; however, mixing in of the Re 6s orbital turns this Re–C antibonding combination into a slightly Re–C bonding orbital ($3a_1$ under C_{2v}, or $2a_1'$ under D_{3h} point symmetry), located just above the five Re–C bonding orbitals. This type of $(n+1)s/nd_{z^2}$ mixing has been analyzed for YCoC [10] and will not be discussed further here.

In the middle of the energy diagram, four carbon-based nonbonding orbitals are located. With a d^5 electron count for Re(II), the 2e'' orbital in trigonal planar $[ReC_3]^{10-}$ (or $2a_2$ orbital in T-shaped $[ReC_3]^{10-}$) is occupied by a single electron. The trigonal planar $[ReC_3]^{10-}$ geometry is favored by 1.5 eV over the T-shaped one. It appears that the major contribution to the stabilization of the trigonal planar form is from the energy lowering of the carbon-based nonbonding orbitals. The energy of the $3b_2$ orbital in the T-shaped form ($1a_2'$ in D_{3h}) is lowered most significantly, because the C–C antibonding interactions are minimized in the trigonal form. The center of gravity for the Re–C bonding orbitals remains essentially the same during the structural distortion. The relative stability of the structures is also indicated by the Re–C overlap populations (OP): in the trigonal planar geometry, the OP's are 0.89 for all three Re–C bonds; whereas for the T-shaped geometry, the OP's are 0.92 for two Re–C bonds and only 0.67 for the third Re–C bond.

Band Structure of Polymeric $[ReC_2]^{6-}$

Now we calculate the band structure for the organometallic polymer $[ReC_2]^{6-}$. 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**).



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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

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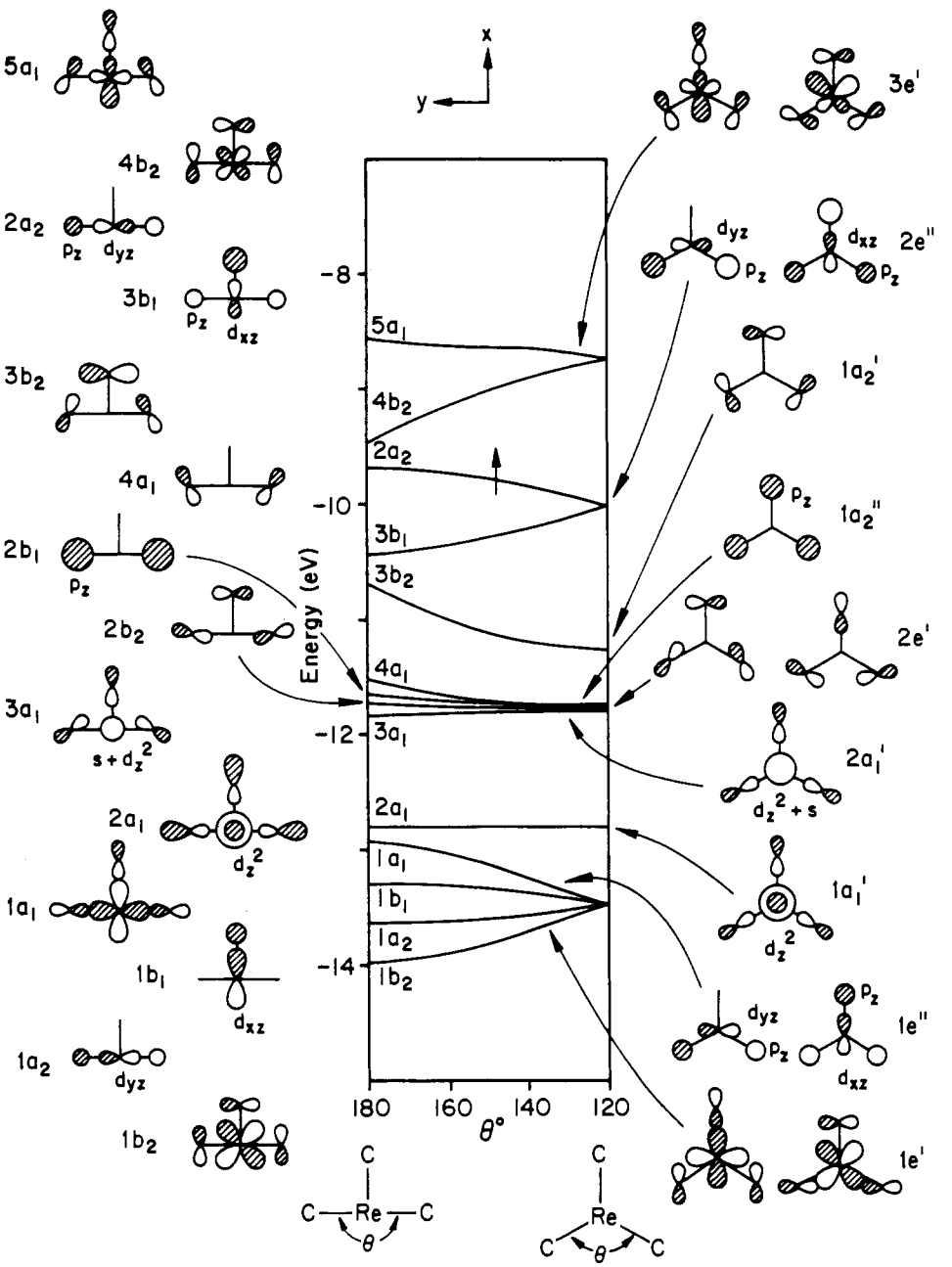


Figure 2. Walsh diagram for the model compound $[ReC_3]^{10-}$: Left side, T-shaped geometry; right side, trigonal planar geometry. The arrow indicates the highest singly occupied MO of the complex.

relate **5** to the experimental structure **2**. Figure 3 shows the band structure for **5**, with selected crystal orbitals drawn out at Γ = 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_1 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_1 screw axis (+ or −). The bands involving Re $5d_{xz}$, $5d_{yz}$ and carbon $2p_z$ orbitals are antisymmetric (A) and those involving Re $5d_{x^2-y^2}$, $5d_{xy}$, $5d_{z^2}$ and carbon $2p_x$, $2p_y$ orbitals are symmetric (S).

We notice immediately the similarity of the ordering of the bands to the molecular orbitals of the model compound $[ReC_3]^{10-}$, **3**. Ten 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 Γ = 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

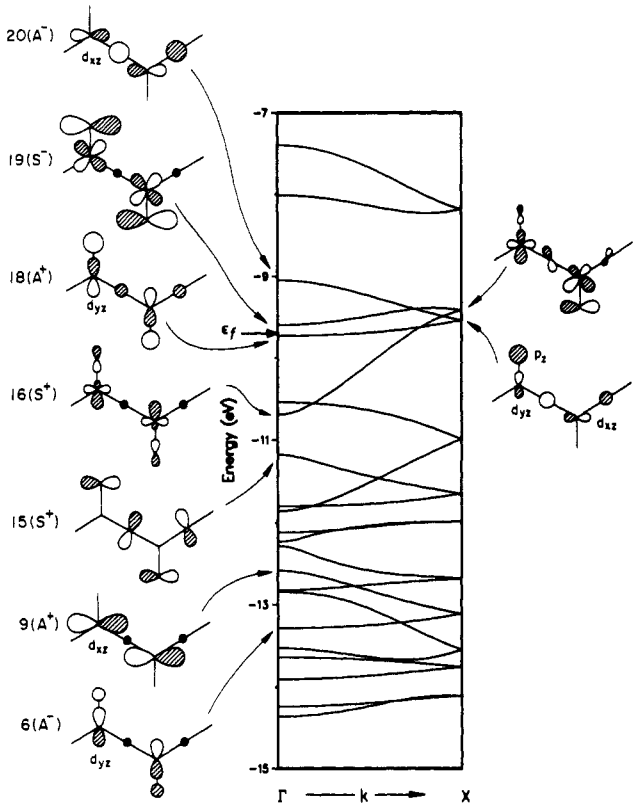
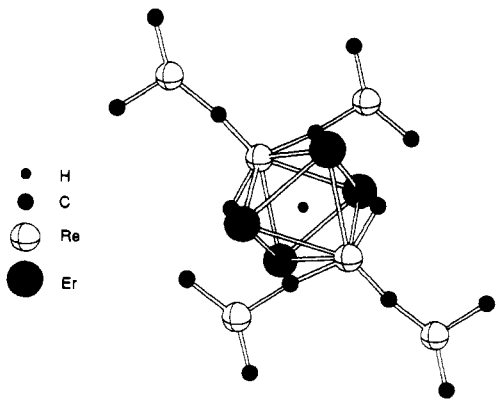


Figure 3. Band structure of **5**.

at much higher energy, in a region of substantial Re–C antibonding. We have a lot of experience with COOP curves, and a generalization that seems to hold is that structures maximize bonding. In most extended structures the Fermi level comes in the region where the overlap population switches from bonding to antibonding. Filling too many antibonding orbitals clearly destroys a structure; there always are alternative geometries available. This polymer is thus unusual.[20]

The generalization that stable structures fill bonding states is sufficiently compelling to make one reviewer of this paper voice what we were initially not brave enough to do—might the composition or structure of the compound be incorrect? The reviewer suggests that it might possibly contain an extra oxide or hydrides. Hydrogens in positions where there are little interactions with Re or C would be hydridic, close to H^-, and could oxidize the ReC_2 chain toward $[ReC_2]^{4-}$, where only Re–C bonding states are filled.

As Jeitschko et al. point out,[2] the Er_2ReC_2 structure may be related to a distorted body-centered structure. There are vacant octahedral voids in this geometry, and one could inquire whether these voids could contain hydrides. Structure **6** shows the largest



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such void, located at one of the 4b special positions, found for us by Dronskowski and Köhler.[21a] The center of the cavity is 2.3 Å from two Re's and 2.5 Å from four Er's; in addition, four carbons are 2.5 and 2.7 Å from the center. A hydrogen atom in this cavity should be quite hydridic, and this we confirmed with detailed calculations. However, there is no calculated reduction for Re–C antibonding when a hydride is introduced into this octahedral cavity. A reexamination of the original structure definitely showed no interstitial atom in this void.[21b]

Given that the bands at the Fermi level are Re–C antibonding for Er_2ReC_2, more stable structures should be formed on removing some electrons from the system. Specifically, $[ReC_2]^{4-}$ would have all the bonding bands filled and all the antibonding bands empty. Substitution of R^{3+} with alkaline earth metals should create such a system. Substitution of Re with group 5 and 6 metals may also yield stable compounds. We suggest synthetic efforts directed at making such compounds, which should have especially strong M–C bonds.

The conducting and magnetic properties of the materials synthesized have not been studied in detail. Our calculations on the single $[ReC_2]^{6-}$ chain and on the whole Er_2ReC_2 crystal lattice indicate that the R_2ReC_2 compounds should be good conductors. The polymeric $[ReC_2]^{6-}$ chains are possibly Pauli-paramagnetic. The magnetic properties of the materials should be determined by both the $[ReC_2]^{6-}$ 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 θ angle in **5** from 180° (fully extended –Re–C–Re–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 θ = 110° (Figure 5a), in good agreement with the experimental structure.

With the θ 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 Er_2ReC_2 (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 the function of ϕ 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 Er_2ReC_2 (**1**), it becomes clear that the terminal carbon would be too close to one of the Er atoms if the ϕ 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 $[ReC_2]^{6-}$ chain (**5**) remains valid as we consider the ReC_2^{6-} sublattice and go on to the whole Er_2ReC_2 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 H_{ii} 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.

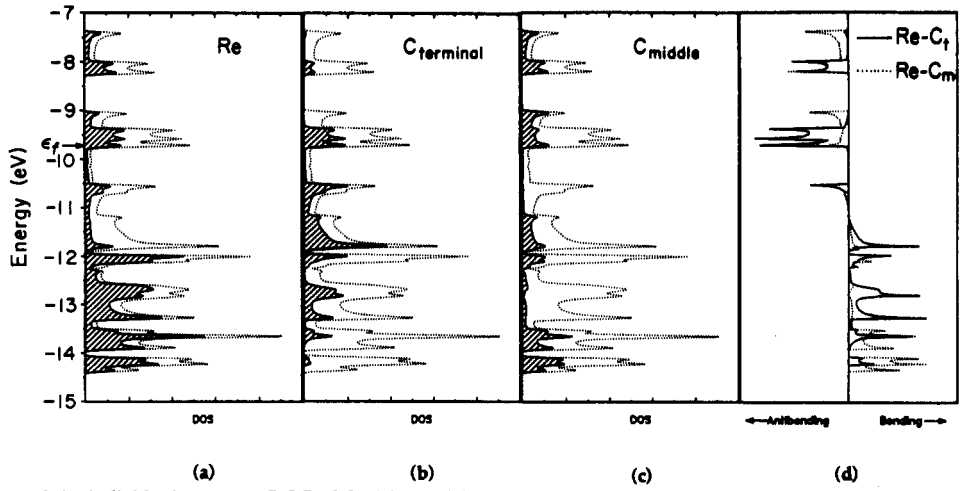
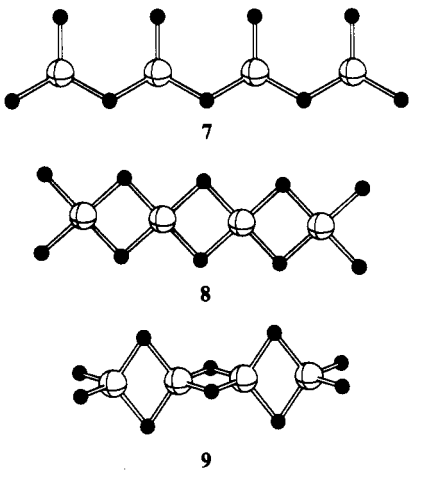


Figure 4. Contribution of the individual atoms to DOS of **5**: (a) Re; (b) terminal carbon; (c) middle carbon; (d) COOP curves for Re–C(terminal) (—) and Re–C(middle) (···) bonds.

Structural Variations

Keeping the 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**.



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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 $Ru_{11}B_8$.[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(C–Re–C) – E_{total}(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 $[ReC_2]^{6-}$, **5** is more stable than all the other structures by at least 0.8 eV. As electrons are added, our calculations predict that isolated ReC_2 units should be preferred, at 25 or 26 electrons. Although such high electron

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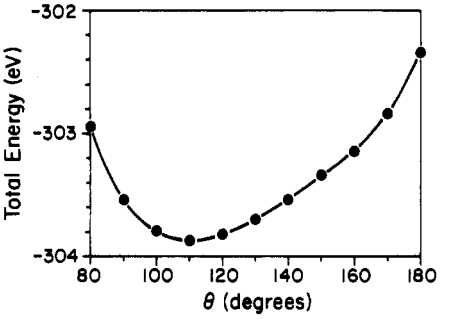
(23) Aselius, J. *Acta Chem. Scand.* **1960**, *14*, 2169. We thank Dr. Jean-François Halet for bringing this reference to our attention.



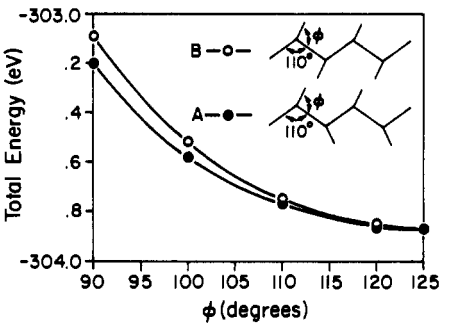


Figure 5. (a) Total energy as the function of θ in **5**. (b) Total energy as the function of ϕ, θ set at 110°.

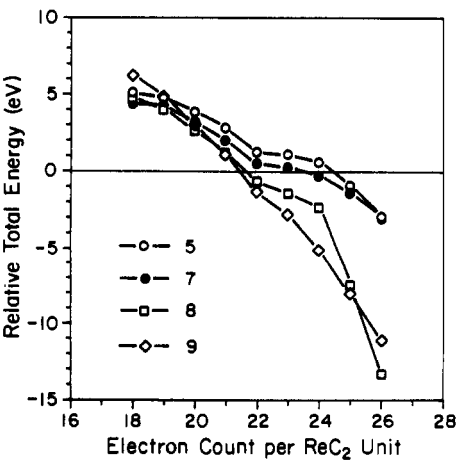


Figure 6. Relative total energy [$=E$(C–Re–C) – E_{total}(i)] as a function of electron count per ReC_2 unit.

Table I. Extended Hückel Parameters

atom	orbital	H_{ii} (eV)	ξ_1	ξ_2	c_1	c_2
Re	6s	−9.36	2.398			
	6p	−5.96	2.372			
	5d	−12.66	5.343	2.277	0.6662	0.5910
Er	6s	−6.0	2.00			
	6p	−4.0	2.00			
	5d	−7.0	3.50	1.30	0.7734	0.4569
C	2s	−21.4	1.625			
	2p	−11.4	1.625			

counts are not realistic for ReC_2, ternary compounds with the U_2IrC_2 structure type do contain isolated linear MC_2 units.[14] They include Th_2NiC_2 and U_2MC_2 (M = Pt, Rh, Ir, Ru, Os),[6,14,15] 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 $[ReC_2]^{6-}$ in Er_2ReC_2 is characterized by substantial Re–C antibonding character at the Fermi level. We predict that reduced valence electron counts might lead to other stable R_2MC_2 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 R_2MC_2 stoichiometry, Er_2ReC_2 and U_2IrC_2, are the most stable with their respective electron counts. Further syntheses of new compounds in this family are encouraged.

Acknowledgment. This work was supported by National Science Foundation Research Grant CHE8912070. We thank Jane Jorgenson for her expert drawings, and two reviewers for their comments, and R. Dronskowski and J. Köhler for a search of possible interstitial sites.

Appendix

Tight-binding extended Hückel calculations, with a weighted H_{ij} approximation, have been applied throughout this paper. The extended Hückel parameters H_{ii} for all atoms were taken from earlier work[24,25] 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.

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