

Deformation and Bonding in a Puckered Re–C Square Net

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Dedicated to Professor Rudolf Hoppe on the Occasion of his 80th Birthday

Abstract. $\text{Sc}_5\text{Re}_2\text{C}_7$ contains unusual Re–C puckered “square” nets, isolated C_3 units, and scandium ions. Its electron count drives the peculiar distortion of the Re–C nets, resulting in quite different Re–C and Re–Re bonding along each direction. Indeed, some of the Re–C interactions emerge as stronger than double bonds. The puckering, in turn, enables a bonding role for the scandium atoms

in addition to their function as electron donors to the nets and the isolated carbide units.

Keywords: Electronic structure; Extended Hückel theory; Transition-metal carbide; Scandium bonding; Metal–carbon multiple bond

Deformation und Bindung in einem gefalteten quadratischen Re–C-Netz

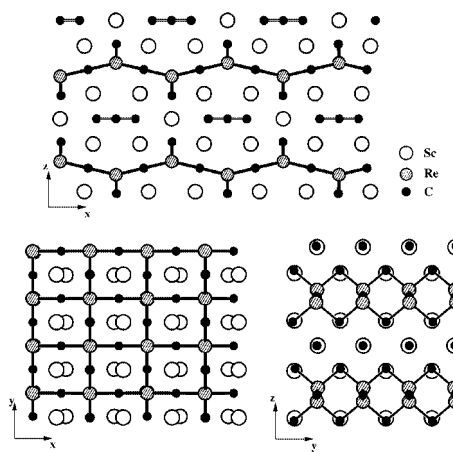
Inhaltsübersicht. $\text{Sc}_5\text{Re}_2\text{C}_7$ enthält ungewöhnliche „quadratische“ Re–C-Netze, isolierte C_3 -Einheiten und Scandium-Ionen. Die Anzahl seiner Elektronen bestimmt die besondere Verzerrung der Re–C-Netze, was ganz verschiedene Re–C- und Re–Re-Bindungen in jeder Richtung zur Folge hat. Tatsächlich erscheinen einige

der Re–C-Wechselwirkungen stärker als Doppelbindungen. Die Faltung erlaubt den Scandium-Atomen andererseits ihre Rolle als Bindungspartner zusätzlich zu ihrer Funktion als Elektronen-Donoren des Netzes und der isolierten Carbid-Einheiten.

Introduction

Ternary transition metal carbides exhibit great structural diversity, containing isolated carbon atoms, C_2 pairs and C_3 groups. One also finds in them interesting metal–carbon networks of varying dimensionality. A decade ago, a new carbide was synthesized by Pöttgen and Jeitschko [1] which contains both C_3 groups and individual C atoms. $\text{Sc}_5\text{Re}_2\text{C}_7$ (shown in three views in **1**) has square nets of rhenium and carbon atoms which are highly distorted through puckering; the bonds in these nets are indicated with heavier black lines. The axes in **1** are assigned for convenience during analysis (placing the nets in the xy plane); our z axis corresponds to the \mathbf{b} axis of the original compound.

The Re–C sheets have two types of carbon atoms (small black circle), each bridging two Re atoms (lined circles) in either a linear or a bent geometry. The linear C_3 units are isolated from each other and from the Re–C nets by the scandium atoms (large white circles), which also separate



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the two-dimensional Re–C networks from each other. The unusual Re–C square nets attracted our interest, leading to the investigation of the electronic structure of the compound reported in this paper.

Assigning electrons

We begin by dissecting the three-dimensional structure of $\text{Sc}_5\text{Re}_2\text{C}_7$ into its chemically meaningful components and distributing the electrons accordingly. Based on the results

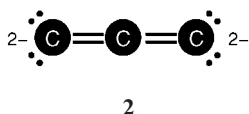
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of this partition, we will then be able to study the effects of electron count in the Re–C networks.

Since the shortest Sc–Sc distance is 3.21 Å, as a first approximation we treat the scandium atoms (or ions) as isolated, providing the Madelung “glue” to hold the entire structure together. A typical formal Sc charge is 3+, which is not unlikely in this structure since Sc has a low electronegativity in comparison with the other atoms in the compound. [2] The C₃ units are quite isolated from each other – and from the rest of the structure – by the Sc matrix, allowing us to consider them separately. The C–C bond length in these C₃ units is 1.34 Å, which suggests a double bond. A closed shell configuration for the C₃ unit (found to be appropriate in some other structures [3]) then requires two additional electrons for each of the two end carbon atoms to complete the octet, giving C₃^{4–} (2) as the formal electron count. So far we have (Sc₅¹⁵⁺)(C₃^{4–}), which implies a charge of 11– on the two-dimensional Re₂C₄ nets.

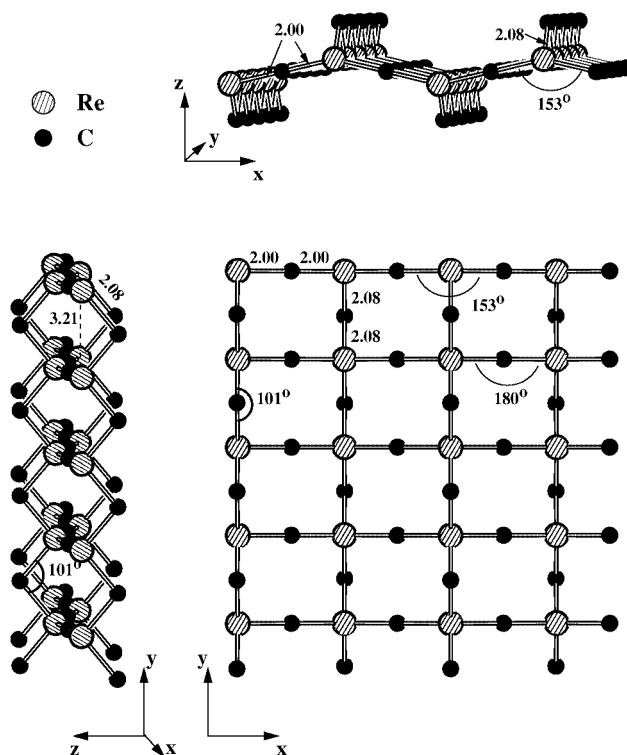


The Re–C nets are shown from the top and from two side views in 1. The side views highlight the puckered nature of the nets, while their similarity to a square net is more obvious in the top view. Within the $\frac{2}{3}[\text{Re}_2\text{C}_4^{1-}]$ net there are no carbon-carbon bonds. Given the relative electronegativities of Re and C (2.2 vs. 2.5) [2], one starting point is to complete the octet at C, *i.e.* C^{4–}, which then leads to a formal Re^{2.5+}. This is within a reasonable range of oxidation states of Re, but the fractional formal charge is a bit odd. Clearly a delocalized band picture will be needed to describe the bonding in this system.

Numerous questions arise. For instance, is it reasonable to assign such a high negative charge (4–) to carbon, considering that the bond lengths between C and Re (2.00 and 2.08 Å) are short enough that one would expect substantial sharing of electrons? Also, what does it mean to have a 2.5+ charge on Re? Might there be an alternation of 3+ and 2+ rhenium, or perhaps a weak bond between neighboring rhenium atoms (at 3.21 Å distance)? Finally, what role do the Sc atoms play in bonding?

Re–C bonding: the carbon point of view

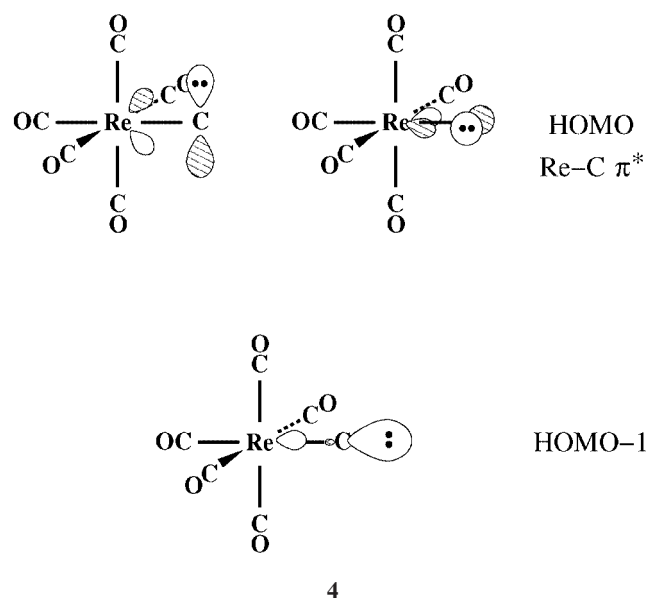
The $\frac{2}{3}[\text{Re}_2\text{C}_4^{1-}]$ substructure (3) is shown below from three different viewpoints, with key bond lengths and angles indicated. The net is significantly distorted from planar, with C–Re–C angles of 101° and 153°. (The corresponding Re–C–Re angles are 101° and 180°, one carbon “bent” and one “linear.”) There are two types of Re–C bonds, one 2.00 Å long (to C_{linear}) and the other slightly longer at 2.08 Å (to C_{bent}, the carbon bent at 101°).



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In the original report [1], the authors suggested that the Re–C bonds are essentially equivalent and could all be considered as having a bond order somewhat less than two. A single carbon with two double bonds (as in allene) should be linear, yet one of the Re–C–Re angles is smaller even than the tetrahedral angle! The Mulliken overlap population (OP), a useful indicator of bonding, is significantly different between the Re–C_{bent} and Re–C_{linear} bonds. We calculate the OP for the shorter Re–C_{linear} bonds to be 0.872, compared with 0.560 for the longer Re–C_{bent} bonds. This drop of about one third in the overlap population is *not* solely due to the slight lengthening of the bond, since similar results (within 10%) were obtained with equal bond lengths for these angles. Clearly the two kinds of Re–C bonds are electronically inequivalent.

To obtain a comparison standard for Re–C bonding, we select as models two discrete molecules having the appropriate electron count for Re–C single and double bonds, respectively. The single Re–C bonds might be modeled by (Re(CO)₅)₂CH₂ or (Re(CO)₅)₂C^{2–}, constructed from fragments of two prototypical single-bonded molecules: ethane and rhenium pentacarbonyl dimer [4]. Unfortunately, these Re–C–Re units cannot be constructed for the 101° Re–C–Re bending angle taken from the solid state structure, because the CO ligands come too close. Therefore we must model the bonds individually with Re(CO)₅CH₃ or Re(CO)₅C^{3–}.



The Re–C OP for $(\text{CO})_5\text{Re}-\text{C}^{3-}$ was 0.516 at 2.00 Å Re–C separation (or 0.483 at 2.08 Å separation). The interaction diagram between the $\text{Re}(\text{CO})_5$ and C^{3-} fragments at 2.08 Å is shown below in Figure 1, with the Re–C molecular orbital overlap population (MOOP) curve [5] for the molecule indicating the degree of Re–C bonding for each energy level. The doubly-degenerate highest occupied molecular orbital (HOMO) in $(\text{CO})_5\text{ReC}^{3-}$ is Re–C π antibonding, a counterpart to the corresponding Re–C π

bonding orbitals below (HOMO-3 and HOMO-4). The Re–C π^* HOMO is derived from two of the formal lone pairs on C, with the third lone pair being the principal component of the HOMO-1, as shown in 4. The true Re–C σ bond is concentrated mostly in an orbital located below the energy window shown. Upon filling of all π and π^* orbitals, we have a net single bond between Re and C and the OP of 0.483 quoted above. A similar situation is found for the model at 2.00 Å Re–C separation.

In Figure 1 at right are the COOP curves for the two types of Re–C bonds in sublattice 3. Most of the Re–C σ bonding states lie below the energy window shown. The sharp peaks at about –13 eV are Re–C π bonding, and the Fermi level lies in a region of Re–C π antibonding. The Re–C_{bent} COOP curve would describe a Re–C single bond if we were filling all of the π and π^* states. However, the integration indicates that only about a third of those π^* states are occupied at our electron count, so the bond should be somewhat stronger than a single bond. The crystal orbital overlap population (COOP) integration (0.560) supports this conclusion.

For a double bond model, we can use the same molecule but with 2 electrons fewer. The Re–C OP for $(\text{CO})_5\text{Re}^+=\text{C}^{2-}$ is 0.715 at 2.00 Å (or 0.661 at 2.08 Å). The π^* level is now half-filled, so the net Re–C bond is stronger. (The interaction diagram and MOOP curve for this model at either Re–C distance are quite similar – except for the electron count – to those shown in Figure 1 for the single bond model, so we do not reproduce them here.) The COOP curve for the shorter Re–C_{linear} bonds in the ex-

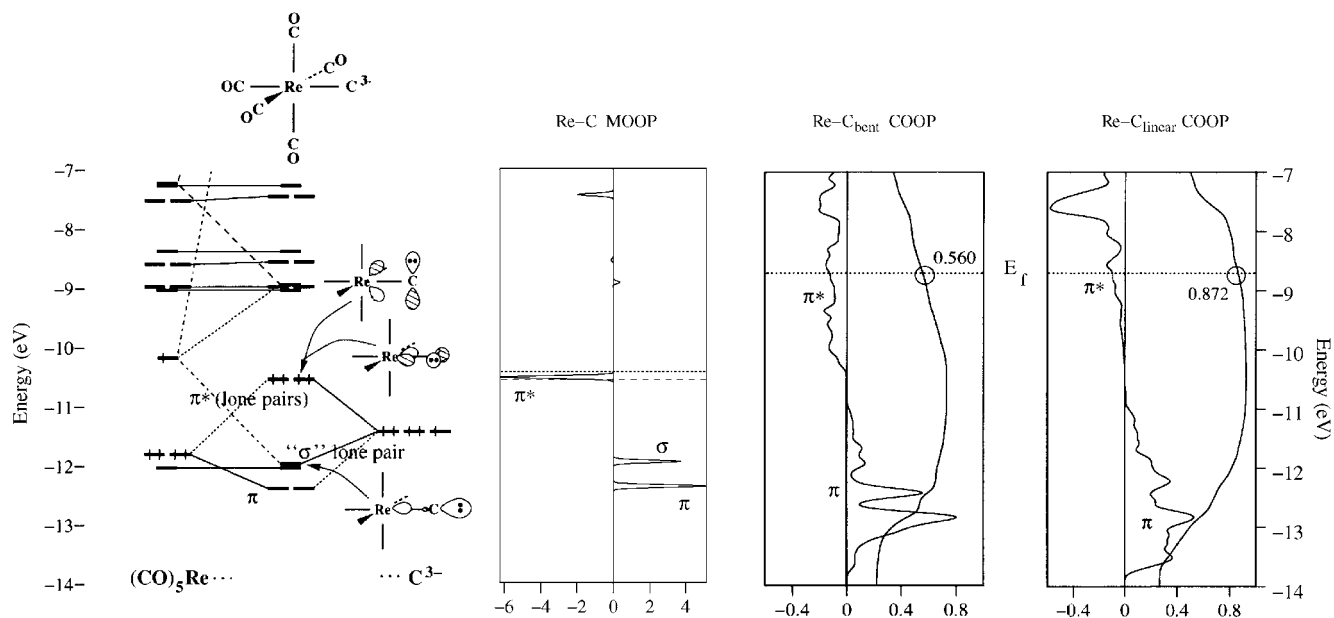


Figure 1 The interaction diagram of $(\text{CO})_5\text{Re}-\text{C}^{3-}$, a model for Re–C single bonding, is shown at left, with the MOOP curve for the model next to it. The principal Re–C bonding and antibonding orbitals in this energy window are labeled; there are additional Re–C σ bonding orbitals lower in energy. The interaction diagram and MOOP curve for $(\text{CO})_5\text{Re}^+=\text{C}^{2-}$, our double-bond model, are quite similar apart from the electron count. At right are the COOP curves for the two types of Re–C bonds in network 3. Many more π^* states are filled in Re–C_{bent} than in Re–C_{linear}, supporting our description of the first as a strong single bond and the second as a very strong double bond.

tended network, **3**, indicates a parallel situation in the solid state. As seen at right in Figure 1, the Fermi level indicates that all of the bonding states and a small fraction (less than 5%) of the Re–C antibonding states are occupied; Re–C bonding is thus nearly maximized. There is clearly more π bonding of the C with both Re atoms: the value of the Re–C COOP is 0.872, which is higher than the OP for the molecular model with a ReC double bond. Overlap populations are not bond orders, but we might even say that in the extended structure one is on the way to a ReC triple bond.

Puckering in the Re–C Network: The Re point of view

From the carbon's point of view, **3** may be roughly described as having a network of Re=C=Re=C... chains running in the *x* direction and approximately single bonded Re–C–Re–C... chains (strongly bent at C) running along *z*. Is this reasonable for the Re atoms, though? Each Re atom is coordinated by four carbon atoms, two *via* double bonds and two *via* single bonds. The charge assignment of the previous section made the Re formally 2.5+ and each carbon formally 4–. From that ionic starting point, two carbon atoms can be thought of as donating four electrons each to the Re through double bonds, and the Re receives

a total of four more electrons from the two singly-bonded carbon atoms. This, plus the “4.5” *d* electrons on the Re, adds up to a “16.5”-electron complex.

There are plenty of 16-electron Re complexes, and a 2+ or 3+ formal oxidation state for Re, while not the most common one, is not unheard of [6]. The electronic structure at the rhenium atoms thus seems approximately right from several viewpoints. However, we would like to look a bit deeper to understand the “16.5” electrons. The coordination at the Re is actually distorted from an idealized square planar geometry (appropriate for 16 electrons) to something between saw-horse (C_{2v} , SF₄-like) and tetrahedral arrangements. The puckering of the Re–C sheet also brings neighboring rhenium atoms within a sheet to 3.21 Å away from each other along the *z* direction in the crystal. These two details will help explain the accommodation of the odd “half electron.”

To choose the molecular model for the metal coordination in **3** we start by “cutting out” a Re, replacing its ligands with H atoms. This just takes into account the σ bonding between Re and its neighbors. The electron count in our resulting model, ReH₄[–], corresponds to Re³⁺, *i.e.* half an electron oxidized relative to the solid state net. In Figure 2 (left) the energy levels are shown for the ReH₄[–] molecular models in a hypothetical D_{4h} square planar geometry, a rectangular geometry, and a C_{2v} puckered rectangular ge-

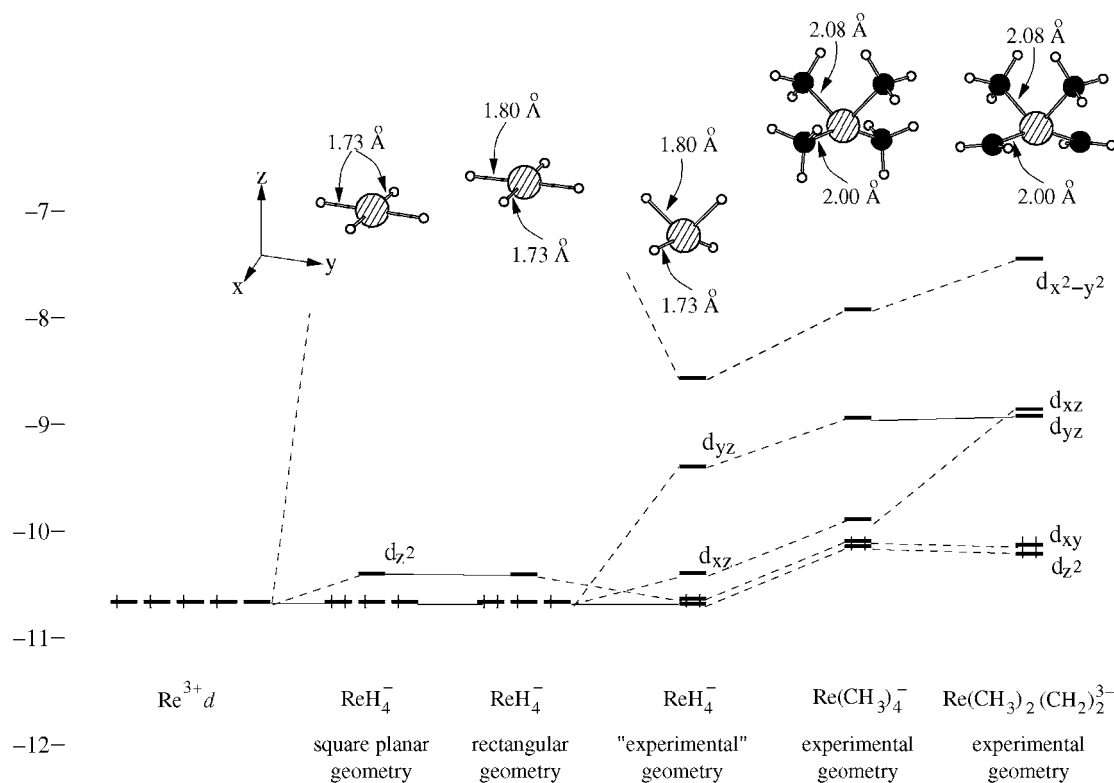


Figure 2 Energy level diagram of $[\text{Re}(\text{CH}_3)_2(\text{CH}_2)_2]^{3-}$, a molecular model of the Re coordination in $\frac{2}{3}[\text{Re}_2\text{C}_4^{1-}]$ (**3**), with experimental Re–C bond lengths and C–Re–C angles (right). For comparison, the energy level diagrams of four models without Re–ligand π interactions are also shown. From left, they are: a square planar $[\text{ReH}_4]^-$ model, a rectangular $[\text{ReH}_4]^-$ model (mimicking the different Re–C bond lengths), a puckered $[\text{ReH}_4]^-$ model, and an analogous puckered $[\text{Re}(\text{CH}_3)_4]^-$ model. The energy levels are labeled by the Re *d* orbitals which dominate each corresponding wavefunction.

ometry with angles as in the experimental structure. The Re–H bond lengths (1.73 and 1.83 Å) are also scaled to model the change in covalent radius from C to H, and the difference between the two kinds of C bonding to the Re. In these models the “puckering axis” is in the z direction, for simplicity of analysis, although we should remember that this direction is defined in the crystal structure as y .

In the square planar coordination, only the $d_{x^2-y^2}$ orbital splits off from the other four orbitals. (See Figure 2 at left.) As two of the Re–H bond lengths are lengthened from 1.73 Å to 1.80 Å, moving to the right in Figure 2, nothing much happens in the d -block. The subsequent deformation to a quasi-sawhorse coordination at the Re moves the H atoms out of plane, and stabilizes the $d_{x^2-y^2}$ and d_{z^2} orbitals (there is now less antibonding character in these) while destabilizing the out-of-plane orbitals (where antibonding with H is turned on). For a low spin d^4 configuration, the d_{z^2} and d_{xy} orbitals would be occupied.

To bring the model for Re coordination closer to reality while still allowing only σ bonds, we replace the H's with carbon-based ligands. An appropriately passivated C ligand would be CH_3 , yielding $\text{Re}(\text{CH}_3)_4^-$, which maintains the d^4 electron count for Re. The energy levels resulting from this substitution, shown near right in Figure 2, are shifted up in energy relative to those of the ReH_4^- model, but they maintain the same order.

To “turn on” the π bonding possibilities between Re and its ligands, we replace the two carbon ligands which are 2 Å away from the Re with CH_2^- . This follows our analysis of Re–C bonding in the previous section. The energy levels shown at right in Figure 2 for the resulting model, $\text{Re}(\text{CH}_2)_2(\text{CH}_3)_2^-$, differ markedly from those of the previous all- σ -bonded model. The additional π interactions between Re and C (which were not possible in previous models) greatly destabilize the $d_{x^2-y^2}$ - and d_{xz} -based orbitals, while leaving the other orbitals at about the same energy.

The net result is that the d_{xz} and d_{yz} orbitals switch places as LUMO and LUMO+1, assuming a low-spin complex. We should point out, however, that these two orbitals are very close in energy. Therefore, from the molecular model it is not clear where the additional 1/2 electron per Re would go. In the extended calculation of the solid state structure, these orbitals form bands which cross the Fermi region so that the additional 1/2 electron per Re occupies both d_{xz} - and d_{yz} -based crystal orbitals. These are Re–C antibonding orbitals (as seen at right in Figure 1), so there is some weakening of the network bonding.

In moving to the extended picture, we should remember that the puckering has a further effect on the Re atoms, bringing them within 3.21 Å of each other along the c direction of the crystal. Could Re–Re interactions be important in determining the 16.5 electron count? Such interactions are actually quite weak. In Figure 3 we plot the Re–Re COOP curve in the extended system, showing the long-range effects of the puckering beyond the immediate coordination sphere of the Re or C. The net COOP (integration of the COOP curve) between rhenium atoms for

${}^2_z[\text{Re}_2\text{C}_4^{10-}]$ is 0.013, while that for ${}^2_z[\text{Re}_2\text{C}_4^{11-}]$ is 0.005. In either case, the puckering of the network has turned on net-antibonding interactions between rhenium atoms in addition to the Re–C antibonding interactions which were discussed earlier. To enhance Re–Re bonding, the network would require either additional electrons to populate higher-energy Re–Re bonding states (see Figure 3) or fewer electrons to depopulate the Re–Re antibonding states. A maximal OP through reduction would be achieved with a 16- charge (Re–Re OP = 0.031), while oxidation to 8- would reach an optimal OP of 0.035. We will see in the next section that the Sc plays an important stabilizing role which results in the oxidation of the network. The Sc interactions with the network cause small changes in the Re–Re COOP curve that lead to a slightly higher Re–Re OP in the final structure than the supposed optimal OP cited above.

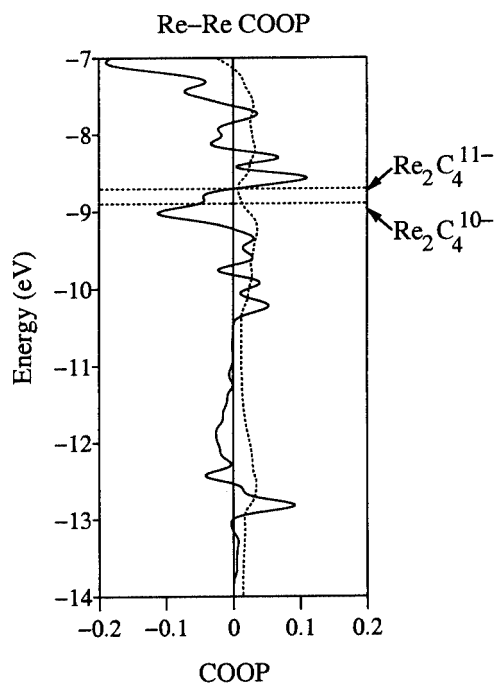


Figure 3 COOP curve between rhenium atoms along the strongly puckered direction in the ${}^2_z[\text{Re}_2\text{C}_4]$ substructure. Fermi levels (horizontal dotted lines) are given for both the formal 11-charge per unit cell expected for the network and a 10-charge corresponding to Re^{3+} . The additional states occupied by the extra “1/2 electron” per Re are Re–Re antibonding.

The full crystal structure

Up to now we have ignored the interactions of the scandium atoms with the Re_2C_4 net, but there are many close Sc–Re and Sc–C contacts. There are also interactions between Sc atoms and the C_3 units. For the most part, though, the two-dimensional Re_2C_4 sheets don’t interact with each other, nor do they interact with the isolated C_3 units.

As a first approximation we treated the Sc atoms simply as donors of 3 electrons each to the rest of the crystal. Now

we can begin to interact the various sublattices by first comparing their Fermi energies – approximating their interactions by a redistribution of electrons – before considering the orbital interactions between them.

Even though the isolated Sc *d* orbitals are put into our calculations at -8.51 eV and *s* orbitals are at -8.87 eV (see Table 1), the Sc–Sc separations in the Sc sublattice are sufficiently short to generate a substantial band width for these diffuse orbitals, as seen in the top center panel of Figure 4. The lowest Sc states (mainly *s* in character) come below the -8.7 eV Fermi level of ${}^2_{\infty}[\text{Re}_2\text{C}_4^{11-}]$ and -10.6 eV Fermi level of the assembly of C_3^{4-} units. (The HOMO of an isolated C_3^{4-} unit is at -11.2 eV.) As a result, there will be some transfer of electrons when the sublattices are combined to achieve the final Fermi level for the entire compound of about -9.7 eV.

The DOS curves shown below (Figure 4) are for the isolated sublattices, with their contribution to the total DOS shown in the bottom panels of the figure for comparison. The overall shape of the contributing sublattice DOS does not change dramatically, so our initial description of the interactions as merely entailing charge transfer is not bad. However, if simple charge transfer were all that occurred, then there would be a net donation from ${}^2_{\infty}[\text{Re}_2\text{C}_4^{11-}]$ to the

Sc^{3+} atoms. Our calculations show that nearly 2 electrons from each C_3^{4-} as well as over 6 electrons from each $\text{Re}_2\text{C}_4^{11-}$ are transferred to the scandium matrix, indicating that there must be some bonding between all of the sublattices.

Sc–C interactions are responsible for most of the perturbations caused in the DOS curves, as well as the remainder of the electron transfer. The Sc atoms raise the coordination of all of the C atoms (except $\text{C}_{\text{central}}$ in the C_3 units) to 6 (octahedral, shown below in Scheme 5). Octahedral coordination by metals or rare earths can stabilize an electron-rich carbon, with “ligands” lining up with carbon lone-pair-type *p* orbitals [7]. These direct Sc–C interactions also increase the Sc contribution to the low-lying states, thus leading to even more transfer of electrons from C to Sc.

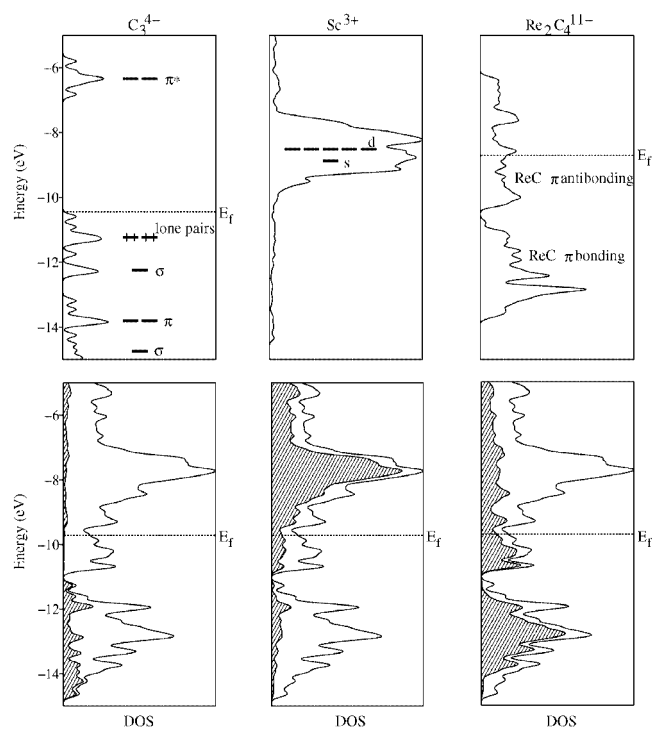
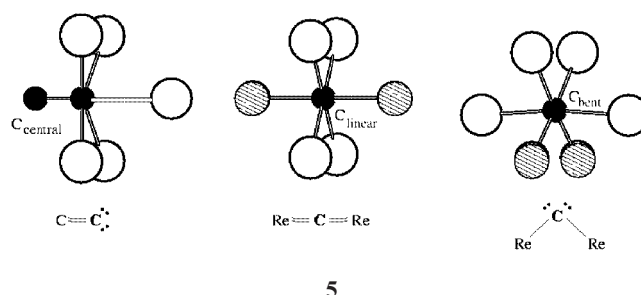


Figure 4 DOS curves for the isolated sublattices are shown above, with Sc^{3+} atoms in the center, C_3^{4-} units at left, and the ${}^2_{\infty}[\text{Re}_2\text{C}_4^{11-}]$ network at right. Superimposed on the DOS plots are the energy levels for the C_3^{4-} molecular units (left) and the Sc atoms (center). In each DOS curve below is the sublattice contribution (shaded area) to the total DOS of $\text{Sc}_5\text{Re}_4\text{C}_7$. The main differences between the isolated sublattice DOS curves and the total DOS curve come from Sc–C interactions, which stabilize the anionic C atoms and transfer electrons to the Sc matrix.

The C “lone pairs” in the Re–C lattice with which the Sc interacts are Re–C non-bonding and antibonding states in the case of C_{bent} , but for C_{linear} they are actually Re–C π bonding states and not really lone pairs. So in the process of interacting with the carbon atoms, the Sc atoms strengthen somewhat the Re– C_{bent} bonds and weaken the Re– C_{linear} bonds. In addition, the states near the Fermi level of ${}^2_{\infty}[\text{Re}_2\text{C}_4^{11-}]$ which were Re–Re antibonding (see Figure 3) are depopulated, leading to significantly stronger (though still small) Re–Re bonding. The Re–Re OP goes from essentially zero to 0.08, about half of the OP for a nominal Re–Re single bond complex (the $\text{Re}_2(\text{CO})_{10}$ dimer) calculated with the Re–Re distance set to 3.21 Å as in our structure.

The double bonds are weakened and the single bonds strengthened from the substantial Sc interactions with the Re–C lattice, but the general picture of electronically inequivalent Re–C double and single bonds (which require a puckered ${}^2_{\infty}[\text{Re}_2\text{C}_4^{11-}]$ network) is maintained. In addition, Re–Re bonding is considerably enhanced by the increased Sc–C interactions, which further supports the puckering. Finally, the puckering allows interactions of several C atoms with each Sc, enabling the stabilization and electron transfer which hold together the various networks and C_3 units.

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Table 1 Parameters used in the extended Hückel calculations.

| Atom | Orbital | H _{ii} | ζ ₁ | c ₁ ^{a)} | ζ ₂ | c ₂ ^{a)} |
|------------------|---------|-----------------|----------------|------------------------------|----------------|------------------------------|
| C | 2s | -21.40 | 1.625 | | | |
| | 2p | -11.40 | 1.625 | | | |
| Sc ^{b)} | 4s | -8.87 | 1.30 | | | |
| | 4p | -2.75 | 1.30 | | | |
| | 3d | -8.51 | 4.35 | 0.4228 | 1.70 | 0.7276 |
| Re | 6s | -8.36 | 2.398 | | | |
| | 6p | -4.96 | 2.372 | | | |
| | 5d | -10.66 | 5.343 | 0.6378 | 2.277 | 0.5910 |

^{a)} Coefficients in double-ζ expansion.

^{b)} Sc parameters were modified from those of Alvarez [18] to eliminate problems with counter-intuitive orbital mixing.

Appendix: Computational details

The calculations presented in this work use the extended Hückel [8–11] tight-binding method [12–14], as implemented in the YAeHMOP package [15]. The off-diagonal elements of the Hamiltonian were evaluated with the modified Wolfsberg-Helmholtz formula [16, 17]. Numerical integrations for the two-dimensional systems were carried out over 16 k-points in the symmetry-unique section of the Brillouin zone, while the three-dimensional structure calculations used the analogous 64 k-points in the corresponding 3-D Brillouin zone. Increasing the number of k-points for the two-dimensional structures did not affect the results. The parameters used in our calculations are listed in Table 1. [18]

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