

Short review

Organometallic structural units in solid state ternary transition metal carbides¹

R. Bruce King

Department of Chemistry, University of Georgia, Athens, GA 30602, USA

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Abstract

Solid state ternary transition metal carbides containing carbon, a transition metal (Cr to Ni and their heavier congeners), and a highly electropositive multivalent metal such as a lanthanide (Ln), Sc, Y, or Th, exhibit a number of structural features resembling those in metal carbonyls and other transition metal derivatives of π -acceptor hydrocarbon ligands. Complete ionization of the electropositive metal to the stable ions Ln^{3+} , Sc^{3+} , Y^{3+} , and Th^{4+} leads to a negatively charged transition metal–carbon subnetwork, which may be regarded as an organometallic net. Many such carbides contain discrete C_2 units with C=C distances in the range 1.32 to 1.47 Å suggestive of double bonding and the C_2^{4-} tetra-anion obtained by the complete deprotonation of ethylene. Thus the carbides Ln_2FeC_4 , Sc_3CoC_4 , and Ln_3MC_4 (M = Fe, Co, Ni, Ru, Rh, Os, Ir) may be considered to contain $1,1\text{-}\mu_2\text{-C}_2^{4-}$, $1,2\text{-}\mu_2\text{-C}_2^{4-}$, and $\mu_3\text{-C}_2^{4-}$ ligands respectively. Other ternary transition metal carbides contain C_2^{2-} ligands in $[\text{M}]=\text{C}=\text{C}$ units derived by complete deprotonation of a terminal vinylidene ligand, $[\text{M}]=\text{C}=\text{CH}_2$. Such terminal deprotonated vinylidene ligands are isoelectronic and isostructural with terminal metal carbonyl groups and are found in trigonal $\text{M}(\text{C}_2)_3$ units isoelectronic with $\text{M}(\text{CO})_3$ units with the transition metal in very low formal oxidation states (e.g. Mn(–V) of $\text{Mn}(\text{C}_2)_3^{11-}$ in $\text{Ln}_3\text{Mn}_2\text{C}_6$ isoelectronic with $\text{Mn}(\text{CO})_3^{5-}$ and Ni(–II) of $\text{Ni}(\text{C}_2)_3^{8-}$ in $\text{Eu}_{3,16}\text{NiC}_6$ isoelectronic with $\text{Ni}(\text{CO})_3^{2-}$). The carbide ScCrC_2 contains a C_2 pair with a longer C–C distance of 1.60 Å, suggesting a C–C single bond and the C_2^{6-} anion obtained by complete deprotonation of ethane. Examples of C_1 ligands found in the solid state ternary transition metal carbides include terminal C^{4-} in Th_2NiC_2 , Y_2ReC_2 , and $\text{Ln}_{12}\text{M}_5\text{C}_{15}$ (M = Mn, Re) and $\mu_2(=\text{C}=\text{C})^{4-}$ in YCoC and Y_2ReC_2 . © 1997 Elsevier Science S.A.

1. Introduction

One of the highlights of chemistry during the past several decades has been the discovery of diverse types of transition metal organometallic compound containing single and/or multiple metal–carbon bonds [1]. In addition, during the past few years, a variety of extended solid state ternary transition metal carbides have been characterized which are indicated by their interatomic distances to contain related types of metal–carbon bonds. In these ternary metal carbides the element other than carbon and the transition metal is a highly electropositive multivalent metal such as a lanthanide (abbreviated as Ln), yttrium, or thorium. Complete ioniza-

tion of the electropositive metal to the stable ions Ln^{3+} , Y^{3+} , or Th^{4+} leads to a negatively charged transition metal–carbon subnetwork, which may be considered to be an organometallic net. Such ternary metal carbides can thus be regarded as negatively charged organometallic polymers imbedded in a matrix of positive ions. In many of these ternary transition metal carbides the transition metal atom can be assigned a low formal oxidation state reminiscent of the metal oxidation states in metal carbonyls and metal–olefin complexes [1].

In previous papers the author has discussed the chemical bonding topology in transition metal polyphosphides [2], superconducting transition metal borides and silicides [3], superconducting alloys [3], and ternary carbides of the late transition metals [4]. This paper extends the previous survey of metal carbides [4] to a wider variety of ternary metal carbides including

¹ This paper is dedicated to Professor Yu.I. Struchkov in recognition of his major contributions to structural inorganic chemistry.

Table 1
Ternary transition metal carbides discussed in this paper

Species	Anion	Bond distances (Å)			Ligand	Electron count		Transition metal formal oxidation state	Polymerization dimensionality
		M–C	C–C	M–M		Anion	Metal		
β -ScCrC ₂	Cr(C ₂) _{3/3} ³⁻	2.03	1.60	3.24	μ_3 -C ₂ ⁶⁻	17	15	Cr(III)	2
α -ScCrC ₂	Cr(C ₂) _{1/2} (C) _{3/3} ³⁻	2.04	1.43(C ₂)	—	μ_3 -C ₂ ⁴⁻	17	15	Cr(III)	2
Sc ₂ CrC ₃	Cr(C ₂) _{3/3} (C) _{3/3} ⁶⁻	2.06	1.88(C ₁)	—	μ_3 -C ⁴⁻	24	18	Cr(II)	3
		2.03	1.47	—	μ_3 -C ₂ ⁴⁻				
		2.07	—	—	μ_2 -C ⁴⁻				
Er ₂ MnC ₄	Mn(C ₂) _{4/2} ⁶⁻	1.99	1.34	2.52	μ_2 -C ⁴⁻	29	13	Mn(II)	1
Y ₂ FeC ₄	Fe(C ₂) _{4/2} ⁶⁻	1.97	1.33	2.50	μ_2 -C ₂ ⁴⁻	30	14 + 2M–M	Fe(II)	1
Y ₂ ReC ₄	ReC _{2/2} C ⁶⁻	1.72	—	—	C ⁴⁻	21	17	Re(II)	1
		2.13	—	—	—	—	—	—	—
		2.34	—	—	μ_2 -C ⁴⁻	—	—	—	—
Gd ₃ Mn ₂ C ₆	Mn(C ₂) _{3/3} ⁵⁻	1.85	1.36	—	μ_3 -C ₂ ⁴⁻	20	18	Mn(–V)	3
	Mn(C ₂) _{6/3} ⁴⁻	2.13	1.36	2.51	—	17	17 + 2M–M	Mn(II)	—
Dy ₁₂ Mn ₅ C ₁₅	MnC ₃ ⁹⁻	1.78	—	—	C ⁴⁻	28	18	Mn(I)	0
	Mn ₃ C ₃ (C ₂) ₃ l ⁸⁻	1.89(C ₂)	1.32	2.84	μ_2 -C ⁴⁻ , C ₂ ²⁻	75	13 + 2M–M	Mn(O)	—
Ho ₁₂ Re ₅ C ₁₅	ReC ₃ ⁹⁻	1.87	—	—	C ⁴⁻	28	18	Re(I)	0
	Re ₃ C ₃ (C ₂) ₃ ¹⁸⁻	1.89(C ₂)	1.42	2.84	μ_2 -C ⁴⁻ , C ₂ ²⁻	75	13 + 2M–M	Re(0)	—
La _{3.67} FeC ₆	Fe(C ₂) ₃ ¹¹⁻	1.82	1.30	—	C ₂ ²⁻	43	19	Fe(–V)	0
YCoC	CoC _{2/2} ³⁻	1.82	—	—	μ_2 -C ⁴⁻	16	16	Co(I)	1
LnCoC ₂	Co(C ₂) _{3/3} ³⁻	1.95–1.98	1.37	—	μ_3 -C ₂ ⁴⁻	20	16	Co(I)	2
Sc ₃ CoC ₄	Co(C ₂) _{3/3} ³⁻	2.09	1.46	—	μ_2 -C ₂ ⁴⁻	34	18	Co(–I)	1
Th ₂ NiC ₂	NiC ₂ ⁸⁻	1.93	—	—	C ⁴⁻	26	14	Ni(0)	0
Eu _{3.16} NiC ₆	Ni(C ₂) ₃ ⁸⁻	1.88	1.27	—	C ₂ ²⁻	42	18	Ni(–II)	0

some early transition metal derivatives. The carbides of interest in this work are listed in Table 1. Some of these ternary transition metal carbides have also been studied by extended Hückel methods, particularly by Hoffmann and co-workers (YCoC [5], Er₂ReC₂ [6], LnCoC₂ [7]).

2. Types of carbon ligand in ternary solid state metal carbides

2.1. Ligands derived from ethylene deprotonation

Many of the ternary solid state transition metal carbides contain C₂ structural units with carbon–carbon distances of 1.32 to 1.47 Å suggestive of carbon–carbon double bonds. Such structural units may be regarded as being derived from the C₂⁴⁻ anion obtained by the complete deprotonation of ethylene. Table 2 summarizes four different known bonding modes of bridging C₂⁴⁻ ligands in metal carbides. Note that there are two known ways that a C₂⁴⁻ ligand can bridge two transi-

tion metals and two known ways that a C₂⁴⁻ ligand can bridge three transition metals. The 1,1-μ-C₂⁴⁻ ligand found in Ln₂MC₄ derivatives (Ln = lanthanide, M = transition metal) is similar to a bridging carbonyl group. The number of electrons donated by a neutral C₂⁴⁻ ligand of a given type listed in Table 2 is obtained by subtracting from the eight valence electrons of the two carbon atoms the four electrons required for the C=C bond and any electrons required for the lone pairs indicated in the structures.

2.2. Ligands derived from ethane deprotonation

The ternary carbide β-ScCrC₂ contains C₂ structural units with a C–C distance of 1.60 Å, which is much longer than any of the C=C distances in any of the carbides listed in Table 2. For this reason the carbon–carbon bonds in the C₂ units of β-ScCrC₂ are interpreted as single bonds, so that these C₂ units are considered to be C₂⁶⁻ derived from the complete deprotonation of ethane.

Table 2
Types Of C₂ ligand found in ternary transition metal carbides

Ligand	Structure	Electrons donated by neutral C ₂ ligand	Examples	C=C or C–C (Å)
1. Ligands derived from ethylene deprotonation (C ₂ ⁴⁻)				
1,2-μ ₂ -C ₂ ⁴⁻		0	Sc ₃ CoC ₄	1.46
1,1-μ ₂ -C ₂ ⁴⁻		0	Er ₂ MnC ₄ Y ₂ FeC ₄	1.36 1.33
1,2-η ² -μ ₃ -C ₂ ⁴⁻		4	α-ScCrC ₂ DyCoC ₂	1.43 1.37
1,1,2-μ ₃ -C ₂ ⁴⁻		2	Sc ₂ CrC ₃	1.47
2. Ligands derived from ethane deprotonation (C ₂ ⁶⁻)				
μ ₃ -η ² -C ₂ ⁶⁻		6	β-ScCrC ₂	1.60
3. Vinylidene ligands (C ₂ ²⁻)				
C ₂ ²⁻		0	La _{3,67} FeC ₆ Eu _{3,16} NiC ₆ Ho ₁₂ Re ₅ C ₁₅ Dy ₁₂ Mn ₅ C ₁₅	1.30 1.27 1.42 1.32
μ ₃ -C ₂ ²⁻		4	Gd ₃ Mn ₂ C ₆ Tb ₃ Mn ₂ C ₆	1.36 1.35

2.3. Ligands derived from vinylidene deprotonation

Terminal C_2 ligands are found in discrete trigonal structural $M(C_2)_3$ units in several carbide structures, including $Ln_3Mn_2C_6$, $Ln_{12}Re_5C_{15}$, $Ln_{3,67}MC_6$ ($M = Mn, Fe, \text{ and } Ru$), and $Eu_{3,16}NiC_6$. Such C_2 ligands are bonded to a single metal atom with rather short metal–carbon bonds, which are interpreted as metal–carbon double bonds. This ligand may be considered to be the dinegative C_2^{2-} derived from the deprotonation of a vinylidene ligand $H_2C=C=[M]$ and thus is isoelectronic and isostructural with a terminal metal carbonyl group, i.e. $C_2^{2-} \approx CO$, so that a charged $M(C_2)_3^{6-}$ unit is isoelectronic with a neutral $M(CO)_3$ unit.

The deprotonated vinylidene ligand can also serve as a bridge between three metal atoms in $Ln_3Mn_2C_6$. In this case one metal atom may be regarded as doubly bonded to the carbene carbon of the C_2^{2-} unit (i.e. $Mn=C = 1.84 \text{ \AA}$) and the other two metal atoms as each singly bonded to the olefinic carbon of the C_2^{2-} unit (i.e. $Mn-C = 2.14 \text{ \AA}$)

2.4. C_1 ligands

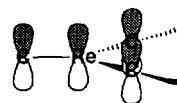
Table 3 lists examples of C_1 ligands found in ternary metal carbides. In the carbide Th_2NiC_2 the terminal carbon atoms are only singly bonded to the nickel atom so that the C^{4-} ligand is isoelectronic and isostructural with the F^- ligand. However, in Y_2ReC_2 , as well as in the ReC_3 units in the more complicated $Ln_{12}Re_5C_{15}$ structure, the terminal carbon atoms are doubly bonded to the rhenium atom so that the $M=C:^{2-}$ unit is isoelectronic with an $M=\ddot{O}$ unit. The μ_2 -carbon atoms in the infinite cobalt–carbon chains of $YCoC$ are similar

Table 3
 C_1 ligands found in ternary transition metal carbides

Ligand	Structure	Examples	M–C (Å)
$[M]-C^{4-}$	$[M]-\overset{\ominus}{\underset{\ominus}{C}}$	Th_2NiC_2	1.93
$[M]=C^{4-}$	$[M]=\overset{\ominus}{\underset{\ominus}{C}}$	Y_2ReC_2 $Ho_{12}Re_5C_{15}$	2.13 1.87
$[M]=C=[M]$	$[M]=C=[M]$	$YCoC$	1.82
$[M]\equiv C-[M]$	$[M]\equiv C-[M]$	Y_2ReC_2	1.72, 2.34
$[M]-C-[M]$	$[M]-\overset{\prime}{C}-[M]$	$Ho_{12}Re_5C_{15}$	2.07
$[M]_3C$	$[M]-\overset{\prime}{C}-[M]$ [M]	$\alpha\text{-ScCrC}_2$	2.06



$CoC_{2/2}^{3-}$ anion
in $YCoC$



$ReCC_{2/2}^{6-}$ anion
in Y_2ReC_2

Fig. 1. Role of metal p orbitals in $M=C$ double bonding in the polymeric anions in $YCoC$ and Y_2ReC_2 .

to the central carbon atom in allene, even to the extent that the $Co=C=Co$ bond angles in $YCoC$ are essentially linear.

In some ternary metal carbides, such as $YCoC$ and Y_2ReC_2 , electron donation from a carbon atom to the transition metal involves formation of a metal–carbon double bond necessarily with both a σ and a π component (Fig. 1). Thus in $YCoC$ with a $=C=Co=C=$ metal environment the $Co=C$ π -bonding requires the cobalt valence orbital manifold to be an eight-orbital sp^2d^5 manifold rather than the seven-orbital spd^5 manifold expected from the linear σ -bonding alone from the two-coordinate cobalt atom. The 'extra' cobalt p orbital of the sp^2d^5 manifold participates in the $Co=C$ $p\pi-p\pi$ bonding. Similarly, in Y_2ReC_2 with a $(=C=)_2Re=C:$ metal environment, the $Re=C$ π -bonding requires the rhenium valence orbital manifold to be a nine-orbital sp^3d^5 manifold rather than the eight-orbital sp^2d^5 manifold expected from the trigonal planar σ -bonding alone from the three-coordinate rhenium atom.

3. The chemical bonding topology of transition metal carbides

3.1. General comments

Table 1 summarizes some of the important structural features of the anionic transition metal–carbon subnetworks in the types of transition metal carbides discussed in this paper. These anionic subnetworks are obtained from the complete ternary transition metal carbide network by removal of the electropositive lanthanide or scandium atom as M^{3+} . An important feature of these anionic transition metal–carbon subnetworks is their polymerization dimensionality [4]. Carbon ligands shared between two or more transition metals in Table 1 are designated by the notations $[M]C_{n/m}$, or $[M](C_2)_{n/m}$ where n is the number of such ligands bonded to the

metal atom [M] and m is the number of metal atoms to which a given C or C₂ ligand is bonded.

3.2. Carbides containing C₂⁴⁻ units derived from ethylene

3.2.1. Ln₂FeC₄

The anionic transition metal–carbon subnetworks of the carbides Ln₂FeC₄ (Fig. 2(a)) consist of infinite [Fe(C₂)_{4/2}]_∞ chains with 30 electrons per FeC₄⁶⁻ unit and 1,1-μ-C₂ ligands bridging pairs of iron atoms [8]. The [Fe(C₂)_{4/2}]_∞ chains contain an infinite chain of Fe–Fe bonds with Fe–Fe distances of 2.50 Å. The previous paper [4] interpreted the C₂ ligands in Ln₂FeC₄ as C₂²⁻ dianions leading to a formal iron oxidation state of -2. If the C₂ ligands in Ln₂FeC₄ are interpreted as tetra-anions, C₂⁴⁻, rather than dianions C₂²⁻, then the formal iron oxidation state is +2 rather than -2.

This change in iron formal oxidation state does not affect the electron counting in Ln₂FeC₄ discussed in the previous paper [4], but only the formal distribution of electrons between iron and carbon. Thus, if the iron–iron bonds are assumed to be single bonds (the 2.50 Å distance is borderline between single and double bonds), then the iron atoms in [Fe(C₂)_{4/2}]_∞ attain the

16-electron configuration required for filling an eight-orbital planar sp²d⁵ manifold as follows:

Neutral iron atom:	8 electrons
4/2 1,1-bridging neutral C ₂ ligands:	0 electrons
Two Fe–Fe single bonds:	2 electrons
–6 charge:	6 electrons
Total iron valence electrons:	16 electrons

If the iron–iron bonds are assumed to be Fe=Fe double bonds, then each iron atom has the favored 18-electron noble gas configuration.

3.2.2. Ln₃MC₄

The anionic transition metal–carbon subnetworks of the carbides Ln₃CoC₄ (Fig. 2(a)) consist of infinite [Co(C₂)_{4/2}]_∞ chains with 34 electrons per CoC₄⁹⁻ unit and 1,2-μ-C₂ ligands bridging pairs of cobalt atoms [9]. Formulating the C₂ ligands as C₂⁴⁻ leads to a formal cobalt oxidation state of -1 analogous to Co(CO)₄⁻. The Co···Co distance of 3.40 Å is too long for a direct Co–Co single bond. The cobalt atoms have the favored 18-electron rare gas configuration as follows:

Neutral cobalt atom:	9 electrons
4/2 1,2-bridging neutral C ₂ ligands:	0 electrons
–9 charge:	9 electrons
Total valence electrons:	18 electrons

The metal atoms in the iron and ruthenium analogues Sc₃FeC₄ and Sc₃RuC₄ have 17 valence electrons and the nickel atom in Sc₃NiC₄ has 19 valence electrons.

3.2.3. LnMC₂

The anionic transition metal–carbon subnetworks of a large group of isostructural carbides of the type LnMC₂ (Ln = lanthanide, M = Fe, Co, Ni) consist of infinite [M(C₂)_{3/3}]_∞ sheets (Fig. 2(b)) [10]. The central cobalt atoms in a [Co(C₂)_{3/3}]_∞ sheet each have 9(Co) + 4(4Co–C) + 3(-3 charge) = 16 electrons as required for a planar cobalt atom with an eight-orbital planar sp²d⁵ manifold. Formulating the carbon pairs as C₂⁴⁻ leads to the formal +1 cobalt oxidation state, so that LnCoC₂, like LnCoC, may formally be regarded as a square planar Co(I) derivative. The metal atoms in the isostructural iron and nickel LnMC₂ derivatives have one less and one more valence electron, respectively, than the ideal 16 electron configuration for a planar metal using an eight-orbital sp²d⁵ manifold.

3.3. A carbide containing a C₂⁶⁻ unit derived from the complete deprotonation of ethane

The carbide β-ScCrC₂ contains discrete C₂ units but with C–C distances of 1.60 Å suggesting single bonds

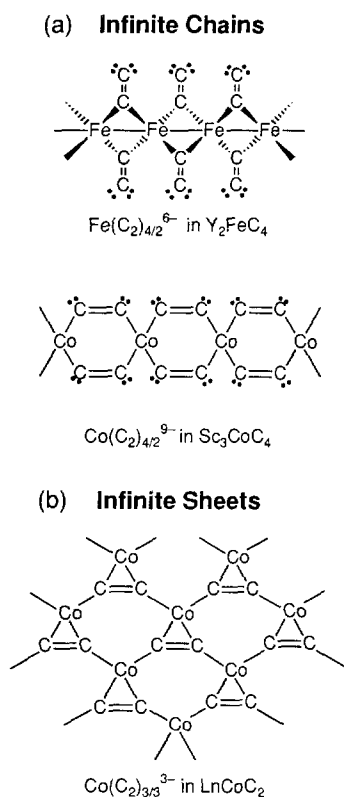


Fig. 2. (a) Infinite chains in the transition metal–carbon subnetworks in Y₂FeC₄ and Sc₃CoC₄. (b) Infinite sheets in the transition metal–carbon subnetwork in LnCoC₂.

and thus a C_2^{6-} ligand derived from the complete deprotonation of ethane [11]. Each C_2^{6-} ligand is bonded pairwise to three different chromium atoms forming a total of six chromium–carbon bonds of length 2.03 Å corresponding to Cr–C single bonds. The chromium–carbon subskeleton of α -ScCrC₂ can then be interpreted to be $[Cr^{III}(C_2)_{3/3}]_{\infty}^{3-}$ with trigonal prismatic Cr(III). The singly bonded *neutral* C_2 ligand can be regarded as a net six-electron donor since only two of the combined eight valence electrons from the two carbon atoms are required for the C–C single bond and there are no lone pairs. The chromium atoms have the 15-electron configuration typical for six-coordinate Cr^{III} complexes as follows:

Neutral Cr atom:	6 electrons
3/3 <i>neutral</i> C_2 units, $3/3 \times 6$:	6 electrons
– 3 charge:	3 electrons
Total valence electrons:	15 electrons

An isomeric α -ScCrC₂ is also known in which the C_2 pairs are randomly distributed between half having a carbon–carbon distance of 1.43 Å, corresponding to a double bond, and the other half having a carbon–carbon distance of 1.88 Å, corresponding to essentially no carbon–carbon bonding [11]. Otherwise the atom connectivities and approximate bond distances in α -ScCrC₂ are very close to those in β -ScCrC₂. The bonding models and electron counting of both modifications of ScCrC₂ can be regarded as very similar, except that the neutral non-bonded C_2 ‘ligands’ (i.e. those with the C···C distances of 1.88 Å) are eight-electron donors and the neutral doubly bonded C_2 ligands (i.e. those with the C=C distances of 1.43 Å) are four-electron donors leading to 15-electron chromium configurations in α -ScCrC₂ as in β -ScCrC₂ discussed above.

3.4. Carbides containing C_2^{2-} units obtained from the deprotonation of vinylidene

3.4.1. $Ln_{3.67}M_2C_6$ ($M = Mn, Fe, Ru$)

These species [12] contain discrete trigonal $M(C_2)_3$ ($M = Mn, Fe, Ru$) units which are assigned a –11 charge to balance out the $Ln_{3.67}$ counteranions, assuming the usual +3 lanthanide oxidation state. The C_2 ligands are the deprotonated vinylidene ligands, C_2^{2-} , isoelectronic with terminal carbonyl groups, so that the trigonal $M(C_2)_3^{11-}$ units are isoelectronic with the hypothetical highly reduced metal carbonyl anions $M(CO)_3^{5-}$ ($M = Mn, Fe, Ru$). The formal transition metal oxidation states in these species are even lower than those observed by Ellis and co-workers [13] in their studies on super-reduced metal carbonyl anions, who obtained $Cr(CO)_4^{4-}$ as their most highly reduced species [14]. The $Mn(C_2)_3^{11-}$ unit found in $Ln_{3.67}Mn_2C_6$ ($\approx Mn(CO)_3^{5-}$) has the favored 18-electron rare gas elec-

tronic configuration, whereas the $M(C_2)_3^{11-}$ units ($M = Fe, Ru$) have a 19-electron configuration, which may correspond to an extra electron in the conduction band.

3.4.2. $Eu_{3.16}NiC_6$

This species [12] also contains a discrete $M(C_2)_3$ unit but appears to require the potentially divalent lanthanide europium as the counteranion, since similar species could not be prepared using lanthanide counteranions that are exclusively trivalent. For this reason there is more ambiguity concerning the negative charge on the $Ni(C_2)_3$ unit. However, an $Ni(C_2)_3^{8-}$ unit isoelectronic with $Ni(CO)_3^{2-}$ would have the favored 18-electron rare gas electronic configuration and would correspond to a reasonable average oxidation state of $8/3.16 = 2.5$ for the europium atoms, i.e. equal amounts of Eu^{2+} and Eu^{3+} .

3.4.3. $Ln_3Mn_2C_6$

The anionic manganese–carbon subnetwork of $Ln_3Mn_2C_6$ [15] is constructed from μ_3 - C_2^{2-} vinylidene units bridging two different types of manganese atoms (Table 2). One of the manganese atoms (Mn2 in Ref. [15]) is bonded to six carbon atoms of six different μ_3 - C_2^{2-} units through Mn–C single bonds (Mn2–C = 2.14 Å), whereas the other manganese atom (Mn1 in Ref. [15]) is bonded to three carbon atoms of three different μ_3 - C_2^{2-} units through Mn=C double bonds (Mn1=C = 1.84 Å) (Fig. 3(a)). In addition, the Mn1–Mn1 distances are 2.50 Å suggestive of Mn–Mn single bonds; thus, each Mn1 atom is singly bonded to two adjacent Mn1 atoms. These considerations lead to a formula $[(Mn^2(C_2)_{6/3})^{4-}\{Mn^1(C_2)_{3/3}\}^{5-}]_{\infty}$ for the an-

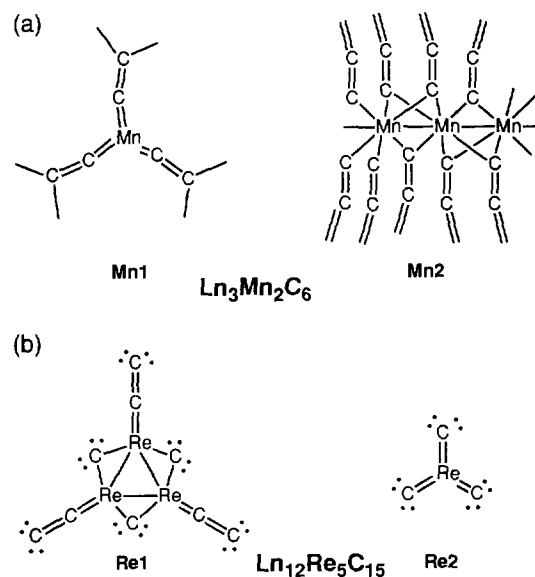


Fig. 3. (a) The environments of the two different types of manganese atom in $Ln_3Mn_2C_6$. (b) The environments of the two different types of rhenium atom in $Ln_{12}Re_5C_{15}$.

3.6.2. $\text{Ln}_{12}\text{M}_5\text{C}_{15}$ ($M = \text{Mn}, \text{Re}$)

These ternary lanthanide transition metal carbides have three different types of carbon ligands and two different type of transition metal atom (Fig. 3(b)) [21,22]. The carbon ligands are of the following three types, as illustrated below for the rhenium derivatives $\text{Ln}_{12}\text{Re}_5\text{C}_{15}$ [21].

(1) A terminal carbide atom (C1 in Ref. [21]) doubly bonded to a single rhenium atom (Re2 in Ref. [21]) with a $\text{Re}=\text{C}$ bond distance of 1.87 Å. If regarded as a neutral carbon atom, this doubly bonded carbon atom is a formal zero-electron donor since its four valence electrons are used for the two lone pairs.

(2) A carbon atom (C4 in Ref. [21]) which bridges two rhenium atoms (both Re1 in Ref. [21]) with $\text{Re}-\text{C}$ bond distances of 2.07 Å. If regarded as a neutral carbon atom, this μ_2 -carbon atom, like C1 discussed above, is a formal zero-electron donor since its four valence electrons are used for the two lone pairs.

(3) A terminal C_2 vinylidene ligand with a 1.42 Å $\text{C}=\text{C}$ distance bonded to Re1 with a fairly short bond (1.89 Å) interpreted as a $\text{Re}=\text{C}$ double bond [21]. This C_2 ligand, considered as a *neutral* species, is also a formal zero-electron donor since four of its eight valence electrons are used for the $\text{C}=\text{C}$ double bond, and the remaining four valence electrons are used for two lone pairs.

Thus all of the carbon atoms in $\text{Ln}_{12}\text{Re}_5\text{C}_{15}$, when considered as neutral ligands, function as formal zero-electron donors.

The rhenium atoms in $\text{Ln}_{12}\text{Re}_5\text{C}_{15}$ are also of two types (Fig. 3(b)). Re1: the Re1 atoms form $\text{Re}_3(\text{C}_2)_3(\mu\text{-C})_3$ triangles with $\text{Re}-\text{Re}$ bond distances of 2.84 Å. Re2: the Re2 atoms form isolated trigonal ReC_3 units involving C1 as noted above.

The rhenium-carbon subnetwork in $\text{Ln}_{12}\text{Re}_5\text{C}_{15}$ may thus be formulated as $[\{\text{Re}_3(\text{C}_2)_3(\mu\text{-C})_3\}\{\text{Re}_2\text{C}_3\}_2]^{36-}$ with two Re_2C_3 units for each $\text{Re}_3(\text{C}_2)_3(\mu\text{-C})_3$ triangle.

If the total negative charge is partitioned between the two types of rhenium unit so as to give the isolated trigonal mononuclear Re_2C_3 units the favored 18-electron rare gas electronic configuration, i.e. $[\{\text{Re}_3(\text{C}_2)_3(\mu\text{-C})_3\}^{14-}\{\text{Re}_2\text{C}_3\}^{11-}]_2$, then the electron counting can proceed as follows:

$1/3 \text{Re}_3(\text{C}_2)_3(\mu\text{-C})_3^{14-}$ unit	
Neutral Re atom:	7 electrons
1 <i>neutral</i> C_2 ligand:	0 electrons
$2/2$ <i>neutral</i> $\mu\text{-C}$ ligand:	0 electrons
Two $\text{Re}-\text{Re}$ single bonds, 2×1 :	2 electrons
$-4\frac{2}{3}$ average negative charge:	$4\frac{2}{3}$ electrons
<i>Total valence electrons:</i>	$13\frac{2}{3}$ electrons

$\text{Re}_2\text{C}_3^{11-}$ unit	
Neutral Re atom:	7 electrons
3 neutral $=\text{C}$ ligands:	0 electrons
-11 negative charge:	11 electrons
<i>Total valence electrons:</i>	18 electrons

The average oxidation state of the Re1 in the $\text{Re}_3(\text{C}_2)_3(\mu\text{-C})_3^{14-}$ unit is zero assuming $\mu\text{-C}^{4-}$ and terminal C_2^{2-} ligands and of the Re2 atoms in the $\text{Re}_2\text{C}_3^{11-}$ units is +1 assuming terminal C^{4-} ligands. The Re2 atoms are assumed to have the favored 18-electron rare gas configuration and to be isoelectronic with species such as $[\text{Re}(\text{CO})_6]^+$. The electronic configuration of the Re1 atoms is somewhat arbitrary since it depends on the order of the $\text{Re}-\text{Re}$ bonds in the triangle.

4. Summary

Solid state ternary transition metal carbides containing carbon, a transition metal, and a highly electropositive multivalent metal such as a lanthanide, Sc, Y, or Th, exhibit a number of structural motifs resembling those in metal carbonyl, alkyl, and carbene complexes. Particularly prevalent in the structures of such compounds are C_2 units with carbon-carbon bond distances suggestive of $\text{C}=\text{C}$ double bonds. Such units, which generally bridge two or three transition metal atoms, may be regarded as C_2^{4-} units obtained by the complete deprotonation of ethylene. Other ternary transition metal carbides contain C_2^{2-} ligands in $[\text{M}]=\text{C}=\text{C}$ units derived by complete deprotonation of a terminal vinylidene ligand, $[\text{M}]=\text{C}=\text{CH}_2$. Such terminal deprotonated vinylidene ligands are isoelectronic with terminal metal carbonyl groups; they are found in trigonal $\text{M}(\text{C}_2)_3$ units isoelectronic with $\text{M}(\text{CO})_3$ units with the transition metal in very low formal oxidation states (e.g. Mn(-V) of $\text{Mn}(\text{C}_2)_3^{11-}$ in $\text{Ln}_{3.67}\text{MnC}_6$ or $\text{Ln}_3\text{Mn}_2\text{C}_6$ isoelectronic with $\text{Mn}(\text{CO})_3^{5-}$ and Ni(-II) of $\text{Ni}(\text{C}_2)_3^{8-}$ in $\text{Eu}_{3.16}\text{NiC}_6$ isoelectronic with $\text{Ni}(\text{CO})_3^{2-}$). Other carbon ligands found in related solid state metal carbides include C_2^{6-} derived from deprotonation of ethane (in $\beta\text{-ScCrC}_2$), terminal C^{4-} ligands either singly or doubly bonded to a transition metal, and bridging linear $=\text{C}=\text{C}=\text{C}$ ligands.

References

- [1] F.P. Pruchnik, *Organometallic Chemistry of the Transition Elements*, Plenum, New York, 1990.
- [2] R.B. King, *Inorg. Chem.*, 28 (1989) 3048.
- [3] R.B. King, *Inorg. Chem.*, 29 (1990) 2164.

- [4] R.B. King, *Russ. Chem. Bull.*, 43 (1994) 1533.
- [5] R. Hoffmann, J. Li and R.A. Wheeler, *J. Am. Chem. Soc.*, 109 (1987) 6600.
- [6] H. Deng and R. Hoffmann, *Inorg. Chem.*, 32 (1993) 1991.
- [7] J. Li and R. Hoffmann, *Chem. Mater.*, 1 (1989) 83.
- [8] M.H. Gerss, W. Jeitschko, L. Boonk, J. Nientiedt, J. Grobe, E. Mörsen and A. Leson, *J. Solid State Chem.*, 70 (1987) 19.
- [9] R.-D. Hoffmann, R. Pöttgen and W. Jeitschko, *J. Solid State Chem.*, 99 (1992) 134.
- [10] W. Jeitschko and M. Gerss, *J. Less-Common Met.*, 116 (1986) 147.
- [11] R. Pöttgen, A.M. Witte, W. Jeitschko and T. Ebel, *J. Solid State Chem.*, 119 (1995) 324.
- [12] A.M. Witte and W. Jeitschko, *Z. Naturforsch. Teil B.*, 51 (1996) 249.
- [13] J.E. Ellis, *Polyhedron*, 8 (1989) 1611.
- [14] J.E. Ellis, K.L. Fjare and T.G. Hayes, *J. Am. Chem. Soc.*, 103 (1981) 6100.
- [15] G.E. Kahnert and W. Jeitschko, *Z. Anorg. Allg. Chem.*, 619 (1993) 93.
- [16] G.N. Harakas and B.R. Whittlesey, *J. Am. Chem. Soc.*, 118 (1996) 4210.
- [17] M.A. Moss and W. Jeitschko, *Z. Anorg. Allg. Chem.*, 603 (1991) 57.
- [18] M.H. Gerss and W. Jeitschko, *Z. Naturforsch. Teil B.*, 41 (1986) 946.
- [19] W. Jeitschko, G. Block, G.E. Kahnert and R.K. Behrens, *J. Solid State Chem.*, 89 (1990) 191.
- [20] A.O. Pecharskaya, E.P. Marusin, O.I. Bodak and M.D. Mazus, *Sov. Phys. Crystallogr.*, 35 (1990) 25.
- [21] R. Pöttgen, G. Block, W. Jeitschko and R.K. Behrens, *Z. Naturforsch. Teil B.*, 49 (1994) 1081.
- [22] U.A. Böcker, W. Jeitschko and G. Block, *J. Alloys Compd.*, 236 (1996) 58.