Reviews

Organometallic motifs in the structures of solid state ternary carbides of the late transition metals

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Solid state ternary transition metal carbides containing carbon, a middle to late transition metal (Re to Ni), and a highly electropositive multivalent metal such as lanthanide, yttrium, or thorium exhibit a number of structural motifs resembling those in metal carbonyls and other transition metal derivatives of strong π-acceptor ligands. This paper presents models for the chemical bonding in the transition metal—carbon subnetworks of the ternary late transition metal carbides LnCoC (Ln = lanthanide), Ln_2ReC_2, Th_2NiC_2, Ln_2FeC_4, Ln_3MC_4 (M = Fe, Co, Ni, Ru, Rh, Os, Ir), Ln_4NiC_5, $Ca_4Ni_3C_5$, and $Er_8Rh_5C_{12}$. Carbide ligands present in such materials include terminal C^{4-} in Th_2NiC_2 and Y_2ReC_2, μ_2-C^{4-} in YCoC or Y_2ReC_2 similar to the central allene carbon atom, 1,2-bridging C_2^{4-} in Sc_3CoC_4 formally derived from ethylene, μ_3-bridging C_2^{4-} in $LnMC_2$ (M = Fe, Co, Ni, Ru) formally derived from ethylene, and 1,1-bridging C_2^{2-} in Ln_2FeC_4 isoelectronic with μ_2-CO group in metal carbonyls.

Key words: metal carbonyls; catalysis; carbon monoxide; formate; water gas shift reaction.

1. Introduction

One of the highlights of chemistry during the past several decades has been the discovery of diverse types of transition metal organometallic compounds exhibiting novel structures and chemical reactivities including species of importance for activation of small molecules in numerous catalytic reactions.[1] A characteristic feature of such transition metal organometallic compounds is the presence of single and/or multiple metal-carbon bonds. 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. The element other than carbon and the transition metal in these ternary metal carbides is a highly electropositive multivalent metal such as a lanthanide (abbreviated as Ln), yttrium, or thorium. Complete ionization 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. The 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 poly-

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phosphides,[2] superconducting transition metal borides and silicides,[3] and superconducting alloys.[3] This paper extends these methods to solid state ternary transition metal carbides with particular emphasis on late transition metal derivatives in which the transition metal atom can attain a closed shell electronic configuration. Some of these ternary transition metal carbides have also been studied by extended Hückel methods, particularly by Hoffmann and collaborators.[4—7]

2. Background

2.1. The transition metal environment

The accessible spd valence orbital manifold of most transition metals consists of nine orbitals (sp^3d^5) and has spherical (isotropic) geometry extending equally in all three dimensions. Filling this accessible spherical spd manifold with electrons from either the central metal atom or its surrounding ligands results in the familiar 18-electron configuration of the next rare gas that governs much of transition metal chemistry. The coordination polyhedra of transition metals using the spherical sp^3d^5 manifold extend equally in all three directions.

A specific feature of the chemical bonding in some derivatives of the late transition and early post-transition metals observed by Nyholm[8] as early as 1961 is the shifting of one or two of the outer p orbitals to such high energies that they no longer participate in chemical bonding and the accessible spd valence orbital manifold is no longer spherical (isotropic). If one p orbital is so shifted to become antibonding, then the accessible spd orbital manifold contains only eight orbitals (sp^2d^5) and has the geometry of a torus or doughnut (Fig.1) with the «missing» p orbital being responsible for the hole in the doughnut. This toroidal sp^2d^5 manifold can only bond in the two dimensions of the plane of the ring of the torus. Filling this two-dimensional sp^2d^5 manifold of eight orbitals with electrons leads to the 16-electron configuration found in square planar complexes of the d^8 transition metals such as Co(I), Rh(I), Ir(I), Ni(II), Pd(II), Pt(II), and Au(III). The clearest example of a toroidal transition metal atom in a ternary transition metal carbide is the distorted square planar Co(I) atom in the CoC_2^{3-} anion of $LnCoC_2$. If two p orbitals are shifted to become antibonding then the accessible spd orbital manifold contains only seven orbitals (spd^5) and has cylindrical geometry extending in one axial dimension much further than in the remaining two dimensions (Fig. 1). Filling this one-dimensional seven-orbital spd^5 manifold with electrons leads to the 14-electron configuration found in two-coordinate linear complexes of d^{10} metals such as Ni(0), Pt(0), Cu(I), Ag(I), Au(I), Hg(II), and Tl(III). The clearest example of a cylindrical transition metal atom in a ternary transition metal carbide is the linear Ni(0) atom in the NiC_2^{8-} anion of Th_2NiC_2.

The p orbitals which are raised to antibonding levels in the toroidal and cylindrical manifolds can participate in $d\sigma \rightarrow p\sigma^*$ or $d\pi \rightarrow p\pi^*$ bonding. Such bonding has been suggested by Dedieu and Hoffmann[9] for Pt(0)—Pt(0) dimers on the basis of extended Hückel calculations. This type of bonding like, for example, the $d\pi \rightarrow p\pi^*$ backbonding in metal carbonyls, does not affect the electron bookkeeping in metal clusters but accounts for bonding rather than non-bonding distances between adjacent metal vertices. The Ni—Ni bonding in $Ca_4Ni_3C_5$ can be interpreted to arise from such interactions.

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. In the cases of transition metal atoms with apparent toroidal and cylindrical valence orbitals manifolds this M=C π-bonding must necessarily involve a p orbital excluded from the toroidal or cylindrical valence orbital manifold so the actual dimensionality of the transition metal valence orbital manifold is one higher than that used exclusively for the σ-bonding (Fig.2). 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 toroidal sp^2d^5 manifold rather than a seven-orbital cylindrical spd^5 manifold expected from the linear σ-bonding alone from the two-coordinate cobalt atom. The «extra» cobalt p orbital of the toroidal sp^2d^5 manifold participates in the Co=C $p\pi$—$p\pi$ bonding. Similarly in Y_2ReC_2 with a $(=C=)_2Re=\ddot{C}$: metal environment the Re=C π-bonding requires the rhenium valence orbital manifold to be a nine-orbital spherical sp^3d^5 manifold rather than an

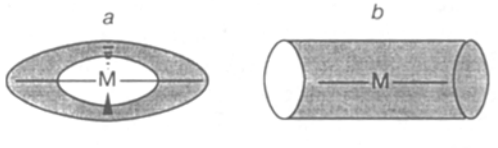


Fig.1. Toroidal (*a*) and cylindrical (*b*) manifolds showing square planar coordination for the toroidal manifold.
a. Toroidal sp^2d^5 manifold (square planar);
b. Cylindrical spd^5 manifold (linear).

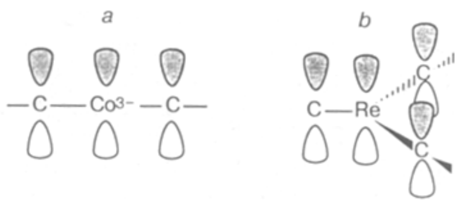


Fig.2. Role of metal p orbitals in M=C double bonding in the polymeric anions in YCoC and Y_2ReC_2.
a. $CoC_{2/2}{}^{3-}$ anion in YCoC; *b*. $ReCC_{2/2}{}^{6-}$ in Y_2ReC_2.

eight-orbital toroidal sp^2d^5 manifold expected from the trigonal planar σ-bonding alone from the three-coordinate rhenium atom.

2.2. The carbon ligand

The carbon ligands found in ternary transition metal carbides (Scheme 1) can be classified into two fundamental types, namely those containing a single carbon atom (C_1 ligands) and those containing bonded carbon pairs (C_2 ligands). The properties of bonded carbon pairs in ternary late transition metal carbides have been reviewed.[6,10]

1. C_1 ligands. The carbide Th_2NiC_2 contains isolated linear C—Ni—C units in which 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. If the carbon atom in such a ligand is formally regarded as a neutral ligand, then it is a formal −2 electron donor (i.e., a two-electron *acceptor*) since it needs to receive one of its three lone electron pairs from the metal atom.

The terminal carbon atoms in Y_2ReC_2 are doubly bonded to the rhenium atom so that the $M{=}\ddot{C}{:}^{2-}$ unit is isoelectronic with an $M{=}\ddot{O}{:}$ unit. If the carbon atom in such a ligand is formally regarded as a neutral ligand then it is a formal zero electron donor since its four valence electrons are used for its lone pairs.

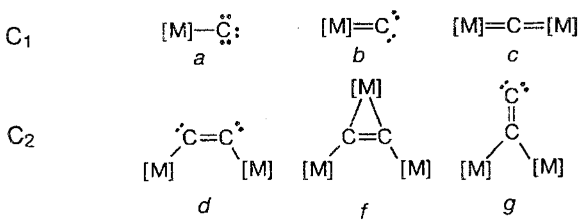
The μ_2-carbon atom in the =C=Co=C= units of YCoC is similar to the central carbon atom in allene even to the extent that the Co—C—Co bond angle in YCoC is essentially linear in accord with its sp hybridization. If the carbon atom in such a bridging =C= ligand is regarded as a neutral ligand then it is a formal two-electron donor to each of the metal atoms that it bridges.

2. C_2 ligands. The carbide Sc_3CoC_4 contains 1,2-bridging C_2 ligands with a C—C distance of 1.46 Å as compared with typical C=C distances of ~1.34 Å and C—C distances of ~1.54 Å in typical simple hydrocarbons. This 1,2-bridging C_2 ligand is formulated as C_2^{4-} formally derived from ethylene, C_2H_4, by loss of its four hydrogens. If the C_2 pair in such a ligand is formally regarded as a neutral ligand, then it is a formal donor of zero electrons to each of the metal atoms that it bridges since all of the eight valence electrons of the two carbon atoms are required for the C=C double bond and the lone pair on each carbon atom.

The carbides $LnCoC_2$ (and related $LnFeC_2$, $LnRuC_2$, and $LnNiC_2$ carbides) contain a μ_3-bridging C_2 ligand bridging three metal atoms. This ligand with a typical C=C distance of 1.37 Å (in $DyCoC_2$) may be regarded as either derived from a 1,2-dimetallated acetylene [M]—C≡C—[M] with the C≡C triple bond of the acetylene π-bonded to a third metal atom or from ethylene by replacement of all four of its hydrogens by metal atoms. The latter view of this ligand as C_2^{4-} leads to more reasonable formal oxidation state assignments for the transition metal atoms. If the C_2 pair in such a ligand is formally regarded as a neutral ligand, then it is a formal donor of four electrons to the three metal atoms that it bridges since only four of the eight valence electrons of the two carbon atoms are required for the C=C double bond remaining after bonding the original C≡C to the third metal atom. Since the structure for a μ_3-bridging C_2 ligand drawn in Scheme 1 has four single bonds to the three metal atoms, it is convenient to consider each M—C bond from such a neutral ligand as representing donation of a single electron to the metal atom.

The carbides Ln_2FeC_4 contain a 1,1-bridging C_2 ligand between a pair of metal atoms with a C=C distance of 1.33 Å in Y_2FeC_4 clearly indicating considerable multiple bonding. This ligand may be regarded as $>C{=}\ddot{C}{:}^{2-}$ isoelectronic and isolobal with a bridging carbonyl group $>C{=}\ddot{O}{:}$. In this connection it is interesting that the 1,1-bridging C_2 ligands in Ln_2FeC_4 are supported by Fe—Fe bonds (Fe—Fe distance of 2.50 Å in Y_2FeC_4) similar to bridging carbonyl groups in polynuclear metal carbonyl derivatives.[1] If the C_2 pair in such a 1,1-bridging C_2 ligand is formally regarded as a neutral ligand, then it is a formal donor of zero electrons to each of the metal atoms that it bridges since all eight valence electrons of the two carbon atoms are required for the C=C double bond and the two lone pairs.

Scheme 1



a. Terminal C^{4-} with M—C in Th_2NiC_2;
b. terminal C^{4-} with M=C in Y_2ReC_2;
c. μ_2-bridging C^{4-} in YCoC or Y_2ReC_2;
d. 1,2-bridging C_2^{4-} in Sc_3CoC_4;
f. μ_3-bridging C_2^{4-} in $LnCoC_2$;
g. 1,1-bridging C_2^{2-} in Y_2FeC_4.

Note. The types of C_1 (*a*, *b*, *c*) and C_2 (*d*, *f*, *g*) ligands found in solid state ternary transition metal carbides. The designation [M] here and elsewhere in this paper denotes a transition metal with all of its ligands other than those explicitly depicted.

3. The chemical bonding topology of ternary transition metal carbides

Table 1 summarizes some of the important structural features of the anionic transition metal—carbon subnet-

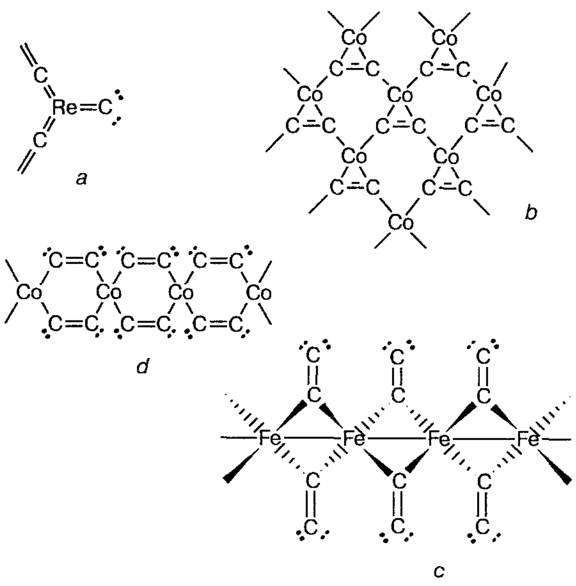
Table 1. Important structural features of the anionic transition metal-carbon subnetworks in ternary transition metal carbides

Species[a]	Anion	Bond distances/Å			Ligand	Electron count		Metal oxidation state	Other transition metals	N^c
		M—C	C—C	M—M		Anion	Metal[b]			
YCoC	$CoC_{2/2}{}^{3-}$	1.82	—	—	μ_2-C^{4-}	16	16P	Co(I)		1
Y_2ReC_2	$ReC_{2/2}C^{6-}$	1.72, 2.18, 2.34	—	—	C^{4-}, μ_2-C^{4-}	21	17	Re(II)		1
$LnCoC_2$	$Co(C_2)_{3/3}{}^{3-}$	1.95, 1.98	1.37	—	μ_3-$C_2{}^{2-}$	20	16P	Co(I)	Fe, Ni	2
Th_2NiC_2	$NiC_2{}^{8-}$	1.93	—	—	C^{4-}	26	14L	Ni(0)		0
Y_2FeC_4	$Fe(C_2)_{4/2}{}^{6-}$	1.97	1.33	2.50	μ_2-$C_2{}^{2-}$	30	14+M—M	Fe(—II)		1
Sc_3CoC_4	$Co(C_2)_{4/2}{}^{9-}$	2.09	1.46	—	μ_2-$C_2{}^{4-}$	34	18	Co(—I)	Fe, Ru	1
$Ln_4Ni_2C_5$	$Ni_2(C_2)_{4/2}{}^{8-}$	1.93, 2.10	1.38	2.63	μ_2-$C_2{}^{2-}$	44	16+M—M			1
$Ca_4Ni_3C_5$	$Ni_3(C_2)_2C^{8-}$	1.83, 1.89	1.20	2.63	C^{4-}, $C_2{}^{2-}$	58	14+M—M	Ni(0)		1

Note. [a] Ln = lanthanide; [b] P = planar metal coordination using an 8-orbital sp^2d^5 valence orbital manifold; L — metal coordination using an 7-orbital spd^5 valence orbital manifold; M—M refers to metal—metal bonding in addition to the valence orbital manifold; [c] *N* — extension of polyanion.

works in the six types of ternary transition metal carbides containing a single type of transition metal that are discussed in this paper. These anionic subnetworks are obtained from the complete ternary transition metal carbide network by removal of the electropositive lanthanide or thorium atom as Ln^{3+} or Th^{4+}. An important feature of these anionic transition metal-carbon subnetworks is its polymerization dimensionality (or *extension* in Jeitschko's terminology). Thus the polymerization dimensionality of isolated transition metal-carbon anions such as the $NiC_2{}^{8-}$ anion in Th_2NiC_2 is zero; the polymerization dimensionality of infinite chain anions such as the $CoC_{2/2}{}^{3-}$ anion in YCoC is one; the polymerization of infinite sheet anions such as the $Co(C_2)_{3/3}{}^{3-}$ anion in $YCoC_2$ is two; etc. Carbon ligands shared between two or more *transition* metals 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 C_2 ligand is bonded. Structures of the infinite anionic transition metal-carbon subnetworks found in the carbides discussed in this section are given in Scheme 2.

Scheme 2



a. $ReC_{2/2}C^{6-}$ in Y_2ReC_2;
b. $Co(C_2)_{3/3}{}^{3-}$ in $LnCoC_2$;
c. $Fe(C_2)_{4/2}{}^{6-}$ in Y_2FeC_4;
d. $Co(C_2)_{4/2}{}^{9-}$ in Sc_3CoC_4.

3.1. Carbides of the type LnCoC

The anionic transition metal-carbon subnetworks of carbides of the type LnCoC such as YCoC consist of =C=Co=C=Co=C=Co= infinite chains with 16 electrons per $CoC^{3-} = CoC_{2/2}{}^{3-}$ unit.[11] The central cobalt atom in such a unit has the 9(Co) + 4(=C) + 3 (−3 charge) = 16 electrons required to fill an eight-orbital toroidal sp^2d^5 manifold consisting of the seven-orbital spd^5 cylindrical manifold plus another p orbital for the π-component of a Co=C double bond. Assignment of the usual +3 and −4 oxidation states to the lanthanide cation and the carbide anion in LnCoC leads to a formal +1 oxidation state for the cobalt atom. If the Co=C double bonds to the =C= ligand are replaced by equivalent bent Co—C single bonds ("banana bonds"), then the cobalt atom in LnCoC may be considered to have square planar coordination which is typical for d^8

transition metals such as Co(I). Extended Hückel calculations[4] confirm the occurrence of extensive π-bonding in the $[CoC_{2/2}{}^{3-}]_\infty$ infinite chains in YCoC.

3.2. Carbides of the type Ln_2ReC_2

The anionic transition metal—carbon subnetworks of carbides of the type Ln_2ReC_2 such as Y_2ReC_2 consist of $[ReC_{2/2}C^{6-}]_\infty$ infinite chains with 21 electrons per $ReC_2{}^{6-}$ unit (Scheme 2).[12] The Re=C bond lengths in Y_2ReC_2 are 1.72 Å and 2.34 Å to the bridging =C= atom and 2.13 Å to the terminal C atom suggesting that the Re=C bond order to the terminal carbon atom is no lower than the average Re=C bond order to the bridging carbon atom implying that all three Re=C bonds are double bonds rather than the Re≡C triple bonds to the terminal carbon atom suggested by Jeitschko and co-workers.[12] Elementary group theory[13] indicates that the rhenium $sp^3d^2(xz,yz)$ orbitals can form three trigonally hybridized σ-bonds to the three carbon atoms as well as one π-bond to each carbon atom perpendicular to the ReC_3 plane. This $sp^3d^2(xz,yz)$ orbital set for the rhenium atom is the same as the set of metal orbitals that are used for the trigonal prismatic hybridization if two "banana" bonds from the rhenium to each carbon atom are used instead of the σ + π(⊥) pairs. The central rhenium atom in an $ReC_{2/2}C^{6-}$ unit in Y_2ReC_2 has a 17 electron configuration obtained as follows:

Neutral rhenium atom	7 electrons
2 bridging (Re=C=) ligands: (2)(2)	4 electrons
1 terminal (Re=$\ddot{C}$:) ligand: (1)(0)	0 electrons
−6 charge	6 electrons
Total valence electrons	17 electrons

This 17-electron configurations for the central rhenium atoms are one less than the favored 18-electron rare gas configuration. However, the minimum Re...Re distances are too long for any significant rhenium-rhenium bonding. Assignment of the usual +3 and −4 oxidation states to the lanthanide and isolated carbon atoms in Y_2ReC_2 leads to a formal +2 oxidation state for its rhenium atom.

3.3. Carbides of the type $LnMC_2$ (M = Fe, Ru, Co, Ni, etc.)

The anionic transition metal-carbon subnetworks of a large group of isostructural carbides of the type $LnMC_2$ (Ln = lanthanide, M = Fe, Co, Ni) consist of infinite $[M(C_2)_{3/3}]_\infty$ sheets (Scheme 2).[14] The central cobalt atoms in a $[Co(C_2)_{3/3}{}^{3-}]_\infty$ sheet each have 9(Co) + 4(4Co−C) + 3(−3 charge) = 16 electrons as required for a planar cobalt atom with an eight-orbital sp^2d^5 toroidal manifold. Formulating the carbon pairs as $C_2{}^{4-}$ from tetrametallated ethylene leads to the formal +1 cobalt oxidation state so that $LnCoC_2$, like LnCoC, may formally be regarded as a square planar Co(I) derivative. The metal atoms in the isostructural iron and nickel $LnMC_2$ derivatives have one less and one more valence electron, respectively, than the ideal 16 electron configuration for a planar metal using an eight-orbital toroidal sp^2d^5 manifold.

3.4. The carbide Th_2NiC_2

The carbide Th_2NiC_2 contains isolated linear $[C{-}Ni{-}C]^{8-}$ anions with 26 valence electrons and Ni−C distances of 1.93 Å suggestive of Ni−C single bonding.[15] Each nickel atom has the 14 electrons required to fill a seven-orbital cylindrical spd^5 manifold as follows:

Neutral nickel atom:	10 electrons
2 singly bonded C^{4-} ligands: (2)(−2)	−4 electrons
−8 charge	8 electrons
Total valence electrons:	14 electrons

Assignment of the usual +4 and −4 oxidation states to the thorium and isolated carbon atoms in Th_2NiC_2 leads to a formal oxidation state of zero for the nickel atoms corresponding to a d^{10} metal configuration. Thus the $NiC_2{}^{8-}$ anion is an example of a linear d^{10} metal derivative similar to those formed by other d^{10} metal ions such as Pt(0), Cu(I), Ag(I), Au(I), Hg(II), Tl(III), etc. Moss and Jeitschko[13] have noted that $NiC_2{}^{8-}$ is isoelectronic with other well-established linear anions such as $HgO_2{}^{2-}$ and $ZnN_2{}^{4-}$.

3.5. The carbides Ln_2FeC_4

The anionic transition metal-carbon subnetworks of the carbides Ln_2FeC_4 consist of infinite $[Fe(C_2)_{4/2}{}^{6-}]_\infty$ chains with 30 electrons per $FeC_4{}^{6-}$ unit and 1,1-bridging C_2 ligands.[16] The $[Fe(C_2)_{4/2}{}^{6-}]_\infty$ chains contain an infinite chain of Fe−Fe bonds with Fe−Fe distances of 2.50 Å. These infinite −Fe−Fe−Fe− chains may related to the observed superconductivity of Y_2FeC_4 below $T_c = 3.6$ K.[14]

The 1,1-bridging C_2 ligands in Ln_2FeC_4 can be formulated as $C_2{}^{2-}$ isoelectronic with a bridging carbonyl group leading to a formal iron oxidation state of −2 analogous to monomeric $Fe(CO)_4{}^{2-}$, although $Fe(CO)_4{}^{2-}$ has only terminal CO groups and obviously no Fe−Fe bonds. 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 $[Fe(C_2)_{4/2}{}^{6-}]_\infty$ attain the 16-electron configuration required for filling a toroidal eight-orbital sp^2d^5 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.

3.6. The carbides Ln_3MC_4 (M = Fe, Co, Ni, Ru, Rh, Os, Ir)

The anionic transition metal-carbon subnetworks of the carbides Ln_3CoC_4 consist of infinite $[Co(C_2)_{4/2}{}^{9-}]_\infty$ chains with 34 electrons per $CoC_4{}^{9-}$ unit and 1,2-bridging C_2 ligands.[17] Formulating the C_2 ligands as $C_2{}^{4-}$ corresponding to the tetradeprotonation of ethylene 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 Sc_3FeC_4 and Sc_3RuC_4 have 17 valence electrons and the nickel atom in Sc_3NiC_4 has 19 valence electrons.

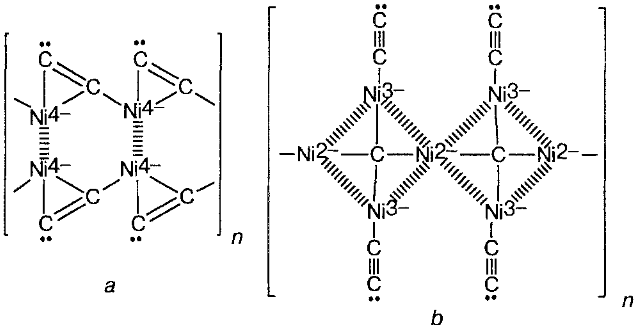
3.7. The carbides $Ln_4Ni_2C_5$ (= $[Ln^{+3}]_4[C^{4-}][Ni_2C_4{}^{8-}]$)

These carbides contain tripositive lanthanide ions (Ln = Er, Tm, Yb, Lu) and isolated carbon atoms that are assumed to be methanide ions, C^{4-}.[18] This leaves an anionic $[Ni_2C_4{}^{8-}]_\infty$ = $[Ni_2(C_2)_{4/2}{}^{8-}]_\infty$ transition metal-carbon subnetwork (Scheme 3). The carbon-carbon distances in the bridging C_2 ligands are 1.38 Å similar to the C_2 carbon-carbon distance in $LnCoC_2$ suggestive of carbon-carbon double bonds. The bridging C_2 ligands require four electrons for the C=C double bond and two electrons for the lone pair on the carbon atom bonded only to a single nickel atom. This leaves two of the eight electrons from a neutral pair of carbon atoms for donation to the two metal atoms to which they are bonded; one of these two electrons is conveniently allocated to each of the nickel atoms bridged by the C_2 ligand. The nickel atoms then have a 16 valence electron configuration obtained as follows:

Neutral nickel atom:	10 electrons
Bonding to two C_2 ligands:	2 electrons
−4 charge	4 electrons
Total valence electrons	16 electrons

Note that this electron counting does not consider any nickel-nickel bonding even though the Ni—Ni distance is 2.63 Å, well within the range for a Ni—Ni single bond. This nickel-nickel bonding can be interpreted as dπ→pπ interactions arising from donation of d electrons from one nickel atom into the empty p_z orbital of the other nickel atom.[9] Such Ni—Ni bonding is indicated by hashed lines in Scheme 3. If the C_2 ligands in the $[Ni_2(C_2)_{4/2}{}^{8-}]_\infty$ subnetwork are considered to be $C_2{}^{4-}$ from tetrametallated ethylene, then the formal oxidation state of the nickel atom is zero.

Scheme 3



a. The $[Ni_2(C_2)_{4/2}{}^{8-}]_\infty$ chain in $Ln_4Ni_2C_5$;
b. The $[Ni_3(C_2)_2C^{8-}]_\infty$ chain in $Ca_4Ni_3C_5$

3.8. The carbide $Ca_4Ni_3C_5$

A repeating unit of the $[Ni_3(C_2)_2C^{8-}]_\infty$ chain in $Ca_4Ni_3C_5$ has two nickel atoms of one type and one nickel atom of another type[19]; these nickel atoms are designated as Ni^{3-} and Ni^{2-}, respectively, in Scheme 3 in accord with the allocation of the −8 charge per Ni_3 unit between the nickel atoms. The terminal C_2 ligands may be regarded as $C_2{}^{2-}$ isoelectronic with terminal CO groups. Since six of the eight carbon electrons are required for the C≡C triple bond and the remaining two carbon electrons for the lone pair remaining on the carbon atom not bonded to nickel, a *neutral* terminal C_2 ligand of this type is a net donor of zero electrons. The isolated μ_4-carbon atom in the middle of a square containing two Ni^{3-} and two Ni^{2-} atoms may be considered to donate one of its four valence electrons to each of these four nickel atoms. If no Ni—Ni bonding is considered, then the following electron-counting schemes lead to the 14 valence electrons required to fill seven-orbital cylindrical spd^5 manifolds on each of the nickel atoms:

For the two Ni^{3-} atoms in the $Ni_3(C_2)_2C^{8-}$ unit:

Neutral nickel atom:	10 electrons
Terminal neutral C≡C: ligand:	0 electrons
Central μ_4-carbon atom:	1 electron
−3 charge	3 electrons
Total valence electrons for Ni^{3-}:	14 electrons

For the Ni^{2-} atom in the $Ni_3(C_2)_2C^{8-}$ unit:

Neutral nickel atom:	10 electrons
Two central μ_4-carbon atoms: (2)(1)	2 electrons
−2 charge	2 electrons
Total valence electrons for Ni^{2-}:	14 electrons

This electron counting scheme again does not consider any nickel−nickel bonding even though the Ni−Ni distances are 2.63 Å, well within the range for Ni−Ni single bonds. The nickel-nickel bonding can be assumed to consist of $d\pi \rightarrow p\pi$ interactions arising from donation of d electrons from one nickel atom into the empty p orbitals of an adjacent nickel atom. If the C_2 ligands in the $Ni_3(C_2)_2C^{8-}$ unit are considered to be C_2^{2-} isoelectronic with a terminal carbonyl group and the isolated carbon atom is considered to be C^{4-} then both Ni^{2-} and Ni^{3-} can be considered to have formal zero oxidation states. Both of the types of nickel atoms in $Ca_4Ni_3C_5$ are thus examples of linearly coordinated d^{10} transition metals similar to the carbide Th_2NiC_2 discussed above.[13]

3.9. The carbide $Er_8Rh_5C_{12}$

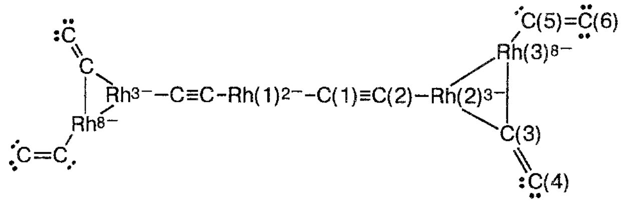
This carbide, at least in one sense, is the most complicated of the late transition metal ternary carbides discussed in this paper since it contains three different types of rhodium atoms and three different types of C_2 units. However, the $Rh_5C_{12}^{24-}$ anion found in this carbide is a finite anion (Scheme 4) unlike the infinite anions found in the other carbides discussed in this paper.[20] In Scheme 4 the rhodium atoms are labelled in brackets so that a possible allocation of the −24 charge on the $Rh_5C_{12}^{24-}$ ion between the five rhodium atoms can be shown. The C_2 ligands are of the following three types:

(1) The C(1)≡C(2) ligand bridging Rh(1) and Rh(2). This C_2 ligand can be interpreted as a bridging neutral alkynyl ligand which is a one-electron donor to each of the rhodium atoms that it bridges.

(2) The C(3)=C(4) ligand bridging Rh(2) and Rh(3), which are also connected by a Rh−Rh bond (2.71 Å). This C_2 ligand is a 1,1-bridging C_2^{2-} isoelectronic with a bridging carbonyl group and similar to the C_2 ligands found in Y_2FeC_4 (Scheme 1). A *neutral* C_2 ligand of this type is a zero-electron donor since four of the eight electrons are required for the C=C double bond and the remaining four electrons are required as two lone pairs on the carbon atom not bonded to the metal atoms.

(3) The terminal C(5)=C(6) ligand bonded to Rh(3). The Rh(3)−C(5)−C(6) angle is 126.1° so that the bond C(5)=C(6) (distance 1.33 Å) must be interpreted as a double bond rather than a triple bond. The C(5)=C(6) ligand thus needs three lone pairs in addition to the four electrons for the C=C double bond so that as a neutral ligand it is a −2 electron donor. The resulting ligand is a C_2^{4-} ligand which is isoelectronic with a *bent* nitrosyl group.

Scheme 4



In allocating the −24 charge on the $Rh_5C_{12}^{24-}$ unit among the five rhodium atoms, it is impossible to give all five rhodium atoms a closed shell electronic configuration. Thus the overall −24 charge of the $Rh_5C_{12}^{24-}$ unit is an even number so that an even-numbered formal charge must be allocated to the central rhodium atom Rh(1) in order to keep the pairs of Rh(2) and Rh(3) atoms equivalent. However, since a neutral Rh(1) atom has an odd number of electrons, namely nine, and an even number of equivalent carbon ligands, namely C(1), the overall electronic configuration of Rh(1) must be an odd number and therefore cannot be a closed shell electronic configuration regardless of whether Rh(1) is assumed to have a cylindrical spd^5 seven-orbital valence manifold requiring 14 electrons (the most likely situation since it is two-coordinate with approximately linear coordination), a toroidal sp^2d^5 eight-orbital valence manifold requiring 16 electrons, or a spherical sp^3d^5 nine-orbital valence manifold requiring 18 electrons.

The allocation of negative charges indicated in Scheme 4 leads to the following electron configurations for the three types of rhodium atoms in $Rh_5C_{12}^{24-}$:

For Rh(1):

Neutral rhodium atom:	9 electrons
Two neutral (−C(1)≡C(2)−) ligands: (2)(1)	2 electrons
−2 charge	2 electrons
Total valence electrons for Rh(1):	13 electrons

For Rh(2):

Neutral rhodium atom:	9 electrons
One neutral (−C(1)≡C(2)−) ligand:	1 electron
One neutral 1,1-bridging C(3)=C(4) ligand:	0 electrons
One Rh−Rh bond	1 electron
−3 charge	3 electrons
Total valence electrons for Rh(2):	14 electrons

For Rh(3):

Neutral rhodium atom:	9 electrons
One neutral 1,1-bridging C(3)=C(4) ligand:	0 electrons
One terminal C(5)=C(6) ligand	−2 electrons
Rh−Rh bond	1 electron
−8 charge	8 electrons
Total valence electrons for Rh(3):	16 electrons

The following points are of interest concerning these apparent electronic configurations of the three types of rhodium atoms:

Rh(1): The 13 valence electron configuration for Rh(1) is one electron short of the 14 valence electrons required for a seven-orbital cylindrical spd^5 electronic configuration consistent with the linear two-coordination of Rh(1).

Rh(2): The 14 valence electron configuration for Rh(2) is two electrons short of the 16 valence electrons required for the eight-orbital toroidal sp^{2}d^5 electronic configuration expected for the apparent planar three-coordination of this rhodium atom. However, the geometry of the packing of the $Rh_5C_{12}^{24-}$ chains in the crystal lattice suggests that a C(5) atom of an adjacent $Rh_5C_{12}^{24-}$ chain is close enough to this Rh(2) so that the electron pair on C(5) can be donated to Rh(2) leading to distorted square planar coordination for Rh(2) with the required 16 valence electrons.

Rh(3): The 16 valence electron configuration is exactly the number of electrons required for the eight-orbital toroidal sp^{2}d^5 electronic configuration expected for the apparent trigonal planar coordination of this rhodium atom.

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