

$(L_nM-C_m-)_x$: Hypothetical organometallic polymers with metallapolyne and metallacumulene character*

Nazzareno Re,^a Antonio Sgamellotti^a and Carlo Floriani^a

^a *Dipartimento di Chimica and Centro di Studio CNR per il Calcolo Intensivo, Università di Perugia, via Elce di Sotto 8, I-06123 Perugia, Italy*

^b *Institut de Chimie Minerale et Analytique, BCH, Université de Lausanne, Switzerland*

A class of $(-L_nM-C_m-)_x$ hypothetical polymers, $m = 2-4$, conceptually derived from experimentally known analogous rigid-rod organometallic polymers and with different electron counts, obtained by varying the metal and the ligands in the ML_n fragment, have been studied using extended-Hückel tight-binding calculations. The results suggest interesting conducting properties, depending on the electron count and the length of the bridging C_m chain.

Much interest has recently been attracted by rigid-rod organometallic polymers¹⁻⁴ because of expected novel properties like non-linear optical behaviour,⁵ liquid crystal properties¹ and one-dimensional conductivity.⁶ Several polymeric species containing transition metals of Groups 8-10 (Fe, Ru, Co, Rh, Ni, Pd, Pt) and a wide class of acetylenic chromophores as bridging ligands have recently been synthesized²⁻⁴ and their physical properties intensively investigated.²⁻⁶ However, in the overwhelming majority of these compounds the energy mismatch between the empty π^* system of the bridging ligands and the filled metal d orbitals leads to a scarce back bonding and therefore to limited π conjugation.^{3,7} As a consequence the experimental band gaps are around 3 eV so that these polymers are regarded as semiconductors to weak conductors in their undoped state.⁶

Recent extended-Hückel band calculations have been performed on a series of polyynes containing transition metals $(L_nM-C\equiv CRC\equiv C-)_x$ ($L = PH_3, CO$ or H ; $n = 2$ or 4 ; $M = Fe, Rh, Pt$ or Cu ; $R = \text{none}, C\equiv C$ or C_6H_4) to study their electronic structures.⁷ The results indicate: (i) a considerable mixing between the filled metal d orbitals and the filled π system of the acetylenic chromophore in the highest occupied crystal orbital (HOCO); (ii) a lowest unoccupied crystal orbital (LUCO) essentially constituted by the empty π^* system of the chromophore; (iii) band gaps in the range 2-3 eV, depending on the considered metal, ligands and chromophores.

Experimental efforts to enhance π conjugation and thus improve the molecular properties of this family of polymers have been directed towards the modification of the acetylenic linkers. This has been achieved by lowering the energy of the π^* system for the linker by extending its π conjugation length or by introducing a heterocycle with a donor atom.³

In this paper we propose a completely different approach to reduce the band gap in rigid-rod organometallic polymers, based on the modification of the metal-ligand groups ML_n , which in turn allows a better exploitation of the higher versatility offered by these organometallic polymers over the conventional π -conjugated organic polymers.⁴ Such an approach has been suggested by the analogy with dinuclear transition-metal complexes containing an acetylide bridge.⁸ Several $\mu-C_2$ bridged dinuclear complexes have been synthesized with structures consistent with all the three possible valence bond descriptions:^{8a,b} $L_nM-C\equiv C-ML_n$, $L_nM=C=C-ML_n$ and $L_nM\equiv C-C\equiv ML_n$. In a recent theoretical paper we studied the factors governing the interaction mode of a bridging C_2 unit

with the metal atoms in these complexes.⁹ This allowed us to distinguish two classes of compounds, depending on the metal, its oxidation state and the nature of the ligand. The first class is constituted by early transition metals (those of the titanium, vanadium and chromium triads) in high oxidation states with mainly π -donor ligands like RO^- . For this class of complexes all the three possible valence bond structures have been found depending on the metal d^n configuration; referring to the isolated ML_n fragment, an acetylenic $M-C\equiv C-M$ structure is found for a d^1 configuration, a cumulenic $M=C=C-M$ structure for a d^2 configuration and a dimetallabutadiyne $M\equiv C-C\equiv M$ structure for a d^3 configuration. The second class is constituted by late transition metals (from the manganese triad to the right) in low oxidation states with mainly π -acceptor ligands (like carbonyls or phosphines). For this class of complexes only the acetylenic $\mu-C\equiv C$ structure has been found, irrespective of the metal d configuration.

These results can be immediately extended to the $(L_nMCC-)_x$ polymeric species and suggest the best strategy to improve π conjugation in this class of compounds. First of all, if the ML_n group is made up by late transition metals with π -acceptor ligands, we expect always a polyynic structure $(L_nM-C\equiv C-)_x$. This is found for essentially the whole class of rigid-rod organometallic polymers with acetylenic chromophores (where the metal moiety is made up by Group 8-10 metals with carbonyl or phosphine ligands). Indeed, this situation clearly corresponds to a polyynic structure for the simplest C_2 linker (corresponding to an acetylene HCCH molecule). For such polymers, the observed crystal structures indicate a metal-carbon distance typical of a single bond while the bond lengths within the acetylenic linkers remain practically unaltered with respect to those of the corresponding free molecule.

By analogy with the dinuclear compounds, a better π conjugation can be obtained using an ML_n group with an early to mid transition metal in a high oxidation state, π -acceptor ligands and a suitable configuration. Taking into account that in a polymeric $(L_nMCC-)_x$ species each metal interacts with two C_2 moieties rather than one, as in the corresponding dinuclear complex (L_nMCCML_n) , the electron counts leading to a metallapolyne, $(L_nM-C\equiv C-)_x$, a metallacumulene $(L_nM=C=C-)_x$, and a metallapolyne, $(L_nM\equiv C-C\equiv)_x$, structure are expected to be d^2 , d^4 and d^6 , respectively. Although based on intuitive valence band (VB) considerations, these criteria are confirmed by our band calculations, although with some modifications, see below.

Related to these hypothetical polymers is the class of lanthanide carbides in which the carbon atoms occurs in discrete pairs.¹⁰ Although these compounds show essentially ionic three-dimensional structures, most of them contain infinite

* Non-SI unit employed: eV $\approx 1.60 \times 10^{-19}$ J.

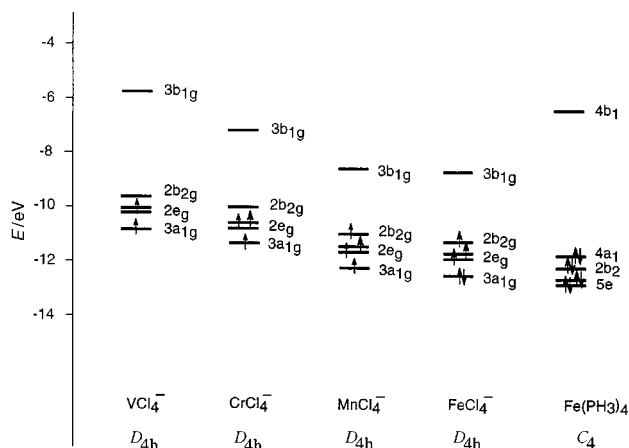


Fig. 1 Energies of the metal orbitals for metal fragments 1–4 and 11

($-M-C_2$)_x parallel chains with C–C distances in the range 1.28–1.30 Å.¹¹ Electronic structure calculations have been carried out for these compounds¹² and show a partial covalent character of the metal–carbon bonds due to a significant d_{π} – p_{π} overlap between the lanthanide d orbitals and the C–C π -antibonding orbitals, thus explaining the observed metallic behaviour.

In this study we use the extended Hückel method¹³ in the tight-binding scheme¹⁴ to study the electronic structure of several ($-L_nM-C_2$)_x hypothetical polymers with different electron counts obtained by varying the metal and the ligands in the ML_n fragment. Analogous polymers with longer bridging carbon chains, ($-L_nM-C_m$)_x, $m = 3$ or 4, have also been considered and the results show a different behaviour according to the even or odd number m of carbon atoms in the bridging chain.

Results and Discussion

We considered hypothetical ($-L_nM-C_2$)_x polymers for early to mid transition metals in high oxidation states and π -donor ligands. The ML_n electron counts from d^2 to d^6 have been considered by taking the square-planar fragments 1–5 which lead to polymers 6–10: VCl_4^- , d^2 1; $CrCl_4^-$, d^3 2; $MnCl_4^-$, d^4 3; $FeCl_4^-$, d^5 4; $FeCl_4^{2-}$, d^6 5; ($-Cl_4V-C_2$)_x⁻, 6; ($-Cl_4Cr-C_2$)_x⁻, 7; ($-Cl_4Mn-C_2$)_x⁻, 8; ($-Cl_4Fe-C_2$)_x⁻, 9; ($-Cl_4Fe-C_2$)_x²⁻, 10. Moreover a typical metal fragment with a late transition metal and π -acceptor ligands, like $Fe(PH_3)_4$ 11, and the corresponding [$-(H_3P)_4Fe-C_2$]_x polymer 12, have been used for comparison.

The energy levels for the metal fragments 1–5 and 11 are reported in Fig. 1 and show the usual four-below-one pattern typical of the d orbitals in a square-planar ligand field. Of particular interest is the energy of the d_{π} orbitals (e_g in 1–5, e in 11) which interact with the π system of the C_2 unit. The energy of these orbitals decreases from 1 to 4 and 5 reflecting the increase of electronegativity along the transition series. A more consistent energy lowering of the d_{π} orbitals is observed for 11 because of the stabilizing effect of the π -acceptor PH_3 ligands. This also leads to a change of the orbital ordering and shifts the d_{π} lower than the d_{z^2} as the lowest metal orbitals.

The band structures of polymers 6, 8 and 12 are shown in Fig. 2 where only the highest occupied and lowest unoccupied crystal orbitals are reported. The different dispersions of the various bands reflect the different extent of overlap of the constituting fragment orbitals and the delocalization of the corresponding crystal orbitals; flat bands indicate localized electrons, steep bands strongly delocalized electrons. The projections of the d metal and carbon p_x and p_y orbitals (the z axis is assumed parallel to the axis of the polymers) of the density of states (DOS) for 6, 8 and 12, reported in Fig. 3, clarify the nature of these bands.

First of all we see that the band structure for polymer 12 is

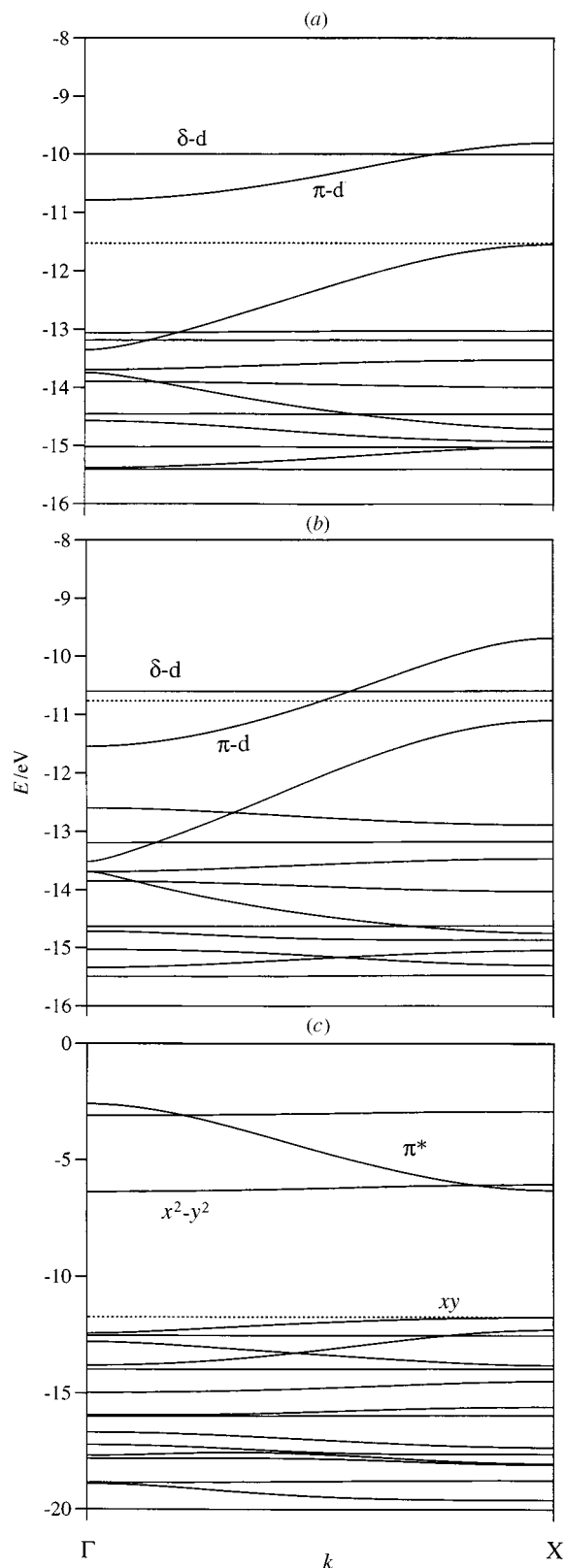


Fig. 2 Band structures of metal polymers: (a) 6, ($-Cl_4V-C_2$)_x⁻, (b) 8, ($-Cl_4Mn-C_2$)_x⁻ and (c) 12, [$-(H_3P)_4Fe-C_2$]_x. The horizontal dashed line indicates the Fermi energy

quite similar to that discussed in ref. 7 for the analogue rigid-rod ($L_nM-C\equiv CRC\equiv C$)_x polymers with Group 8–10 metals and carbonyl or phosphine ligands; the highest occupied crystal orbitals of the valence band are of mainly d_{π} character, while the lowest unoccupied crystal orbitals in the conduction band are essentially made up by the π^* orbitals of the C_2 moiety, see Figs. 2(c) and 3(c). A large band gap, 4.8 eV, is observed due to the low conjugation of the C_2 linker.

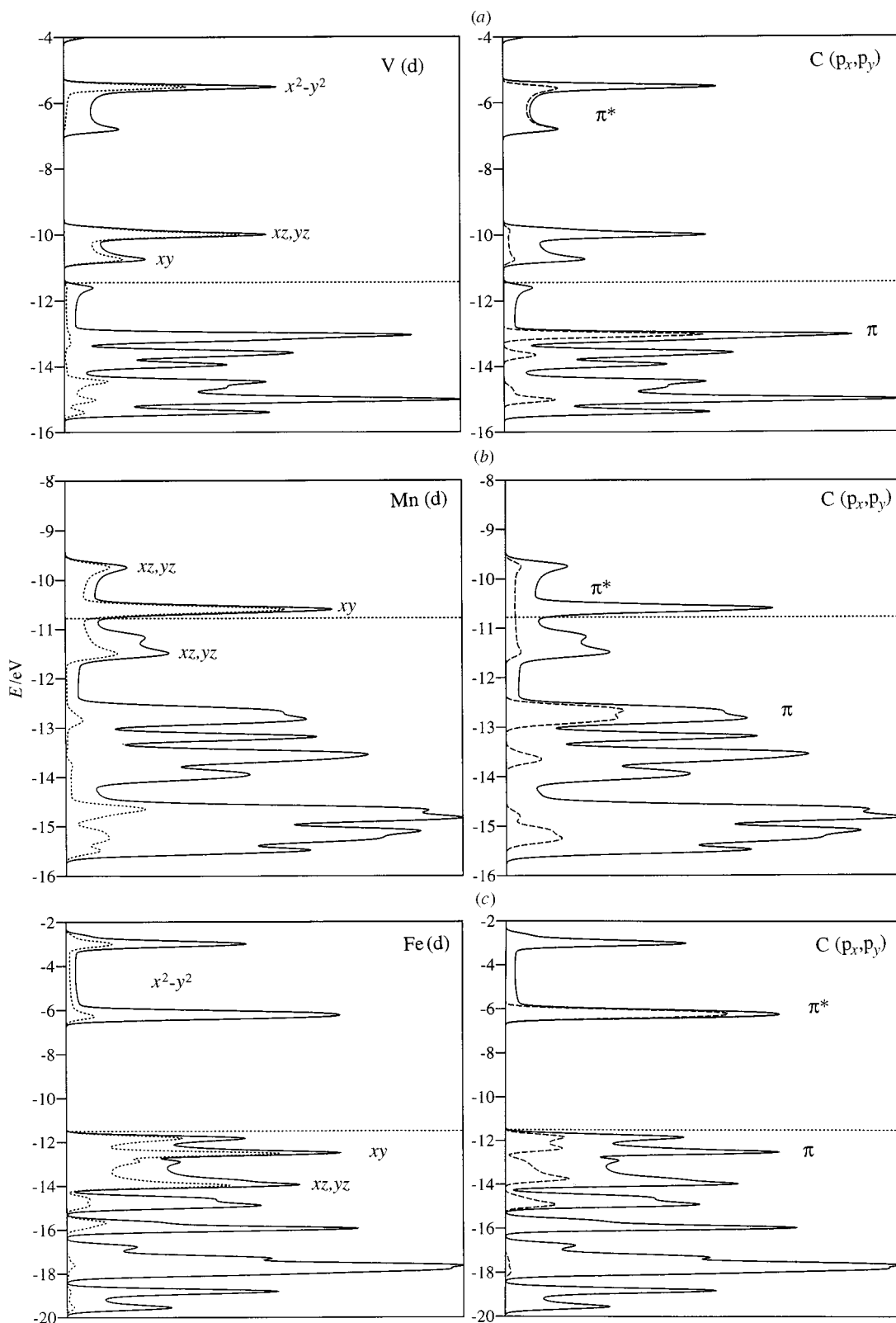


Fig. 3 Density of states (solid lines) with the projection of the metal d orbitals (dashed lines; on the left) and carbon p_x and p_y orbitals (dash-dotted lines; on the right) for metal polymers: (a) **6**, (b) **8** and (c) **12**. The horizontal dashed line indicates the Fermi energy

A completely different situation is found for polymer **6** where the highest occupied crystal orbitals have a high contribution from the occupied σ and π orbitals of the C_2 moiety (strongly mixed with ligands orbitals of comparable energy) while the two lowest unoccupied crystal orbitals are essentially metal d orbitals, see Figs. 2(a) and 3(a). The acetylenic nature of **6**, expected by analogy with the dinuclear analogues, is confirmed by the crystal orbital overlap population (COOP) curves for C–C and V–C π bonding reported in Fig. 4. Fig. 4(a) (on the

left) shows that the C–C π bonding levels are fully populated below the Fermi energy while the C–C π^* antibonding levels are essentially not populated. At the same time, however, Fig. 4(a) (on the right) shows a slight population of the V–C π bonding levels below the Fermi energy which indicates a partial π contribution to the V–C bond. In spite of the same polyynic structure, **6** shows a band gap (0.7 eV) much smaller than that calculated for **12** (4.8 eV). This is essentially due to the much lower energy of the LUCO in **6** (mainly d_{π} orbitals of

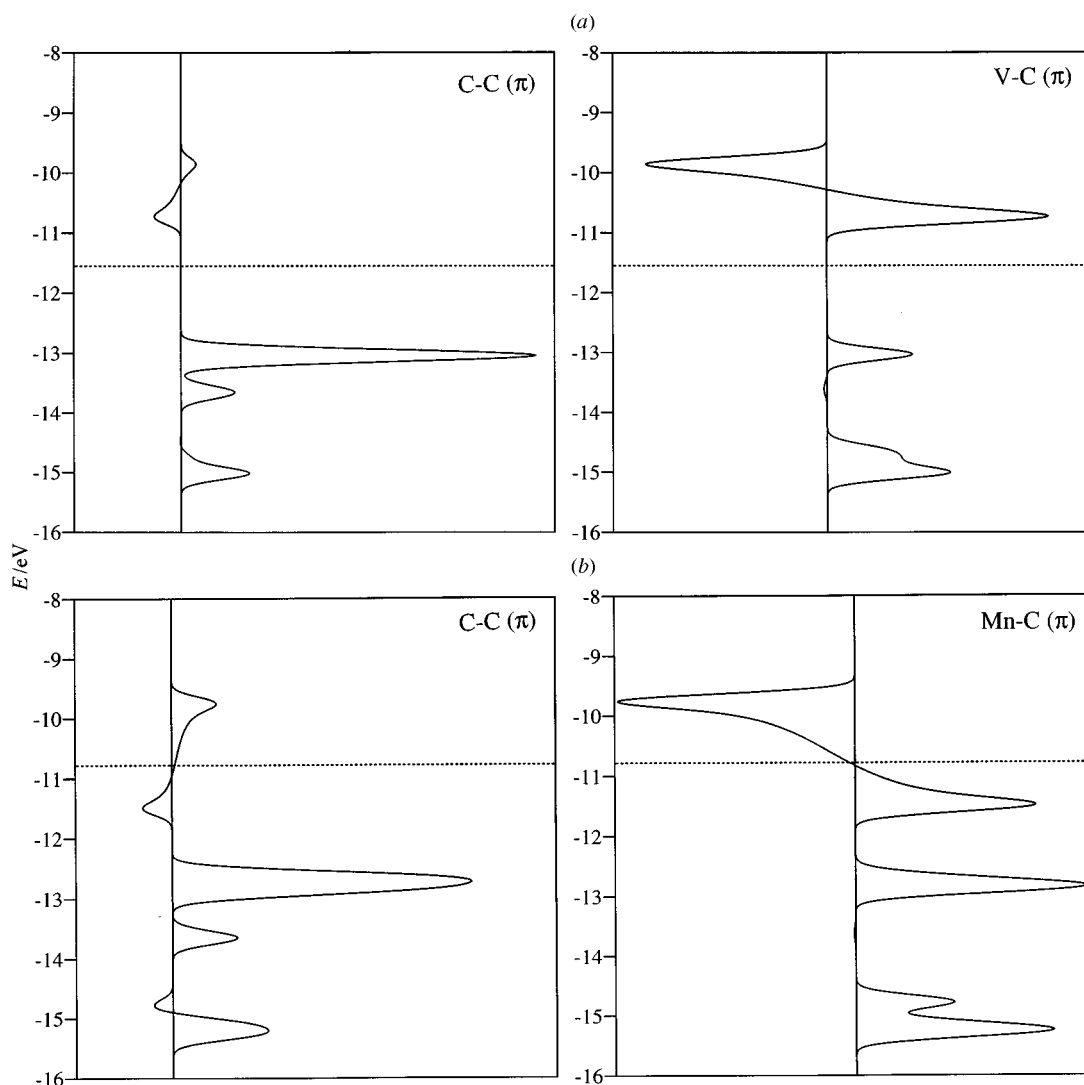


Fig. 4 The COOP curves for C-C π (on the left) and M-C π (on the right) bonding of metal polymers: (a) **6** and (b) **8**

vanadium) than in **12** (mainly π^* orbitals of the C_2 unit). Moreover, at variance with **12**, **6** is an indirect semiconductor, *i.e.* the maximum of the HOCO and the minimum of the LUCO fall at different points of the k space. In more detail, the band structure of **6** reported in Fig. 2(a) shows a set of two low-lying empty bands clearly isolated from the next higher bands (about 3 eV). The doubly degenerate LUCO (hereafter called π -d) is made up by the vanadium d_{xz} and d_{yz} orbitals substantially mixed with the π^* orbital of C_2 as evidenced by the significant slope and is crossed in its upper edge by a flat band of vanadium d_{xy} (hereafter called δ -d).

A partial filling of the two low-lying empty bands of polymer **6** is expected for metal electron counts higher than d^2 . This is confirmed by the band structures of **8** reported in Fig. 2(b) and the corresponding density of states (DOS) curve in Fig. 3(b). A cumulenic structure is expected for the hypothetical polymer **8** by analogy with the dinuclear analogues. This is substantiated by the COOP curves for C-C and Mn-C π bonding in Fig. 4(b) which shows significant population of the C-C π^* antibonding and Mn-C π bonding levels below the Fermi energy. For this d^4 electron count the π -d band is half filled and **8** is therefore susceptible to a Peierls distortion which opens a band gap at the Fermi level. For this simple linear system we expect a pairing distortion toward an alternate metallapolyne structure, like $\cdots-M\equiv C-C\equiv M-C\equiv C-M\equiv C-\cdots$, **13**. The band structure of such a paired system is compared in Fig. 5 with that of the undistorted polymer **8**, prepared for dimerization by doubling the unit cell, and shows a band gap of *ca.* 1.0 eV at the Fermi

level. The square planar $MnCl_4^-$ d^4 fragment can be considered isolobal with a carbon atom¹⁵ so that it is interesting to compare the behaviour of **8** with that of pure carbon polymer $(C)_x$. Such a species is known as karbin¹⁶ and is thought to exist in two different geometries corresponding to a cumulene, **14**, and a polyynes, **15**, structure: $\cdots=C=C=C=C=C=\cdots$, **14**; $\cdots-C\equiv C-C\equiv C-C\equiv C-\cdots$, **15**. The band structure of the cumulene polymer with equidistant carbon atoms (C-C 1.30 Å) is shown in Fig. 6(a) where the bands are labelled as σ and π . The doubly degenerate π band is half-filled and is therefore subjected to a Peierls distortion which leads to alternating C-C bond lengths along the chain (*i.e.* to the polyynic structure **15**) and a concomitant opening of a band gap of 2.1 eV at the Fermi level. This is illustrated by the band structure in Fig. 6(b) (calculated for C-C 1.21 and 1.39 Å) which shows also the familiar 'folding back' due to the doubling of the unit cell. Such a pairing distortion leads to an average energy decrease of *ca.* 0.35 eV per carbon as compared to the symmetric structure. It is interesting to compare this energy decrease, which reflects the driving force to pairing, with that calculated for the metallacumulene polymers **8**. Upon pairing of **8** to **13** we observe a decrease in the average energy of 0.59 eV per L_nMCC unit, *i.e.* of 0.19 eV per atomic unit (M or C) along the chain, which is much lower than the energy decrease for pairing of **14** to **15**. Such a reduced tendency to pairing of **8** as compared to that of **14** is also shown by the smaller band gap opened at the Fermi level (1.0 vs. 2.1 eV).

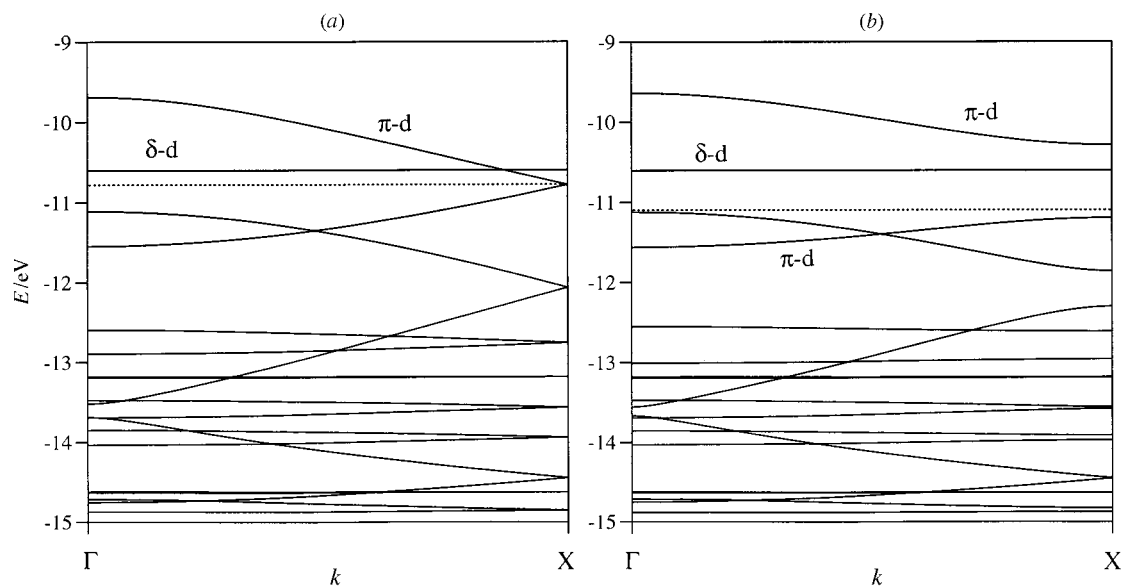


Fig. 5 Band structures of the symmetric (a) and paired (b) metal polymer **8**

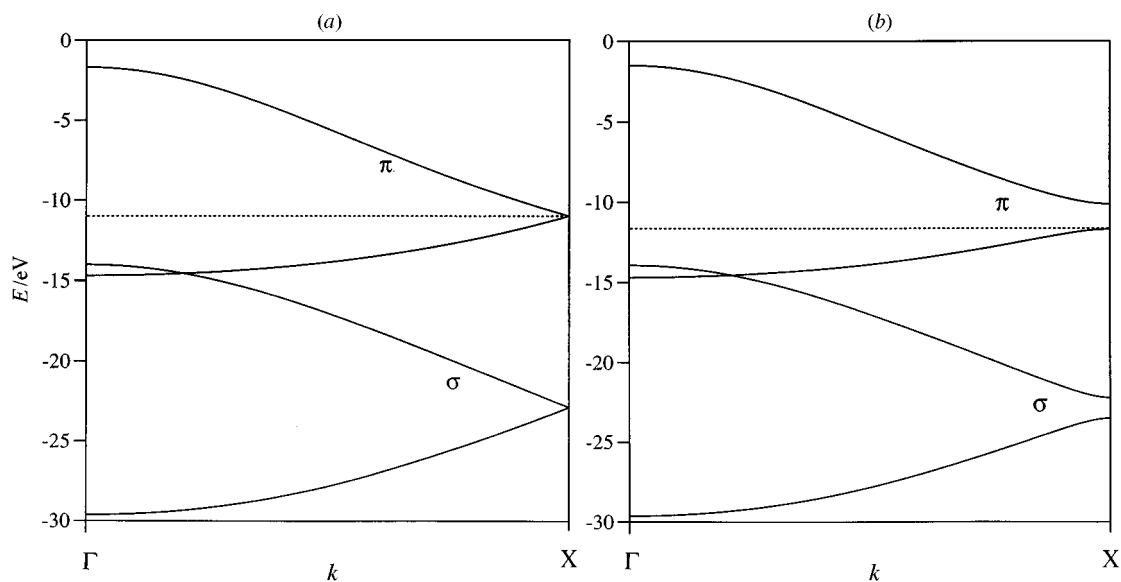


Fig. 6 Band structures of the undistorted **14** (a) and distorted **15** (b) linear carbon chain (C)_x

An even lower tendency to a Peierls distortion is expected for the hypothetical polymers **7** and **9** with d^3 and d^5 electron counts. Indeed, in these systems the π -d band is $\frac{1}{4}$ and $\frac{3}{4}$ filled, respectively. Therefore, although the simplest possible VB structures $\cdots =M-C=C-M=C=C-M-\cdots$, **16**, and $\cdots =M\equiv C-C\equiv M=C=C-M\equiv\cdots$, **17**, already involve a chain pairing, only a tetramerization is expected to open a band gap at the Fermi level. As the driving force for the distortion drops off with the size of the distorted unit cell,^{17,18} we expect a lower tendency to Peierls distortion for **7** and **9** as compared to **8**.

In polymer **10**, with a d^6 electron count, a complete filling of the π -d band cannot be reached due to its crossing with the second low-lying δ -d band. Indeed, as a consequence of the d-orbital stabilization upon shifting to the right of the transition series, the δ -d band lies slightly below the π -d band and is therefore completely filled, thus leaving the π -d band half-filled which is the same situation found for **8** and suggesting an essentially cumulenic structure in which every metal has a doubly occupied d orbital of δ symmetry: $\cdots =M=C=C=M=C=C=M=C=C-\cdots$. We therefore expect for **10** a behaviour analogous to that of **8**, with a possible Peierls distortion leading to a paired structure like **13**. In this case, however, the lower energy of the d_π orbitals leads to a reduced mixing with the high energy π^*

orbitals of C_2 as compared to **8**, and therefore to a narrower π -d band.

A complete filling of the δ -d and π -d bands is expected for a d^8 electron count as confirmed by the band structure of polymer **12**, with a $Fe(PH_3)_4$ metal fragment, but does not lead to the expected metallapolyene $\cdots -M\equiv C-C\equiv M=C-C\equiv M\equiv\cdots$ structure because of the energy mismatch between the metal d_π orbitals and the π^* orbitals of C_2 . This is due to the low energy of the d_π orbitals of the $Fe(PH_3)_4$ metal fragment (further stabilized by the π -acceptor phosphine ligands) which mix with the bonding π orbitals of C_2 leading to a low-lying, almost flat, band.

Some care should be taken about the above results predicting conducting properties for some of the considered polymers. Indeed the extended-Hückel method does not give a proper treatment of electron repulsion in high-valent metal complexes and could overestimate the $M-CC \pi^*$ interaction favouring a full delocalization of the d electrons over localized paramagnetism. However, it has been shown previously both experimentally⁸ and theoretically⁹ that $M-CC \pi^*$ interactions in these systems are sufficiently high to lead to delocalized cumulenic structures, $M=C=C=M$, in several molecular C_2 -bridged complexes, thus supporting our predictions.

Table 1 Summary of band structure for metal polymers **6–10**, **12** and **22–25**: energies of the d_π orbitals for the corresponding metal fragment, $\varepsilon(d_\pi)$; bandwidths of the π -d band, Fermi energies, E_f , and energy gaps, Δ (all in eV). For **25** the two values of $\varepsilon(d_\pi)$ and band width refer to the non-degenerate d_{xz} and d_{yz} orbitals and the corresponding π -d bands

ML_n	$\varepsilon(d_\pi)$	Band width (π -d)	E_f	Δ
6	-10.1	1.0	-11.5	0.7
7	-10.5	0.9	-10.9	—
8	-10.9	1.8	-10.8	—
9	-11.4	1.2	-11.5	—
10	-11.4	1.2	-11.9	—
12	-12.3	—	-11.8	4.8
22	-10.5	2.0	-10.6	—
23	-11.8	1.6	-11.2	—
24	-11.3	1.7	-11.0	—
25	-11.0, -10.5	1.8, 1.9	-10.7	—

Conjugation as a function of the metal fragment

In the hypothetical polymers considered up to now the MCl_4^- metal fragments ($M = V, Cr, Mn$ or Fe) constitute a chemically plausible building block through a wide range of the transition series. We will extend our study to $(L_nM-CC^-)_x$ polymers based on different metal fragments, limiting our attention to the most interesting d^4 electron count. We will consider the following ML_n , d^4 , fragments which differ from $MnCl_4^-$ **3** in the metal, ligands and co-ordination geometry, $CrCl_4^{2-}$ **18**, $Mn(OH)_4^-$ **19**, $MnCl_3$ **20**, $Cr(acacen)$ **21** [$H_2acacen = 4,4'$ -ethylenedinitrilobis-(pentan-2-one)], and the corresponding polymers, $(-Cl_4Cr-C_2^-)_x$ **22**, $[-(HO)_4Mn-C_2^-]_x$ **23**, $(Cl_3Mn-C_2^-)_x$ **24** and $[-(acacen)Cr-C_2^-]_x$ **25**. The same $M-C$ and $C-C$ distances as in **8** were employed in order to separate the effect of the change in metal fragment.

The main parameters characterizing the band structures of these polymers are compared in Table 1 with those for **6–10** and **12**. As expected, the average energy of the π -d band (which for these d^4 systems coincides with the Fermi energy) is directly related to the energy of the d_π orbitals of the corresponding metal fragments. At the same time, the π -d bandwidth increases on increasing the d_π energies, reflecting the greater mixing between the d_π orbitals and the π^* orbitals of C_2 . Therefore, the higher the d_π orbitals the more disperse is the π -d band and better is the conjugation along the chain. On the basis of simple considerations, we expect the energies of the d_π orbitals in a ML_n fragment to increase (i) on moving from the right to the left of the transition series, (ii) using stronger π -donor ligands,

and (iii) on going from the first to the second and third transition series. The first two effects are substantiated by the first column of Table 1.

Particularly interesting is the case of polymer **25** based on the $Cr(acacen)$ fragment. Indeed, in such a fragment the π -donating nature of the Schiff-base ligand leads to high d_π orbitals which therefore mix appreciably with the π^* orbital of C_2 . Moreover, in **25** there are two flat low-lying empty bands consisting mainly of the π^* system of the Schiff-base ligand, with the lowest one only 1.1 eV above the Fermi level. The more important difference concerning the metal properties of the polymer is, however, the doubling of the π -d band. This is due to the lower symmetry of the metal fragment (C_{2v} rather than D_{4h} or D_{3h} as for all the other fragments) which leads to a splitting of the two components (d_{xz} and d_{yz}) of the π -d band by about 0.5 eV. The main consequence of this doubling is that the band gap opened at the Fermi level by the pairing distortion to the alternate metallapolyene structure **13** is reduced by about the splitting energy so that the system is expected to be less susceptible to such a Peierls distortion. This effect is similar to the well known stabilization against a Peierls distortion of a one-dimensional system with a partially occupied band due to interchain interaction which is also attributed to the doubling of the partially occupied band.¹⁸ Accordingly, upon pairing of **25**, we observed a decrease in the average energy of 0.32 eV per L_nMCC unit, almost half that for **8**.

Longer carbon chains as linker

Let us now extend our study to polymers containing longer bridging units C_m . In general terms, a lengthening of the bridging C_2 carbon chain leads to a higher π and a lower π^* systems and is therefore expected to improve the conjugation along the organometallic polymer. A quite different situation is, however, expected for bridging chains with an odd or an even number of carbon atoms. Such a difference is already observed in the simple HC_nH series, much more stable for even n ,¹⁹ and arises from the different nature of the ground state for compounds with an even or an odd number of carbon atoms, a stable closed-shell singlet in the former case and a reactive open-shell triplet in the latter case.²⁰

Fig. 7 shows the band structures of the polymers $(-Cl_4V-C_3^-)_x$ **26** and $(-Cl_4V-C_4^-)_x$ **27** with a d^2 electron count and C_3 and C_4 bridging ligands, respectively. Polymer **27** shows a band structure analogous to that of **6** with a doubly occupied HOCO of mainly C_4 character and the empty π -d band of mainly metal d_π character as LUCO. Note that the increase in energy of the

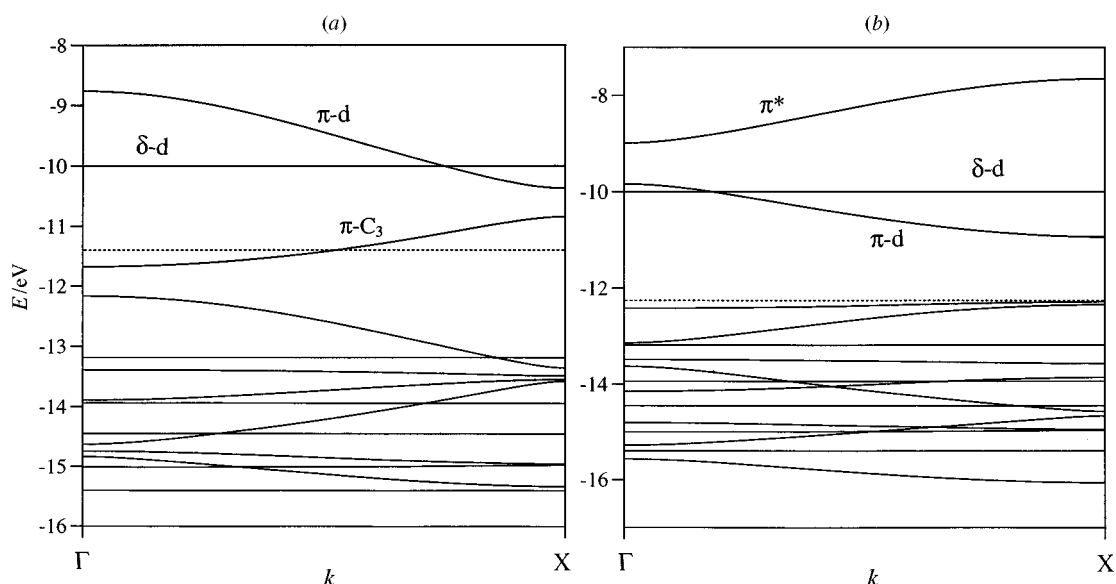
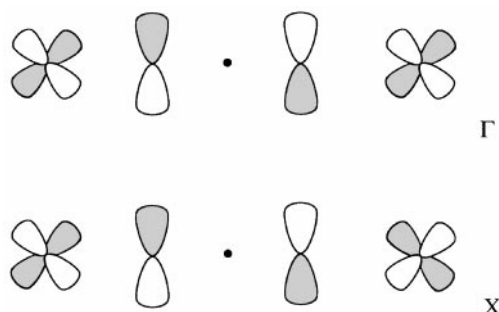


Fig. 7 Band structures of metal polymers: (a) **26**, $(-Cl_4V-C_3^-)_x$, (b) **27**, $(-Cl_4V-C_4^-)_x$



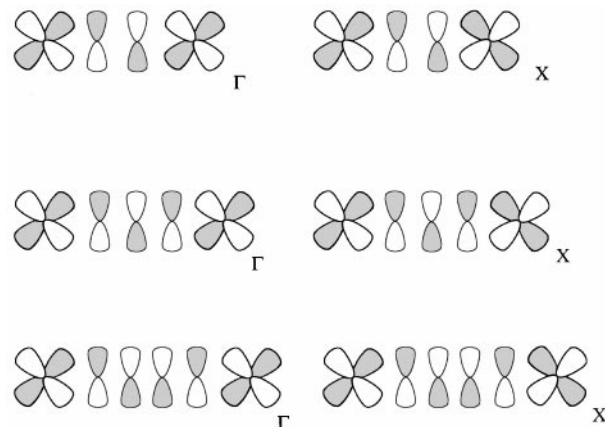
Scheme 1

occupied π system of the carbon chain on passing from C_2 to C_4 leads to a higher energy for the corresponding band and an increase of its metal character, while the parallel lowering of the unoccupied π^* system leads to a lower energy of the LUCO and an increase of its π^* character. However, the stabilization of the σ band leads to a slight increase of the band gap (from 0.7 to 1.2 eV) in spite of a higher conjugation along the chain.

A different band structure is observed for polymer **26** which shows a partially occupied band of strongly mixed C_3 and metal d_π character which almost reaches, at the zone edge, the empty π -d band. This doubly degenerate band is mainly constituted by the non-bonding π orbital of the C_3 unit and the corresponding crystal orbitals at the zone centre and zone edge are shown in Scheme 1. For a d^2 electron count, this band (hereafter called π - C_3) is half-filled and would lead to a metallic behaviour. The bonding in this polymer can be seen in a different way based on the experimental²¹ and theoretical²⁰ evidence that the C_3 molecule is relatively stable with a $^1\Sigma_g^+$ ground state corresponding to a $:C=C=C:$ configuration. This supports an interpretation of the σ V-C bond as formed by the donation of the terminal lone pair of the C_3 unit to an empty vanadium d orbital which leaves a formally vanadium(III), d^2 , metal centre and suggests for **26** a cumulenic character. From this point of view, the behaviour of **26** is similar to that of **8**. An analogous cumulenic structure can be expected for every $(-Cl_4V-C_{2k+1})_x^-$ polymer with a bridging chain made up by an odd number of carbon atoms, still based on the general evidence^{20,21} that all the C_{2k+1} molecules are relatively stable with a $^1\Sigma_g^+$ ground state corresponding to a $:C(=C=)_{2k+1}C:$ configuration. Owing to the presence of a half-filled band, **26** is susceptible to a Peierls distortion with the opening of a band gap at the Fermi level. We expect a pairing distortion leading to an alternate partial metallapolyne character. A lower tendency to pairing is expected for a d^3 electron count which would lead to a $\frac{3}{4}$ -filled π - C_3 band, stabilization of which requires a tetramerization of the unit cell.

For a d^4 electron count, like in $(-Cl_4Mn-C_3)_x^-$, the π - C_3 band is filled and would lead to a semiconductor behaviour. Moreover, the M-C π -bonding and C-M π -antibonding nature of the higher levels of the π - C_3 band close to the zone edge (see Scheme 1) would suggest a partial alternate metallapolyne character, *i.e.* $\cdots-M\equiv C-C\equiv C-M\equiv C-C\equiv C-M\equiv\cdots$. Higher electron counts would lead to a partial filling of the π -d band and the same considerations discussed for the corresponding polymers with a C_2 linker apply. Notice that the dispersion relations of the π -d band in polymers **26** and **27** are different from that observed for **6** [compare Figs. 2(a) and 7]. This difference is due to the different symmetries of the lowest unoccupied π orbitals of C_3 and C_4 , symmetric (S), and C_2 , antisymmetric (A), with respect to the symmetry plane bisecting the carbon chain which lead to different bonding-antibonding π interactions between the metal and the last carbon atom of the unit cell, see the corresponding crystal orbitals at the zone centre and zone edge in Scheme 2.

The sign of the dispersion relations for the main frontier bands of π symmetry of a generic $(-Cl_4M-C_m)_x^-$ polymer



Scheme 2

LUMO	A—	A—	S—	S—
HOMO	S—↑—	S—↑↓—	A—↑—	A—↑↓—
$m \bmod 4$	1	2	3	0

Scheme 3

depends only on the number $m \bmod 4$ (where the arithmetic operation $\bmod 4$ stands for subtraction from m of the maximum multiple of 4) and is foreseen from Scheme 3²² which shows the symmetries (A for $m \bmod 4 = 1$ or 2, and S for $m \bmod 4 = 0$ or 3) of the lowest unoccupied π orbitals of C_m . From this, extending the arguments employed in Scheme 2 it follows that for $(-L_4M-C_m)_x$ polymers with $m \bmod 4 = 3$ or 0 (like **26** or **27**) the energy of the π -d band increases on going from Γ to X while the opposite trend is observed if $m \bmod 4 = 1$ or 2 (like **6**). This may have important consequences on the physical behaviour of these compounds, note for instance that the $(-L_4V-C_m)_x$ polymers will be semiconductors with an indirect or direct gap, respectively, depending whether $m \bmod 4 = 2$ (like **6**) or 0 (like **27**).

Conclusion

We have analysed $(-L_nM-C_m)_x$ hypothetical polymers, $m = 2-4$, analogues of a series of experimentally known rigid-rod organometallic polymers. The hypothesized polymers are based on early transition-metal fragments with π -donor ligands at variance with the known analogues which are based on late transition-metal fragments with π -acceptor ligands. The electronic structures of several possible polymers with different electron counts, obtained by varying the metal and the ligands in the ML_n fragment, have been characterized using extended-Hückel tight-binding calculations.

The electronic properties of these one-dimensional systems depend on the electron count of the ML_n metal fragment and the length of the bridging C_m chain. For some of these hypothetical systems our calculations indicate completely filled bands with band gaps around 1 eV, at variance with the known polymers which show experimental band gaps of around 3 eV. Some of the considered hypothetical systems present partially filled bands and are therefore expected to undergo Peierls distortions leading, however, to low-band-gap semiconducting behaviour. A few compounds show completely filled M-C and C-C bonding bands and mainly unfilled antibonding bands and are expected to be quite stable, thus resulting in promising synthetic targets.

The analysis on the $M-C_m-M-$ polymers emphasized a crucial role of the metallic fragment and in particular of the ancillary ligand, promising properties being foreseen for a tetradentate Schiff base supporting a d^3 or d^4 early transition metal ion. Such polymers are expected to be little sensitive to Peierls distortions and could show conducting properties.

Table A1 Atomic parameters used in the extended-Hückel calculations

Atom	Orbital	H_{ii}/eV	ζ_1	C_1	ζ_2	C_2
H	1s	-13.60	1.30			
C	2s	-21.40	1.625			
	2p	-11.40	1.625			
N	2s	-26.00	1.950			
	2p	-13.40	1.950			
O	2s	-32.30	2.200			
	2p	-14.80	1.975			
V	4s	-8.81	1.300			
	4p	-5.52	1.300			
	3d	-11.00	0.4755	4.750	0.7052	1.700
Cr	4s	-8.66	1.700			
	4p	-5.24	1.700			
Mn	3d	-11.22	0.5058	4.95	0.6747	1.800
	4s	-9.75	0.970			
	4p	-5.89	0.970			
Fe	3d	-11.67	0.514	5.150	0.693	1.700
	4s	-9.10	1.900			
	4p	-5.32	1.900			
	3d	-12.60	5.350	0.505	2.000	0.6260

Table A2 Main geometrical parameters (Å) employed in the extended-Hückel calculations

Polymer	M-C	C-M	C-C	M-L
6	2.05	2.05	1.21	2.42
7	2.00	2.00	1.21	2.42
8	1.90	1.90	1.29	2.41
8 (paired)	2.00, 1.80	2.00, 1.80	1.21, 1.38	2.41
9	1.80	1.80	1.25	2.40
10	1.85	1.85	1.29	2.40
12	1.92	1.92	1.21	2.41
26	2.00	2.00	1.29, 1.29	2.40
27	2.00	2.00	1.21, 1.38	2.40

The experimental entry is particularly encouraged by the wide experience we acquired in the use of macrocyclic ligands in the organometallic chemistry of early transition metals. The variety of macrocyclic ligands employed, from Schiff base²³ to dibenzotetramethyltetraazaannulene²⁴ to porphyrinogen²⁵ allowed the change of some crucial parameters like p donation and p acceptance, the symmetry and geometrical constants.

Appendix

All the extended-Hückel calculations presented in this work were performed using the YAEHMOP package.²⁶ The parameters used in the calculations are listed in Table A1. A set of 80 K points in the Brillouin zone was used to average property calculations. The geometrical parameters employed in the calculations were taken, whenever available, from the experimental data for $C_{sp}-C_{sp}$ and $M-C_{sp}$ single, double and triple bonds and are listed in Table A2. The C-C bond distances in polymers **26** and **27** have been assigned by analogy with the HC_3H (cumulene-like) and HC_4H (butadiyne-like) molecules.²⁰

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References

- 1 K. Sonogashira, S. Kataoka, S. Takahashi and N. Hagihara, *J. Organomet. Chem.*, 1978, **160**, 319; N. Hagihara, S. Sonogashira and S. Takahashi, *Adv. Polym. Sci.*, 1980, **41**, 149; S. Takahashi, H. Monmoto, E. Murato, K. Kataoka, K. Sonogashira and

- N. Hagihara, *J. Polym. Sci., Polym. Chem. Ed.*, 1982, **20**, 565 and refs. therein; T. Kaharu, S. Matsubara and S. Takahashi, *J. Mater. Chem.*, 1991, **1**, 145.
- 2 M. S. Kahn, S. J. Davies, A. K. Kakkar, D. Schwartz, B. Ling, B. F. G. Johnson and J. Lewis, *J. Organomet. Chem.*, 1992, **424**, 87; M. S. Kahn, D. J. Schwartz, N. A. Paska, A. K. Kakkar, B. Lin, P. R. Raithby and J. Lewis, *Z. Anorg. Allg. Chem.*, 1992, **616**, 121; S. J. Davies, B. F. G. Johnson, M. S. Kahn and J. Lewis, *J. Chem. Soc., Chem. Commun.*, 1991, 187; M. S. Kahn, A. K. Kakkar, S. L. Ingham, P. R. Raithby, J. Lewis, B. Spencer, F. Wittmann and R. H. Friend, *J. Organomet. Chem.*, 1994, **472**, 247.
- 3 (a) K. A. Bunten and A. K. Kakkar, *J. Mater. Chem.*, 1995, **5**, 2041; (b) R. D. Markwell, I. S. Butler, A. K. Kakkar, M. S. Kahn, Z. H. Al-Zakwani and J. Lewis, *Organometallics*, 1996, **15**, 2331; (c) M. S. Kahn, A. K. Kakkar, N. J. Long, J. Lewis, P. R. Raithby, P. Nguyen, T. B. Marder, F. Wittmann and R. H. Friend, *J. Mater. Chem.*, 1994, **4**, 1227.
- 4 M. H. Chisholm, *Angew. Chem., Int. Ed. Engl.*, 1991, **30**, 673; H. Nishihara, in *Handbook of Organic Conductive Molecules and Polymers*, ed. H. S. Nalwa, Wiley, Chichester, 1997, vol. 2, p. 799; M. C. Böhm, *One-Dimensional Organometallic Materials*, Springer, Berlin, 1987.
- 5 J. L. Bredas and R. R. Chance (Editors), *Conjugate Polymers Materials: Opportunities in Electronic, Optoelectronic and Molecular Electronics*, NATO ASI Series, Kluwer, Dordrecht, 1990, vol. 182; P. N. Prasad and D. J. Williams, *Introduction to Non Linear Optical Effects in Molecules and Polymers*, Wiley-Interscience, New York, 1991.
- 6 A. E. Dray, F. Wittmann, R. H. Friend, A. M. Donald, M. S. Khan, J. Lewis and B. F. G. Johnson, *Synth. Met.*, 1991, **41**, 871; J. Lewis, M. S. Kahn, A. K. Kakkar, B. F. G. Johnson, T. B. Marder, H. B. Fyfe, F. Wittmann, R. H. Friend and A. E. Dray, *J. Organomet. Chem.*, 1992, **425**, 165.
- 7 G. Frapper and M. Kertesz, *Inorg. Chem.*, 1993, **32**, 732.
- 8 (a) F. Diederich and Y. Rubin, *Angew. Chem., Int. Ed. Engl.*, 1992, **31**, 1101 and refs. therein; (b) H. Lang, *Angew. Chem., Int. Ed. Engl.*, 1994, **33**, 547 and refs. therein; (c) W. Beck, B. Niemer and M. Wieser, *Angew. Chem., Int. Ed. Engl.*, 1993, **32**, 923; (d) D. R. Neithamer, R. E. LaPointe, R. A. Wheeler, D. S. Richeson, G. D. Van Duyne and P. T. Wolzkanski, *J. Am. Chem. Soc.*, 1989, **111**, 9056; (e) K. G. Caulton, R. H. Cayton, M. H. Chisholm, J. C. Huffman, E. B. Lobkovsky and Z. Xue, *Organometallics*, 1991, **11**, 321; (f) F. De Angelis, E. Solari, C. Floriani, A. Chiesi-Villa and R. Rizzoli, *Angew. Chem., Int. Ed. Engl.*, 1995, **34**, 1092.
- 9 P. Belanzoni, N. Re, M. Rosi, A. Sgamellotti and C. Floriani, *Organometallics*, 1996, **15**, 4264; *J. Chem. Soc., Dalton Trans.*, 1997, 4773.
- 10 F. A. Cotton, *Advanced Inorganic Chemistry*, 5th edn, Wiley, New York, 1988; N. N. Greenwood and A. Earnshaw, *Chemistry of the Elements*, Pergamon, New York, 1984; G. J. Miller, in *The Chemistry of Transition Metal Carbides and Nitrides*, ed. S. T. Oyama, Chapman & Hall, Glasgow, 1996, p. 134.
- 11 A. F. Wells, *Structural Inorganic Chemistry*, 5th edn, Clarendon, Oxford, 1984.
- 12 J. R. Long, J.-F. Halet, J.-Y. Saillard and R. Hoffmann, *New. J. Chem.*, 1992, **16**, 839; J. R. Long, H.-J. Meyer and R. Hoffmann, *Inorg. Chem.*, 1992, **31**, 1734.
- 13 R. Hoffmann, *J. Chem. Phys.*, 1963, **39**, 1397; R. Hoffmann and W. N. Lipscomb, *J. Chem. Phys.*, 1962, **37**, 2872.
- 14 M.-H. Whangbo and R. Hoffmann, *J. Am. Chem. Soc.*, 1978, **100**, 6093; M.-H. Whangbo, R. Hoffmann and R. B. Woodward, *Proc. R. Soc. London, Ser. A*, 1979, **366**, 23.
- 15 R. Hoffmann, *Angew. Chem., Int. Ed. Engl.*, 1982, **21**, 711.
- 16 V. M. Mel'nichenko, A. M. Sladkov and Yu. N. Nikulin, *Usp. Khim.*, 1982, **51**, 736; *Russ. Chem. Rev.*, 1982, **51**, 421; R. L. Lagow, J. J. Kampana, H.-C. Wei, S. L. Battle, J. W. Genge, D. A. Laude, C. J. Harper, R. Bau, R. C. Stevens, J. F. Haw and E. Munson, *Science*, 1995, **267**, 362.
- 17 R. Hoffmann, *Solids and Surfaces: A Chemist's View of Bonding in Extended Structures*, VCH, Weinheim, 1988.
- 18 J. K. Burdett, *A Chemical Bonding in Solids*, Oxford University Press, New York, 1995.
- 19 J. R. Heath, Q. Zhang, S. C. O'Brien, R. F. Curl, H. W. Kroto and R. E. Smalley, *J. Am. Chem. Soc.*, 1987, **109**, 359.
- 20 Q. Fan and G. V. Pfeiffer, *Chem. Phys. Lett.*, 1989, **162**, 462.
- 21 W. Weltner, jun. and R. J. Van Zee, *Chem. Rev.*, 1989, **89**, 1713.
- 22 I. Gutman and N. Trinajstić, *Top. Curr. Chem.*, 1973, **42**, 1.
- 23 V. L. Goedken and J. A. Ladd, *J. Chem. Soc., Chem. Commun.*, 1981, 910; 1982, 142; S. Ciurli, C. Floriani, A. Chiesi-Villa and C. Guastini, *J. Chem. Soc., Chem. Commun.*, 1986, 1401; C. Floriani, M. Mazzanti, S. Ciurli, A. Chiesi-Villa and C. Guastini, *J. Chem. Soc., Dalton Trans.*, 1988, 1361; S. De Angelis, E. Solari,

- E. Gallo, C. Floriani, A. Chiesi-Villa and C. Rizzoli, *Inorg. Chem.*, 1992, **31**, 2520.
- 24 C. Floriani, E. Solari, F. Corazza, A. Chiesi-Villa and C. Guastini, *Angew. Chem., Int. Ed. Engl.*, 1989, **28**, 64; F. Corazza, E. Solari, C. Floriani, A. Chiesi-Villa and C. Guastini, *J. Chem. Soc., Dalton Trans.*, 1990, 1335; E. Solari, C. Floriani, A. Chiesi-Villa and C. Rizzoli, *J. Chem. Soc., Dalton Trans.*, 1992, 367.
- 25 J. Jubb, C. Floriani, A. Chiesi-Villa and C. Rizzoli, *J. Am. Chem. Soc.*, 1992, **114**, 6571; U. Piarulli, C. Floriani, A. Chiesi-Villa and C. Rizzoli, *J. Chem. Soc., Chem. Commun.*, 1994, 895; C. Floriani, *Transition Metals in Supramolecular Chemistry*, eds. L. Fabbri and A. Poggi, NATO ASI Series, Kluwer, Dordrecht, 1994, vol. 448, pp. 191–209; U. Piarulli, E. Solari, C. Floriani, A. Chiesi-Villa and C. Rizzoli, *J. Am. Chem. Soc.*, 1996, **118**, 3634; C. Floriani, *Pure Appl. Chem.*, 1996, **68**, 1 and refs. therein.
- 26 G. Landrum, YAEHMOP, Yet Another Extended Huckel Molecular Orbital Package, version 1.0, Cornell University, Ithaca, NY, 1995.

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