Bull. Chem. Soc. Jpn., 68, 1515—1521(1995)

Accounts

Organometallic π-Conjugated Systems

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(Received December 8, 1994)

Chemistry of transition metal complexes of organic conjugated systems, e.g. 1,3-diene, cyclobutadiene, and hexapentaene, is reviewed mainly based upon the author's investigation. Some recent examples of dπ–pπ conjugated systems with multiple metal–metal and metal–carbon bonds are also described.

Conjugation in organic chemistry is represented by extended pπ–pπ interactions. Typical one-dimensional conjugation is found in *trans*-polyacetylene which is well-known for its high conductivity upon doping. Cyclic conjugation is an important feature of aromatics and annulenes. Here, the unique electromagnetic properties together with their chemical reactivities are characteristics of conjugation.

The conjugation in organometallic chemistry may be defined as extended π-interactions involving metal–carbon bondings. Two distinctive categories can be found in the organometallic conjugated systems. One is metal π-complexes of organic conjugated systems. The other is conjugated π-systems containing metal–carbon multiple bonds. Unique properties of dπ–pπ interactions coupled with extended pπ–pπ interactions are thus setting highly interesting items in the study of the new conjugated systems.

The uniqueness of the organometallic π-systems containing various transition metals exists in their large variety in electronic and molecular structures. Schematic illustrations for typical two cases are shown in Fig. 1. Please note the change of orbital sign upon involvement of a dπ-orbital in the conjugation system.

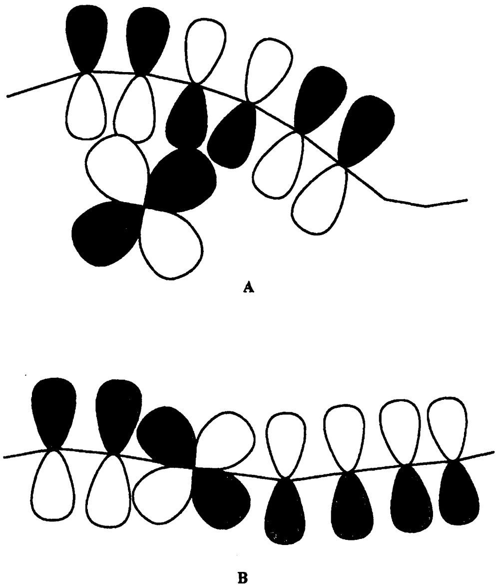


Fig. 1. Schematic illustrations of two different types of organometallic π-conjugated systems.

In this connection it is important to point out that almost all the transition metals are able to form polyene–metal complexes by suitable choice of supporting co-ligands. Later transition metal ions such as copper(I), silver(I), and platinum(II) have been well-known to form such organometallics just at ambient conditions. These electron-rich metal ions are selective for olefins or acetylenes in donor solvents such as water or alcohols under air. Since 1960, many polyene–metal complexes of iron, cobalt, and other metals have been prepared. Recent progress in organometallic chemistry provides us remarkable new methods for the synthesis of polyene complexes of early transition metals such as zirconium(II) and lanthanum(III).[1] These electron-deficient metal ions are highly reactive to air and to donor solvents and formation of polyene complexes had been thought quite impossible. However, the use of electron-rich multicenter ligands, such as cyclopentadienyls, coupled with new preparative methods has provided a novel area of polyene–metal complexes. One typical example is a *trans-trans-trans*-1,6-diphenylhexatriene complex of zirconocene.[2] Here the triene is coordinated in *s-trans* conformation to Zr which is stabilized by two cyclopentadienyl ligands. The conjugated triene system is considerably perturbed by the bonding with low-valent zirconium which is both electron-donating (π-type) and -attracting (σ-type) in varying degrees. The situation is basically different from the simple protonation or doping (with e.g. iodine) of conventional conjugated systems.

The example described above illustrates a rich area of chemistry of organometallic π-conjugated systems. In this account I will briefly summarize recent advances in this area by taking some of new relevant examples from literatures and from results of our group.

Metal Complexes of π-Conjugated Systems

The simplest π-conjugated organic system is butadiene, i.e. "1,3-diene." Its first metal complex of composition, $C_4H_6Fe(CO)_3$, was reported in 1930 by Rheilen.3) However, this did not attract much attention at that time since the nature of bonding was obscure due to lack of any similar compounds. After the discovery of ferrocene, this complex was rediscovered by Hallam and Pauson in 19584) and bonding similar to ferrocene was proposed. Remarkably high thermal stability toward dissociation of butadiene was noted and ascribed to the partial involvement of di-sigma-bonded structure as shown in Fig. 2.

Since then many 1,3-diene complexes were prepared starting from the diene or the tetraene and relevant metal complexes of mostly low-valent state. Some of the typical examples are shown in Fig. 3.

The η^4-C_8H_8 complex shown in Fig. 3 is highly fluxional even at −100 °C in solution where the metal atom moves around the conjugated systems.5)

The nature of the metal–diene bonding has been investigated by combination of physical methods e.g. X-ray analysis and NMR spectroscopy. In particular, the bond lengths of coordinating dienes and C–H and C–C coupling constants in the NMR parameters give important information about the diene–metal bonding. Although many diene complexes of late transition metals are similar in terms of metal diene bonding, so-called π^2-mode where the orbital hybridization at the diene terminal is sp^2. However, the bonding in the early transition metal is quite different. Here, strong σ-bonding is found at the diene terminals and the hybridization approaches sp^3. Then the bonding is designated as σ^2-π in accordance to the C–C bond lengths of the diene skeleton as shown in Fig. 4.

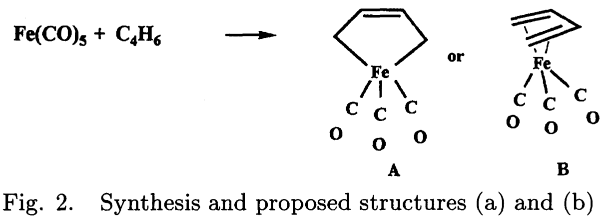


Fig. 2. Synthesis and proposed structures (a) and (b) of butadiene(tricarbonyl)iron.

The description above indicates an important aspect of basic chemistry of interaction of conjugated system to transition metal atoms. One of such features is quite strong interaction of 1,3-dienes with early transition metal atoms such as zirconium and hafnium. The interaction with later metals is always weaker. This trend is in good agreement to that observed for chemisorption of various small molecules on metal surfaces where the interaction of unsaturated organics is stronger with early transition metal.

It is important to note that the coordinating diene is always assuming the *s-cis* conformation in all the complexes described here. Actually *s-trans* conformation of diene was thought to be very unfavorable to make strong coordination. This concept prevailed for more than 20 years. However, such *s-trans* conformation was confirmed in the zirconocene–diene systems in 1980 by the pioneering work of G. Erker and ours at almost the same time.6) The *s-trans* butadiene complex was first prepared by the photochemical method of Erker from diphenylzirconocene. Later the endiylmagnesium method was used to prepare 1,4-diphenylbutadiene complex where *s-trans* coordination at the diene part is highly preferred.

The nature of diene–metal bonding here is different from the conventional ones. Detailed MO analysis indicated the bonding to be doubly π-bonded, but requires some more conjugation at the diene and more spatial extension of metal d-orbitals.6) Further research

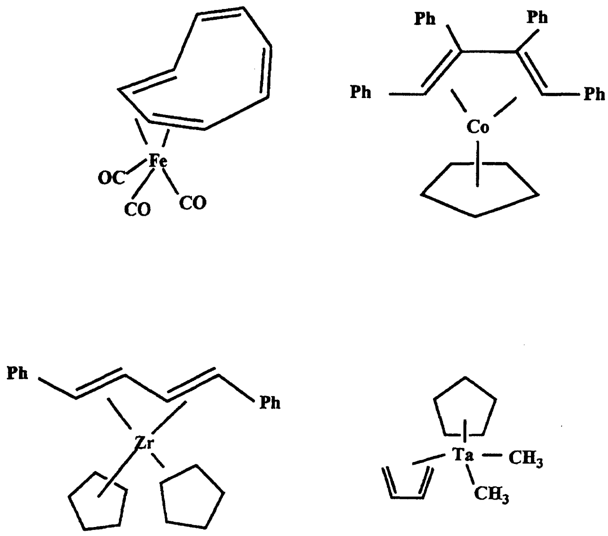


Fig. 3. Some specific examples of polyene–metal complexes.

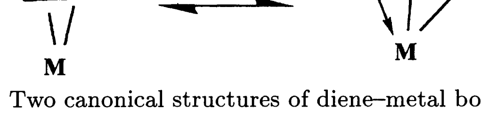
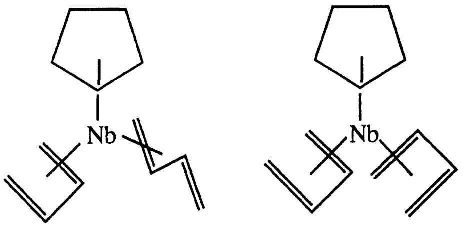


Fig. 4. Two canonical structures of diene–metal bonding.

in the synthesis of other examples indicated preference of 2nd row transition metal rather than the 3rd ones for the *s-trans* bonding.[6] For example, among the known bis(diene) complexes of niobium and tantalum, CpM(diene)$_2$, M=Nb and Ta, only in the case of Nb with butadiene we have found one of the diene ligands coordinated as *s-trans* conformation (see Fig. 5).[7a] Here, the *s-cis* diene assumes the supine geometry and therefore is more strongly bound to Nb. The (*s-trans*)(*s-cis*)-bis(butadiene) isomer is formed in equilibrium with the bis(*s-cis*) isomer, but complete separation to each pure isomer has not been accomplished at that time by us. Later the bis(*s-cis*) isomer was separated pure and the structure was confirmed by Herberich.[7c] For the (*s-trans*)(*s-cis*) isomer, all attempts by us and others have failed since the overall molecular structure is so similar and therefore repeated recrystallization has been totally unsuccessful.

These diene–niobium and –tantalum complexes are recently found to be initiators of ethylene polymerization where one of the diene ligands remains attached to the metal furnishing the required 14-electronic configuration at the metal for effective living polymerization (see Fig. 6).[7b]

The smallest cyclic π-conjugation is found in cyclobutadiene. The π-complex of which was predicted to be much more stable relative to the uncomplexed one. The first π-complex of unsubstituted cyclobutadiene was prepared with silver(I) and the tetramethyl analogue with nickel(II) by C. D. Nenitzescu and R. Criegee in 1959.[8] Soon after these pioneering works, tetraphenylcyclobutadiene complexes of iron and cobalt was prepared from cycloaddition of two molecules of diphenylacetylene (see Fig. 7) and these were found to have remarkable thermal and air stability.[9] The basis for the stability is attributed to their stable 18-electron configuration. When comparison was made with similar benzene π-complexes for the thermal stability, these cyclobutadiene complexes of Fe and Co are more stable in general. A 3-dimensional aromaticity involving the whole metal systems has thus been proposed.



(a) (b)

Fig. 5. Geometry of butadiene coordination in bis(butadiene)cyclopentadienylniobium, a) bis(*s-cis*) isomer, b) (*s-cis*)(*s-trans*) isomer.

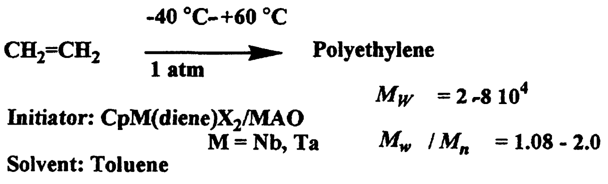
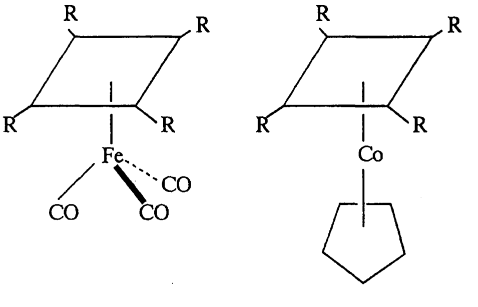


Fig. 6. Living polymerization of ethylene by initiator systems, Cp(1,3-diene)MX$_2$/methylaluminoxane, M=Nb, Ta.

Utilizing the extended π-system of coordinated tetraphenylcyclobutadiene, electrical conductivity of solid samples of the Co complex was examined after iodine doping. A value (4×10^{-6} S cm^{-1}) indicating semi-conducting region was obtained. (see Table 1). The conductivity was ascribed to the conjugation of the metal orbitals with aromatic substituents.

Cumulenes with conjugation, e.g. butatrienes and hexapentaenes, form stable complexes with two or more Fe(CO)$_3$ groups. Unsubstituted butatriene generated from 1,4-dibromo-2-butyne and zinc gave air-stable red crystals of composition, $C_4H_4[Fe(CO)_3]_2$ where two overlapping π-allyl coordinations on the Fe–Fe dinuclear structure was observed.[10] Similar coordination has been observed with the tetramethyl- and tetraphenyl derivatives. Unsubstituted hexapentaene was also found to give stable complexes upon reaction of 1,6-dibromo-2,4-hexadiyne with iron carbonyls in 1965 in 3% yield.[11] Later Iyoda et al. examined the structure in 1991 by careful separation of the product to find two isomers. One deep red isomer (isomer (a)) was found to have structure as shown in Fig. 8. Two Fe$_2$(CO)$_6$ moi-



(a) (b)

Fig. 7. Typical examples of cyclobutadiene complexes.

Table 1. Electrical Conductivity of Organometallic Conjugated Systems after Doping with Iodine[19]

Precursor complex	Conductivity[a)] /S cm^{-1}
Fe(CO)$_3$(1,4-diphenylbutadiene)	2×10^{-5}
Fe(CO)$_3$(1,6-diphenylhexatriene)	5×10^{-5}
Fe(CO)$_3$(1,8-diphenyloctatetraene)	6×10^{-5}
[Fe(CO)$_3$]$_2$(1,3,7,9-decatetraene)	5×10^{-5}
Co(C$_5$H$_5$)(tetraphenylcyclobutadiene)	4×10^{-6}
Cr(CO)$_3$(η^6-1,4-diphenylbutadiene)	5×10^{-5}

a) The extent of the doping as expressed by the molar ratio of iodine to metal, I$_2$/metal, is 0.03 to 0.09 in all of the cases.

eties are coordinated up and below to the planar zig-zag carbon chain of C_6H_4. An inversion center is found at the center of the carbon chain where the C–C bond length is relatively large, 1.454(9) Å. The other deep red isomer (isomer (b)) has a non-planar zig-zag chain with with two $Fe_2(CO)_6$ groups as shown in Fig. 8. Here a C_2 axis is found at the center of the molecule. This isomer is more unstable and changes into the isomer (a) upon heating at 100 °C.[12)]

In all the cases, high reactivity of unsubstituted cumulenes was quenched by the π-complexation and the resulting molecular structures are characterized by the formation of uniquely cumulated π-allyl systems. Extended Hückel calculations on these isomers indicated presence of positively charged iron atoms strongly bound to carbons in essentially covalent manner.[12)] Interestingly, the two innermost carbons are in 5-coordinated state. Here, some similarity may be found in future for carbons in carbon-rich iron carbides (FeC_n, not known at present).

Conjugated π-Systems Containing Metal–Carbon σ- and π-Bonds (Metallated π-Systems)

When organic conjugated systems are directly combined to the metal atom(s) by σ-bonding, novel organometallic conjugated systems result (see Fig. 1). Organometallic compounds containing dienyl ligands or metallacyclopentadiene ring(s) are numerous and does not need special mention here. Metal atoms directly bound to very long conjugated π-systems are important for their enhanced physical properties characterizable to extended conjugation. For example, a series of straight linear polymers containing diacetylene ligands has been reported by N. Hagihara, K. Sonogashira, and S. Takahashi in 1973 (Fig. 9).[13)] These polymers were prepared e.g. by oxidative polycondensation of diethynylbis(tributylphosphine)metal by the $CuI/NEt_3/O_2$ system. The use of tributylphosphine is important for solubilyzing the polymers thus formed. In the case of M = Pt, high-molecular weight polymers (M_w = ca. 80000) were obtained and found to be soluble in hexanes and have properties of liquid crystals in solution. Thus, their optical properties are unique. Recently, these polymers attracted attention as non-linear optical polymers (NLO polymers) since the conjugation through the main chain causes high response to the incident light.[14)]

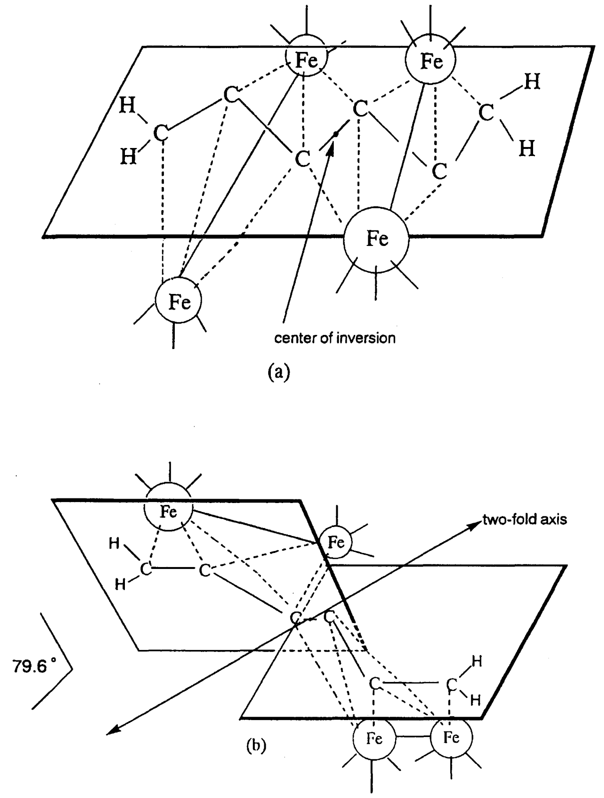
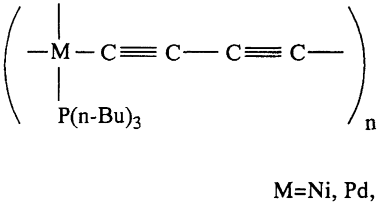


Fig. 8. Schematic structure of two isomers of the hexapentaene complex.

Metal Complexes of Larger Cyclic Conjugated Systems

Planar and non-planar complexes of cyclooctatetraene have been known since 1959.[9)] Depending on the demand of the metal, cyclooctatetraene donates 4 to 6 electrons to the metal in the late transition metal complexes and coordinates in non-planar structure. In some cases of early transition metal such as lanthanoids or actinoids, cyclooctatetraene accepts two electrons to become planar and aromatic (10π-system). Many examples are now found to contain planar C_8H_8 rings for lanthanoids complexes. Recently, a very simple direct reaction of cyclooctatetraene with lanthanum metals and appropriate ligands such as organic disulfides, RS–SR, occurs to give a series of planar cyclooctatetraene–lanthanoid complexes with thiolato ligands.[15b)]

Palladium complexes of phenalene were prepared and found to be fluxional at high temperature (Fig. 10).[15a)] Remarkable mobility of metal atom along the conjugated systems is thus found and indicates further possible extension of research into still larger cyclic conjugated systems.



$$\left(-\underset{P(n\text{-}Bu)_3}{\overset{P(n\text{-}Bu)_3}{M}}-C\equiv C-C\equiv C- \right)_n$$

M=Ni, Pd, Pt

n=~100(Pt)

Fig. 9. Repeating structure of straight linear polymers containing diacetylide–metal chains.

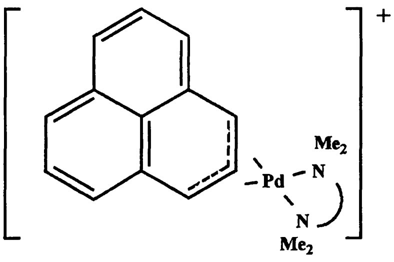


Fig. 10. Structure of phenalenyl (TMEDA)palladium cation.

Mono- and Polymetalladienes and Polymetallacumulenes

Recently, a number of compounds containing multiple metal–metal bonding have been reported and attracting attention of chemists. Organometallic compounds with this kind of metal–metal bonds are also well known.$^{16)}$ For example, octaalkyldichromium(II,II), $[R_4Cr{=}CrR_4]^{4-}$, and the related compounds have been prepared. Multiple metal–carbon bonds are found in metal–carbene or metal–alkylidene complexes. Alkylidene complexes may be regarded as metallamonoene systems and vinylalkylidene complexes as metalladiene systems. In this way polymetalladienes and polymetallapolyenes are defined. Actually many preparative attempts for preparation of these compounds have been done in recent years and some successful results are now emerging. However, I will not describe these fully at this time. I will focus on the conjugation of the metal–metal multiple bonding with carbon–carbon π-bonding as shown schematically in Fig. 11. The example (a) is the simplest example of 1,2-dimetalla-1,3-diene. Typical examples of polymetallacumulenes are also presented in (c) and (d).

Addition of alkyl, alkenyl, or aryl groups on the axial positions of the M_4M quadruple bonds has been tried in an attempt to extend the conjugation further.$^{16)}$ However, it has been quite difficult to attach any of these organometallic groups by direct reaction.$^{16)}$ The lability of a donor ligand on the axial position of M_4M has been noted and attributed to the high trans-effect of the M_4M bond.

A strategy for circumvent this situation was found recently. Double axial addition of platinum(I) and palladium(I) on the Mo4Mo bonds was successful with assistance of a novel O–N–P tridentate ligand (abbreviated as pyphos) as shown in Fig. 12.$^{17)}$

M=M-C=C **M=C-C=C**

(a) **(b)**

M=C=C=M **C=M=M=C**

(c) **(d)**

Fig. 11. Typical examples of polymetalladienes and polymetallacumulenes as shown schematically.

Straight linear conjugated dπ-systems were thus obtained by reduction at the late transition metal part, e.g. Pt or Pd, to give a straight linear tetrametal chain, M–Mo–Mo–M, M = Pt, Pd.$^{17)}$ Consideration of the bonding between Mo and Pt (or Pd) bonds indicated multiple-bonding consisting of (a) σ-type donation of the filled orbitals on Mo(II) to Pt(I) and (b) π-type back donation of the filled dπ orbital on the Pt(I) to the π* orbital of Mo(II). The structure and bonding in the linear tetrametal part of the molecule are shown schematically in Fig. 13.

Starting from this complex, an easy access to organometallic conjugated systems is possible by simple ligand exchange of the halo ligands on Pd(I) or Pt(I) with e.g. alkynyl ligands.

It is expected that a further variety of metals may be introduced in place of Mo or Pd and investigation of their physical as well as chemical properties will give novel aspects of chemistry of these conjugated systems in near future.

Recently, an polymeric example of a conjugated system containing metal–carbyne and heteroaromatic π-systems and the first example of dimetallacumulene was reported as shown in Fig. 14.$^{18)}$

Various differently π-conjugated organometallic sys-

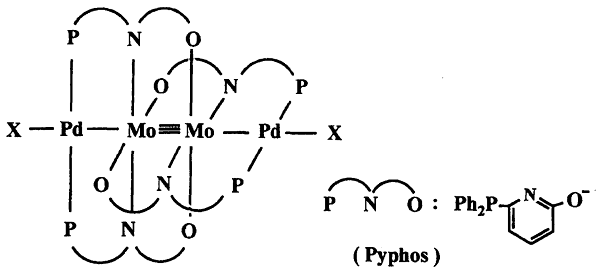


Fig. 12. Schematic picture of the double axial Pd(I)-addition product at the quadruply-bonded dimolybdenum(II) induced by chelated pyphos ligands.

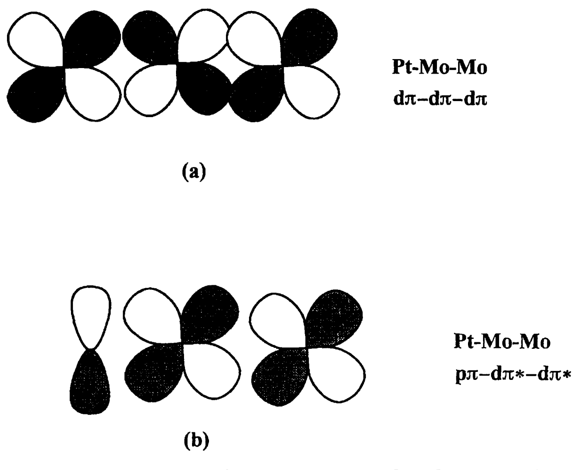


Fig. 13. Examples of schematic π-orbital interactions of the linear trimetal part, Pt–Mo–Mo.

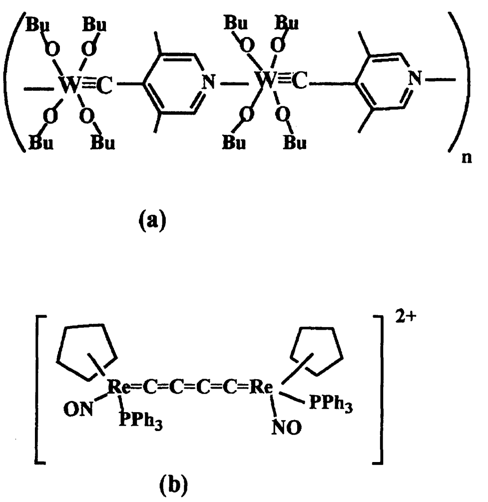


Fig. 14. Recent examples of conjugated systems containing (a) metal–carbyne complex in the main chain and (b) dimetallahexapentaene structure.

tems of the types described above are possible and will be prepared to find novel properties.

Physical Properties of Organometallic π-Conjugated Systems

Semi-conducting properties of doped solids of some of the diene and other polyene metal complexes have been investigated. Thus polycrystalline samples of α-ω-diphenylpolyene(tricarbonyl)iron of the general formula, $Ph(CH{=}CH)_nPh\ Fe(CO)_3$ were iodine-doped to give deep brown pellets of metallic luster.[19] The electric conductivity increased with the number of double bonds in the complexes: $2{\cdot}10^{-5}\ S\,cm^{-1}$ to $6{\cdot}10^{-5}\ S\,cm^{-1}$ as shown in Table 1. Solids of phenyl- or naphthyl-substituted ferrocenes are also made semi-conducting upon similar doping at 1—3% level.[19] Intermolecular charge transfer between conjugated parts of each molecules is thus considered important.

Organometallic polymers containing a diene–metal moiety at the pendant groups have been prepared.[20] Thus, cationic polymerization of vinyl monomers containing a diene(tricarbonyl)iron or -ruthenium group provided polymers with molecular weight sufficient to afford self-standing films as shown in Fig. 15.

Upon iodine-doping, these films became semi-conductive (ca. $5{\times}10^{-4}\ S\,cm^{-1}$) at room temperature. The chemical changes during the doping were investigated by Moessbauer spectra and formation of some iodine-addition products, mostly $FeI_2(CO)_2$(diene) species, in the polymer was found. The polymer thus have mixed-valency to some extent which leads to the observed conductivity.

Recently, a unique thermochromism was found for the 1,4-diphenylbutadiene complex of zirconocene where deep red color gradually turns bright red upon chilling to ca. 90 K. This indicates a thermal change of the nature of metal–diene bonding which is unprecedented.[2]

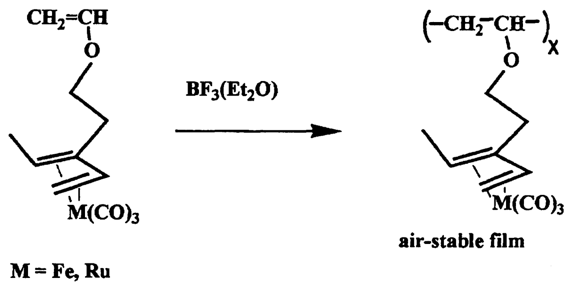


Fig. 15. Chemical structure of a semiconducting film prepared from vinyl-polymerization of an organometallic triene complex.

The field of organometallic conjugated systems is just extending the scope now as described above and will be investigated in an increasing rate to find novel and exciting aspects in future.

The author appreciates the co-operation of the persons whose names are in the references for their efforts. The latest part of the research described in this account is supported by a Grant-in-Aid for the Specially Promoted Research No. 06101004 from the Ministry of Education, Science and Culture.

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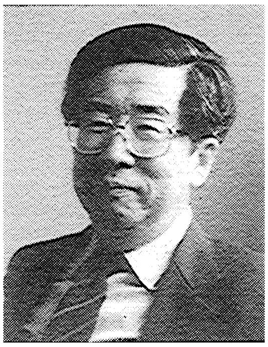

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