Reviews

Binuclear ladder-type complexes as building blocks for the synthesis of novel polynuclear systems

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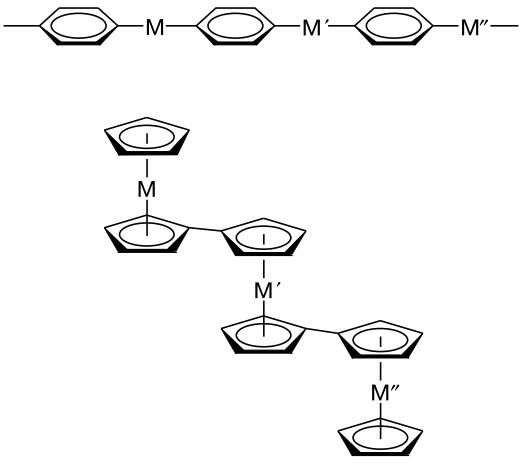
Summarized are reactivity studies of binuclear ladder complexes in the metallation reaction that has been applied to prepare novel homo- and heteropolynuclear transition metal complexes. The electron transfer through π-ligand-metal-σ,π-ligand-metal chain has been studied by IR spectroscopy and cyclic voltammetry techniques.

Key words: ladder complexes, carbonyl(cyclopentadienyl)metal complexes, reactivity, rearrangement, IR spectra, electrochemisrtry.

Over the past decades, bi- and polynuclear transition metal complexes incorporating π-conjugated bridging organic ligands have attracted considerable attention of organometallic chemists. Interest in these compounds is due to their unique physicochemical properties that make them of potential value as basic components to be used in catalytic, photochemical, and electrochemical systems. The examples of such complexes are organometallic linear chains representing a new class of conductive one-dimensional molecular wires[1] as well as bi- and trinuclear metallocenes.[2]



Two series of ladder complexes were synthesized, *i.e.*, binuclear Fe—Mn, Mo—Mn, and W—Mn complexes with bridging η^1,η^5-cyclopentadienyl ligand were obtained by cymantrene metallation followed by treatment with $Cp(CO)_nMHal$ (n = 2, M = Fe; n = 3, M = Mo, W)[3,4,5],

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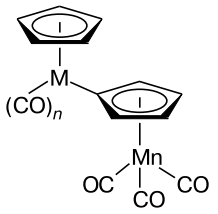
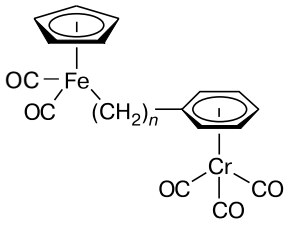
and binuclear Fe—Cr complexes with bridging η^1,η^6-phenyl ligand were obtained by refluxing $Cp((CO)_2FeR$ (R = Ph, CH_2Ph) with $Cr(CO)_6$ in 1,4-dioxane.[6]



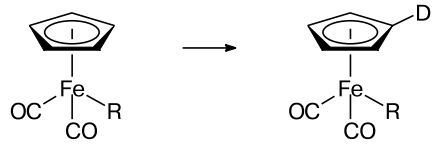
n = 2, M = Fe
n = 3, M = Mo, W



n = 0, 1

While evaluating carbonyl(cyclopentadienyl)iron complex with η^1-bound ligands, η^5-$C_5H_5(CO)_2Fe$-η^1-R (R = Alk or Ar), in metallation by *n*-butyllithium (THF, −78 °C), we have found[7] that metallation occurs selectively on η^5-cyclopentadienyl ring in 80% yield (Scheme 1).

Scheme 1

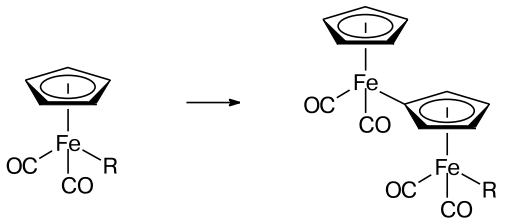


R = Ph, CH_2Ph

Reagents and conditions: *n*-BuLi, D_2O.

We exploited this property in lithiation of the complexes $Cp(CO)_2FeR$ (R = Me, CH_2Ph) followed by reacting the lithio derivative with the electrophilic reagent $Cp(CO)_2FeI$ to yield binuclear Fe—Fe complex bridged by η^1,η^5-cyclopentadienyl ligand[8] (Scheme 2).

Scheme 2



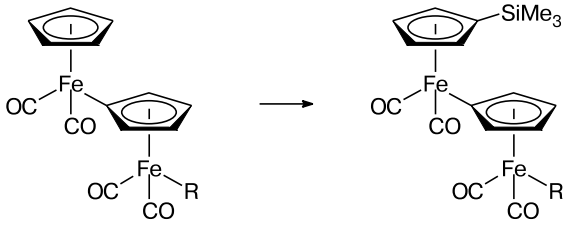
1, 2

R = CH_2Ph (**1**), Me (**2**)

Reagents, conditions, and yield: *n*-BuLi, $Cp(CO)_2FeI$, 20%.

The discovered selective metallation of η^5-cyclopentadienyl ring in these systems was found to hold also in the case ligand R is a transition metal complex itself (complexes **1** and **2**). Metallation of binuclear complexes η^5-$C_5H_5(CO)_2Fe$-η^1,η^5-$C_5H_4(CO)_2Fe$-η^1-R (**1**, **2**) also occurs exclusively onto η^5- rather than η^1,η^5-cyclopentadienyl ring[9] (Scheme 3).

Scheme 3

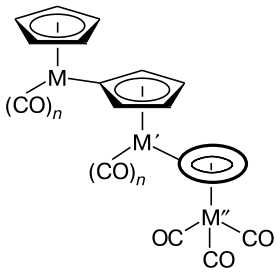


1, 2

R = CH_2Ph (**1**), Me (**2**)

Reagents, conditions, and yield: *n*-BuLi, Me_3SiCl, 20%.

The found property allows regarding binuclear ladder-type complexes as potential building blocks for polyheteronuclear molecular systems based on transition metals and η^1,η^5-cyclopentadienyl or η^1,η^6-arene bridging ligands.



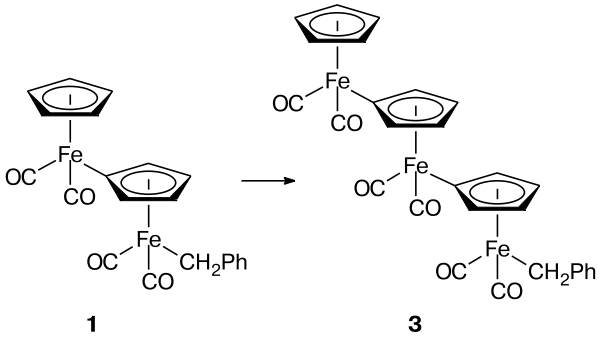
= C_5H_4 or C_6H_5

It is an interesting subject to construct such complexes bridged by ligands having delocalized π-systems that serve as conduits for electron transfer between the metal centers, and explore the intramolecular charge transfer through π-ligand—metal—σ,π-ligand—metal chain.

This report summarizes our metallation studies of binuclear ladder complexes and presents the examples of applying such metallation reactions to prepare novel transition metal complexes of higher nuclearity.

Metallation of binuclear complex η^1,η^5-$C_5H_5(CO)_2$-Fe-η^1,η^5-$C_5H_4(CO)_2Fe$-η^1-CH_2Ph (**1**) by *n*-butyllithium (THF, −78 °C) with the following treatment of the lithiated derivative with electrophilic reagent η^5-C_5H_5-$(CO)_2FeCl$ was demonstrated to give trinuclear complex η^5-$C_5H_5(CO)_2Fe$-η^1,η^5-$C_5H_4(CO)_2Fe$-η^1,η^5-$C_5H_4(CO)_2$-Fe-η^1-CH_2Ph (**3**, yield 12%) with three iron atoms and two bridging η^1,η^5-cyclopentadienyl ligands[10] (Scheme 4).

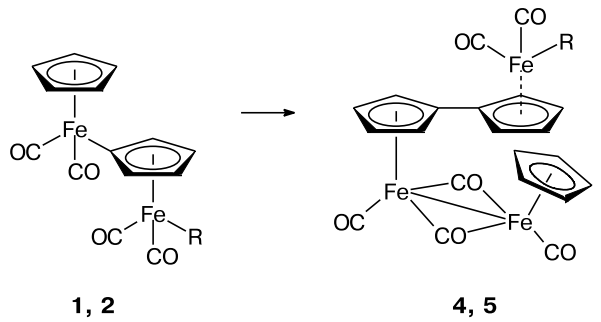
Scheme 4



Reagents and conditions: *n*-BuLi, $Cp(CO)_2FeCl$.

Using η^5-$C_5H_5(CO)_2FeI$ instead of electrophilic reagent does not afford complex **3** but leads to trinuclear complex η^5,η^5-$PhCH_2(CO)_2Fe(C_5H_4—C_5H_4)(CO)Fe$-μ-$(CO)_2Fe(CO)\eta^5—C_5H_5$ (**4**) resulting from migration of ligand η^1,η^5-$C_5H_4(CO)_2FeCH_2Ph$ from iron atom on η^5-cyclopentadienyl ring with the following interaction between η^5-$C_5H_5(CO)_2FeI$ and the iron-centered anion.[9] The complex of similar structure, η^5,η^5-$Me(CO)_2Fe$-$(C_5H_4—C_5H_4)(CO)Fe$-μ-$(CO)_2Fe(CO)\eta^5$-C_5H_5 (**5**, yield 20%) was derived from binuclear complex **2** under the same conditions (Scheme 5).

Scheme 5



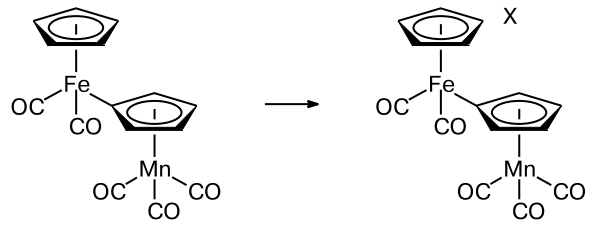
R = CH_2Ph (**4**), Me (**5**)

Reagents and conditions: *n*-BuLi, $Cp(CO)_2FeI$.

In this case, in contrast to the known rearrangements with η^1-bound to transition metal (Fe, Mo, W, Re) simple groups ER_3 (E = Si, Sn, Ge, Pb; R = CHO, —C=CPh, —C≡C, $P(=O)(OMe)_2$, *etc.*) migrating to cyclopentadienyl ring,[11] the migrating group is a complex organometallic fragment. The possibility of such rearrangement depends on a number of factors, *i.e.*, the particular metal and ligand η^1-coordinated to it, character of electrophilic and metallating agents, *etc.*[11] In our case the nature of electrophilic reagent appears to be the dominating influence since replacing chlorine with iodine in (cyclopentadienyl)iron dicarbonyl complex has altered the reaction pathway substantially.

Further it was found[12] that metallation of binuclear complex η^5-$C_5H_5(CO)_2Fe$-η^1,η^5-$C_5H_4Mn(CO)_3$ (**6**) structurally analogous with **1** and **2** occurs exclusively on η^5-cyclopentadienyl ring similarly to **1** and **2** under the same conditions (*n*-BuLi, THF, −78 °C). Treatment of the lithiated complex derived from **6** with electrophilic reagents CO_2, C_3F_7I, and Ph_2PCl afforded monosubstituted functional derivatives η^5-$HOOCC_5H_4(CO)_2Fe$-η^1,η^5-$C_5H_4Mn(CO)_3$ (**7**),[12] η^5-$IC_5H_4(CO)_2Fe$-η^1,η^5-$C_5H_4Mn(CO)_3$ (**8**),[13] and η^5-$Ph_2PC_5H_4(CO)_2Fe$-η^1,η^5-$C_5H_4Mn(CO)_3$ (**9**)[14] in 53, 45, and 60% yield, respectively (Scheme 6).

Scheme 6



X = COOH (**7**), I (**8**), PPh_2 (**9**)

Reagents and conditions: *n*-BuLi, CO_2 (**7**); *n*-BuLi, C_3F_7I (**8**); *n*-BuLi, Ph_2PCl (**9**).

The analogous metallation of complex **6** and its derivatives **7**, **8**, and **9** with subsequent treatment by various electrophilic agents was used to obtain a range of new tri-, tetra-, penta-, and hexanuclear complexes. Specifically, reacting η^5-$C_5H_5(CO)_2FeI$ with the lithiated complex **6** resulted in trinuclear complex η^5-$C_5H_5(CO)_2Fe$-η^1,η^5-$C_5H_4(CO)_2Fe$-η^1,η^5-$C_5H_4Mn(CO)_3$ (**10**) with Fe—Fe—Mn sequence of metals and two bridging η^1,η^5-cyclopentadienyl ligands.[9] As was mentioned above, in the case of binuclear ligands **1** and **2**, $Cp(CO)_2FeI$ used instead of $Cp(CO)_2FeCl$ as a stronger electrophile mainly attacks Fe—Alkyl σ-bond which is labile to electrophilic substitution so that selective metallation of cyclopentadienyl ring cannot be achieved. Complex **6** has no such bond and thus can be treated with iodide to direct the reaction on cyclopentadienyl ring. Treatment of the lithio derivative of **6** with complexes η^5-$C_5H_5(CO)_3MCl$ (M = Mo or W) gave trinuclear systems, η^5-$C_5H_5(CO)_3$-Mo-η^1,η^5-$C_5H_4(CO)_2Fe$-η^1,η^5-$C_5H_4Mn(CO)_3$ (**11**) and η^5-$C_5H_5(CO)_3W$-η^1,η^5-$C_5H_4(CO)_2Fe$-η^1,η^5-$C_5H_4Mn(CO)_3$ (**12**) with Mo—Fe—Mn and W—Fe—Mn sequence of metals, respectively, and two bridging η^1,η^5-cyclopentadienyl ligands.[15]

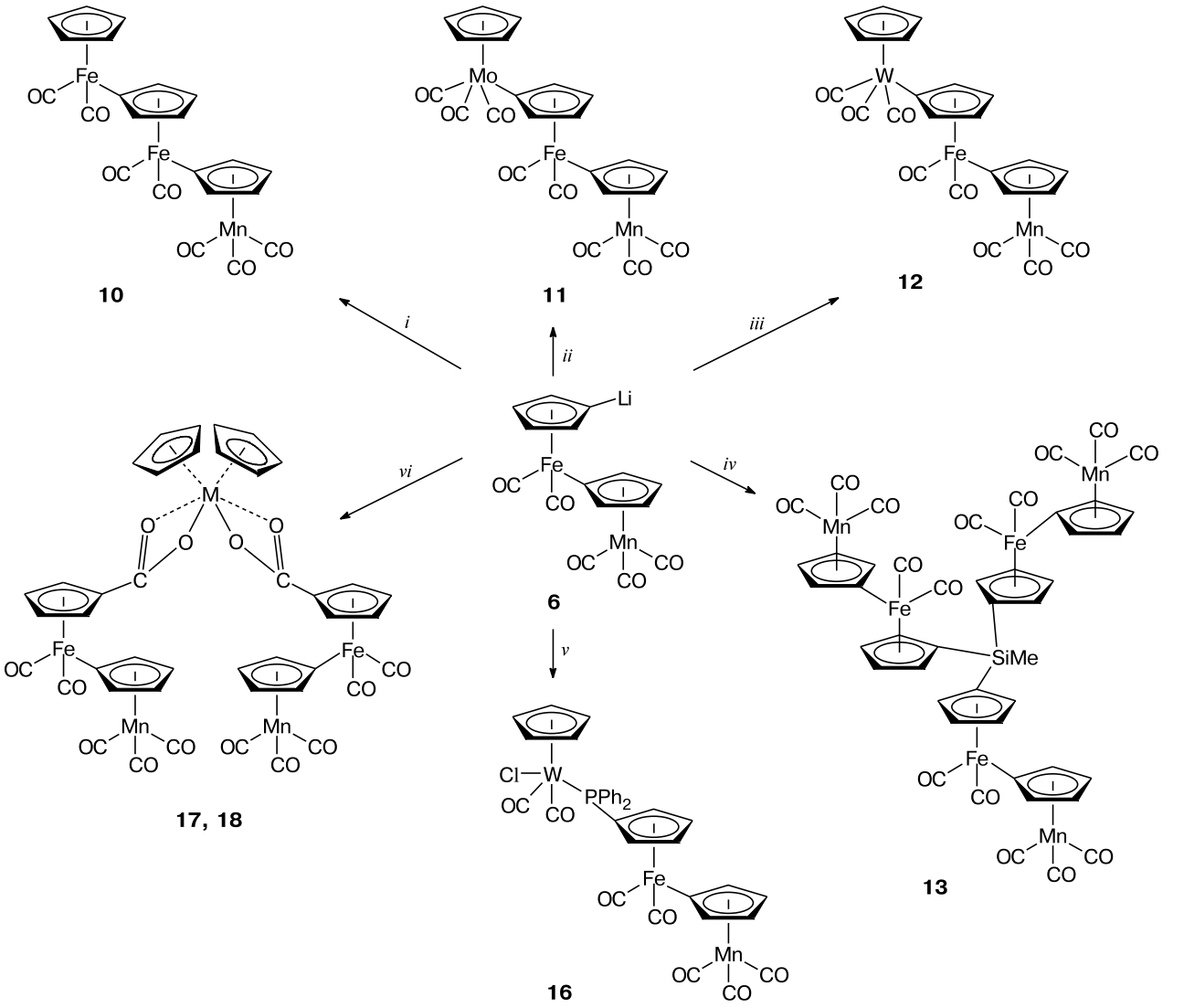
By reacting the lithio derivative of **6** with $MeSiCl_3$ (3 : 1) we have synthesized hexanuclear propeller-type complex $MeSi[-\eta^1,\eta^5\text{-}C_5H_4(CO)_2Fe\text{-}\eta^1,\eta^5\text{-}C_5H_4Mn(CO)_3]_3$ (**13**) containing three iron and three manganese atoms and six bridging η^1,η^5-cyclopentadienyl ligands.[16] Metallation of complex $\eta^5\text{-}C_5H_5(CO)_2Fe\text{-}\eta^1,\eta^5\text{-}C_5H_4Mn(CO)_2PPh_3$ (**14**) followed by treatment with $MeSiCl_3$ (3 : 1) leads to the similar hexanuclear complex $MeSi[-\eta^1,\eta^5\text{-}C_5H_4(CO)_2\text{-}Fe\text{-}\eta^1,\eta^5\text{-}C_5H_4Mn(CO)_2PPh_3]_3$ (**15**).[14]

The propeller-type trinuclear complexes were synthesized previously by reacting lithiated derivatives of $\eta^5\text{-}C_5H_5(CO)_nMR$ (M = Fe, Mn or W, R = Me, Et or CH_2Ph) with trichlorosilanes R^1SiCl_3 (R^1 = Me, $(CH_2)_3Cl$ or *m*-, *p*-$(CH_2)_2C_6H_4CH_2Cl$).[17]

Binuclear complex $\eta^5\text{-}PPh_2C_5H_4(CO)_2Fe\text{-}\eta^1,\eta^5\text{-}C_5H_4\text{-}Mn(CO)_3$ (**9**) was reacted with $\eta^5\text{-}C_5H_5(CO)_3WCl$ in the presence of Me_3NO to synthesize trinuclear complex $\eta^5\text{-}C_5H_5(CO)_2ClW\text{-}\eta^1,\eta^5\text{-}Ph_2PC_5H_4(CO)_2Fe\text{-}\eta^1,\eta^5\text{-}C_5H_4Mn(CO)_3$ (**16**) with W—Fe—Mn metals sequence and bridging ligands $\eta^1,\eta^5\text{-}PPh_2C_5H_4$ and $\eta^1,\eta^5\text{-}C_5H_4$.[14] Binuclear complex of similar structure is described in Ref. 18.

Treatment of $(\eta^5\text{-}C_5H_5)_2MCl_2$ (M = Ti or Zr) with the acid **7** sodium salt gave pentanuclear complexes

Scheme 7

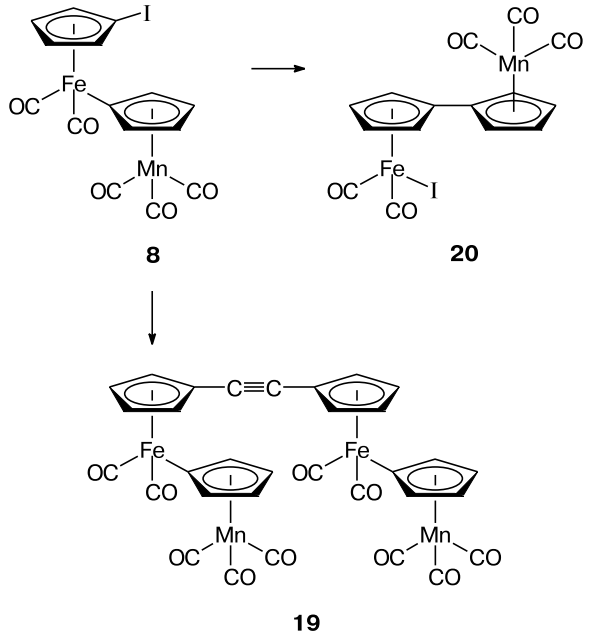


Reagents and conditions: *i*. $Cp(CO)_2FeI$; *ii*. $Cp(CO)_3MoCl$; *iii*. $Cp(CO)_3WCl$, *iv*. 1/3 equiv. $SiMeCl_3$, *v*. PPh_2Cl, $Cp(CO)_3WCl$, *vi*. CO_2, NaH, Cp_2MCl_2 (M = Ti or Zr); yields 15—30%.

$(\eta^5\text{-}C_5H_5)_2M\text{-}[O_2CC_5H_4(CO)_2Fe\text{-}\eta^1,\eta^5\text{-}C_5H_4Mn(CO)_3]_2$ (M = Ti (**17**), Zr (**18**)) with Ti—Fe—Mn and Zr—Fe—Mn metal sequences and bridging ligands $\eta^1,\eta^5\text{-}O_2CC_5H_4$ and $\eta^1,\eta^5\text{-}C_5H_4$.[19] The synthesis of structurally similar trinuclear complexes containing Fe besides Ti or Zr was reported in Ref. 20 (Scheme 7).

Stille cross-coupling between iodo-derivative $\eta^5\text{-}IC_5H_4(CO)_2Fe\text{-}\eta^1,\eta^5\text{-}C_5H_4Mn(CO)_3$ (**8**) and $Me_3SnC{\equiv}CSnMe_3$ in the presence of $PdCl_2(MeCN)_2$ afforded tetranuclear complex $\mu\text{-}(C{\equiv}C)[\text{-}\eta^5\text{-}C_5H_4(CO)_2Fe\text{-}\eta^1,\eta^5\text{-}C_5H_4Mn(CO)_3]_2$ (**19**, yield 3%) carrying acetylene group between cyclopentadienyl rings. The main product of this reaction is binuclear complex $I(CO)_2Fe\text{-}\eta^5,\eta^5\text{-}C_5H_4\text{-}C_5H_4Mn(CO)_3$ (**20**, yield 28%) resulting from $PdCl_2(MeCN)_2$-catalyzed intramolecular rearrangement of iodine and cymantrene ligand in **8** (Scheme 8).[21]

Scheme 8



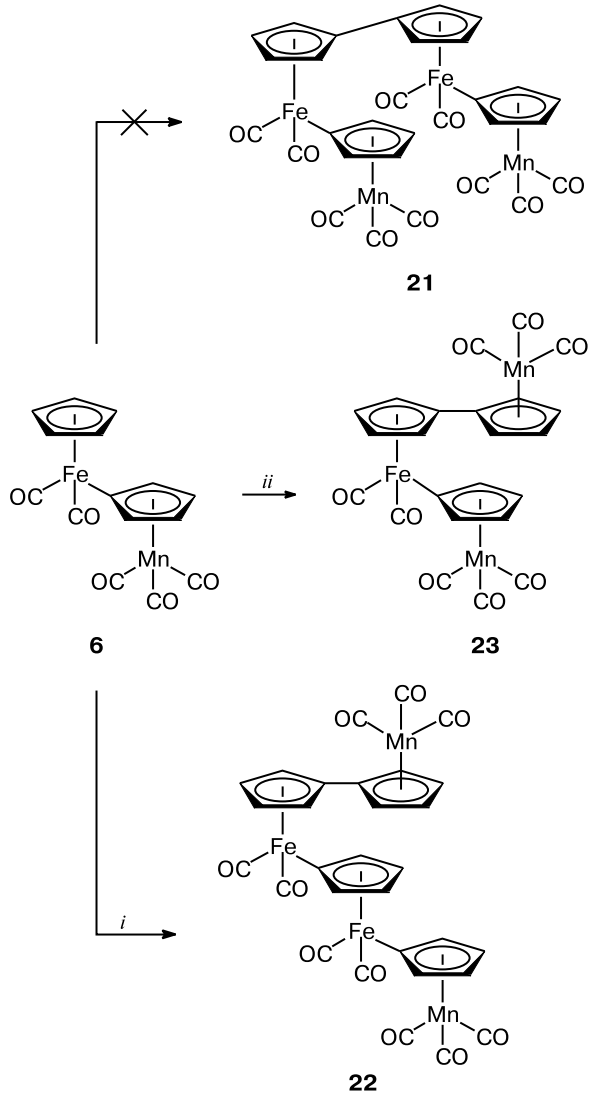
Reagents and conditions: $Me_3SnC{\equiv}CSnMe_3$, $PdCl_2(MeCN)_2$, DMF, ~20 °C.

The similar intramolecular regio-exchange of iodine and methyl group has been observed earlier on attempted synthesis of $Me(CO)_nM(C_5H_4{-}C_5H_4)TiCl_2C_5H_5$ (M = Fe, n = 2; M = Mo, W, n = 3) starting from $IC_5H_4(CO)_nM$ Me and $Me_3SnC_5H_4TiCl_2C_5H_5$ (see Ref. 22).

The attempted dimerization of Fe—Mn complex **6** though the cyclopentadienyl ring by Wurtz coupling of lithio derivative $\eta^5\text{-}LiC_5H_4(CO)_2Fe\text{-}\eta^1,\eta^5\text{-}C_5H_4Mn(CO)_3$ with $\eta^5\text{-}IC_5H_4(CO)_2Fe\text{-}\eta^1,\eta^5\text{-}C_5H_4Mn(CO)_3$ (**8**) has not afforded the expected tetranuclear complex $\eta^5,\eta^5\text{-}(C_5H_4{-}C_5H_4)[(CO)_2Fe\text{-}\eta^1,\eta^5\text{-}C_5H_4Mn(CO)_3]_2$ (**21**) but instead resulted in a tetranuclear complex $(CO)_3Mn\text{-}\eta^5,\eta^5\text{-}(C_5H_4{-}C_5H_4)(CO)_2Fe\text{-}\eta^1,\eta^5\text{-}C_5H_4(CO)_2Fe\text{-}\eta^1,\eta^5\text{-}C_5H_4\text{-}Mn(CO)_3$ (**22**)[13] which is a product of rearrangement involving migration of cymantrenyl ligand from iron atom on cyclopentadienyl ring with subsequent interaction of electrophilic reagent **8** with the generated iron-centered anion.

The treatment of lithio derivative of **6** with anhydrous $CuCl_2$ (again targeted to yield complex **21**) also gave the product of migration of cymantrenyl ligand from iron atom on cyclopentadienyl ring, $(CO)_3Mn\text{-}\eta^5,\eta^5\text{-}(C_5H_4{-}C_5H_4)(CO)_2Fe\text{-}\eta^1,\eta^5\text{-}C_5H_4Mn(CO)_3$ (**23**) in 10% isolated yield (Scheme 9)[21].

Scheme 9

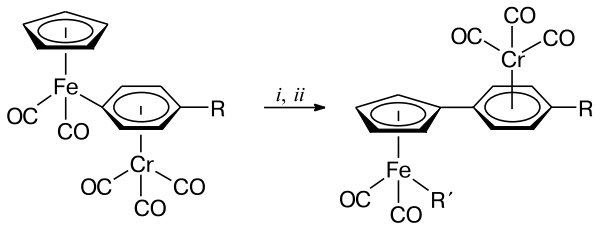


Reagents and conditions: *i*. *n*-BuLi, $IC_5H_4(CO)_2FeC_5H_4Mn(CO)_3$; *ii*. *n*-BuLi, $CuCl_2$.

The rearrangement of σ-cymantrenyl ligand from Mo atom on Cp ring was observed previously at thermal treatment of η^5-$C_5H_5(CO)_3Mo$-η^1,η^5-$C_5H_4Mn(CO)_3$ (169—171 °C), as a result the authors[5] have isolated trinuclear complex η^5,η^5-$(CO)_3Mn(C_5H_4—C_5H_4)(CO)_3$-Mo—Mo$(CO)_3\eta^5$-$C_5H_5$.

Another building block that we have utilized in constructing trinuclear ladder systems is binuclear complex η^5-$C_5H_5(CO)_2Fe$-η^1,η^6-$C_6H_5Cr(CO)_3$ (**24**) containing iron and chromium atoms in combination with η^1,η^6-bridging phenyl ligand. It turned out, however, that under metallation of this complex followed by treatment with electrophilic agent, migration of phenyl ligand coordinated with $Cr(CO)_3$ from iron atom on cyclopentadienyl ring is very facile. In particular, treatment of the lithiated derivatives of **24** (*n*-BuLi, THF, −78 °C) with $PhCH_2Cl$, as well as interaction of the lithiated derivative of η^5-$C_5H_5(CO)_2Fe$-η^1,η^6-$(C_6H_4$-*p*-Me$)Cr(CO)_3$ (**25**) with dimethyl sulfate (Me_2SO_4) resulted in isolation of binuclear complexes $PhCH_2(CO)_2Fe$-η^5,η^6-$(C_5H_4—C_6H_5)Cr(CO)_3$ (**26**) or $Me(CO)_2Fe$-η^5,η^6-$(C_5H_4—C_6H_4$-*p*-Me$)Cr(CO)_3$ (**27**), respectively (Scheme 10).[23,24] Thus, binuclear complex **24** cannot be used as a precursor for a trinuclear ladder structure. However the revealed intramolecular rearrangement that attends metallation in complex **24** is of utmost interest, in addition presenting the example of organometallic fragment migration generating new C—C bond in the coordination sphere of a transition metal (Scheme 10).

Scheme 10



24, 25 **26, 27**

R = H (**24**), Me (**25**);
R = H, R′ = CH_2Ph (**26**), R = Me, R′ = Me (**27**)

Reagents and conditions: *i*. *n*-BuLi, $PhCH_2Cl$; *ii*. *n*-BuLi, Me_2SO_4, MeI; yields 14 (**26**) and 20% (**27**).

There was reported a synthesis[25] in which complex $[PhC_5H_4(CO)_3W]_2$ was formed *via* phenyl migration from W atom on Cp ring under thermal treatment of $Cp(CO)_3WPh$. Under the metallation conditions, such migration does not occur as we have shown[23] for the complex $Cp(CO)_2FePh$.

The synthesized by us polynuclear complexes were characterized by microanalysis, X-ray diffraction, mass-spectrometry, IR and ^{1}H NMR spectroscopies.

Thus, metallaltion of binuclear ladder complexes may proceed, depending on reagents and conditions, with the metal—σ-ligand bond being retained throughout the reaction or may involve intramolecular migration of the σ-bound ligand from metal on cyclopentadienyl ring. In case the rearrangement does not take place, one can synthesize a range of novel tri-, penta-, and hexanuclear ladder complexes and explore the electron transfer through their π-ligand—metal—σ,π-ligand—metal bond system.

Intramolecular charge transfer in bi- and polynuclear complexes has been studied by IR spectroscopy[26,27] and by cyclic voltammetry.[19,24,28]

Carbonyl ligands contained in the complexes under study are known as convenient spectroscopic indicators to track electronic effects of substituents. The spectra were interpreted by consideration of local symmetry for each metal carbonyl moiety, taking into account contributions of all of the latter into ν(CO) band positions.

Assembling of mono- and binuclear precursors into bi- and polynuclear successor complexes, respectively, is accompanied by electron redistribution. Electronic effect of electron-donating $Cp(CO)_nM$ groups (M = Fe, *n* = 2; M = Mo, W, *n* = 3), as well as electron-withdrawing $M(CO)_3$ groups (M = Mn or Cr) is transmitted through the bridging η^1,η^5-cyclopentadienyl or η^1,η^6-phenyl ligands, being reflected in alteration of vibrational frequencies of carbonyl groups compared to the mono- or dinuclear precursor complexes.[26,27]

The analysis of ν(CO) frequency in binuclear ladder complexes **1** (Fe—Fe), **6** (Fe—Mn), and **24** (Fe—Cr) has shown that $Cp(CO)_2Fe$ group (a strong electron donor) transfers its electronic effect through η^1,η^5- or η^1,η^6-bridging cyclopentadienyl or phenyl ligands, respectively, resulting in a substantial lowering of ν(CO) frequencies of carbonyl groups attached to Fe, Mn, or Cr atoms relative to the corresponding mononuclear complexes $Cp(CO)_2FeR$ (R = Alk or Ar), $CpMn(CO)_3$ or $C_6H_6Cr(CO)_3$. The electron-withdrawing $C_5H_4(CO)_2FeR$, $C_5H_4Mn(CO)_3$ or $C_6H_5Cr(CO)_3$ groups in their turn enhance stretching frequencies of the carbonyls at Fe atom considerably compared to the values found in mononuclear complexes $Cp(CO)_2FeR$. Noticeably, the ν(CO) frequencies at Fe atom are shifted nearly equally for $C_5H_4(CO)_2Fe$ and $C_5H_4Mn(CO)_3$ groups, indicating their nearly equal electron-withdrawing abilities.[26,27]

In a trinuclear Fe—Fe—Mn ladder complex **10** composed of three metal carbonyl moities, the "top-step" ν(CO) frequencies (that is, belonging to the carbonyl attached to Fe atom) are under electron-withdrawing influence of two metal carbonyl moities that causes their blue shift with respect to positions in binuclear complex **1**. The "bottom step" in **10** is in its turn affected by two electron-donating groups, hence ν(CO) frequencies at Mn atom are down-shifted from ν(CO) of $CpMn(CO)_3$ moiety and differ only slightly from ν(CO) at Mn in a

binuclear counterpart **6**. Thus, electronic effects are attenuated from the top to bottom step of the ladder. In the central fragment of complex **10**, $C_5H_4(CO)_2Fe$, electron-donating influence of the "top" and electron-withdrawing influence of the "bottom" moieties are equilibrated so that ν(CO) frequencies of the carbonyls at Fe atom in $C_5H_4(CO)_2Fe$ are close to ν(CO) observed in mononuclear complexes $Cp(CO)_2FeR$ (see Ref. 26 and 27).

In trinuclear complexes **11** (Mo—Fe—Mn) and **12** (W—Fe—Mn), ν(CO) frequencies assigned to $Fe(CO)_2$ and $Mn(CO)_3$ moities are in close agreement with the corresponding ν(CO) frequencies in Fe—Fe—Mn complex **10**, which implies that $Cp(CO)_2Fe$, $Cp(CO)_3Mo$, and $Cp(CO)_3W$ moieties are nearly equally strong electron donors.[22]

In a trinuclear W—Fe—Mn complex **16**, electron-donating influence of $CpW(CO)_2$ moiety is compensated by electron-withdrawing influence of chlorine. This effect of $Cp(CO)_2ClW$ moiety is reflected in that ν(CO) frequences in the neighbor $Fe(CO)_2$ group are shifted to higher wavenumbers relative to those in complex **9**, with attenuation through-bond as approaching remote $Mn(CO)_3$ group. In $W(CO)_2$ group, ν(CO) frequencies are markedly (90 cm^{-1}) red-shifted compared to complex $Cp(CO)_3WCl$ due to the strong electron-donating influence of the phosphine ligand.[14]

In pentanuclear complexes **17** and **18**, the carbonyl frequencies of $Fe(CO)_2$ group are substantially up-shifted relative to ν(CO) in binuclear Fe—Mn complex **6** as result of electron-withdrawing influence of carboxylate ligands.[19]

In hexanuclear complexes **13** and **15**, ν(CO) frequencies coincide precisely with ν(CO) in binuclear complexes **6** and **14**, indicating that electronic effects of $C_5H_4(CO)_2Fe—C_5H_4Mn(CO)_3$ or $C_5H_4(CO)_2Fe—C_5H_4Mn(CO)_2PPh_3$ moieties are not transmitted through Si atom.[16,14]

Thus, alteration of carbonyl stretching frequencies ν(CO) in the ladder structures discussed above is diagnostic of the transfer of electronic effects from organometallic fragments through η^1,η^5-cyclopentadienyl or η^1,η^6-phenyl bridging ligands.

Electrochemical data obtained for di- and polynuclear ladder complexes are consistent with the IR data; the general conclusion that follows is that in these compounds that can be considered as integral systems with the high degree of interunit communication, localization sites of electronic effects are different for oxidation and reduction. Oxidation is directed on the atoms π-bound to the bridge (Mn, Cr) with the π-bond being cleaved and σ-bond remaining intact. Reduction of the complexes involves the orbitals localized on the Fe—C σ-bond with electron transfer followed by the rapid σ-bond cleavage. Consequently, by applying cathodic or anodic potential it is possible to selectively cleave σ- or π-bond, respectively.

The comparison of the oxidation potentials E^{ox} for such pair as binuclear Fe—Mn complex **6** and cymantrene (1.06 and 1.29 eV, respectively) may lead to the conclusion that the electron-donating influence of $Cp(CO)_2Fe$ moiety is transmitted through the bridging cyclopentadienyl ligand, facilitating the oxidation.[28]

However, in comparing the reduction potentials $-E^{red}$ of the same binuclear Fe—Mn complex **6** and $Cp(CO)_2FePh$ (2.20 and 2.31 eV, respectively) or binuclear Fe—Cr complex **24** and $Cp(CO)_2FePh$ (2.06 and 2.14 eV, respectively) it is seen that electron-withdrawing influence of $Mn(CO)_3$ or $Cr(CO)_3$ groups is transmitted through cyclopentadienyl or phenyl ligand, respectively, thus facilitating reduction.[28] More detailed electrochemical characterization of the particular complexes is given in the original articles.[19,24,28]

In summary, the results obtained are indicative of the "top-down" electron transfer in the ladder structures through the bridging η^1,η^5-cyclopentadienyl or η^1,η^6-arene ligands, with the extent of transfer depending on the nature of the bridging ligand.

In our view, synthesis and research of novel ladder complexes with versatile combinations of transition metals and various σ,π-bridging ligands, as well as the attempt of deep insight into the mechanisms behind the revealed intramolecular rearrangements generating new C—C bonds in the metal coordination sphere constitute an important task that is also highly motivated by applicability considerations.

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