On the Way to Delocalized Organometallic Polymers: Triple- and Quadruple-Decker Pentalene Complexes of Iron and Cobalt

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*Summary: A new class of triple- and quadruple-decker complexes of iron and cobalt derived from pentalene was prepared. The triple-deckers are prepared through the reaction of the bis(hydropentalenyl)iron monolithium salt 2 with Cp*M(acac) (M = Fe, Co). Two types of iron quadruple-deckers were also prepared, the first through the reaction of 2 with Fe(acac)$_2$, and the second through the reaction of 3 with n-butyllithium followed by Cp*Fe(acac).*

There has been a great interest in the synthesis and properties of one-dimensional organometallic polymers based on sandwich compounds due to their potential applications as advanced materials.[1] The possibility that polymers derived from transition-metal complexes of pentalene (Chart I) might show interesting electrical and/or magnetic properties associated with electron delocalization and electronic cooperative interactions in odd electron systems has motivated us to prepare several model monomers related to such polymers and examine their properties (Chart II).

Of particular relevance for the Cp*M(pentalene)M′Cp* (Cp* = η^5-C_5Me_5) mixed valence derivatives are the results of the X-ray studies, which show equivalent metallic centers,[2] and ^{57}Fe Mössbauer spectroscopic studies, indicating full delocalization for the monocationic system [Cp*Fe(pentalene)FeCp*]$^+$BF$_4^-$ over the entire range 1.5–300 K.[3]

Since one approach to the design of electrically conducting metallocene-type polymers is that the requirements for the desired electrical properties are inherent to the individual molecules, the species shown in Chart II can be envisioned as the subunits of a potential one-dimensional conducting material. In this context, the synthesis of dimeric, trimeric, and oligomeric metallocene-type complexes have attracted increasing interest.[4-9]

Along this line, we wish to report a synthetic route to iron and cobalt triple- and quadruple-decker complexes derived from pentalene, which can be considered as small segments and/or the building blocks of a polymer of the type shown in Chart I.

Chart I. Hypothethical One-Dimensional Structure of a Pentalene Transition-Metal Polymer

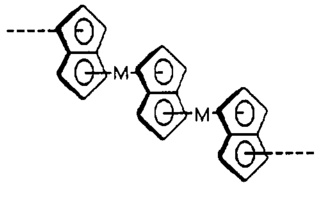
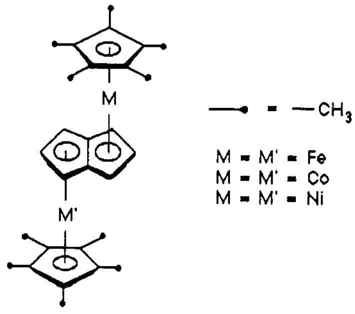


Chart II. Bis[pentamethylcyclopentadienyl)metal]pentalene Complexes



The reaction of bis(hydropentalenyl)iron[10](1, 1 equiv) with n-butyllithium (1.6 M in hexanes, 1 equiv) generates exclusively the monoanionic lithium salt 2,[10] which, under reaction with Cp*Fe(acac)[11] or Cp*Co(acac),[11] affords in high yields the 34- and 35-electron complexes Cp*Fe(C_8H_6)Fe(C_8H_7) (3) and Cp*Co(C_8H_6)Fe(C_8H_7) (4), re-

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(1) See for example: (a) Böhm, M. C. *Lect. Notes Chem.* **1987**, 45. (b) Carraher, C. E.; Linville, R. J.; Manek, T. A.; Blaxall, H. S.; Taylor, J. R.; Torre, L. P. In *Conductive Polymers*; Seymour, R. B., Ed.; Plenum Press: New York, 1981; p 77. (c) Carraher, C. E.; Pittman, C. U. In *Metal-Containing Polymer Systems*; Sheats, J. E.; Carraher, C. E., Pittman, C. U., Eds.; Plenum Press: New York, 1985; p 1. (d) Grimes, R. N. *Pure Appl. Chem.* **1987**, *59*, 847.

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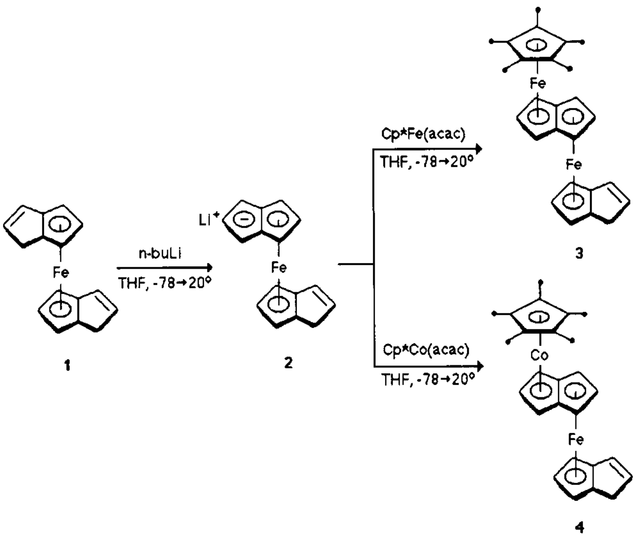
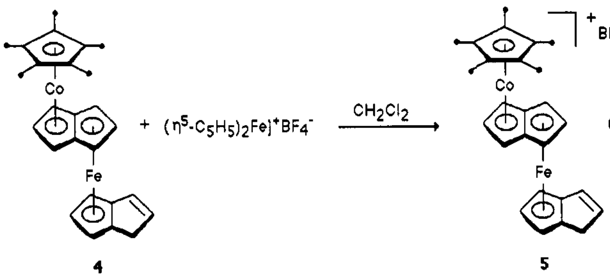
Scheme I



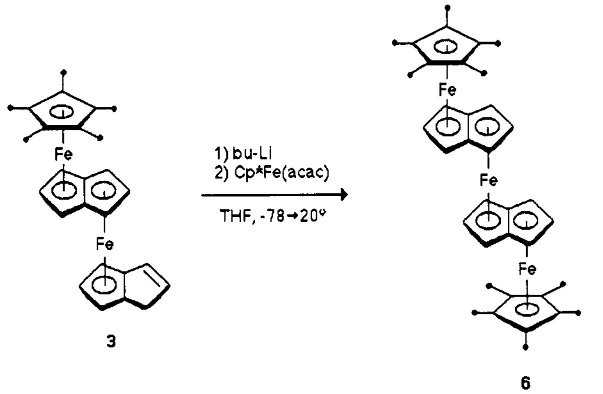
spectively. Complexes 3 and 4 are obtained after removal of the solvent under vacuum and extraction with hexane to remove insoluble Li(acac), followed by crystallization from hexane (Scheme I).[12]

Although 4 is paramagnetic, it can be conveniently characterized through the ^{1}H- and ^{13}C-NMR spectra of the oxidized derivative 5, isoelectronic with 3, obtained as dark blue crystals after oxidation with ferrocenium tetrafluoroborate (eq 1), precipitation of the salt with diethyl ether to remove ferrocene, and crystallization by ether/dichloromethane diffusion.



(1)

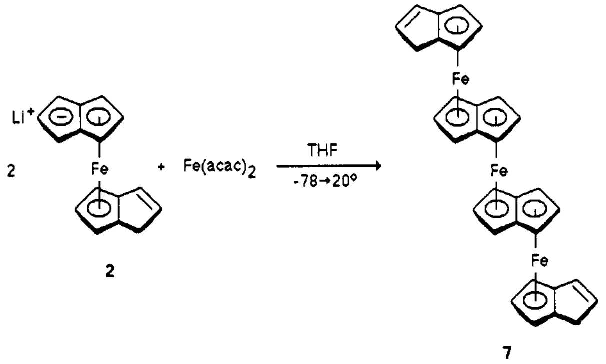
Compound 3 (1 equiv) reacts with *n*-butyllithium (1.6 M in hexanes, 1 equiv) and subsequently with Cp*Fe-(acac) (1 equiv) to afford the quadruple-decker complex $(Cp^*Fe)_2[(C_8H_6)_2Fe]$ (6) (eq 2) in 51% yield as a brown



(2)

microcrystalline powder after removal of the solvent under vacuum, extraction with hot hexane, followed by slow crystallization from hexane. Complex 6 is very air sensitive but thermall stable at 110 °C (boiling toluene).

Interestingly, compound 2 (2 equiv) reacts with bis-(2,4-pentanedionato)iron(II),[11,13] $Fe(acac)_2$ (1 equiv), to afford the quadruple-decker compound $[(C_8H_7)Fe]_2[(C_8H_6)_2Fe]$ (7) (eq 3) in 40% yield after removal of the solvent under vacuum, extraction with hot toluene, and crystallization from boiling toluene.



(3)

Compound 7 is isolated as a green crystalline powder, which is very air sensitive but thermally stable. The structure of 7 was assigned on the basis of elemental analysis, its infrared spectrum, which is remarkably similar to that of 1[14,15] and shows a strong absorption at 718 cm^{-1}, probably due to an olefin C–H out of plane vibration,[15] and its mass spectrum, which is expected to be consistent with that of 1. Indeed, the mass spectrum of 7 shows clearly the molecular ion peak and the most important fragmentations (peaks of greater intensity than 20% of the base peak) are the same as those observed for 1.[16] Unfortunately, due to the low solubility of 7 (about 400 mg/L in boiling toluene), we have as yet not been able to get ^{1}H- and ^{13}C-NMR spectra.

As compound 6 is a convenient model to see if detrapping is still operating in systems with more than two metal centers, the quadruple-decker complex 7 represents, in principle, a convenient building block for organometallic species derived from pentalene. Also, it seems plausible that by changing the metal in eqs 2 and 3, a number of other heterometallic derivatives could be synthesized.

Further study to examine this possibility and to determine the degree of delocalization in the trinuclear species described is now in progress.

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Supplementary Material Available: Text giving typical experimental procedures and spectral and analytical data for the products obtained (4 pages). Ordering information is given on any current masthead page.

OM930395D

(12) All new compounds were characterized by NMR (except 4, which is paramagnetic, and 7, which is discussed in the text), IR, and mass spectra and by elemental analysis (see the supplementary material).

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(14) The infrared spectra (4000–600 cm^{-1}, Nujoll mull) show the following: (1) 3086 (m), 3053 (m), 1627 (w), 1544 (w), 1310 (s), 1265 (s), 1231 (s), 1169 (m), 1116 (m), 1012 (s), 923 (s), 884 (w), 852 (w), 816 (w), 796 (s), 713 (vs), 641 (vs) (see also ref 13); (7) 3082 (m), 1629 (w), 1307 (w), 1253 (s), 1244 (s), 1168 (w), 1087 (s), 1003 (vs), 924 (s), 877 (w), 815 (w), 774 (w), 718 (vs), 640 (vs).

(15) Katz, T. J.; Mrowca, J. J. *J. Am. Chem. Soc.* **1967**, *89*, 1105.

(16) The mass spectra (EI) *m/z* (relative intensity) show the following (peaks of greater intensity than 10% of the base peak): (1) 262 (M^+, 100), 158 ($C_8H_6Fe^+$, 23), 102 ($C_8H_6^+$, 14) (high resolution mass calcd for $C_{16}H_{14}Fe$ 262.0524, found 262.0500) (see also ref 13); (7) 578 (M^+, 2), 522 ($C_{32}H_{26}Fe_2^+$, 16), 262 ($C_{16}H_{14}Fe^+$, 100), 158 ($C_8H_6Fe^+$, 22), 102 ($C_8H_6^+$, 22) (high resolution mass calcd for $C_{32}H_{26}Fe_3$ 578.0082, found 578.0075).