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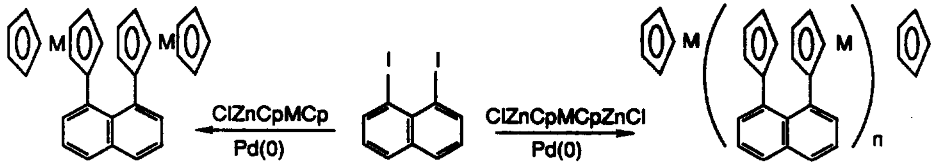
FACE-TO-FACE METALLOCENES. THE SYNTHESIS OF A CYMANTRENE-FERROCENE TRIAD.

Dana A. Gronbeck, Stephen A. Matchett, Myron Rosenblum*
Department of Chemistry, Brandeis University
Waltham, MA 02254

Summary: 1,8-diiodonaphthalene is converted through successive coupling with cyclopentadienylcopper dimethyl sulfide followed by complexation with iron and then manganese tricarbonyl to the trimetallic complex 7 in which adjacent cyclopentadienylmanganese tricarbonyl and ferrocene units are held face-to-face.

Columnar, or stacked organometallic arrays represent a comparatively new class of 'one dimensional' molecular system of current theoretical[1] and synthetic interest. The forerunner of this class of substance, $Cp_3Ni_2^+$ BF_4^- first reported in 1972[2], has since been joined by tripledeck metal complexes incorporating either borole[3], P_6[4] or benzene decks[5], and by more highly extended members of this genre in which iron, cobalt or nickel is bifacially bonded to triboroles[6], diboroles[7] and thiadiborolenes[7]. Within this general class may also be included those complexes in which the architectural unit is a monofacially coordinated paracyclophane type of unit. Among these, are a number of multideck benzeneruthenium[8], cyclopentadienyl- iron[9], nickel and cobalt complexes[10], as well as indenyliron[11], and cyclobutadienecobalt[12] complexes. The recently reported *trans* doubly-coordinated oligomeric naphthalenechromium[13], the triple deck indenyliron, cobalt and nickel complexes[14] as well as the trimeric helicenecobalt complexes[15] also preserve the spirit of this enterprise.

We have earlier reported the synthesis of the first members of a class of face-to-face metallocenes 1 (M=Fe, Ru), and of structurally related polymers 2, through Pd catalyzed coupling of metallocenylchlorozinc complexes with 1,8-diiodonaphthalene[16]. We now report the preparation of the first heterometallic member of this structural class 7, incorporating cymantrene and ferrocene nuclei.

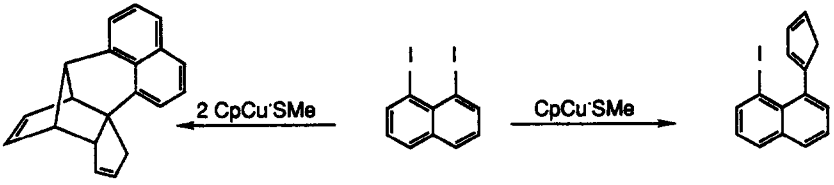


1

2

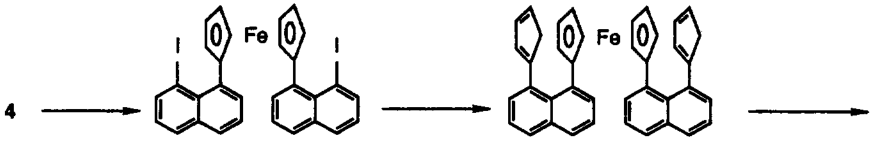
M = Fe, Ru

When cross coupling of 1,8-diiodonaphthalene with cyclopentadienylcopper dimethyl sulfide is carried out employing three molar equivalents of copper reagent (THF, -23°, 24 h), the initial product, 1,8-bis-cyclopentadienylnaphthalene, has been shown to undergo successive sigmatropic rearrangement and intramolecular Diel-Alder cyclization to give 3[17]. A closer examination of this reaction has now shown that the replacement of the first iodine by cyclopentadienyl takes place significantly faster than the does the second halogen, making possible the stepwise replacement of halogen groups.

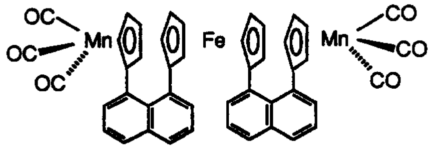


3 **4**

Thus, treatment of 1,8-diiodonapthalene with 1.5 molar equivalent of cyclopentadienylcopper dimethylsulfide under controlled conditions (THF, -23°, 2h) gave 1-iodo-8-cyclopentadienylnaphthalene 4, as a yellow oil, in 37% yield[18]. This was converted, by successive treatment with LDA (-78°, 20 min), followed by ferrous chloride[19] (-20°, 24 h) to 1,1'-bis-(8-iodo-1-naphthyl)ferrocene 5, isolated in 33% yield as a bright red solid (dec. 171°). Repetition of the coupling reaction, using cyclopentadienylcopper dimethyl sulfide (THF, -23°, 20 h) gave 1,1'-bis-(8-cyclopentadienyl-1-naphthyl)ferrocene 6 as a red solid, dec. 130° (55%). This substance was then treated successively with LDA (THF, -78°, 20 min) and $Mn(CO)_5Br$ to give the trinuclear Mn-Fe-Mn complex 7 (10%) as a bright red-orange solid, m.p. 107.5-108°[20].



5 **6**



7

The ^{1}H-NMR spectrum of **7** shows the cyclopentadienyl ring protons of the ferrocene and cymantrene nuclei as pairs of triplets associated with α and β ring protons. The higher field signals at δ 3.91 and 4.01 are assigned respectively to the β and α ferrocene ring protons, while the lower field signals at δ 4.37 and 4.80 are assigned to the corresponding β and α cymantrene protons[21]. It seems likely that the cyclopentadienyl rings in **7** are not perpendicular to the naphthalene ring plane, but that as for **1** (M=Fe, Ru) the dihedral angle between these ring planes is close to 45°. Under these circumstances, the presence of a single resonance for α and β ring protons for each of the metallocene center requires facile rotation of the face-to-face cyclopentadienyl rings about their *ipso* centers. Such a rotation, as has been observed in **1** and **2**, exchanges conformationally inequivalent α and β cyclopentadienyl ring protons for both metallocenes.

The synthetic methodolgy used to prepare face-to-face metallocenyl stacks such as **7** is more flexible than that previous employed for the synthesis of this class of compound, and should provide a more general approach to these systems. Experiments, now in progress, are designed to test the application of this methodology to the synthesis of homo- and heterometallic triad complexes of other metals as well as to the synthesis of polymeric stacked metallocenes related to these.

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20. 1H NMR (300 MHz, MeCN-d3) δ 3.91 (t, 4H, J = 1.6 Hz Cp H_β), 4.01 (t, 4H, J = 1.6 Hz, Cp H_α), 4.37 (t, 4H, J = 2.1 Hz, Cp H_β), 4.80 (t, 4H, J = 2.1 Hz, Cp H_α), 7.18 (dd, 2H, J = 7.9, 6.8 Hz, Ar H_3), 7.44 (dd, 2H, J = 8.4, 7.0 Hz, Ar H_6), 7.56 (dd, 2H, J = 7.0, 1.0 Hz, Ar H_7), 7.73 (dd, 2H, J = 7.9, 1.0 Hz, Ar H_4), 7.81 (dd, 2H, J = 8.4 Hz, Ar H_5), 7.87 (dd, 2H, J = 6.8, 1.0 Hz, Ar H_2); Mass Spectrum, m/z (rel. intensity): 842 (17.8, $C_{46}H_{28}FeMn_2O_6$), 758 (10.7, $C_{43}H_{28}FeMn_2O_3$), 703 (53.8, $C_{43}H_{28}FeMnO_3$), 639 (5.9, $C_{38}H_{24}FeMnO_3$), 619 (47.3, $C_{40}H_{28}FeMn$), 564 (32.0, $C_{40}H_{28}Fe$), 500 (35.5, $C_{35}H_{24}Fe$, base peak), 254 (32.5, $C_{20}H_{14}$);

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