

Polydecker sandwich complexes

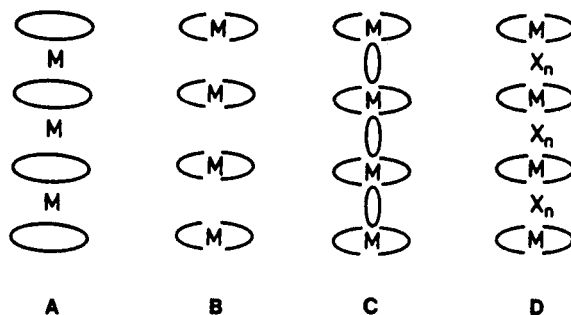
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Abstract - Derivatives of the polydecker sandwich complexes $[(\eta^5, \mu-2,3\text{-dihydro-1,3-diboroly})\text{nickel}]_n$ and $[(\eta^5, \mu-2,3\text{-dihydro-1,3-diboroly})\text{rhodium}]_n$ are synthesized via polycondensation reactions of triple-decker complexes. The structures of the black oxygen-sensitive polymers have been studied by EXAFS. They exhibit different conductivities: the nickel polymer is a semiconductor (10^{-2} Scm^{-1}), whereas the rhodium compound is an insulator ($10^{-10} \text{ Scm}^{-1}$).

INTRODUCTION

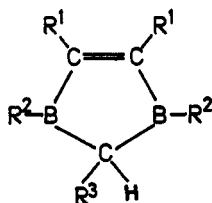
Polydecker sandwich complexes belong to the class of the low-dimensional compounds (ref.1). They should exhibit anisotropic properties of which the electrical conductivity along the metal chain is of highest interest. In polymers of type **A** the metals are coupled via planar cyclic ligands, whereas in the coordination polymers **B** (ref.2) the metals have direct contact via z^2 orbitals. Polymers **C** and **D** contain chalcogen or halogen as well as heterocycles as bridging ligands (ref.3). This report describes the strategy to construct polydecker sandwich complexes with bridging 2,3-dihydro-1,3-diboroly ligands.



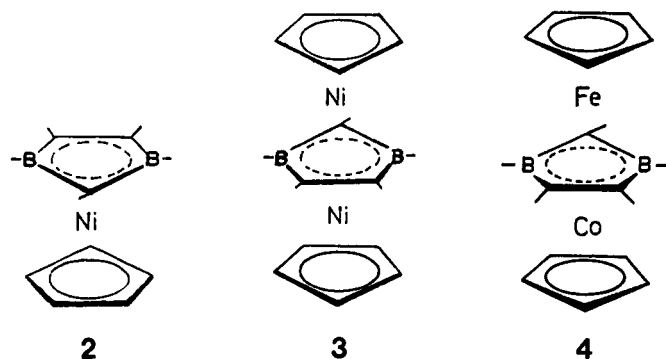
2,3-DIHYDRO-1,3-DIBOROLYL DERIVATIVES AS LIGANDS

Since the early days of metallocene chemistry the possibility of preparing polymeric cyclopentadienylmetal complexes has been discussed. However, no compound of the type $[(\eta^5, \mu-C_5H_5)M]_n$ has been described, although the first triple-decker sandwich $[(\eta^5-C_5H_5)_3Ni_2]^+$ contains a bridging C_5H_5 ligand (ref.4). MNDO calculations show that a variety of five-membered Π -ligands from cyclopentadienyl to the boron homocycle B_5H_5 may be incorporated in polydecker sandwich complexes (ref.1). We have studied the boron heterocycle **1**, a 3e-donor ligand after abstraction of a hydrogen atom from C2, to use it as bridging ligand (ref.5). **1a** was first prepared via a thermal ring closure of hexaethyl-1,2-cis-diborylethene (ref.6).

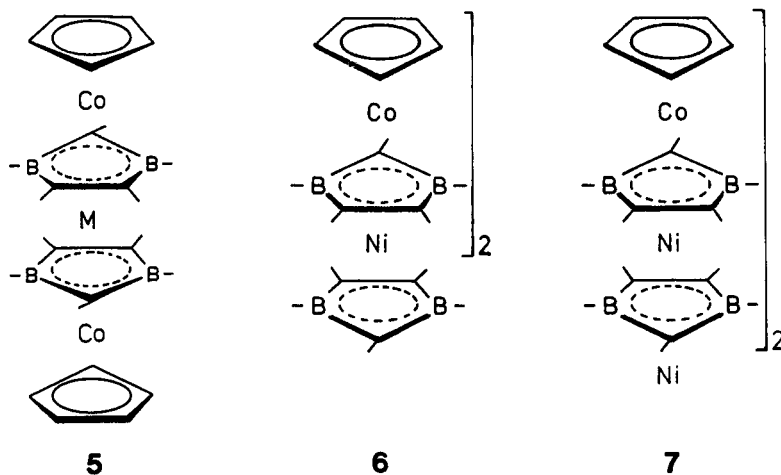
1	R ¹	R ²	R ³
a	Et	Et	Me
b	Et	Me	H
c	Me	Me	H
d	Me	Me	Me



In the meantime we have developed alternative routes (ref.7-9) to synthesize the tetra- and pentaalkyl derivatives 1b-d. The high acceptor power of the 2,3-dihydro-1,3-diborolyl ligand (1a-H) was discovered when the diamagnetic nickel sandwich 2a was stacked with $(C_5H_5)Ni$ to give the paramagnetic triple-decker 3a, having 33 valence electrons (VE). Besides diamagnetic 4, the 30 VE analogue of ferrocene, triple-decker complexes with the metals FeFe (29VE), CoCo (31 VE), and CoNi (32 VE) could be prepared (ref.7).



Reduction of 3 yields the diamagnetic anion, in agreement with MO calculations for triple-decker complexes (ref.10). Our strategy for constructing tetradeccker sandwich complexes led to a large number of colored paramagnetic and diamagnetic compounds 5 (M=Cr,Mn,Fe,Co, Ni,Cu,Zn) (ref.5,9). Further development yielded the first examples of pentadecker 6 and hexadecker sandwich complexes 7.



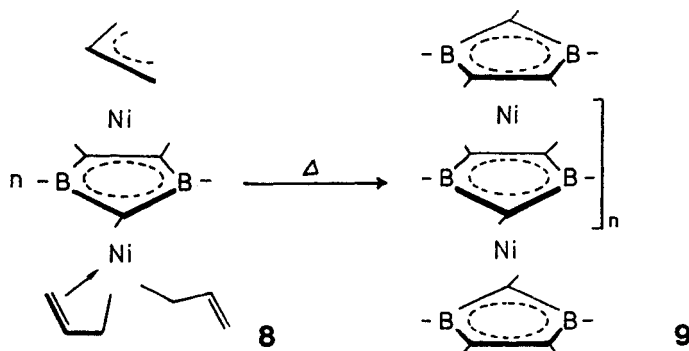
ELECTRON COUNT IN MULTIDECKER COMPOUNDS

In oligodecker sandwich complexes the optimum number of valence electrons is given by $12n + 6$, where n is the number of stacks (metal + ligand). Thus for $n = 1$: 18 VE, $n=2$: 30 VE, $n=3$: 42 VE are counted. Examples are the diamagnetic triple-decker 4 (30 VE) and the paramagnetic tetradeccker 5, M=Fe : 42 VE (high-spin Fe(II)). 6 has 57 VE and is easily reduced to the diamagnetic anion. Diamagnetic 7 contains 70 VE (ref.5). Polydecker complexes with (1-H) as bridging ligand will yield an electron count $(3+d^m)$, where m is the number of d electrons. Thus the incorporation of Co or Rh leads to polydecker complexes with $12n$ valence electrons, in a Ni or Pd polydecker 13 VE per stack are present.

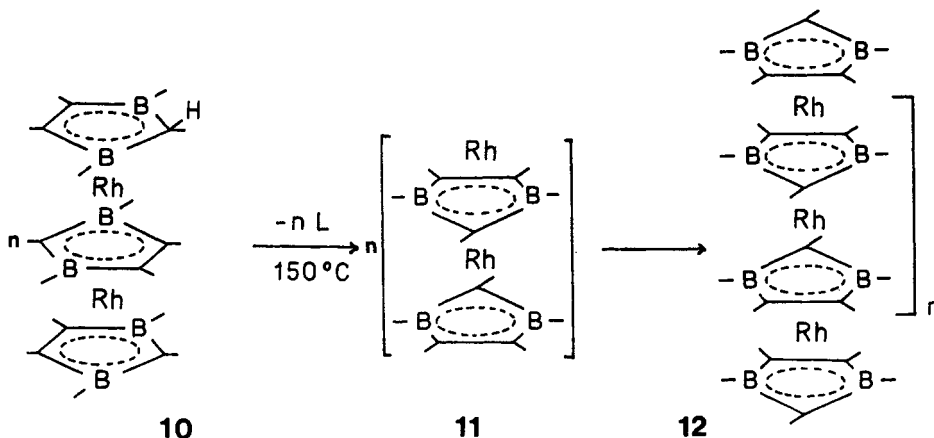
SYNTHESIS OF POLYDECKER SANDWICH COMPLEXES

For the formation of polydecker complexes suitable starting materials are needed. Reaction of a sandwich complex dianion with a metal dication should lead to the desired polymer, however the only complex dianion $[Pt(\underline{1a-H})_2]^{2-}$ is oxidized by Fe^{2+} ions. We have studied the polycondensation reactions of

tris(allyl)nickel-(μ -2,3-dihydro-1,3-diboroly) complexes **8**, which on heating to 120 - 150°C in vacuo yield black polymeric products **9**, bis(allyl)nickel and hexadiene (ref. 11,12). The material is thermally stable up to 500°C, but it is readily attacked by oxygen at ambient temperature. It does not dissolve in toluene, tetrahydrofuran or methylenechloride. **8b,c** are obtained from **1b,c** and Ni(C₃H₅)₂ at -80°C.



The second polymer was formed by heating the green rhodium triple-decker **10a** in vacuo. Elimination of the terminal 2,3-dihydro-1,3-diborol ligand **1a** occurs, leaving the reactive double stack **11** behind, which undergoes stacking to the black polymer. **12a** is less sensitive to oxygen than **9b**, it does not change on heating up to 500°C (ref.13).



STRUCTURE AND CONDUCTIVITY OF **9** AND **12**

Both polydeckers are amorphous and insoluble in organic solvents. Therefore a determination of the average molecular weight is not possible. EXAFS studies of **9** at 120, 300 and 340 K confirm the polydecker sandwich structure (ref.11,12). A 1:1 ratio of Ni to ligand was observed. At 120 K shorter Ni-B,C distances (2.15(2) Å) and longer Ni-B,C distances (2.56(2) Å) were observed, requiring two Ni...Ni distances, which were found at 3.35(2) and 3.8-3.9 Å, respectively. These findings may be interpreted with Peierls distortion. Preliminary results of an EXAFS study of the rhodium polymer **12** indicate a Rh...Rh distance of 3.6 Å (ref.14).

Conductivity measurement on the nickel polymer gave results which are characteristic for a hopping mechanism; the four-probe measurements at room temperature yielded a conductivity of 10⁻² S cm⁻¹, which is similar to that of germanium. In contrast the rhodium polymer is an insulator, the conductivity is 10⁻¹⁰ S cm⁻¹. The high sensitivity toward oxygen results in a drop of the conductivity when the sample is exposed to air. Thus the use of **9** as a semiconductor is hampered. However chemical alteration of the ligand and the switch to less electron - rich metals (e.g. iron) could have stabilizing effects.

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