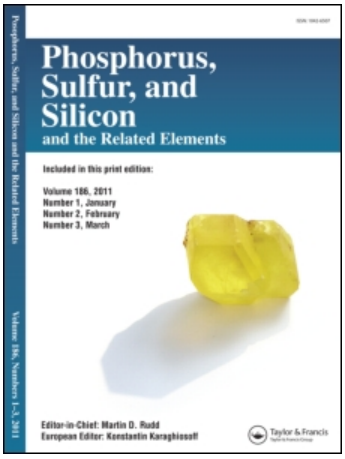

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[3]Ferrocenophanes Containing Heteroelements

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[3]FERROCENOPHANES CONTAINING HETEROELEMENTS

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Abstract The synthesis and characterization of 1,3-dichalcogena-[3]ferrocenophanes are described in which the central position of the triatomic bridge may be occupied by various main group and transition metal elements. Trinuclear [3]ferrocenophanes $Fe\{(C_5H_4E)Y[(EC_5H_4)_2Fe]\}_2$ (Y = P, As, Sb) were obtained from the reactions of 1,1'-bis(trimethylstannyl-chalcogenato)-ferrocenes, $Fe(C_5H_4E\text{-}SnMe_3)_2$ (E = S, Se, Te), with the trichlorides PCl_3, $AsCl_3$ and $SbCl_3$, respectively. Heterobimetallic complexes $[Fe(C_5H_4E)_2]M(L)(\eta^5\text{-}C_5Me_5)$ (M(L) = $Rh(PMe_3)$, $Ir(PMe_3)$, $Ir(PPh_3)$ and $Ir(CN^tBu)$) were prepared by reacting dilithium 1,1'-ferrocene-dichalcogenates $Fe(C_5H_4ELi)_2$ (E = S, Se, Te) with η^5-pentamethylcyclopentadienyl halfsandwich compounds $(\eta^5\text{-}C_5Me_5)M(L)Cl_2$. X-Ray data confirm the absence of bonding interactions between the two metals, Fe and M.

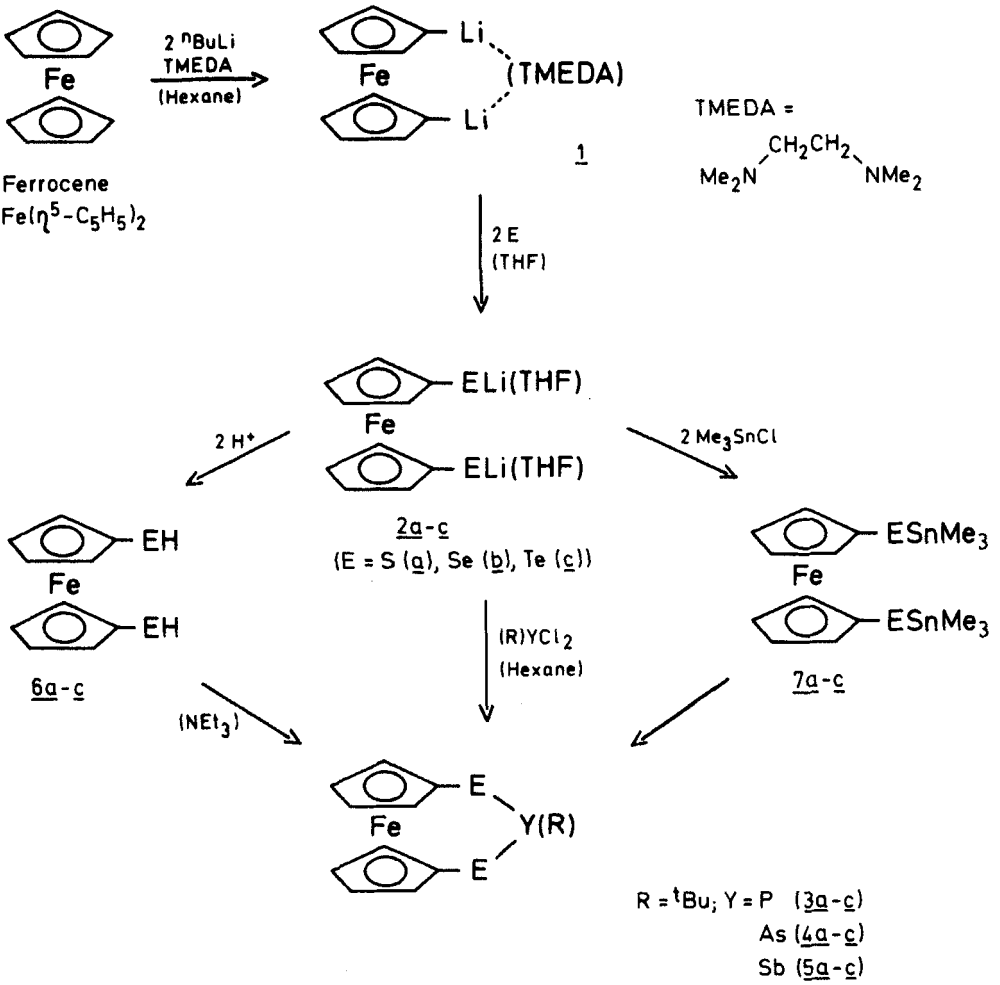
INTRODUCTION

Inorganic ring systems incorporating organometallic sandwich complexes of the ferrocene type contain a redox-active metal center in a sterically well-protected cavity. The smallest rings which are able to accommodate a metallocene unit without deformation of the sandwich structure (with its two planar, parallel cyclopentadienyl ligands) are [3]ferrocenophanes. Previous studies have shown that 1,3-dithia- and 1,3-diselena-[3]ferrocenophanes can be easily obtained[1] via TMEDA-stabilized 1,1'-dilithio-ferrocene (1)[4]. However, 1,3-ditellura-[3]ferrocenophanes have been unknown until recently[5,6].

SYNTHETIC PROCEDURES

Insertion of chalcogens E (E = S (a), Se (b), Te (c)) into the carbon-lithium bonds of 1 leads to dilithium 1,1'-ferrocene-dichalcogenates

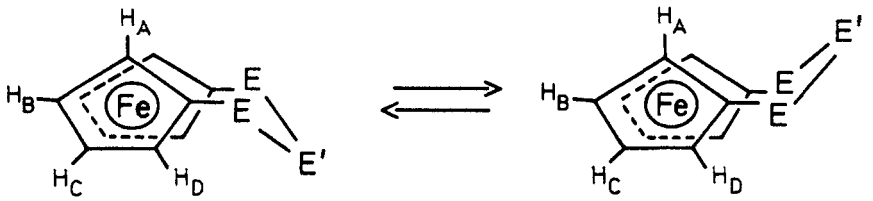
(2a[7], 2b[7], 2c) which are versatile precursor compounds for the synthesis of [3]ferrocenophanes. Thus, the reactions of 2a-c with organoelement dihalides $(R)YCl_2$ (Y = P, As, Sb; R = tert.butyl) can be used to prepare 1,3-dichalcogena-[3]ferrocenophanes containing phosphorus, arsenic and antimony in the central bridge position, e. g. 3a-c, 4a-c and 5a-c.



Other reactive educts which are available for the synthesis of 1,3-dichalcogena-[3]ferrocenophanes include the 1,1'-ferrocene dichalcogenols (E = S (6a)[4,7], Se (6b)[7,8], Te (6c)) and the 1,1'-bis(trimethylstannyl-chalcogenato)ferrocenes (7a-c).

MONONUCLEAR 1,3-DICHALCOGENA-[3]FERROCENOPHANES

All nine possible 1,2,3-trichalcogena-[3]ferrocenophanes $Fe(C_5H_4E)_2E'$ (E = S, Se, Te; E' = S, Se, Te) are known (cf.[6]). Their ^1H and ^{13}C NMR spectra are temperature-dependent in solution, indicating a restricted bridge reversal motion at higher temperatures (above 25°C)[9,10].

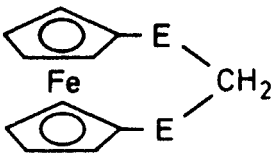


E = S, Se, Te
E' = S, Se, Te

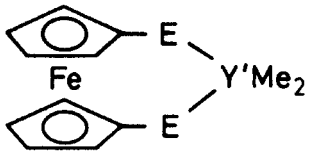
The static low-temperature conformers contain two sets of four different ring protons in an $[ABCD]_2$ spin system. In the high-temperature limiting ^1H NMR spectrum two pseudo-triplets are observed which correspond to an $[[AB]_2]_2$ spin system. Calculations suggest that the mechanism of the bridge inversion process involves a transition state with staggered cyclopentadienyl rings[10]. The bridge reversal barriers depend on the size of the bridge and decrease on going from the sulfur to the tellurium compounds, e. g. $Fe(C_5H_4S)_2S$ has the highest ($\Delta G^{\ddagger}$(298K) = 80.4 ±0.2 kJ·mol^{-1})[9] and $Fe(C_5H_4Te)_2Te$ the lowest (51.8 ±0.2 kJ·mol^{-1})[10] barrier.

The ^1H and ^{13}C NMR solution spectra of the 2-(tert.butyl)-phospha-, 2-(tert.butyl)arsa- and 2-(tert.butyl)stiba-[3]ferrocenophanes (3a-c, 4a-c and 5a-c) at room temperature are consistent with rigid structures. In all nine cases the ^1H NMR spectra show the $[ABCD]_2$ pattern characteristic of two sets of four magnetically inequivalent cyclopentadienyl protons, and five different carbon atoms are observed in the ^{13}C NMR spectra, as expected for a static trigonal-pyramidal bridge center. According to an X-ray structure analysis carried out for $Fe(C_5H_4S)_2As(Ph)$ the organic substituent occupies the less sterically crowded exo position[11].

On the other hand, rapid configurational interchange in solution at room temperature can be deduced from the ^1H and ^{13}C NMR spectra of the methylene-bridged 1,3-dichalcogena-[3]ferrocenophanes, $Fe(C_5H_4E)_2(CH_2)$ (E = S (8a)[7,12] ($\Delta G^{\ddagger}$(298K) = 47.90 ±0.23 kJ·mol^{-1})[13], Se (8b)[14], Te (8c)[6]), as well as for the dimethylsila- and dimethylstanna-bridged compounds 9a-c and 10a-c, respectively (E = S[12], Se[14] and Te). The typical $[[AB]_2]_2$ pattern showing two pseudo-triplets for the cyclopentadienyl protons is always observed in the ^1H NMR spectra if the bridging atom in the center is tetrahedrally coordinated (C_6D_6 solutions, 25°C).



8a-c

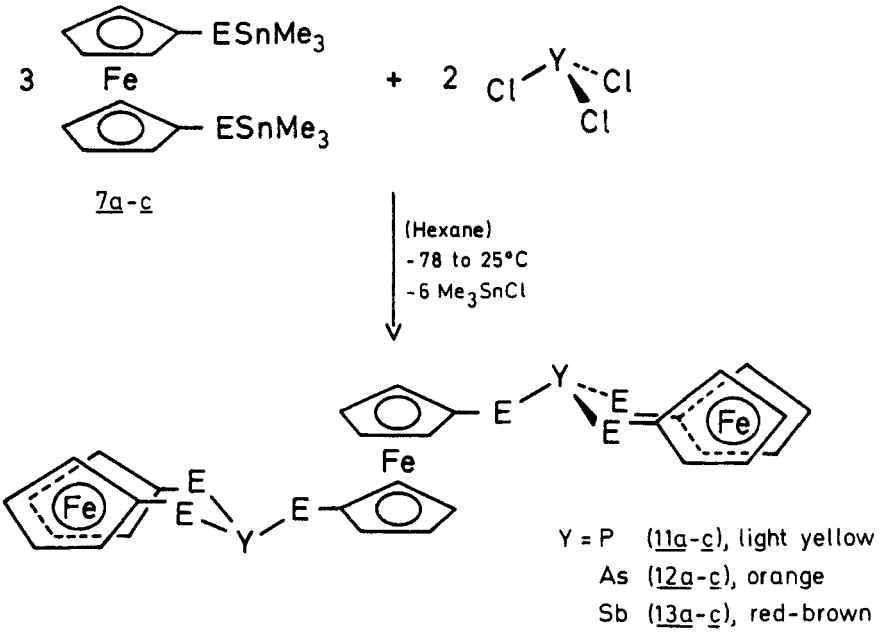


Y' = Si (9a-c)
Sn (10a-c)

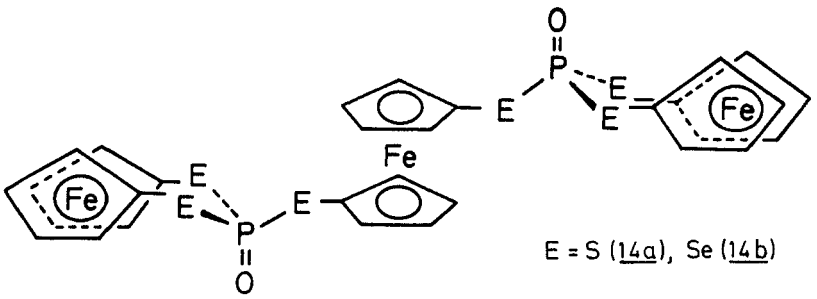
The $[[AB]_2]_2$ spin system leading to two pseudo-triplets in the ^1H NMR spectra is also characteristic of 2-bora-1,3-dichalcogena-[3]ferrocenophanes such as $Fe(C_5H_4E)_2B(NEt_2)$ (E = S (cf.[15]), Se, Te).

BI- AND TRINUCLEAR 1,3-DICHALCOGENA-[3]FERROCENOPHANES

The reactions of the 1,1'-bis(trimethylstannyl-chalcogenato)ferrocenes (7a-c) with trichlorides YCl_3 (Y = P, As, Sb) lead to trinuclear products in which two [3]ferrocenophane units are linked through a 1,1'-ferrocenedichalcogenato bridge:

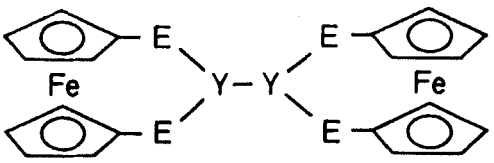


The trinuclear compounds are only sparingly soluble in organic solvents. The ^{1}H and ^{13}C NMR spectra (in C_6D_6 solution) indicate rigid structures. The phosphorus complexes 11a,b which are formed in high yields (80-90%) have been oxidized by m-chloro perbenzoic acid to give 14a,b:

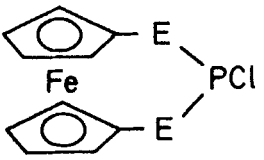


According to the Mössbauer spectra[16] of the trinuclear complexes 11a,b, 12a,b and 13a,b, only one type of iron center appears to be present, which might be taken as indication for charge delocalization within the molecule. If the dilithium 1,1'-ferrocene-dichalcogenates 2a,b

are used for the reactions with YCl_3 instead of 7a,b, the trinuclear products 11a,b and 12a,b are still formed preferentially, but binuclear side-products such as 15a,b and 16a,b can also be extracted from the black reaction mixtures using methylene chloride. In the phosphorus series, the precursor 2-chlorophospha-[3]ferrocenophanes have been isolated in low (ca 5%) yield.

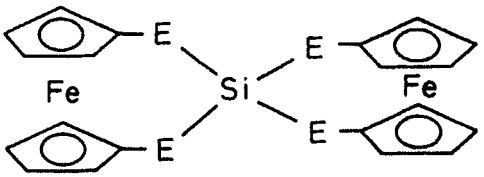


Y = P (15a,b); As (16a,b)



E = S (17a), Se (17b)

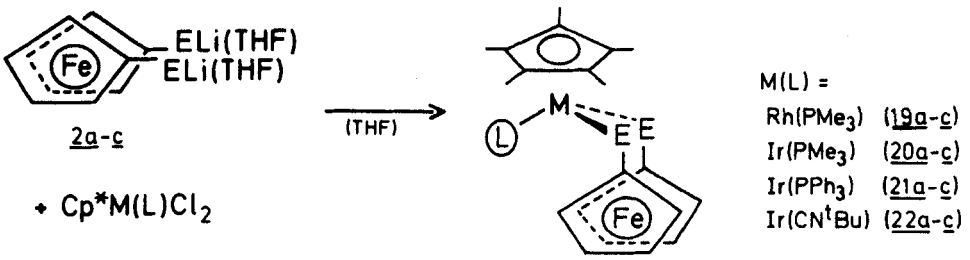
Attempts to synthesize trinuclear ferrocenophane derivatives containing silicon as the heteroatom have been unsuccessful. The reactions of 2a,b with $MeSiCl_3$ stopped at the stage of the mononuclear [3]ferrocenophanes $Fe(C_5H_4E)_2Si(Me)Cl$ (E = S, Se), whereas with Si_2Cl_6 spirosilanes 18a,b were obtained. The spirosilanes 18a-c are directly formed in the reactions of 2a-c with $SiCl_4$ in a molar ratio 2:1.



E = S (18a), Se (18b), Te (18c)

2-METALLA-1,3-DICHALCOGENA-[3]FERROCENOPHANES

Heterobimetallic compounds are formed when the 1,1'-ferrocenedichalcogenate anions from 2a-c are introduced as chelating (4-electron) ligands into the coordination sphere of a transition metal complex, e. g.



The halfsandwich compounds 19-22 are expected to be suitable models for the study of intramolecular interactions. The metal M has the formal oxidation state +3, and one hemisphere of the coordination shell is completely shielded by the voluminous η^5-pentamethylcyclopentadienyl ligand. The ^1H and ^{13}C solution NMR spectra at room temperature are, once more, characteristic of rigid [3]ferrocenophane structures.

The distances d(M·····Fe) are too long for direct bonding interactions in halfsandwich complexes such as $[Fe(C_5H_4S)_2]Rh(PMe_3)Cp^*$ (19a) (430.4 pm)[17], $[Fe(C_5H_4S)_2]Mo(NO)L$ (L = tris(3,5-dimethylpyrazolyl)borate) (414.7(2) pm)[18] and $[Fe(C_5H_4Se)_2]V(O)Cp^*$ (401.4(2) pm)[3] as well as in $[Fe(C_5H_4Se)_2]FeCl_2$ (387 pm)[19]. However, a weak iron-to- metal dative bond has been assumed on the basis of structural data for platinum(II) and palladium(II) complexes of the type $[Fe(C_5H_4S)_2]M(PPh_3)$ (M = Pd (287.8(1) pm)[20], Pt (293.5(2) pm)[21]) and for the ruthenocenophane complex $[Ru(C_5H_4S)_2]Ni(PPh_3)$ (286.4(1) pm)[22].

ACKNOWLEDGEMENT

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