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Preliminary communication

REACTIONS OF ORGANOSULPHUR COMPOUNDS WITH METAL ATOMS

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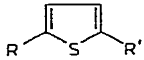
Summary

Co-condensation of metal atoms (Cr, Fe) and thiophenes,  ($R = R' = H$, Me; $R = H$, $R' =$ Me) at −196°C leads to desulphurization of the thiophene, and warm-up of the iron-thiophene co-condensate in a CO atmosphere produces tricarbonylferracyclopentadienetricarbonyliron, $C_4H_2RR'Fe_2(CO)_6$; co-condensation of CH_3SCH_2Cl with Pd atoms, followed by addition of Ph_3P in methylene chloride at −196°C, gives $(Ph_3P)Pd(\pi\text{-}CH_2SCH_3)Cl$, whereas Ni atoms dehalogenate CH_3SCH_2Cl.

The synthesis of bis(arene)metal complexes [1] and of π-allylnickel halides [2] have been notable successes in the preparation of organometallic complexes by the metal atom route. In this communication we describe experiments designed to extend the direct approach of metal atom syntheses to the preparation of metal complexes with (a) thiophenes and (b) the CH_3SCH_2 group**. This is the first report of reactions of organosulphur compounds with metal vapours, although the desulphurization of tetrahydrothiophene by atomic carbon has been described [3].

The direct reaction of metal vapours with arenes is a versatile route to bis(arene)metal complexes [4], which has recently been applied to the synthesis of bis(2,6-dimethylpyridine)chromium [5]. Although complexes of thiophenes with the $Cr(CO)_3$ group are well known [6], no neutral bis(thiophene) metal compounds have been reported [7]***. We have therefore investigated the reactions of thiophenes with Fe and Cr vapours at −196°C.

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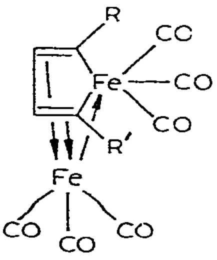
**The ligands (a) and (b) can be regarded as sulphur analogues of arenes and the methylallyl group, respectively, in which the sulphur atom has replaced a C=C group.

***In ref. 7 is described the electrochemical reduction of the bis(tetramethylthiophene)iron(II) cation and it is suggested to be possible to isolate bis(tetramethylthiophene)iron(0).

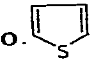
Metal atom-thiophene reactions

The co-condensation of Fe atoms with thiophene, 2-methyl- or 2,5-dimethylthiophene at −196°C gives a plum-coloured matrix which retains its colour on melting up to ca. −20°C. In contrast to bis(arene)iron complexes [8], the thermal stability of this coloured complex appears to be independent of alkyl substitution on the thiophene. When the Fe/thiophene co-condensate was allowed to warm up in an atmosphere of CO, orange-brown crystals of I were isolated in ca. 5% yield and identified by comparison of their IR, NMR and mass spectra with authentic samples prepared from the appropriate thiophene and either $Fe(CO)_5$ [9] or $Fe_3(CO)_{12}$ [9,10].

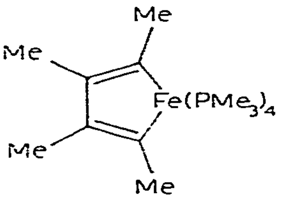


(I)

The metal residues, after washing with benzene and drying, contained 11—17% sulphur. Similarly, co-condensation of Cr atoms with thiophenes at −196°C resulted in desulphurization of the thiophene (10—13.5% sulphur in the metal residues) and no organometallic product was isolated.

The following experiments indicate that desulphurization occurs immediately on co-condensation rather than formation of an unstable dithiophenemetal complex followed by desulphurization on warm-up. (i) Whereas addition of cyclopentadiene to an Fe/benzene co-condensate at −196°C produces ferrocene in 40% yield [1], no ferrocene is obtained when an Fe/thiophene co-condensate is treated in a similar manner. (ii) When the Cr/thiophene co-condensate is allowed to warm up from −196°C in a CO atmosphere, no  $Cr(CO)_3$ was isolated.

Addition of 1,3-butadiene, 1,5-cyclooctadiene, or trimethylphosphine to the Fe/thiophene co-condensate at −196°C, followed by warming to −100°C yields red solutions which decompose above −20°C. It was hoped that the trimethylphosphine reaction would yield an analogue of the volatile iron heterocycle II [11] but the instability of the reaction product precluded isolation.



(II)

CH_3SCH_2 Complexes

The ability of the CH_3SCH_2 group to function as a 3-electron ligand was established some years ago [12], and the isolation of some π-CH_3SCH_2 palladium derivatives has recently been reported [13]. We describe here studies of the possible synthesis of π-CH_3SCH_2 derivatives of nickel and palladium by the reaction of CH_3SCH_2Cl with the appropriate metal vapour at −196°C.

When nickel vapour is co-condensed with CH_3SCH_2Cl at −196°C dehalogenation occurs to give nickel(II) chloride and 2,5-dithiahexane. With Pd atoms and CH_3SCH_2Cl, the red condensate evolves bubbles as it warms up and the gaseous products have been shown to contain ethylene (IR). Addition of Ph_3P in methylene chloride to the co-condensate at 20°C produced orange crystals of $(Ph_3P)_2Pd(SCH_3)Cl \cdot xCH_2Cl_2$ (from CH_2Cl_2/Et_2O) identified by NMR and chemical analysis. The migration of SCH_3 to palladium can be preempted by addition of Ph_3P/CH_2Cl_2 to the co-condensate at −196°C. Yellow crystals of $(Ph_3P)Pd(CH_2SCH_3)Cl$ were formed in 21% yield, after recrystallization from CH_2Cl_2/Et_2O at −78°C. Found: C, 51.4; H, 4.5; Cl, 8.3. $C_{20}H_{20}ClPPdS$ calcd.: C, 51.6; H, 4.3; Cl, 7.6%.

^1H NMR (CH_2Cl_2) at 25°C showed signals at δ 2.23s, 2.70s and 7.6m ppm corresponding to CH_3S, CH_2S, and $(C_6H_5)_3P$ protons, respectively, in the expected intensity ratios (cf. lit. [13]: ^1H NMR ($CDCl_3$) at −30°C, δ 2.34 ppm (d, J(HP) 4 Hz) and δ 2.68 ppm (d, J(HP) 2 Hz)). These authors report that each signal coalesces to a singlet at ca. 40°C, probably due to rapid phosphine exchange [14]. These results are best explained by an initial oxidative insertion of Pd into the C—Cl bond of CH_3SCH_2Cl [14], as depicted in Scheme 1.

$$\begin{tikzcd}
\mathrm{Pd_g + CH_3SCH_2Cl} \arrow[r, "\text{cocondense}", "-196^\circ\mathrm{C}"'] & {} \\
{\mathrm{[ClPd(CH_2SCH_3)]_2\,?}} \arrow[r, "20^\circ\mathrm{C}"] \arrow[d, "\begin{array}{l}\mathrm{PPh_3 + CH_2Cl_2}\\ \text{warm to } 20^\circ\mathrm{C}\end{array}"] & {\mathrm{[ClPdSCH_3]_n\,? + C_2H_4} + \text{hydrocarbons}} \arrow[d, "\mathrm{PPh_3 + CH_2Cl_2}"] \\
\mathrm{(PPh_3)Pd(CH_2SCH_3)Cl} & \mathrm{(Ph_3P)_2Pd(SCH_3)Cl \cdot \mathit{x}CH_2Cl_2}
\end{tikzcd}$$

SCHEME 1

Thus initial studies of the reactions of organosulphur compounds with metal vapours suggest that simple metal—ligand interactions may be complicated by the affinity of metals for sulphur leading to processes such as desulphurization or RS migration to the metal. Specific techniques will have to be developed to prevent such processes e.g. addition of ligands to ensure coordinative saturation of the metal, or reduction of the basicity of the organosulphur ligand by complexation prior to the co-condensation reaction.

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