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1-Arsa- and 1,1′-Diarsaferrocenes

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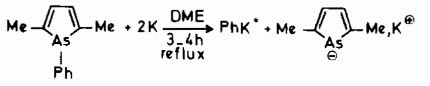
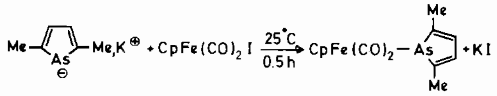
The discovery of arsacymantrenes [1, 2] has proven that arsolyl anions were able to give stable π-aromatic complexes with transition metals. Thus we were prompted to investigate the synthesis of 1-arsa and 1,1-diarsaferrocenes which were potentially the most interesting compounds among this new class of complexes.

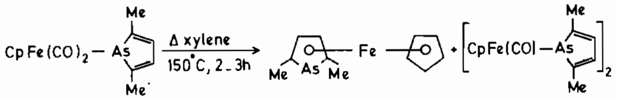
In a preliminary attempt to obtain 2,5-dimethyl-1-arsaferrocene we allowed to react directly 2,5-dimethyl-1-phenylarsole [3] with an equimolecular amount of dicyclopentadienyl tetracarbonyl diiron at 150 °C in boiling xylene according to a procedure which was successfully developed for the synthesis of phosphaferrocenes [4, 5]. The formation of minute amounts of arsaferrocenes was detected by ^{1}H NMR but we were unable to recover it in a pure state. Thus we tried an indirect approach. At first the arsole was reacted with potassium in dimethoxyethane to afford the corresponding 2,5-dimethylarsolylpotassium [6]:



The arsolyl anion was then was allowed to react *in situ* with cyclopentadienyl dicarbonyliron iodide:



The red σ-complex thus obtained was purified by chromatography (silica gel, benzene–pentane 50:50) and only characterized by I.R. spectroscopy: ν(CO) = 2010, 1965 cm^{-1} (hexadecane) (see the corresponding data for a similar phospholyl complex [7]). The decomposition of this σ-complex in boiling xylene yielded two new arsolyl complexes:



2,5-Dimethylarsaferrocene (overall yield ≅30%) is an orange solid (crystallized in methanol –70 °C; m.p. ≅70 °C) which is eluted on silica gel by a pentane–benzene mixture (80:20). It was unambiguously characterized by elemental analysis and spectroscopy. In the mass spectrum (15 eV) the molecular peak (m/2 276) is also the base peak. The ^{1}H and ^{13}C NMR data are given in the Table.

The dimeric σ-complex (overall yield 10%) is a green solid (crystallized in methanol 25 °C; m.p. 250 °C with decomposition) which is eluted on silica gel by benzene. It is a mixture of "*cis*" and "*trans*" complexes ("*cis*": "*trans*" ratio ≅90:10) in which the arsolyls act as 3-electron bridging ligands through their arsenic atoms. In the "*cis*" complex, since the arsolyl planes are quite probably perpendicular to the Fe••Fe axis, two methyl(Me) and two CH groups (one on each arsolyl) are on the same side of the Fe–As–Fe–As moiety as the cyclopentadienyl groups. Thus they are probably more shielded than the two methyl (Me′) and two CH groups on the other side of this moiety. On the contrary in the "*trans*" complex both methyl and CH groups are fully equivalent. A similar situation was encountered in the analogous dimeric complexes in which the arsolyls were replaced by AsMe$_2$ ligands [8]. The ^{1}H NMR (100 MHZ, CDCl$_3$, internal TMS) and IR (KBr) data are given hereafter:

TABLE. NMR Data[a] of Arsa- and Diarsaferrocenes.

	2,5-Dimethyl-1-arsaferrocene		2,2′,5,5′-Tetramethyl-1,1′-diarsaferrocene	
	^{1}H NMR	^{13}C NMR	^{1}H NMR	^{13}C NMR
CH$_3$	1.93	19.24	1.91	18.90
C$_\beta$H	5.09	82.62	5.09	86.10
C$_\alpha$		106.60		108.50
C$_5$H$_5$	4.18	71.24		

[a] δ in ppm, CDCl$_3$, internal TMS.

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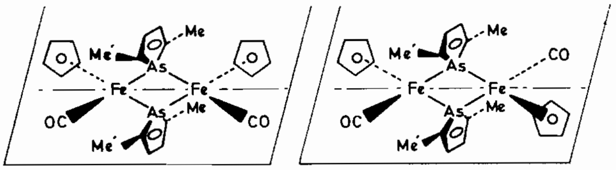
*PhK is destroyed by boiling DME.

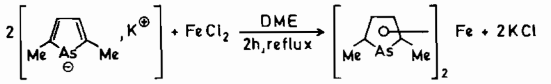


"cis" complex "trans" complex

^{1}H NMR:	Me δ 2.50 and 2.78 ppm	Me δ 2.67 ppm
	CH δ 6.09 and 6.37 ppm	CH δ 6.18 ppm
	Cp δ 3.98 ppm	Cp δ 4.12 ppm
IR	ν(CO) 1926 cm^{-1}	ν(CO) 1899 cm^{-1}

The CH elemental analysis agrees well with the proposed formula. The mass spectrum (70 eV or 15 eV) does not contain the molecular peak; the highest peak of m/e 397 (I = 3–4%) corresponds to the loss of the two carbonyls and of one of the two arsolyl bridges; the base peak of m/e 276 corresponds to 2,5-dimethylarsaferrocene.

The synthesis of 2,2′,5,5′-tetramethyl-1,1′-diarsaferrocene was much simpler: we used the same approach as for the preparation of 1,1′-diphosphaferrocenes [9]. We just reacted 2,5-dimethylarsolylpotassium with anhydrous ferrous chloride:



The diarsaferrocene (overall yield ≅40%) is a red solid (m.p. ≅34 °C) which is eluted on silica gel by a pentane–benzene mixture (80:20). It was characterized by elemental analysis and spectroscopy. In the mass spectrum (70 eV) the molecular peak (m/e 336) is once again the base peak. The ^{1}H and ^{13}C NMR data are given in the Table. The close analogy with the corresponding monoarsaferrocenes is obvious from these data.

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