*Journal of Organometallic Chemistry*, 344 (1988) C31–C34
Elsevier Sequoia S.A., Lausanne – Printed in The Netherlands

**Preliminary communication**

# $Pd(BF_4)_2$ complexes of 1,1′-bis[(alkyl- or aryl-)thio]- and 1,1′-bis(diphenylphosphino)-ferrocenes. Bond formation between the Fe and Pd atoms

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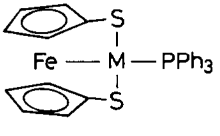
(Received November 13th, 1987)

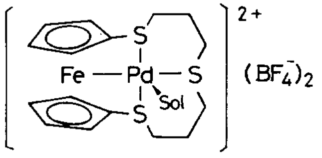
## Abstract

1,1′-Bis[(alkyl- or phenyl-)thio]- and 1,1′-bis(diphenylphosphino)-ferrocenes react with $(CH_3CN)_4Pd(BF_4)_2$ in the presence of triphenylphosphine to give 1/1 complexes in good yields. Spectral data have confirmed the presence of an Fe–Pd dative bond in these complexes.

It was first reported by Bishop and Davison [1] that ferrocene derivatives with donor atoms at 1,1′-positions can coordinate to some transition metals through donor atoms. After this discovery, many such complexes were prepared, but no interaction between the iron atom of the ferrocene moiety and the metal atom coordinated to the donor atoms was found [2]. Recently, the palladium(II) (**1a**) [3] and platinum(II) complexes (**1b**) [4] of 1,1′-ferrocenedithiolate were reported to possess a weak dative bond between the iron atom and the palladium(II) or platinum(II) atom. The $Pd(BF_4)_2$ complexes of trithia[$n$]ferrocenophanes ($n = 7$ or 9) (**2**) were also reported to contain a similar Fe–Pd bond [5]. Here we describe the synthesis of $Pd(BF_4)_2$ complexes of 1,1′-bis[(alkyl- or phenyl-)thio]- and 1,1′-bis(diphenylphosphino)-ferrocenes having an Fe–Pd dative bond.

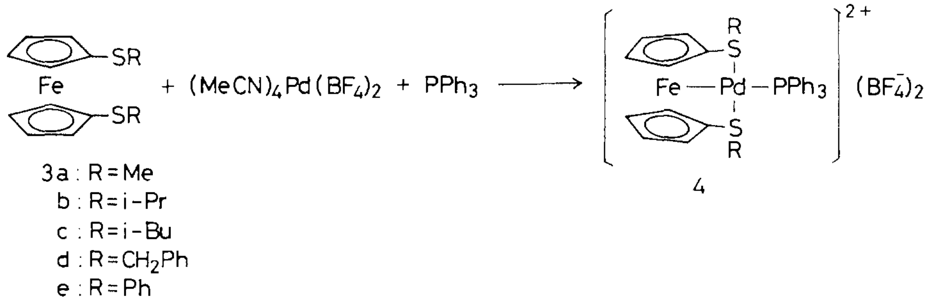


1a : M = Pd
b : M = Pt

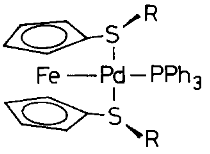


2

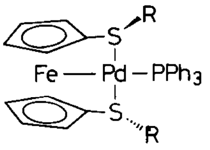
1,1′-Bis(methylthio)ferrocene (**3a**) reacts with $(CH_3CN)_4Pd(BF_4)_2$ in acetone in the presence of one equivalent of triphenylphosphine to give a 1/1 cationic complex, triphenylphosphine[1,1′-bis(methylthio)ferrocene-*S,S′,Fe*]palladium(II) tetrafluoroborate (**4a**), as fine black needles, m.p. 252° C (dec). In a similar manner, the isopropyl (**4b**), isobutyl (**4c**), benzyl (**4d**), and phenyl derivatives (**4e**) were obtained in good yields. Complex **4b** was also obtained in moderate yield from the reaction of dichloro[1,1′-bis(isobutylthio)ferrocene-*S,S′*]palladium(II) with two equivalents of $AgBF_4$, in the presence of triphenylphosphine. In the IR spectrum of **4a**, for example, the out-of-bending vibration, which is diagnostic of the oxidation state of ferrocene, was observed at 848 $cm^{-1}$, the position of which was shifted considerably to high frequency compared with the free ligand **3a** (824 $cm^{-1}$) and the corresponding $PdCl_2$ complex (832 $cm^{-1}$). This suggests that the iron atom of the ferrocene moiety in **3a** is significantly perturbed by the complexation with $Pd(BF_4)_2$. For complexes **1a** [4] and **2** the corresponding bands appeared at 838 and 844 $cm^{-1}$ [5], respectively. In the visible spectrum of **4a**, three adsorption bands were observed at 380 9ε 5730), 450 (16500), 580 nm (sh, 484). The spectrum is very similar to that of **2**, in which an Fe–Pd bond is suggested.



The $^1H$ NMR spectrum (400 MHz, acetone-$d_6$) of all the complexes, **4a–4e**, gave two sets of four pseudo-singlets of equal intensity for the ferrocene ring protons. The shapes of the remaining regions of the spectra were dependent on the nature of the R-substituent on sulfur. For the methyl derivatives **4a**, for example, the major set contains four signals at $\delta$ 6.26, 6.07, 4.13, and 3.73 ppm. The minor set consists of four signals at $\delta$ 6.32, 5.96, 4.19, and 3.83 ppm. In both sets, the four ring proton signals were separated into two signals at lower field near $\delta$ 6.0 ppm, and two signals at higher field near $\delta$ 4.0 ppm, which were assigned to the $\beta$- and $\alpha$-protons of the ferrocene rings, respectively [4]. Such a large separation between the $\alpha$- and $\beta$-protons of the Cp-rings of a ferrocene ring has never been observed in the $PdCl_2$ complexes of **3** [6,7]. This can only be explained in terms of the anisotropy of the metal–metal bond between the Fe atom of a ferrocene nucleus and the palladium(II) atom coordinated to the sulfur atoms in the substituents at the 1,1′-positions, because a similar separation was observed in the complexes **1a** and **1b**, which were found by X-ray diffraction study to contain a weak dative bond between the Fe atom of the ferrocene moiety and the metal atom coordinated to the donor atoms [3,4]. That the ferrocene ring protons in the complexes **4a–4e** occur as two sets of the four different environments at room temperature indicates the presence of two isomers, *syn*- (**4A**) and *anti*-bonded (**4B**). This indicates the rigidity of the structure of the complexes



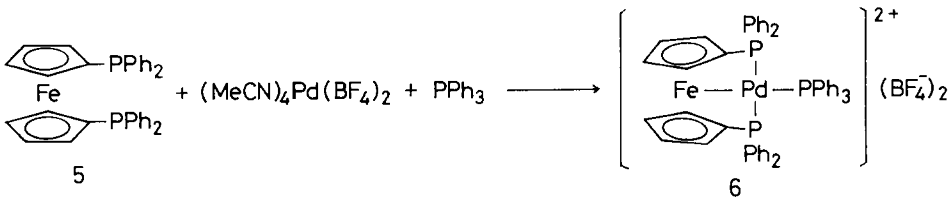
4A



4B

**4a–4e**, in contrast to the corresponding $PdX_2$ complexes which showed their static spectra only below $-30\,^\circ$C [7]. That there was no interconversion of the isomers **4A** and **4B** at room temperature may be also consistent with the presence of a bonding interaction between Fe and Pd$^{II}$ atoms. The isomer ratio could be also estimated from the $^{31}$P NMR spectrum of **4a–4e**. The major and the minor isomers of **4a**, for example, produce signals at $\delta$ 23.9 and 23.6 ppm (with an integration ratio of 2/1), respectively relative to phosphoric acid as the external reference. The major isomer in this series of complexes seems to be the *anti*-isomer in light of the steric hindrance by the R substituents.

Similarly, 1,1′-Bis(diphenylphosphino)ferrocene (**5**) reacts with $(CH_3CN)_4Pd(BF_4)_2$ in the presence of triphenylphosphine to give a 1/1 complex (**6**) as dark green needles in moderate yield. In the $^1$H NMR spectrum (90 MHz, acetone-$d_6$) of **6**, the Cp ring protons produce two broad singlets at $\delta$ 5.98 and 4.85 ppm. This pattern of Cp ring proton resonances is different from that of the corresponding complexes $PdCl_2$ [2,8] and (NBD)Rh$^I$ [9]. This suggests that complex **6** has a symmetrical structure and therefore likely to have dative Fe–Pd bond. The electronic spectrum of **6** showed three absorption maxima at 380 ($\epsilon$ 14500), 477 (7300), 624 nm (sh, 1000). This spectrum is rather similar to that of **4**, although the relative intensities of the peaks are somewhat different from each other, indicating that there is a structural similarity between **4** and **5**.



**Acknowledgements.** We thank Dr. Yoshiharu Toida and Dr. Misako Imachi, Bulker Japan Co. INC., for 400 MHz $^1$H NMR measurement. This work is supported by a Grant-in-Aid for Scientific Research No. 61540362 from the Ministry of Education, Science, and Culture of Japan.

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