Journal of Organometallic Chemistry, 377 (1989) 327–337
Elsevier Sequoia S.A., Lausanne – Printed in The Netherlands
JOM 20284

Synthesis and some properties of $Pd(BF_4)_2$ and $Pt(BF_4)_2$ complexes of 1,1′-bis[(alkyl- or phenyl-)chalcogeno]ferrocenes

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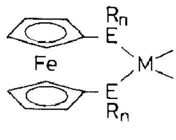
(Received June 7th, 1989)

Abstract

1,1′-Bis(alkylthio and -phenylthio)ferrocenes react with $(MeCN)_4Pd(BF_4)_2$ in the presence of triphenylphosphine to give stable 1/1 complexes in good yields. 1,1′-Bis(alkylseleno)ferrocenes and 1,1′-bis(phenylthio and phenylseleno)ferrocenes to give similar 1/1 complexes. Some platinum analogs were prepared from the reaction of the corresponding dichloro-complexes with $AgBF_4$ in the presence of triphenylphosphine. The spectral data indicate that there is a dative metal–metal bond between the iron atom of the ferrocene and the palladium(II) or platinum(II) atom in these complexes.

Introduction

Recently, much interest has been focused on the chemistry of heterobimetallic complexes [1,2]. Such species are expected to have a unique reactivity because of the adjacent metals. Ferrocene derivatives with potential donor atoms at the 1,1′-positions are capable of coordinating to some transition metals through the donor atoms and are among the best organometallic ligands for preparing hetero bimetallic complexes. The first such complexes (**1**) were prepared by Bishop and Davison [3], and since then many have been prepared [4–7]. Some of these complexes exhibit high catalytic activity for selective cross-coupling [8], selective hydroformylation [9], and asymmetric hydrogenation [10] reactions. However, no interaction between the iron atom of a ferrocene moiety and the metal atom coordinated to the donor atoms has been found. Recently, the palladium(II) (**2a**) [11] and platinum(II) complexes (**2b**) [12] of 1,1′-ferrocenedithiolate were synthesized and were shown by X-ray diffraction to possess a weak dative bond between the iron and the palladium (II) or platinum(II) atoms. The $Pd(BF_4)_2$ complexes of trithia[*n*]ferrocenophanes ($n = 7$ or 9) (**3**) have been reported to have a similar Fe–Pd bond [13,14]. In these complexes, the Pd^{II} or Pt^{II} atom should show a unique chemistry. Here we describe the synthesis and the various spectra of the $Pd(BF_4)_2$ and $Pt(BF_4)_2$ complexes of 1,1′-bis[(alkyl- or phenyl)chalcogeno]ferrocenes, which have dative Fe–Pd and Fe–Pt bonds, respectively. [15].



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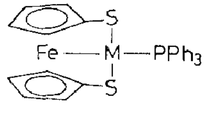
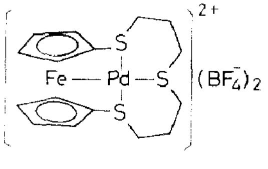


2a : M = Pd
2b : M = Pt



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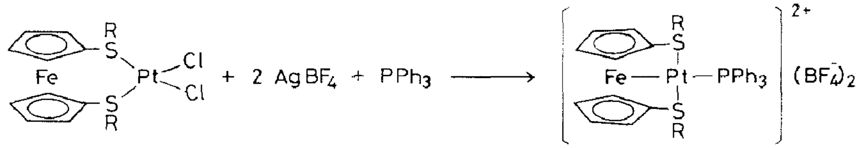
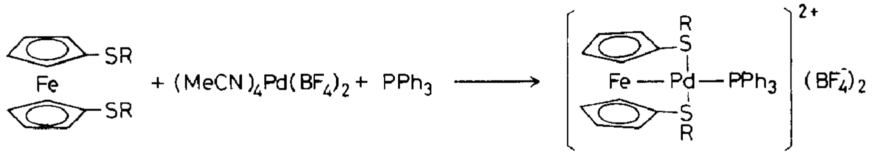
Results and discussion

Treatment of 1,1′-bis(methylthio)ferrocene (**4a**) with $(MeCN)_4Pd(BF_4)_2$, that had been prepared previously from the reaction of $(MeCN)_2PdCl_2$ with $AgBF_4$ in acetone [16], in the presence of one equivalent of triphenylphosphine gave a cationic 1/1 complex, triphenylphosphine[1,1′-bis(methylthio)ferrocene-*S*,*S*,*Fe*]palladium(II) tetrafluoroborate (**5a**), as stable, fine needles, m.p. 258°C (dec.), in good yield. Similarly, the isopropyl (**5b**), n-butyl (**5c**), isobutyl (**5d**), benzyl (**5e**), and phenyl derivatives (**5f**) have been obtained in moderate to good yields. The complex (**5g**) of 1,10-dithia[10]ferrocenophane [17] was also prepared. The novel 1,1′-bis(t-butylthio)ferrocene was allowed to react with $(MeCN)_4Pd(BF_4)_2$, though no pure product could be isolated, the presence of a similar 1/1 complex (**5h**) was confirmed from the ^1H NMR spectrum. Complexes **5b** and **5d** were alternatively prepared in moderate yields from the reaction of the corresponding dichloro[1,1′-bis(alkylthio)ferrocene-*S*,*S*]palladium(II) with two equivalents of $AgBF_4$ in the presence of one equivalent of triphenylphosphine. Use of this route gives the platinum analogs, **6a** (R = Me) and **6d** (R = i-Bu), starting from the corresponding dichloro[1,1′-bis(alkylthio)ferrocene-*S*,*S*]platinum(II) [7] in moderate yields. The successful double abstraction of the chloro ligand from the $PtCl_2$ complexes with $AgBF_4$ does not preclude the fact that two chloro ligands could be abstracted by a Ag^+ ion in the presence of the nitrogen donor from dichloro[1,1′-bis(diphenylphos-



6a : R = Me
6d : R = i-Bu



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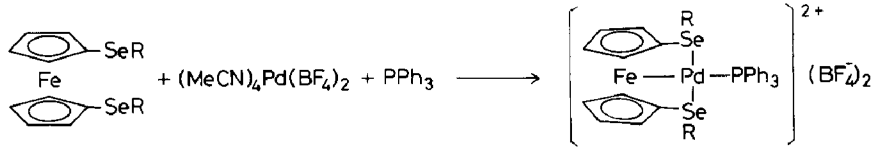
a : R=Me, b : R=i-Pr, c : R=n-Bu, d : R=i-Bu, e : R=CH_2Ph

f : R=Ph, g : R,R=$(CH_2)_6$ h : R=t-Bu



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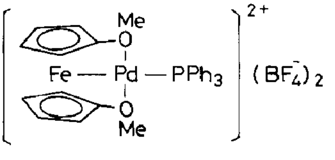
8a : R=Me

8f : R=Ph

phino)ferrocene-*P*,*P*]platinum(II) [18]. The two selenium analogs of the complex **5**, **8a** (R = Me) and **8f** (R = Ph), have been prepared by the reaction of 1,1′-bis(methylseleno)- and 1,1′-bis(phenylseleno)ferrocene [19] with $(MeCN)_4Pd(BF_4)_2$ in the presence of one equivalent of triphenylphosphine. In a similar reaction, 1,1′-dimethoxylferrocene with $(MeCN)_4Pd(BF_4)_2$ in acetone, a cationic complex (**9a**) was isolated as unstable, fine needles in excellent yield; **9a** was confirmed by elemental analysis to be a 1/1 complex, but could not give satisfactory spectral data because of its instability. The results are listed in Table 1.



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In the IR spectra of the Pd complexes described above, the out-of-plane bending vibration, which is indicative of the oxidation state of ferrocene [20], is shifted considerably to higher frequency compared with the free ligands and the corresponding $PdCl_2$ complexes as shown in Table 2. For example, the out-of-plane bending vibration of **5a** is observed at 848 cm^{-1}, whereas those of the corresponding free ligand and $PdCl_2$ complex appear at 824 and 832 cm^{-1}. This suggests that the iron atom of the ferrocene moiety of **5a** is significantly perturbed by the complexation with $Pd(BF_4)_2$. A similar large shift to high frequency of this band has also been observed in complexes **3** (844 cm^{-1}) [13,14] and **2a** (830 and 838 cm^{-1}) [11]. The presence of a dative Fe–Pd bond in **2a** was confirmed by an X-ray diffraction study [11,21]. The features of the selenium analogs **8a** and **8f** and of the Pt^{II} analogs **6a** and **6d**, differ little from those of the Pd complexes **5a**–**5g**.

The electronic spectra of the Pd(II) complexes showed three absorption in the visible region (Table 2). The absorption maxima for **5a** are observed at 580sh (ϵ

Table 1

Melting points, yields, and elemental analyses

Compounds	M.p. (°C)	Yield (%)	Anal. (Found (calcd.) (%))	
			C	H
5a	258(dec.)	93	43.93	3.66
			(43.91)	(3.56)
5b	179	79	46.70	4.49
			(46.59)	(4.25)
5c	200	76	47.78	4.84
			(47.80)	(4.67)
5d	215	61	48.03	4.57
			(47.80)	(4.67)
5e	243(dec.)	66	52.42	4.41
			(52.43)	(4.20) [a]
5f	202	56	50.89	3.65
			(50.86)	(3.56)
5g	260(dec.)	91	48.01	4.50
			(47.90)	(4.36)
6a	270(dec.)	89	40.98	3.71
			(40.98)	(3.65) [a]
6d	227	46	44.68	4.50
			(44.93)	(4.29)
8a	214(dec.)	67	39.41	3.20
			(39.45)	(3.20)
8f	222(dec.)	56	44.95	3.17
			(45.00)	(3.44) [b]
9a	184(dec.)	67	45.97	3.63
			(45.70)	(3.71)

[a] Includes one equivalent of acetone. [b] Includes half an equivalent of dichloromethane.

484), 450 (16500), and 380 nm (5730). This absorption pattern is similar to that of the bisthiolate complex **2a**, although all absorptions are shifted to longer wavelengths. Thus, the structural features which are similar to those of **2a** are kept in the

Table 2

The out-of-plane bending vibration and visible spectra

Compounds	Out-of-plane bending vibration (cm^{-1})	λ_{max} (nm)
5a	848	580sh(484) 450(16500) 380(5730)
5b	848	580sh(436) 466(11100) 376(4930)
5c	856	580sh(467) 450(10300) 366(3800)
5d	842	580sh(400) 450(15600) 358(5580)
5e	846	580sh(361) 452(14300)
5f	852	604sh(348) 466(11100) 366(5240)
5g	842	640sh(489) 490(11900) 402(4710)
6a	850	480sh(583) 378(11500)
6d	851	480sh(583) 380(13700)
8a	843	600sh(637) 477(14200) 378(7000)
8f	846	620sh(200) 492 (5070) 382(1560)
9a	824, 842	778 (340) 523 (319) 340(5238)
2a	830, 838	515sh(709) 402 (5960) 360(5970)

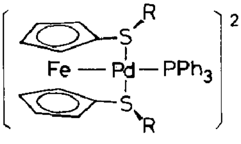
Table 3

The ^1H chemical shifts of the ferrocenyl ring protons (400 MHz, acetone-d_6)

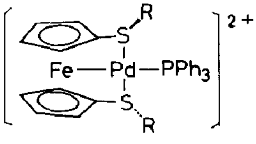
Compounds	*Anti*-isomer				*Syn*-isomer				*Anti*/*syn* ratio
	$H_{2,5}$		$H_{3,4}$		$H_{2,5}$		$H_{3,4}$		
5a	3.72	4.13	6.06	6.26	3.83	4.19	5.96	6.32	2.0
5b	3.79	4.27	6.14	6.22	3.88	4.64	5.79	6.58	1.0
5c	3.71	4.11	6.12	6.28	3.82	4.19	6.04	6.31	2.0
5d	3.73	4.11	6.11	6.27	3.82	4.18	6.06	6.27	1.5
5e	3.63	4.36	6.01	6.25	3.81	4.38	6.10	6.18	2.0
5f	3.79	4.30	5.76	6.45	4.05	4.15	6.16	6.19	6.5
5g	–	–	–	–	3.98	4.41	6.03	6.38	0.0
5h	3.82	4.03	6.00	6.16	3.95	4.07	5.89	6.23	1.5
6a	3.96	4.33	6.19	6.36	4.02	4.39	6.10	6.41	2.0
6d	3.96	4.32	6.21	6.35	4.00	4.39	6.20	6.32	1.5
8a	3.60	4.02	6.00	6.15	3.94	4.04	5.88	6.22	2.0
8f	3.72	4.32	5.59	6.47	4.00	4.19	6.07	6.12	8.0

cationic complexes **5**. Either of the absorptions, 580 or 450 nm seems to be related to the formation of the Fe–Pd dative bond, because square-planar Pd^{II} complexes show no absorption above 370 nm [16] and the free ligand shows only a weak absorption at 440 nm (ϵ 100). The same absorptions in **8a** and **8f** are shifted slightly ($\Delta \sim 20$ nm) to longer wavelengths region compared with those in **5a** and **5f**, respectively. The shift to the longer wavelengths may reflect the decrease in the bonding interaction owing to the decreased donor ability of the hetero-atom in the order: $S^- > SR > SeR$.

The ^1H NMR spectra (400 MHz, acetone-d_6) of all the complexes **5a–5f, 6a, 6d, 8a**, and **8f** show two sets of four pseudo-singlets of equal intensities for the Cp-ring protons of the ferrocene moiety at room temperature (Table 3). The shapes of the remaining regions of the spectra were dependent on the nature of the R-substituent on the sulfur. For example, the n-butyl derivatives **5c** show four signals at δ 6.28, 6.12, 4.11, and 3.71 as the major set for the ferrocene ring protons; the minor set consists of four signals at δ 6.31, 6.04, 4.19, and 3.82. The appearance of four signals for the ferrocene ring protons indicates that the ferrocene ring protons are in an unsymmetrical arrangement. The ^1H NMR spectrum of the complex **5g**, whose ligand has a bridging alkyl chain containing the same number of carbon atoms between the two sulfur atoms as that in **5c**, however, shows only one set of four proton signals for the ferrocene ring, viz. at δ 6.38, 6.03, 4.41, and 3.98. For the two sulfur atoms of 1,10-dithia[10]ferrocenophane to coordinate to a Pd(II) atom, the alkyl chain on the sulfur atoms must be oriented in the same direction because of its steric demand. Consequently, in the complex **5g** there is only one isomer that has *syn*-configuration with respect to the stereochemistry on the sulfur stoms. The ^1H NMR data of the complexes **5a–5f**, are consistent with the presence of two isomers, viz., the *syn*- (**5A**) and the *anti*-isomer (**5B**), as shown in Fig. 5. A comparison of the chemical shifts of the Cp-ring protons of **5a–5f** in the lower-field



5A



5B

region with that of **5g**, shows that the *anti*-isomer in **5a–5f** predominates over the *syn*-isomer. The same phenomena were observed for the complexes **6a, 6d, 8a**, and **8f**. That there are *two* isomers and that there is *no* interconversion between them at room temperature, in **6a, 6d, 8a**, and **8f**, is in sharp contrast to the fact that the PdX_2 complexes of **4a–4f** are fluxional at room temperature because of *S*-inversion and bridge reversal; **4a–4f** show their static spectra only below −30 °C [22]. Such structural rigidity in the $Pd(BF_4)_2$ and $Pt(BF_4)_2$ complexes probably arises from the presence of some bonding interaction between the Fe and Pd^{II} atoms. The four signals from each isomer of the Pd^{II} and Pt^{II} complexes were assigned to the $H_{2,5}$ and $H_{3,4}$ of the ferrocene ring by H,H-COSY. For example, in the H,H-COSY spectrum of complex **5g**, the signals at δ 3.98 and 4.41 are not coherent with each other, but are coherent with the signals at δ 6.03 and 6.38, respectively, indicating that the signals at high and low fields can be assigned to $H_{2,5}$ and $H_{3,4}$, respectively. Thus the coordination of the heteroatoms in the 1,1′-disubstituted ferrocenes to metal atoms usually brings about a lowfield shift in both the $H_{2,5}$ and the $H_{3,4}$ resonances; those of $H_{2,5}$ appear at lower field than those of $H_{3,4}$. For example, the $H_{2,5}$ and $H_{3,4}$ resonances in the $PdCl_2$ complex of 1,1′-bis(isobutylthio)ferrocene appeared at δ 5.28 and 4.42, respectively [23]. The low-field shift is probably caused by the magnetic anisotropy or by the inductive effect of the metal halide [7]. In contrast, the $H_{2,5}$ signals from the $Pd(BF_4)_2$ complex (**5d**) are at higher field than those of the free ligand (**4d**) and the $H_{3,4}$ resonances appear at very low field (Table 3). Such a large separation and reversal of the chemical shifts of the $H_{2,5}$ and $H_{3,4}$ in the complexes **5** cannot be elucidated merely by the inductive or field effect of the coordinating metal ions. The most likely explanation is in terms of the anisotropy of the metal–metal bond between the Fe atom of a ferrocene nucleus and the Pd^{II} or Pt^{II} atom coordinated to the sulfur atoms in the substituents at the 1,1′-positions, because similar separation and reversal of the $H_{2,5}$ and $H_{3,4}$ resonances has also been observed in complexes **2a** and **2b**, which were shown by X-ray diffraction study to contain weak, dative Fe–Pd and Fe–Pt bonds, respectively [11,12]. The same phenomena have been observed in the complexes, **6a, 6d, 8a**, and **8f**, in spite of the fact that a selenium atom replaced the sulfur atom in **6a** and **6d**, and that a Pt^{II} replaced the Pd^{II} atom in **8a** and **8f**, (Table 3). Consequently, a similar dative metal–metal bond must exist in these complexes.

In the ^{13}C NMR spectrum of the complex **5a**, for example, the $C_{2,5}$ resonances of the main isomer were observed at δ 69.65 and 71.27 ppm and the $C_{3,4}$ resonances appeared at δ 85.56 and 86.46 ppm (Table 4). The assignment of such signals to the $C_{2,5}$ and $C_{3,4}$ was made from the C,H-COSY data for **5a**. The carbon signals at δ 85.56 and 86.46 ppm are coherent with the proton signals at δ 6.06 and 6.26, assigned to the $H_{3,4}$ resonances, respectively. Similarly, there is good coherence between the carbon signals at 69.65 and 71.27 ppm and the $H_{2,5}$ signals at δ 3.72 and 4.13, respectively. From this assignment it follows that complexation with a Pd^{II} ion the bridge-head carbon signal shifts to a higher field than that of the corresponding free ligand (Δ 3.25 ppm) and the separation between the $C_{2,5}$ and $C_{3,4}$ signals increases greatly (Δ 15.78 ppm). Coordination of $PdCl_2$ to 1,1′-bis(isobutylthio)ferrocene causes a similar highfield shift of the bridge-head carbon signal compared with the free ligand (Δ 3.44 ppm), but only a small separation between the $C_{2,5}$ and $C_{3,4}$ signals (Δ 4.51 ppm) [7]. The change in the $C_{2,5}$ and $C_{3,4}$ signals between the $Pd(BF_4)_2$ complex and the $PdCl_2$ complex is striking and is mainly

Table 4

The ^{13}C chemical shifts of the ferrocenyl ring carbons (100 MHz, acetone-d_6)

Compounds	*Anti*-isomer					*Syn*-isomer				
	C_1	$C_{2,5}$		$C_{3,4}$		C_1	$C_{2,5}$		$C_{3,4}$	
5a	80.75	69.65	71.27	85.56	86.46	82.56	70.12	70.57	85.56	86.38
5b	79.00	71.01	71.83	85.96	87.58	–	–	–	–	–
5c	79.00	70.64	71.04	85.91	86.98	81.11	70.75	70.79	85.83	86.77
5d	79.51	70.49	71.02	85.79	86.82	81.51	70.70	70.73	85.53	86.78
5e	83.04	69.61	71.18	86.45	87.12	80.06	70.70	70.73	85.31	87.22
5f	83.01	69.60	71.17	86.50	87.12	– [b]	71.10	71.81	86.02	87.63
5g	–	–	–	–	–	82.64	71.03	72.03	86.71	87.92
6a	– [b]	69.79	70.95	85.87	86.45	– [b]	70.19	70.39	85.81	86.17
6d	74.31 [a]	70.60	70.61	85.97	86.86	76.13 [a]	70.53	70.54	85.63	86.89
8a	80.05	70.72	71.13	84.11	85.40	81.72	70.40	71.18	84.29	85.02
8f	83.42	70.93	71.03	85.10	86.60	–	–	–	–	–

[a] *J*(P–C) 4.0 Hz, *J*(Pt–C) 25.6 Hz. [b] This signal was not observed owing to its low intensity.

attributable to the large lowfield shift of the $C_{3,4}$ signals. The deshielding of the $C_{3,4}$ atoms is probably responsible in part for the lowfield shift of the $H_{3,4}$ resonances in the ^1H NMR spectrum of **5a**. Therefore, the large separation between the $H_{2,5}$ and $H_{3,4}$ resonances in the complexes **5**, **6**, and **8** cannot solely be the result of the magnetic anisotropy of the Fe–M dative bond, although such a large separation of the ferrocenyl ring-proton signals remained in the thiolate complexes, **2a** and **2b**. At this point, it is interesting to note that Cowie et al. [21] have suggested three canonical structures for the thiolate complex **2a**, two of which contain a fulvene-like structure in the cyclopentadienyl rings of the ferrocene moiety. The deshielding of the $H_{3,4}$ compared with that of the $H_{2,5}$ and the large separation between them in the complexes **5**, **6**, and **8** are also observed in the α-ferrocenylcarbonium cations [$H_{2,5}$, δ 4.72; $H_{3,4}$, 6.32] [24,25]. The lowfield shift of the $C_{3,4}$ resonances compared with that of the $C_{2,5}$ [$C_{2,5} = \Delta$ 17.6 ppm and $C_{3,4} = \Delta$ 27.4 ppm] and large separation between these carbons (Δ 10.1 ppm) are observed when the carbon chemical shifts in the ferrocenylcarbonium cations are compared with those in the corresponding alcohols [26]. These facts suggest that the fulvene-like canonical structure of the cyclopentadienyl rings of the ferrocene moiety contributes to the actual structure in **5**, **6**, and **8** much more so than that in **2a**, because X-ray diffraction reveals that ferrocenyldiphenylcarbonium cation can be described as being a fulvenecyclopentadienyliron cation [27].

The ^{31}P chemical shift of the Pd^{II} complexes **5a**–**5f** was observed in the narrow range 23.5–25.5 ppm (relative to 85% H_3PO_4) (Table 5). This is significantly smaller than that in the dithiolato complex **2a** (δ 39.50 ppm). The replacement of the sulfur atoms in **5a** and **5f** by selenium atoms has little effect on the ^{31}P chemical shift (Δ ca. +3.5 ppm). On the other hand, in the Pt^{II} complexes **6a** and **6d** the ^{31}P signals appeared at δ 11.0–12.0 ppm, whereas the corresponding signal in the dithiolato complex **2b** was observed at 23.34 ppm. Since the ^{31}P signals in bis(triphenylphosphine)(1,1′-ferrocenedithiolato-*S*,*S*)platinum(II) (**10**) [12] is observed at 20.02 ppm, the difference between **6a** (or **6d**) and **2b** (and by analogy, between **5a**–**5f** and **2a**) in the ^{31}P chemical shift seems to be mainly due to the difference between the thiolate and the sulfide ligands. It is well known [28] that the ^{195}Pt–^{31}P coupling constant

Table 5

The ^{31}P NMR data (160 MHz, acetone-d_6)

Compounds	*Anti*-isomer	*Syn*-isomer	*Anti/syn* ratio
5a	23.44	23.74	2.1
5b	25.03	26.74	1.1
5c	23.89	24.14	1.7
5d	24.27	24.70	1.5
5e	24.27	24.70	2.3
5f	24.65	25.52	6.5
5g	–	23.85	–
6a	11.45 (*J* 4588 Hz)	11.08 (*J* 4565 Hz)	2.3
6d	11.96 (*J* 4598 Hz)	11.88 (*J* 4574 Hz)	1.3
8a	26.82	27.71	1.4
8f	28.31	28.90	7.5

The value in parentheses is the $^{195}Pt-^{31}P$ coupling constant.

reveals the nature of the Pt–P bond and is also sensitive to the nature of the *trans* ligand. The relevant coupling constants for **6a** are 4588 (*anti*-isomer) and 4565 Hz (*syn*-isomer), and those for **6d** are 4598 (*anti*-isomer) and 4574 Hz (*syn*-isomer). These values are significantly smaller than that for the dithiolato complex **2b** (5416 Hz) and differ markedly from that for the bis(phosphine) complex **10** (2905 Hz). These results suggest that the complexes **6a** and **6d** have structures similar to that of complex **2b**. In addition the Pt–P bond distance in **6a** and **6d** is somewhat longer than that in **2b**.

The Mössbauer spectral data are listed in Table 6. The $Pd(BF_4)_2$ complexes **5a, 5b, 5e**, and **5f** show QS values similar to that for the free ligand **4a**, and the $PdCl_2$ complex of **4a**, which may suggest that these complexes show no direct metal–metal bonding (cf. $HgCl_2$ adduct of [2]ferrocenophane has a large *QS* value (3.29 mm s^{-1})) [29]. However, only a small decrease in the *QS* value was observed for the bithiolate complex **2a** (*QS* = 1.99 mm s^{-1}) [14], in which a weak dative Fe–Pd bond

Table 6

Mössbauer spectral data

Compounds	Conditions	*IS* (mm s^{-1})	*QS* (mm s^{-1})
4a	liq. N_2	0.50	2.35
4a·$PdCl_2$	liq. N_2	0.49	2.32
	R.T.	0.44	2.30
5a	liq. N_2	0.54	2.44
5b	R.T.	0.46	2.30
5e	R.T.	0.48	2.38
5f	R.T.	0.47	2.38
2a[a]	R.T.	0.48	1.99
3[a]	R.T.	0.49	2.36

[a] Ref. 14.

has been confirmed by X-ray diffraction. A similar *QS* value (2.36 mm s^{-1}) has been obtained for the $Pd(BF_4)_2$ complex of 1,5,9-trithia[9]ferrocenophane [14]. Definite conclusions on Fe–Pd bonding cannot be drawn from the Mössbauer spectral data.

In summary, the cationic complexes of some sulfide and selenide derivatives of ferrocene with $Pd(BF_4)_2$ or $Pt(BF_4)_2$ were prepared and their visible, IR, and NMR spectral data suggest that there is a weak metal–metal bond between the Fe atom of the ferrocene nucleus and the Pd^{II} or Pt^{II} atom coordinated to the sulfur atoms. The ^1H and ^{13}C NMR spectra data also indicate that the fulvene-like canonical structure is responsible for the actual structure of these complexes more so than that of complex **2**.

Experimental

The melting points were measured by Differential Scanning Calorimeter (Seiko DSC-20). The IR spectra were recorded on a Hitachi 270-50 Infrared Spectrometer. The ^1H, ^{13}C, and ^{31}P NMR spectra were recorded on a Bruker AM-400 spectrometer, with TMS and H_3PO_4 as the standards. The electronic spectra were recorded on a Hitachi 340 spectrometer. The mass spectra were measured on by Shimadzu QP-1000.

Materials. 1,1′-Ferrocenedithiol was prepared from 1,2,3-trithia[3]ferrocenophane [30]. Dichlorobis(acetonitrile)palladium(II) and -platinum(II) were prepared by published procedures [16]. 1,1-Bis(methylthio)ferrocene [31], 1,1′-bis(alkyl- and phenylchalcogeno)ferrocenes and their dichloropalladium(II) and -platinum(II) complexes [6] were prepared by procedures described previously. Silver(I) tetrafluoroborate, 1-iodobutane and t-butyl disulfide were commercial products. Triphenylphosphine was recrystallized from ethanol before use.

1,1′-Bis(n-butylthio)ferrocene (4c)

To a suspension of 1,1′-ferrocenedithiol (1 g, 4 mmol) in ethanol (50 ml) was added a 40% aq solution of sodium hydroxide (1 ml) under nitrogen. 1-Iodobutane (1.6 g, 8.8 ml) was added to the resulting red solution of 1,1′-ferrocenedithiolate. The solution was stirred for 3 h at room temperature. After the reaction mixture had been evaporated in a vacuum, the residue was chromatographed on silica gel by elution with hexane-toluene (3 : 1). The second (the main) fraction gave **4c** as an orange oil in 63% yield. Found: C, 59.55; H, 7.06. $C_{18}H_{20}FeS_2$ calcd.: C, 59.66; H, 7.23%. MS: m/z 362 (M^+).

1,1′-Bis(t-butylthio)ferrocene (4d)

To ferrocene (2 g, 8 mmol), in a 200 ml round bottom flask equipped with a dropping funnel, a nitrogen inlet (one side) and a rubber septum (the other side), was added n-BuLi (1.55 *M* solution hexane, 20 ml) by an injector. Tetramethylethylenediamine (4.5 ml, 30 mmol) was slowly added dropwise to the flask over 20 min under nitrogen, and the mixture was stirred for 7 h. Then t-butyl disulfide (4.2 g 17.6 mmol) was added via the dropping funnel to the orange solution at room temperature. The mixture was refluxed for 24 h. About 20 ml of water was added, and the precipitate that formed was filtered off and washed several times with benzene (10 ml). The residue was chromatographed on silica gel by elution with hexane-toluene (4 : 1). The second fraction, gave t-butylthioferrocene as yellow needles in 42.3% yield, m.p. 60–61° C. Found: C, 61.08; H, 6.56. $C_{14}H_{18}FeS$ calcd.: C, 61.32; H, 6.61%. The third fraction gave **4d** as yellow needles in 9.3% yield, m.p. 81–82° C. Found: C, 59.83; H, 7.18. $C_{18}H_{20}FeS_2$ calcd.: C, 59.66; H, 7.23%. MS: m/z 362 (M^+).

*Dichloro[1,1′-bis(n-butylthio)ferrocene-*S,S′*]palladium(II)*

To a solution of 1,1′-bis(n-butylthio)ferrocene (**4c**) (36 mg, 0.1 mmol) in acetonitrile (10 ml) was added a solution of dichlorobis(acetonitrile)palladium(II) (26 mg, 0.1 mmol) in acetonitrile (10 ml) with stirring at room temperature. After the solution had been keep for 1 h, the resulting crystals were collected by filtration and recrystallized from CH_2Cl_2-hexane to give the title complex as dark-brown crystals (48 mg, 88%), m.p. 249° C (dec.). Found: C, 36.87; H, 4.34. $C_{19}H_{28}Cl_2Fe$-PdS_2 calcd.: C, 36.54; H, 4.51%.

The following dichloropalladium complexes were prepared by the procedure described above:

*Dichloro[1,1′-bis(methylselena)ferrocene-*S,S′*]palladium(II).* Dark brown crystals (92%), m.p. 234° C (dec.). Found: C, 26.49; H, 2.56. $C_{12}H_{14}Cl_2FePdSe_2$ calcd.: C, 26.23; H, 2.56%.

*Dichloro[1,1′-bis(phenylselena)ferrocene-*S,S′*]palladium(II).* Dark brown crystals (78%), m.p. 256° C (dec.). Found: C, 39.47; H, 3.00. $C_{22}H_{18}Cl_2FePdSe_2$ calcd.: C, 39.24; H, 2.69%.

*(Triphenylphosphine)[1,1′-bis(methylthio)ferrocene-*S,S′,Fe*]palladium(II) tetrafluoroborate (5a)*

Addition of **4a** (28 mg, 0.1 mmol) to a mixture of $(MeCN)_2PdCl_2$ (26 mg, 0.1 mmol), $AgBF_4$ (40 mg, 0.2 mmol), and PPh_3 (26 mg, 0.1 mmol) in dry acetone (10 ml) with stirring gave a dark-brown solution. The solution was stirred for 1 h at room temperature, then it was filtered, and the filtrate was evaporated under reduced pressure. The residue was recrystallized from acetone-ether to give **5a** as dark-brown crystals (68 mg).

The complexes **5b–5g** were prepared by the procedure described above. M.p., yield, and elemental analysis data were listed in Table 1.

*(Triphenylphosphine)[1,1′-bis(methylthio)ferrocene-*S,S′,Fe*]platinum(II) tetrafluoroborate (6a)*

Dichloro[1,1′-bis(methylthio)ferrocene]platinum(II) (**4a**) (55 mg, 0.1 mmol) was added to a mixture of $AgBF_4$ (40 mg, 0.2 mmol) and PPh_3 (26 mg, 0.1 mmol) in dry and nitrogen-saturated acetone (10 ml) under nitrogen. The mixture was refluxed for 2 h with stirring. The resulting red mixture was filtered, and the filtrate was diluted with dry, nitrogen-saturated diethyl ether. The solution was kept overnight in a refrigerator, and the resulting dark brown crystals (88 mg) were collected by filtration.

(Triphenylphosphine)[1,1′-bis(isobutylthio)ferrocene-*S,S′, Fe*)platinum(II) tetrafluoroborate (**6d**) was prepared in the same way. The m.p., yield, and elemental analysis data are listed in Table 1.

Acknowledgement

The present work was supported by a Grant-in-Aid for Science Research (No. 63540382) from the Ministry of Education, Science and Culture.

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