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Preparation of Novel Platinum and Palladium Complexes by Reaction of 1,1′-Metallocenedichalcogenols with Tetrakis(triphenylphosphine)palladium(0) or -platinum(0). The Important Role of the Coordinating Ability of the Metal Atom of the Metallocene in Product Formation

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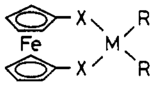
The reaction of 1,1′-metallocenedichalcogenol, $M(\eta\text{-}C_5H_4XH)_2$ (M = Fe or Ru, X = S or Se), with tetrakis(triphenylphosphine)platinum(0) at room temperature gave the mono(phosphine) complexes (1,1′-metallocenedichalcogenolato-*X,X′,M*)(triphenylphosphine)platinum(II) in good yield, while in a similar reaction at 0 °C an intermediate platinum complex was obtained. When the intermediate was heated to 60 °C, the above mono(phosphine) complex was obtained in quantitative yield together with triphenylphosphine. The mono(phosphine) palladium complexes were also obtained by a similar method, although the intermediate could not be isolated. The structure of (1,1′-ferrocenedithiolato-*S,S′,Pt*)(triphenylphosphine)platinum(II) has been determined by the single-crystal X-ray diffraction method. The crystal is monoclinic with space group $P2_1/c$, and the cell constants are a = 14.166 (1) Å, b = 17.208 (4) Å, c = 12.227 (1) Å, β = 92.52 (1)°, and Z = 4. The structure has been refined to a final R value of 0.053. The crystals are solvated by benzene (ratio of 1:1). The distance between the iron and platinum atoms is 2.935 (2) Å. Two Cp rings have an eclipsed conformation and are tilted by 21.0 (7)° from the parallel plane. From the ^{1}H NMR spectral and X-ray analysis data, the mono(phosphine) complexes have an electronic interaction between the metal of the metallocene nucleus (Fe or Ru) and the metal (Pt or Pd) located at the 2-position of the bridge. The interaction appears to be a dative bond of the iron or ruthenium atom to the palladium(II) or platinum(II) atom.

Introduction

The coordination of the nonbonding electrons (e_{2g} electrons) of the iron atom in the ferrocene nucleus to the vacant orbitals of a transition metal has become a topic of interest in recent years. Such a bonding interaction was reported for the first time by Sano et al.[1] in ([2](1,1′)-ferrocenophane)metal halide adducts. Whitesides et al.[2] and McCulloch et al.[3] reported that there was no evidence of interaction between the iron atom and the platinum atom in compounds 1, 2, 3, and 4, respectively. In this connection, Seyferth et al.[4] carried out a reaction of trithia[3](1,1′)ferrocenophane (**6a**) with tetrakis(triphenylphosphine)palladium(0) (**7a**) in order to prepare (1,1′-ferrocenedithiolato-*S,S′*)bis(triphenylphosphine)palladium(II) (**8a**). However, the product of the reaction was an unexpected complex (**9a**). Judging from the coordinating ability of the palladium atom and the X-ray analysis of **9a**, it followed that the iron atom of the ferrocene nucleus had a bond with the palladium(II) atom.[4] Complex **9a** is a structurally interesting compound, and, moreover, it may be closely related to catalytic and physiological activities.[5] Therefore, we here report a systematic synthetic study of (1,1′-metallocenedichalcogenolato-*X,X′*,-



1 : X=S(i-Bu), M=Pd, R=Cl
2 : X=PPh$_2$, M=Pt, R=n-Bu
3 : X=PPh$_2$, M=Pd, R=Cl

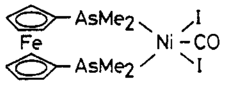


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Table I. Yield, Melting Point, and ^{1}H NMR Data for 8 and 9

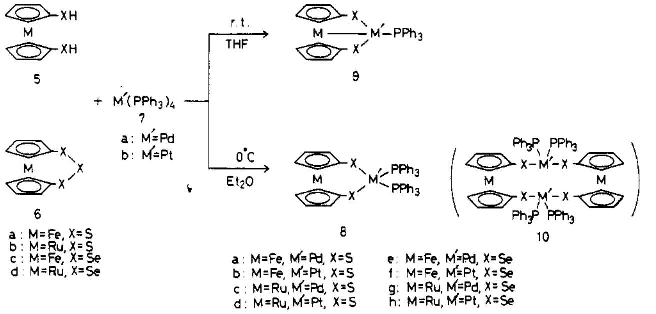
compd	yield, %	mp, °C	^{1}H NMR (90 MHz, in $CDCl_3$, δ)^d
8b	65^a	*c*	3.73 (t, J = 1.8 Hz, 8 H), 3.99 (t, J = 1.8 Hz, 8 H), 6.96–7.64 (m, 60 H)
8d	28^a	*c*	4.24 (t, J = 1.5 Hz, 8 H), 4.38 (t, J = 1.5 Hz, 8 H), 6.97–7.80 (m, 60 H)
8f	45^b	*c*	3.73 (br, 8 H), 3.89 (br, 8 H), 7.16–7.80 (m, 60 H)
8h	20^b	*c*	4.36 (t, J = 1.6 Hz, 8 H), 4.51 (t, J = 1.6 Hz, 8 H), 6.96–7.76 (m, 60 H)
9a	44^a	108.0–110.0	2.86 (t, J = 2.0 Hz, 4 H), 5.16 (t, J = 2.0 Hz, 4 H), 7.16–7.82 (m, 15 H)
9b	18^b	250.0 dec	3.04 (t, J = 1.9 Hz, 4 H), 5.20 (t, J = 1.9 Hz, 4 H), 7.25–7.92 (m, 15 H)
9c	62^a	250.0–252.0	3.57 (t, J = 1.8 Hz, 4 H), 5.16 (t, J = 1.8 Hz, 4 H), 7.25–7.78 (m, 15 H)
9d	38^a	268.0–269.5	3.75 (t, J = 1.8 Hz, 4 H), 5.17 (t, J = 1.8 Hz, 4 H), 7.25–7.83 (m, 15 H)
9g	68^a	245.0 dec	3.63 (t, J = 1.9 Hz, 4 H), 5.11 (t, J = 1.9 Hz, 4 H), 7.25–7.81 (m, 15 H)
9h	60^a	218.5–219.5	3.81 (t, J = 1.8 Hz, 4 H), 5.11 (t, J = 1.8 Hz, 4 H), 7.25–7.80 (m, 15 H)

[a] Reaction of 5 and 6. [b] By the Seyferth method. [c] The melting point could not measured because the sample was isomerized to 9 and triphenylphosphine on heating. [d] The ^{1}H NMR spectra of **9a**, **9c**, **9d**, and **9g** showed the peak of benzene ring protons due to the solvated benzene. Also, ^{1}H NMR spectrum of **9b** showed the peaks of methyl and benzene ring protons due to the solvated toluene.

M)(triphenylphosphine)platinum(II) and -palladium(II) (**9**) in which a modified method of Seyferth et al.[4] was used, and the important role of the coordinating ability of the metal atom of metallocene in the intermediate of the complex formation was demonstrated. Furthermore, we describe structural studies of the platinum complex **9b** by spectroscopic and X-ray methods.

Results and Discussion

The synthetic reaction was carried out as follows: a solution of 1,1′-metallocenedichalcogenol (**5**) and the tetrakis(triphenylphosphine) complex **7** of platinum and/or palladium in THF was stirred for 1 h at room temperature in a nitrogen atmosphere. Complexes **9a**, **9c**, **9g**, and **9h** were obtained by this method. Complexes **9b** and **9d** were obtained by the Seyferth method[4] since they were not obtainable by the above method. However, complexes **9e** and **9f** could not be obtained by either method. The structures of **9b–9d**, **9g**, and **9h** were determined by elemental analysis, the parent peaks in their mass spectra, and the similarity of their ^{1}H NMR spectra with that of **9a**[4] (Table I). The kind of chalcogen atom present influenced the complex formation in the ferrocene series, while no effect was observed in the ruthenocene series. The fact that the ferrocene complexes **9e** and **9f** could not be obtained could be explained by the following: The C–Se and M–Se (M = Pd or Pt) bonds are a little longer than those of the C–S and M–S (M = Pd or Pt) bonds, respectively, because the covalent radii of Se and S atoms are 1.17 and 1.02 Å, respectively.[14] As a result, the Fe–M (M = Pd or Pt) distance will become too long to provide a stable complex. In the Ru complexes **9g** and **9h**, the lengthening of the Ru–M (M = Pd or Pt) distance resulting from the long Se–C and Se–M distances would be compensated for by the expanded 4d orbital of a Ru atom compared with the 3d orbital of an Fe atom. The steric crowding in complexes **9e** and **9f** may also have contributed to the failure of their formation, because the van der Waals radii of a Se atom (2.00 Å) is larger than that of a S atom (1.85 Å).[14]



The reaction of **5** with **7** was dependent on the reaction temperature and the solvent used. For example, when a solution of 1,1′-ruthenocenedithiol (**5b**) and tetrakis(triphenylphosphine)platinum(0) (**7b**) was stirred in THF at room temperature, two products, the mono(phosphine) complex **9d** and the bis(phosphine) complex (**8d**), were obtained in 38% and 28% yields, respectively. When the same reaction was carried out at 0 °C by using diethyl ether as the solvent, only the bis(phosphine) complex **8d** was obtained in 78% yield. The bis(phosphine) complexes **8b**, **8d**, **8f**, and **8h** (M = Pt) were isolated by this method, although **8a**, **8c**, **8e**, and **8g** (M = Pd) could not be obtained. The reaction of **6** and **7** also exhibited a similar temperature dependence. The structures of **8b**, **8d**, **8f**, and **8h** were elucidated by using their elemental analysis, mass and ^{1}H NMR spectra, and gel permeation chromatography. For example, in the ^{1}H NMR spectrum of **8b**, the α- and β-ring protons of the ferrocene nucleus appeared at δ 3.73 and 3.99, respectively. The pattern of the Cp ring protons in **8** is in striking contrast to the wide splitting of the α- and β-proton signals in the mono(phosphine) complexes (see Table I). The mass spectrum of **8b** was taken by means of CIMS technique in which heating was avoided, chosen because of the thermal instability of the complexes **8** (vide infra). The peak corresponding to $M^+ - PPh_3$ (m/z 705) as well as the peak corresponding to $2 \times (M^+ - PPh_3)$ (m/z 1409) was observed. This mass spectrum is rationalized in terms of the facile conversion of **8** to **9** (vide infra). All attempts to measure the molecular weight of **8** using ebullioscopic and cryoscopic methods were unsuccessful because of their thermal instability both in the solid state and in solution. We examined the gel permeation chromatograms of **9a**, **9b**, and **8b**. Compound **9a** had a shorter retention time (7.55 min) than **9b** (7.65 min). Compound **8b** showed a peak with a retention time of 7.60 min. The retention time of **8b** is close to those of **9a** and **9b**, suggesting that **8b** has a molecular weight similar to those of **9a** and **9b**. Thus, we can tentatively assign a bis(phosphine) structure to **8**, although the dimeric complex **10** cannot be ruled out.

When chloroform solutions of the bis(phosphine) complexes **8b**, **8d**, and **8h** were heated to 60 °C, the corresponding mono(phosphine) complexes **9b**, **9d**, and **9h** were obtained in quantitative yield together with triphenylphosphine, although in the bis(phosphine) complex **8f** a similar reaction could not be observed. Thus, on heating, the bis(phosphine) complexes **8** were smoothly converted to the corresponding thermodynamically stable mono(phosphine) complexes **9**, so that their melting points could

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Table II. Electronic Spectra for 8 and 9

compd	λ, nm (ε)
8b	266 (50 500), 339 (13 300), 366 (15 300)
8d	267 (39 300), 312 (15 500), 425 (1520)
8f	385 (5210), 458 (2700), 472 (2570)
8h	296 (27 400), 346 (15 800),
9a	274 (25 400), 363 (8400), 403 (8490)
9b	254 (28 400), 288 (14 700), 366 (10 000)
9c	260 (18 900), 317 (14 100), 502 (131)
9d	289 (18 100), 312 (10 200), 474 (426)
9g	268 (22 700), 332 (17 600), 541 (425)
9h	258 (23 600), 293 (16 900), 345 (6630), 509 (122)

not be measured. From the above results, we assume that the bis(phosphine) complex **8** is an intermediate in the reaction of **5** or **6** with **7**. Therefore, we suppose that the likeliest reaction mechanism is as follows: (1) a S–S or S–H bond of **5** or **6** oxidatively adds to a zerovalent Pd or Pt atom, followed by elimination of a sulfur atom or a hydrogen molecule to give first the bis(phopshine) intermediate **8**; (2) 1 mol of triphenylphosphine leaves from **8** to give the coordinately unsaturated mono(phosphine) complex; (3) the metallocene metal coordinates to the coordinately unsaturated M′ atom generating the mono(phosphine) complex **9**. In this transformation, the coordination ability of the metallocene metal to the platinum or palladium atom seems to play an important role.

It is worthwhile to discuss here the ^1H NMR spectral data of **8** and **9** summarized in Table I. The chemical shift differences between the two triplets of the α- and β-protons of the Cp rings of some 2-metalla[3]ferrocenophanes having a $Fe(\eta\text{-}C_5H_4S)_2$ moiety are only 0.9 ppm at best.[3,6] In complexes **9a–d**, **9g**, and **9h**, however, the resonances of the α- and β-protons showed great differences, 1.3–2.3 ppm. These results probably are due to the following possible reasons: (1) the great tilting of the two Cp rings of a metallocene nucleus; (2) the anisotropic effect of the bond between M and M′ on the α-protons; (3) the anisotropic effect of the bond between X and M′ on the α-protons. However, possibilities 1 and 3 seem less reasonable for such great chemical shift differences because of the following facts: (a) the chemical shift differences between the α- and β-protons of 1,1,2,2-tetramethyl[2]ferrocenophane,[7] in which the two Cp rings are tilted by 23° from the plane, are only 0.54 ppm; (b) the corresponding differences of $Fe(\eta\text{-}C_5H_4S\text{-}i\text{-}Bu)_2M^{II}X_2$ (M = Pd or Pt, X = Cl or Br) are 0.69–0.89 ppm.[3] Therefore, it may be suggested that the anisotropic effect of the dative bond between M and M′ (vide infra) is mainly attributable to such a great chemical shift difference. The two triplets in the NMR spectrum of **9** were assigned in similar manner to the other 1,3-dithia-2-metalla[3]metallocenes.[8] The high-field triplet was assigned to the α-protons, and the low-field triplet was assigned to the β-protons because, in complexes **9a**, **9d**, **9g**, and **9h**, the low-field triplets (corresponding to the β-protons) appeared only within a narrow range, from 5.11 to 5.20 ppm, while the high-field triplets (corresponding to the α-protons) appeared within a wide range, from 2.86 to 3.81 ppm. Such differences could be explained by the assumption that the anisotropic effect of the M–M′ bond affects the α-protons of the Cp rings. Moreover, for example, in complexes **9a** and **9c**, the low-field triplet (β-protons) shows the same δ values, while the chemical shift differences between the high-field triplets (α-protons) is 0.71 ppm. This large difference is elucidated by the following: in complex **9c**, the anisotropic effect of the M–M′ bond on the α-protons is less effective compared with complex **9a** because the distance between the two Cp rings in ruthenocene[9] is greater by 0.32 Å than that of ferrocene.[10]

Table III. Fractional Atomic Coordinates (×10⁴) and Thermal Parameters (Å²) for 9b

atom	*x*	*y*	*z*	$B_{eq}{}^a/B_{iso}$
Pt	1822.4 (3)	5279.6 (2)	3572.9 (3)	2.8
Fe	1091 (2)	6464 (1)	5025 (1)	4.6
S(1)	2159 (3)	4620 (2)	5186 (2)	4.9
S(2)	1299 (3)	6133 (2)	2252 (2)	4.2
P	2515 (2)	4521 (2)	2388 (2)	3.0
C(1)	1666 (9)	5446 (7)	5777 (8)	4.0
C(2)	2211 (11)	6142 (8)	6062 (10)	5.7
C(3)	1588 (15)	6633 (9)	6575 (10)	8.3
C(4)	696 (13)	6297 (9)	6612 (10)	7.5
C(5)	723 (11)	5581 (8)	6074 (10)	5.5
C(6)	947 (9)	6685 (6)	3324 (8)	3.6
C(7)	1494 (12)	7265 (7)	3879 (9)	5.8
C(8)	871 (15)	7599 (7)	4678 (11)	8.2
C(9)	0 (13)	7212 (10)	4624 (12)	7.8
C(10)	62 (10)	6671 (8)	3795 (11)	5.6
C(11)	2412 (9)	3454 (6)	2484 (9)	3.4
C(12)	2034 (13)	3110 (7)	3387 (11)	6.8
C(13)	2005 (15)	2303 (8)	3467 (13)	8.8
C(14)	2334 (11)	1851 (7)	2629 (12)	6.0
C(15)	2709 (13)	2179 (7)	1758 (12)	6.8
C(16)	2754 (12)	2989 (8)	1672 (11)	6.4
C(21)	3776 (8)	4697 (7)	2403 (9)	3.9
C(22)	4318 (11)	4503 (10)	1534 (14)	7.7
C(23)	5285 (11)	4643 (13)	1576 (15)	9.4
C(24)	5731 (11)	4931 (11)	2528 (17)	9.5
C(25)	5211 (12)	5136 (13)	3295 (14)	10.3
C(26)	4213 (11)	5027 (10)	3259 (12)	7.5
C(31)	2073 (8)	4678 (7)	986 (8)	3.4
C(32)	1275 (10)	4292 (8)	610 (10)	5.1
C(33)	874 (12)	4432 (9)	−407 (12)	6.9
C(34)	1239 (13)	4939 (9)	−1097 (11)	7.3
C(35)	2024 (11)	5361 (9)	−751 (10)	6.5
C(36)	2420 (10)	5229 (8)	299 (9)	5.2
C(B1)	418 (2)	804 (2)	639 (2)	17.2 (0.9)
C(B2)	519 (2)	781 (2)	629 (3)	22.3 (1.3)
C(B3)	531 (2)	712 (2)	557 (2)	19.6 (1.1)
C(B4)	490 (2)	713 (2)	464 (2)	17.4 (1.0)
C(B5)	417 (2)	750 (2)	458 (2)	18.2 (1.0)
C(B6)	366 (2)	780 (2)	549 (2)	15.2 (0.8)

[a] Hamilton, W. C. *Act Crystallogr.* **1959**, *12*, 609.

The electronic spectra of complexes **8** and **9** are presented in Table II. The ruthenocene complexes **9a**, **9d**, **9g**, and **9h** showed absorption bands at 258–289, 293–346, and 474–541 nm. The first two absorptions are assignable to the ruthenocene moiety[11] and the triphenylphosphine moiety,[12] respectively. The third absorptions may be attributable to the charge-transfer band due to the Ru–Pt (or Pd) interaction because the absorption bands could not be observed in the starting materials. Also, in the ferrocene complexes **9b** and **9c**, the d–d transition band due to the Fe–Pt(II) and/or Fe–Pd(II) bonds could not be observed probably because of their overlap with the d–d transition of the ferrocene nucleus. In contrast with the mono(phosphine) complexes, there is no absorption band in the spectra of **8b**, **8d**, **8f**, and **8g** above 400 nm. On the basis of these results, it seems that there is direct metal–metal interaction between the ruthenium atom in the ruthenocene nucleus and the palladium(II) and/or platinum(II) atoms at the 2-position in the bridge in the bis(phosphine) complexes **8**.

Complex **9b** was further characterized by a single-crystal X-ray diffraction study. The final atomic parameters and selected bond lengths and bond angles for complex **9b** are presented in Tables III and IV, respectively. An ORTEP drawing of the structure is shown in Figure 1, along with the atomic labels used. Complex **9b** has molecular features quite similar to the Pd analogue **9a** obtained by Seyferth et al.[4] The ferrocene moiety of complex **9b** is very similar to that of the other ferrocenophanes. The Fe–C distances in the Cp rings ranged from 2.01 (2) to 2.125 (13) Å, and

Table IV. Bond Lengths (Å) and Angles (deg) with Estimated Standard Deviations in Parentheses for 9b

	Bond Lengths		
Pt–Fe	2.935 (2)	C(13)–C(14)	1.38 (2)
Pt–S(1)	2.299 (4)	C(14)–C(15)	1.33 (2)
Pt–S(2)	2.294 (4)	C(15)–C(16)	1.400 (18)
Pt–P	2.201 (3)	C(21)–C(22)	1.38 (2)
S(1)–C(1)	1.752 (12)	C(21)–C(26)	1.320 (19)
S(2)–C(6)	1.710 (11)	C(22)–C(23)	1.39 (2)
P–C(11)	1.848 (11)	C(23)–C(24)	1.39 (3)
P–C(21)	1.811 (11)	C(24)–C(25)	1.26 (2)
P–C(31)	1.819 (10)	C(25)–C(26)	1.42 (2)
C(1)–C(2)	1.459 (18)	C(31)–C(32)	1.372 (17)
C(1)–C(5)	1.419 (19)	C(31)–C(36)	1.372 (17)
C(2)–C(3)	1.39 (2)	C(32)–C(33)	1.366 (19)
C(3)–C(4)	1.39 (3)	C(33)–C(34)	1.33 (2)
C(4)–C(5)	1.40 (2)	C(34)–C(35)	1.38 (2)
C(6)–C(7)	1.418 (17)	C(35)–C(36)	1.399 (18)
C(6)–C(10)	1.403 (18)	C(B1)–C(B2)	1.49 (4)
C(7)–C(8)	1.46 (2)	C(B1)–C(B6)	1.36 (4)
C(8)–C(9)	1.40 (3)	C(B2)–C(B3)	1.49 (5)
C(9)–C(10)	1.38 (2)	C(B3)–C(B4)	1.25 (4)
C(11)–C(12)	1.380 (18)	C(B4)–C(B5)	1.21 (4)
C(11)–C(16)	1.379 (18)	C(B5)–C(B6)	1.46 (4)
C(12)–C(13)	1.394 (19)		
	Bond Angles		
Pt–S(1)–C(1)	83.6 (4)	C(12)–C(11)–C(16)	119.3 (7)
Pt–S(2)–C(6)	85.2 (4)	C(11)–C(12)–C(13)	119.8 (10)
Pt–P–C(11)	120.0 (4)	C(12)–C(13)–C(14)	119.7 (13)
Pt–P–C(21)	111.3 (4)	C(13)–C(14)–C(15)	120.7 (9)
Pt–P–C(31)	112.9 (4)	C(14)–C(15)–C(16)	120.2 (11)
Fe–Pt–S(1)	83.5 (1)	C(11)–C(16)–C(15)	120.2 (11)
Fe–Pt–S(2)	82.0 (1)	P–C(21)–C(22)	122.3 (7)
Fe–Pt–P	170.9 (1)	P–C(21)–C(26)	120.6 (7)
S(1)–Pt–S(2)	165.4 (1)	C(22)–C(21)–C(26)	117.2 (8)
C(11)–P–C(21)	104.2 (1)	C(21)–C(22)–C(23)	120.7 (14)
C(11)–P–C(31)	100.5 (1)	C(22)–C(23)–C(24)	120.2 (14)
C(21)–P–C(31)	106.5 (1)	C(23)–C(24)–C(25)	117.5 (12)
S(1)–C(1)–C(5)	129.4 (7)	C(24)–C(25)–C(26)	123.2 (16)
S(1)–C(1)–C(2)	123.3 (7)	C(21)–C(26)–C(25)	120.8 (12)
C(2)–C(1)–C(5)	107.3 (6)	P–C(31)–C(32)	119.3 (6)
C(1)–C(2)–C(3)	105.5 (8)	P–C(31)–C(36)	124.2 (7)
C(2)–C(3)–C(4)	110.9 (8)	C(32)–C(31)–C(36)	116.2 (8)
C(3)–C(4)–C(5)	107.8 (10)	C(31)–C(32)–C(33)	121.6 (10)
C(1)–C(5)–C(4)	108.1 (8)	C(32)–C(33)–C(34)	122.2 (13)
S(2)–C(6)–C(7)	125.9 (8)	C(33)–C(34)–C(35)	118.7 (12)
S(2)–C(6)–C(10)	126.9 (7)	C(34)–C(35)–C(36)	118.8 (10)
C(7)–C(6)–C(10)	107.2 (6)	C(31)–C(36)–C(35)	122.3 (10)
C(6)–C(7)–C(8)	105.3 (8)	C(B2)–C(B1)–C(B6)	110.7 (19)
C(7)–C(8)–C(9)	109.7 (8)	C(B1)–C(B2)–C(B3)	113 (2)
C(8)–C(9)–C(10)	105.7 (10)	C(B2)–C(B3)–C(B4)	119 (2)
C(6)–C(10)–C(9)	112.1 (9)	C(B3)–C(B4)–C(B5)	114 (3)
P–C(11)–C(16)	119.9 (6)	C(B4)–C(B5)–C(B6)	127 (3)
P–C(11)–C(12)	120.8 (6)	C(B1)–C(B6)–C(B5)	116 (2)

Table V. Selected Bond Angles (deg) with Esd's for $Fe(\eta\text{-}C_5H_4S)_2(PPh_3)Pt$

S(1)–Pt–S(2)	165.3 (1)	P–C(11)–C(16)	120.4 (6)
S(1)–Pt–P	101.5 (1)	P–C(11)–C(12)	121.1 (6)
S(2)–Pt–P	93.2 (1)	C(12)–C(11)–C(16)	118.4 (7)
Pt–S(1)–C(1)	83.7 (1)	C(11)–C(12)–C(13)	120.6 (11)
Pt–S(2)–C(6)	85.4 (1)	C(12)–C(13)–C(14)	118.9 (13)
Pt–P–C(11)	120.2 (1)	C(13)–C(14)–C(15)	121.1 (9)
Pt–P–C(21)	111.2 (1)	C(14)–C(15)–C(16)	120.0 (13)
Pt–P–C(31)	112.7 (1)	C(11)–C(16)–C(15)	121.1 (12)
C(11)–P–C(21)	104.2 (1)	P–C(21)–C(22)	121.3 (7)
C(11)–P–C(31)	100.6 (1)	P–C(21)–C(26)	120.4 (7)
C(21)–P–C(31)	106.6 (1)	C(22)–C(21)–C(26)	118.3 (9)
S(1)–C(1)–C(5)	129.8 (8)	C(21)–C(22)–C(23)	118.1 (14)
S(1)–C(1)–C(2)	123.5 (8)	C(22)–C(23)–C(24)	121.8 (17)
C(2)–C(1)–C(5)	106.7 (6)	C(23)–C(24)–C(25)	117.5 (12)
C(1)–C(2)–C(3)	106.3 (9)	C(24)–C(25)–C(26)	122.4 (18)
C(2)–C(3)–C(4)	110.5 (9)	C(21)–C(26)–C(25)	120.9 (14)
C(3)–C(4)–C(5)	106.5 (10)	P–C(31)–C(32)	119.0 (6)
C(1)–C(5)–C(4)	109.0 (7)	P–C(31)–C(36)	123.3 (7)
S(2)–C(6)–C(7)	125.8 (8)	C(32)–C(31)–C(36)	117.2 (8)
S(2)–C(6)–C(10)	126.5 (7)	C(31)–C(32)–C(33)	121.0 (10)
C(7)–C(6)–C(10)	107.7 (6)	C(32)–C(33)–C(34)	122.3 (14)
C(6)–C(7)–C(8)	105.0 (9)	C(33)–C(34)–C(35)	119.0 (13)
C(7)–C(8)–C(9)	109.6 (8)	C(34)–C(35)–C(36)	119.9 (11)
C(8)–C(9)–C(10)	106.3 (11)	C(31)–C(36)–C(35)	120.4 (10)
C(6)–C(10)–C(9)	111.4 (9)		

their average value was 2.06 Å. The C–C distances in the Cp rings ranged from 1.38 (2) to 1.46 (2) Å, and their average value was 1.41 (2) Å. Also, the C–C–C angles in the two Cp rings ranged from 105.3 (8) to 126.9 (7)°, and their average value was 111.0°.

These bond lengths and bond angles are in agreement with reported values for other 2-metalla[3]ferrocenophanes[3,13] and **9a**.[4] The bond angle (165.4 (1)°) of S–Pt–S in **9b** is similar to that (165.2°) of the Pd analogue **9a**[4] but is remarkably larger than that of the other [3]metallocenophanes[3] containing the metal atom at the 2-position in the bridge. For example, in complexes **1** and **4**, the bond angles of S–Pd–S and As–Ni–As are 83.9 and 93.49°, respectively.[3,17] Therefore, the bridge chain in the **9b** is held in the position at which the distance between Fe and Pt can be the shortest and the Pt(II) atom has a distorted tetragonal configuration, as observed in the Pd analogue **9a**.

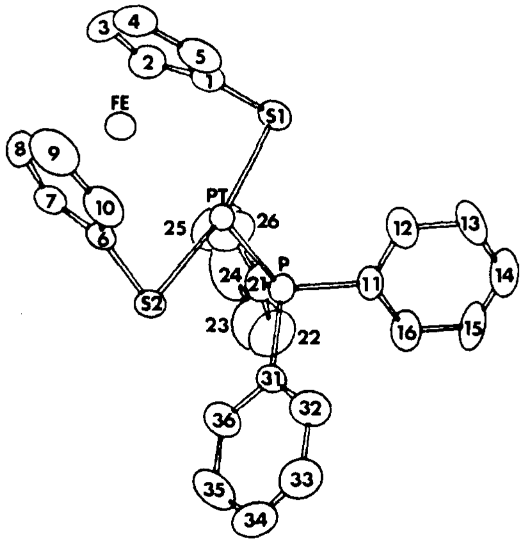

Figure 1. An ORTEP drawing of **9b**.

The Fe–Pt distance was found to be 2.935 (2) Å, while the distances between Fe and Pd or Ni in complexes **1** and **4** were 3.810 and 4.348 Å, respectively.[3,17] The value of the Fe–Pt distance is comparable to the Fe–Pd distance (2.878 Å) in complex **9a**, in which the presence of a weak dative bond is proposed on the basis of the Fe–Pd distance.[4] The Fe–Pt distance (2.935 (2) Å) is somewhat longer than the sum (2.54 Å) of the covalent radii[14] of Fe and Pt atoms. However, the Fe–Pt bond in complex **9b** is necessary for obtaining a stable electron configuration (16-electron configuration) around the Pt(II) atom. Therefore, this bond will necessarily be a weak dative bond from the Fe atom to the Pt(II) atom. The rather long distance between the Fe and Pt atoms, however, is not unreasonable as Pt–Pt single-bond distances[15] up to 2.77 Å and Fe–Fe distances up to 2.89 Å[16] have been reported.

The Fe–Pt distance (2.935 Å) in complex **9b** is a little longer than the Fe–Pd distance (2.878 Å) in complex **9a** even if we take the difference (0.02 Å) of the covalent radii of Pt and Pd atoms into consideration. This suggests that the Fe–Pt bond in **9b** seems to be somewhat weaker than the Fe–Pd bond in **9a**, and the unsaturation of the Pt atom in **9b** may be increased compared with that of the Pd atom

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[17] Pierpont, D. G.; Einsenberg, R. *Inorg. Chem.* **1972**, *11*, 823.

in **9a**. This suggestion is supported by the other bond distances around the Pt atom. The Pt–S distance (average 2.297 Å) in **9b** is at the short end of the range observed (2.280–2.350 Å) in some (thiolato)platinum(II) complexes[18-21] and is a little shorter than that (2.302 Å)[4] in complex **9a**. Furthermore, the Pt–P distance (2.203 Å) is also one of the most shortest distances observed (2.218–2.359 Å) in typical Pt–PPh_3 complexes[22-28] and is slightly shorter than that (2.241 Å)[4] in complex **9a**. Thus, the increased Fe–Pt distance is apparently reflected in the decreased Pt–S and Pt–P distances. The Cp rings take an eclipsed conformatiion to each other, and the dihedral angle between the rings is 21.0 (7)°, while the dihedral angles of the complexes **1** and **4** are 1.9 and almost 0°, respectively.[3,17] The slight tilting of the ferrocene Cp rings observed in **9a** and **9b**, compared with that of wedge-shaped metallocenes, suggests that the Fe–M (M = Pd or Pt) is rather weak, as indicated by Seyferth et al.[4]

In summary, the mono(phosphine) complexes **9** are readily prepared from tetrakis(triphenylphosphine)platinum or -palladium and chalcogen containing a 1,1′-metallocenyl, **5** or **6**. A presumed reaction intermediate **8** has been isolated. The structural features of **9a** and **9b** are similar, and a weak dative bond between the ferrocenyl Fe atom and the M atom (M = Pt or Pd) is suggested on the basis of short distances observed.

Experimental Section

The melting points are uncorrected. The ^1H NMR spectra were obtained on a JEOL FX-90Q spectrometer, Me_4Si being chosen as an internal standard. The electronic spectra were measured on a Hitachi 340 spectrometer. The mass spectra were taken by using a Hitachi M-80 spectrometer.

Materials. All solvents and reagents were used as purchased unless otherwise specified. 1,2,3-Trithia[3]ruthenocenophane,[29] 1,1′-ferrocenedithiol, 1,1′-ruthenocenedithiol,[29] 1,2,3-triselena[3]ferrocenophane,[30] 1,2,3-triselena[3]ruthenocenophane,[31] tetrakis(triphenylphosphine)palladium(0),[32] and tetrakis(triphenylphosphine)platinum(0)[33] were prepared according to the literature procedures. Merk Kieselgel 60 and Wako Alumina (activated, about 200 mesh) were used for column chromatography.

Reaction of 5 and 7. [Fe(η-C_5H_4S)$_2$]Pd(PPh_3) (9a). A solution of ferrocene-1,1′-dithiol (**5a**) (0.252 g, 1.01 mmol) and tetrakis(triphenylphosphine)palladium(0) (**7a**) (0.847 g, 0.734 mmol) in THF (80 mL) was stirred for 0.5 h at room temperature under a nitrogen atmosphere. The reaction mixture was concentrated in vacuo, and the residue was chromatographed on activated alumina by using 1:1 benzene/hexane solution as the eluent. The first fraction contained triphenylphosphine only. The second fraction was collected and concentrated in vacuo. The residue was dissolved in a minimum amount of chloroform, and then hexane was added dropwise to the solution until dark red plates precipitated. The crystals were collected by filtration and recrystallized from benzene to give **9a** as dark red columnar crystals in 44% yield. MS: *m/z* 616 (M^+). Anal. Calcd for $C_{28}H_{23}S_2PFePd{\cdot}C_6H_6$: C, 58.76; H, 4.21. Found: C, 58.76; H, 4.22.

[Ru(η-C_5H_4S)$_2$]Pd(PPh_3) (9c). Compound **9c** was obtained from ruthenocene-1,1′-dithiol (**5c**) (0.254 g, 0.832 mmol) and **7a** (1.39 g, 1.20 mmol), as light orange columnar crystals in 62% yield, in a similar manner to that described for **9a**, except that the eluent for the column chromatography was benzene. MS: *m/z* 662 (M^+). Anal. Calcd for $C_{28}H_{23}S_2PPdRu{\cdot}{}^1/_2C_6H_6$: C, 53.10; H, 3.75. Found: C, 53.09; H, 3.69.

[Ru(η-C_5H_4S)$_2$]Pt(PPh_3) (9d). Compound **9d** was obtained from **5b** (0.194 g, 0.0656 mmol) and tetrakis(triphenylphosphine)platinum(0) (**7b**) (0.647 g, 0.520 mmol), as light orange plates in 38% yield, in a similar manner to that described for **9a**, except that the eluent for column chromatography was 1:1 chloroform/hexane. MS: *m/z* 751 (M^+). Anal. Calcd for $C_{28}H_{23}S_2PPtRu{\cdot}{}^1/_2C_6H_6$: C, 47.13; H, 3.32. Found: C, 47.07; H, 3.23.

[Ru(η-C_5H_4Se)$_2$]Pd(PPh_3) (9g). Compound **9g** was obtained from ruthenocene-1,1′-diselenol (**5g**) (0.142 g, 0.338 mmol) and **7a** (0.491 g, 0.426 mmol), as red-orange columnar crystals in 68% yield, in a similar manner to that described for **9a**, except that silica gel was used for column chromatography instead of activated alumina and the eluent was 1:1 chloroform/hexane. MS: *m/z* 757 (M^+). Anal. Calcd for $C_{28}H_{23}Se_2PPdRu{\cdot}{}^1/_2C_6H_6$: C, 48.97; H, 3.50. Found: C, 48.70; H, 3.76.

[Ru(η-C_5H_4Se)$_2$]Pt(PPh_3) (9h). Compound **9h** was obtained from **5d** (0.032 g, 0.082 mmol) and **7b** (0.102 g, 0.082 mmol), as pink plates in 60% yield, in a similar manner to that described for **9a**, except that silica gel was used for column chromatography instead of activated alumina and that the eluent was 1:1 chloroform/hexane. MS: *m/z* 846 (M^+). Anal. Calcd for $C_{28}H_{23}Se_2PPtRu$: C, 39.82; H, 2.74. Found: C, 39.68; H, 2.63.

[Fe(η-C_5H_4S)$_2$]Pt(PPh_3)$_2$ (8b). A suspension of **5a** (0.059 g, 0.234 mmol) and **7b** (0.259 g, 0.208 mmol) in THF (30 mL) was stirred for 1 h at room temperature under a nitrogen atmosphere. The reaction mixture was concentrated in vacuo below 20 °C. The residue was chromatographed on activated alumina by using 1:2 chloroform/hexane as eluent. The first colorless fraction contained only triphenylphosphine. The second orange fraction was collected and concentrated in vacuo below 20 °C. The residue was dissolved in a minimum amount of chloroform, and then hexane was added dropwise to the solution until the precipitate was formed. The precipitate was collected by filtration and washed with hexane to give **8b** as an orange powder in 65% yield. Anal. Calcd for $C_{46}H_{38}S_2P_2FePt$: C, 56.05; H, 3.98. Found: C, 55.82; H, 3.91.

[Ru(η-C_5H_4S)$_2$]Pt(PPh_3)$_2$ (8d). Compound **8d** was obtained from **5b** (0.261 g, 0.884 mmol) and **7b** (1.08 g, 0.872 mmol), as a yellow powder in 73% yield, in a similar manner to that described for **8b**, except that the solvent was diethyl ether and the reaction temperature was 0 °C. Furthermore, the eluent for column chromatography was 1:1 chloroform/hexane. Anal. Calcd for $C_{46}H_{38}S_2P_2PtRu$: C, 54.54; H, 3.78. Found: C, 54.22; H, 3.86.

Reaction of 6 and 7. [Fe(η-C_5H_4Se)$_2$]Pt(PPh_3)$_2$ (8f). A solution of 1,2,3-triselena[3]ferrocenophane (**6c**) (0.248 g, 0.591 mmol) and **7b** (0.620 g, 0.499 mmol) in THF (90 mL) was stirred for 1 h at 0 °C. The reaction mixture was concentrated in vacuo at the temperature below 20 °C. The residue was chromatographed on silica gel using 4:5 THF/hexane as eluent. The first colorless fraction contained only triphenylphosphine. The second red fraction was collected and concentrated in vacuo. The residue was dissolved in a minimum amount of chloroform, and hexane was added dropwise to the solution until a precipitate was formed. The precipitate was collected by filtration and washed with hexane to give **8f** as dark red powder in 45% yield. Anal. Calcd for $C_{46}H_{38}Se_2P_2FePt$: C, 56.05; H, 3.98. Found: C, 55.79; H, 3.81.

[Ru(η-C_5H_4Se)$_2$]Pt(PPh_3)$_2$ (8h). Compound **8h** was obtained from 1,2,3-triselena[3]ruthenocenophane (**6d**) (0.203 g, 0.436

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mmol) and **7b** (0.309 g, 0.248 mmol), as a yellow powder in 20% yield, in a similar manner to that described for **8f**, except that the reaction temperature was 0 °C and the eluent was 1:1 chloroform/hexane. Anal. Calcd for $C_{46}H_{38}Se_2P_2PtRu$: C, 49.92; H, 3.46. Found: C, 49.63; H, 3.48.

$[Fe(\eta\text{-}C_5H_4S)_2]Pt(PPh_3)$ (9b). A solution of 1,2,3-trithia[3]ferrocenophane (**6a**) (0.470 g, 1.43 mmol) and **7b** (1.85 g, 1.49 mmol) in THF (50 mL) was stirred for 2 h at room temperature. The solution was concentrated in vacuo, and the residue was chromatographed on silica gel by using chloroform as the eluent. The first colorless fraction contained only triphenylphosphine. The second red fraction was collected and concentrated in vacuo. The residue was dissolved in a minimum amount of chloroform, and then hexane was added dropwise to the solution until red plates precipitated. The plates were collected by filtration and recrystallized from benzene/hexane/toluene (1:1:1) to give **9b** as red columnar crystals in 18% yield. MS: *m/z* 705 (M^+). Anal. Calcd for $C_{28}H_{23}S_2PFePt\cdot{}^1/_2$Ph-Me: C, 51.14; H, 3.29%. Found: C, 51.21; H, 3.42.

$Ru(\eta\text{-}C_5H_4SeH)_2$ (5d). Compound **6d** (0.343 g, 0.763 mmol) was added to a suspension of lithium aluminum hydride (0.196 g, 5.16 mmol) in anhydrous diethyl ether (70 mL) under nitrogen. Stirring was continued at the reflux temperature for 5 h, and the mixture then was cooled to ice-water temperature. To the mixture was added dropwise 1.5% aqueous potassium hydroxide solution (50 mL), and the aqueous layer was separated. The aqueous solution was extracted with two 30-mL portions of diethyl ether. The aqueous solution was acidified with concentrated hydrochloric acid until it became weakly acidic and then extracted with three 30-mL portions of diethyl ether. The combined extracts were dried and concentrated to give **5d** as colorless crystals in 46% yield (mp 200.0–201.0 °C).

Conversion of 8 into 9. General Procedure. A solution of **8b** (7 mg, 0.0036 mmol) in 30 mL of chloroform was heated to 60 °C and stirred for 0.5 h under nitrogen. The mixture was cooled and then concentrated in vacuo. The residue was chromatographed on silica gel by using benzene as the eluent. The first colorless fraction contained triphenylphosphine. The recovery of triphenylphosphine was 95%. The red second fraction was collected and concentrated to give **9b**. The yield of **9b** was 96%.

The conversion of **8d** and **8h** into **9d** and **9h** was confirmed by comparison of the ^{1}H NMR spectra before and after the conversion, instead of isolation, respectively.

Gel Permeation Chromatography. Compounds **9a**, **9b**, and **8b** were submitted to gel permeation chromatography (GPC), using a Hitachi 635 high-pressure liquid chromatograph and a Hitachi GL-R410 or GL-R420 as a GPC column. Tetrahydrofuran was used as a eluting solvent. UV detection at 240 nm was used. Compounds **9a**, **9b**, and **8b** showed a single peak having retention times of 7.55, 7.65, and 7.60 min, respectively.

X-ray Crystallography of 9b. A crystal of dimensions 0.4 × 0.3 × 0.15 mm, obtained from benzene/hexane, was used for the intensity measurement. Lattice constants were determined by least-squares fit of angular settings of 20 reflections within range $15 \leq 2\theta \leq 30°$. Intensity data were obtained on a Rigaku AFC-5R apparatus equipped with graphite-monochromatized Mo Kα radiation and using the θ–2θ scan technique ($2\theta \leq 50°$). During data collection three standards, measured before every 200 reflections, showed a gradual decay up to 4%. Corrections of the intensity measurements were made by using a linear rescale function based on the standard intensities. Of 5258 independent reflections measured, only 4223 were considered as observed on the basis of the criterion $F_o \geq 2\sigma(F_o)$. All intensities were corrected for Lorentz and polarization effects but not for absorption.

Crystal Data. $C_{28}H_{23}S_2PFePt\cdot C_6H_6$: mol wt 783.6, monoclinic, $P2_1/c$, a = 14.166 (1) Å, b = 17.208 (4) Å, c = 12.227 (1) Å; β = 92.52 (1)°; U = 2977.6 (8) Å^3; Z = 4; D_{calcd} = 1.75 g cm^{-3}; μ(Mo Kα) = 5.4 mm^{-1}; T = 297 K. The structure was solved by the heavy-atom methods and refined by block-diagonal least-squares methods. The disordered benzene solvate molecule, which could not determine the exact coordination, was located in the cavity of the crystal structure. The carbon atoms were allowed to refine with a fixed occupancy factor of 1.0 and isotropic temperature factors because they gave the lowest R values. Positions of the hydrogen atoms, except those attached to the solvent carbon atoms, were estimated from standard geometry. The final refinements with anisotropic temperature factors for the non-hydrogen atoms except the solvent molecule and isotropic temperature factors for the solvent carbon atoms and hydrogen atoms lowered the R value to 0.053 (R_w = 0.050, $w = 1/\sigma(F_o)$). The goodness of fit was 4.92. Maximum and minimum heights in the final difference Fourier synthesis were +1.1 and −1.0 e A^{-3}, respectively, located within 1.4 Å from the Pt atom. The maximum and average shifts in the final cycle of refinement were 0.54 and 0.07, respectively, of the corresponding standard deviation. The anomalous dispersion corrections were applied to the scattering factors of Pt, Fe, S, and P.[34]

Supplementary Material Available: Tables of anisotropic thermal parameters and fractional atomic coordinates and isotropic thermal parameters for hydrogen atoms (2 pages); a listing of observed and calculated structure factors (26 pages). Ordering information is given on any current masthead page.

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