Synthesis of Heterobimetallic Fe−M (M = Ni, Pd, Pt) Complexes Containing the 1,1′-Ferrocenedithiolato Ligand and Their Conversion to Trinuclear Complexes

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The reaction of [$NiCl_2(PMe_2Ph)_2$] with $fc(SH)_2$ (fcS_2 = 1,1′-ferrocenedithiolato) afforded the Ni−Fe heterobimetallic complex containing an Fe→Ni dative bond [$Ni(S_2fc)(PMe_2Ph)$] (**1**) with concurrent liberation of one of the PMe_2Ph ligands. In contrast, similar treatment of [MCl_2(dppe)] (M = Ni, Pd, Pt; dppe = $Ph_2PCH_2CH_2PPh_2$) gave a series of group 10 metal−ferrocenedithiolato complexes [$M(S_2fc)$(dppe)] (**2**) which do not contain such a dative bond. Furthermore, oxidation of complexes **2** with 1 equiv of [$(\eta^5\text{-}C_5H_5)_2Fe$][$PF_6$] resulted in the formation of 1,1′-ferrocenedithiolato-bridged complexes [$\{M(\text{dppe})\}_2(\mu\text{-}S_2fc)$][$PF_6$]$_2$ (**3**) along with poly(1,1′-ferrocenylene disulfide). Complexes **2** were also converted into the Fe−Ru−M heterotrimetallic complexes [(*p*-cymene)RuCl(μ-S_2fc)M(dppe)][PF_6] (**4**; *p*-cymene = 4-isopropyltoluene) by the reaction of **2** with [(*p*-cymene)$RuCl_2$]$_2$ and NH_4PF_6 in acetonitrile. The detailed structures of **1**, [$Ni(S_2fc)$(dppe)] (**2a**), [$Pd(S_2fc)$(dppe)] (**2b**), [$\{Ni(\text{dppe})\}_2$(μ-S_2fc)][PF_6]$_2$ (**3a**), and [(*p*-cymene)RuCl(μ-S_2fc)Ni(dppe)][PF_6] (**4a**) have been determined by X-ray crystallography.

Introduction

Ferrocene compounds containing heteroelements are versatile building blocks for polynuclear complexes.[1] They possess electrochemically active iron centers as well as unique cylindrical shapes and, as exemplified by ferrocenylphosphine complexes, exhibit remarkable activities and selectivities in numerous catalytic reactions.[2] Thus syntheses and functions of transition metal complexes containing ferrocene moieties have been attracting much attention in recent years.

In the course of our extensive study on the preparation and reactivities of the thiolato-bridged diruthenium, dirhodium, and diiridium complexes,[3] we have recently synthesized a series of ferrocenechalcogenolato-bridged diruthenium complexes such as [Cp*Ru(μ_2-*s-trans*-CH_2=CHCH=CH_2)(μ_2-EFc)$_2$RuCp*] (Cp* = η^5-C_5Me_5; E = S, Se, Te; Fc = ferrocenyl).[3c] We now turn our attention to the group 10 metal complexes with ferrocene-substituted thiolato ligands since the resultant mixed-metal thiolato complexes containing group 8 and group 10 metals might have some relevance to the active site of Ni−Fe hydrogenases.[4] In this paper, we describe the syntheses and structures of the Ni−Fe heterobimetallic complex [$Ni(S_2fc)(PMe_2Ph)$] (**1**; S_2fc = 1,1′-ferrocenedithiolato) containing an Fe→Ni dative bond and a series of 1,1′-ferrocenedithiolato group 10 metal complexes [$M(S_2fc)$(dppe)] (**2**; M = Ni, Pd, Pt) without a metal−metal bond. Formation of the trinuclear complexes containing M_2Fe and MRuFe cores [$\{M(\text{dppe})\}_2$(μ-S_2fc)][PF_6]$_2$ (**3**) and [(*p*-cymene)RuCl(μ-S_2fc)M(dppe)][PF_6] (**4**) from **2** is also reported.

Results and Discussion

Preparation and Structure of the Ni−Fe Heterobimetallic Complex [$Ni(S_2fc)(PMe_2Ph)$] (1) Containing an Fe→Ni Dative Bond. Although the 1,1′-ferrocene- or 1,1′-ruthenocenedithiolato complexes [M{$(SC_5H_4)_2$M′}(PPh_3)] (M = Ni, Pd, Pt; M′ = Fe, Ru) containing M′→M dative bonds were previously prepared by the reactions of [$M(PPh_3)_4$] with 1,1′-metallocenedithiols or 1,2,3-trithia[3](1,1′)metallocenophanes,[5−7] the Ni−Fe complex [$Ni(S_2fc)(PPh_3)$] has been a missing link in this series; attempts to obtain this complex have failed.[7] Thus we have employed the more electron-donating dimethylphenylphos-

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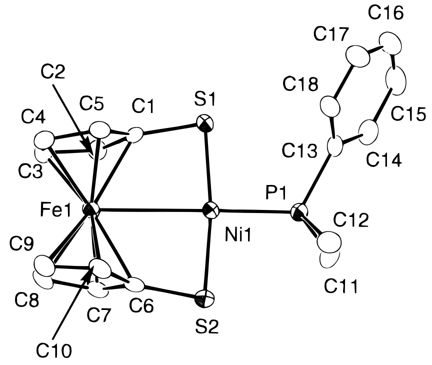
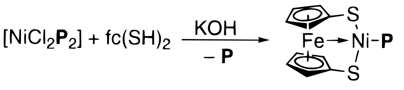


Figure 1. ORTEP drawing for **1**. Hydrogen atoms are omitted for clarity.

Table 1. Selected Bond Lengths (Å) and Angles (deg) for **1**

Ni(1)−Fe(1)	2.886(1)	Ni(1)−P(1)	2.136(2)
Ni(1)−S(1)	2.140(2)	Ni(1)−S(2)	2.159(2)
C(1)−C(2)	1.429(7)	C(6)−C(7)	1.426(7)
C(2)−C(3)	1.381(8)	C(7)−C(8)	1.388(8)
C(3)−C4)	1.423(8)	C(8)−C(9)	1.417(8)
C(4)−C(5)	1.386(8)	C(9)−C(10)	1.384(8)
C(1)−C(5)	1.440(8)	C(6)−C(10)	1.424(7)
S(1)−Ni(1)−P(1)	95.15(7)	S(2)−Ni(1)−P(1)	92.69(7)
S(1)−Ni(1)−Fe(1)	85.72(5)	S(2)−Ni(1)−Fe(1)	86.45(6)
Fe(1)−Ni(1)−P(1)	179.09(6)	S(1)−Ni(1)−S(2)	172.10(7)

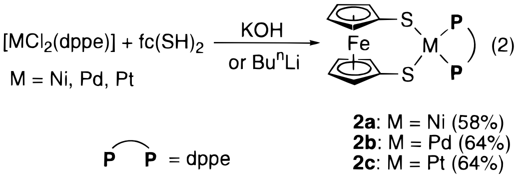
phine as an ancillary ligand. When [$NiCl_2(PMe_2Ph)_2$] was allowed to react with 1 equiv of 1,1′-ferrocenedithiol in the presence of potassium hydroxide at room temperature, the Ni−Fe heterobimetallic complex [$Ni(S_2fc)(PMe_2Ph)$] (**1**) was obtained in moderate yield (eq 1). The ^1H NMR spectrum of **1** exhibits signals ascribed to the 1,1′-ferrocenedithiolato and the phosphine ligands in a ratio of 1:1. The two triplets assignable to the cyclopentadienyl protons appear significantly apart from each other (4.99 and 2.89 ppm) as are observed in other complexes containing dative bonds from the iron atom in the ferrocene moieties.[6,9] We have no evidence for the formation of the bis(phosphine) complex [$Ni(S_2fc)(PMe_2Ph)_2$], although both [$Pt(S_2fc)(PPh_3)$] and [$Pt(S_2fc)(PPh_3)_2$] have been obtained from the reaction of [$Pt(PPh_3)_4$] with $fc(SH)_2$ depending upon the reaction conditions.[6] In addition, **1** did not react with donor ligands such as PMe_2Ph and CO.



$P = PMe_2Ph$ **1** (1)

To clarify the detailed structure of **1**, an X-ray analysis has been performed; an ORTEP drawing of **1** is depicted in Figure 1, and selected bond distances and angles are listed in Table 1. Complex **1** is isostructural with the palladium and platinum analogues [$M(S_2fc)(PPh_3)$] (M = Pd, Pt).[5,6] The nickel and iron atoms are bridged by two μ_2-η^1:η^5-C_5H_4S groups. The coordination geometry around the nickel atom is distorted square planar with the two sulfur atoms in mutually trans positions, and the iron atom is located trans to the phosphine ligand. The remarkably acute Ni−S−C angles (82.6(2) and 84.4(2)°) as well as the Ni−Fe distance of 2.886(1) Å in **1** suggest the presence of a dative bond from the iron atom to the nickel atom, which gives the nickel center a stable 16-electron configuration. The Ni−Fe distance is, however, significantly longer than those found in the Ni−Fe heterometallic clusters reported so far (2.41−2.45 Å)[8] and comparable to the metal−metal distances in [$Pd(S_2fc)(PPh_3)$] (2.878(1) Å)[5] and [$Ni(S_2rc)(PPh_3)$] (2.864(1) Å; S_2rc = 1,1′-ruthenocenedithiolato)[7] despite the smaller covalent radii of the first-row transition metals compared to the second-row ones, suggesting a weaker metal−metal interaction in **1**. Such a long Ni−Fe distance may be due to the steric demand of the bridging C_5H_4S ligands since the Ni−S−C angles are significantly acute as described above. The resultant weaker donation from the iron atom is apparently compensated by the more electron-donating nature of the dimethylphenylphosphine ligand, which has led to the successful isolation of **1**. Thus **1** is the first Ni−Fe heterobimetallic complex containing a dative bond from the iron atom in the ferrocene moiety to the nickel atom. The Ni−P distance (2.136(2) Å) and the Ni−S distances (2.140(2) and 2.159(2) Å) in **1** are comparable to those in the 1,1′-ruthenocenedithiolato analogue of **1** [$Ni(S_2rc)(PPh_3)$] (Ni−P, 2.140(1); Ni−S, 2.176(1) and 2.155(1) Å)[7] and a mononuclear nickel(II) complex [$Ni(SCH_2CH_2PPh_2)_2$] (Ni−P, 2.186(1); Ni−S, 2.174(1) Å).[10] The two cyclopentadienyl rings in **1** are tilted with a dihedral angle of 14.8°, which is slightly smaller than the corresponding angle in [$Pd(S_2fc)(PPh_3)$] (19.6°).[5] In the two cyclopentadienyl rings in **1**, the pattern of alternating "long" (1.417(8)−1.440(8) Å) and "short" (1.381(8)−1.388(8) Å) C−C bond lengths is observed, although the high estimated standard deviations associated with these distances render this variation statistically insignificant at the 2σ level. The S−C distances of 1.729(6) and 1.736(6) Å appear somewhat shorter than normal. This bond alternation as well as the tilting of the cyclopentadienyl rings suggests some contribution of a cyclopentadienethione-type canonical structure as proposed for [$Pd(S_2fc)(PPh_3)$].[5b]

Preparation and Structures of M−Fe Heterobimetallic Complexes [$M(S_2fc)(dppe)$] (2; M = Ni, Pd, Pt) with No Direct M−Fe Interactions. In contrast to the formation of **1** and the concurrent liberation of one of the coordinated phosphine ligands (eq 1), treatment of the bidentate phosphine complex [$NiCl_2(dppe)$] with $fc(SH)_2$ at ambient temperature in the presence of potassium hydroxide afforded the 1,1′-ferrocenedithiolato−diphosphine complex [$Ni(S_2fc)(dppe)$] (**2a**) in moderate yield (eq 2). Although [$MCl_2(dppe)$] (M = Pd, Pt) did not react with $fc(SH)_2$ under the same conditions, the corresponding palladium and platinum complexes [$M(S_2fc)(dppe)$] (**2b**, M = Pd; **2c**, M = Pt) were successfully obtained by the reactions of [$MCl_2(dppe)$] with $fc(SLi)_2$. In contrast to **1**, the ^1H NMR spectra of **2** show two triplets for the cyclopentadienyl protons in the narrow range of 3.8−4.2 ppm along with the signals assignable to one dppe ligand. The $^{31}P\{^1H\}$ NMR spectra display only one singlet, which is further accompanied by the ^{195}Pt satellites in the platinum complex **2c**.



(2)

2a: M = Ni (58%)
2b: M = Pd (64%)
2c: M = Pt (64%)

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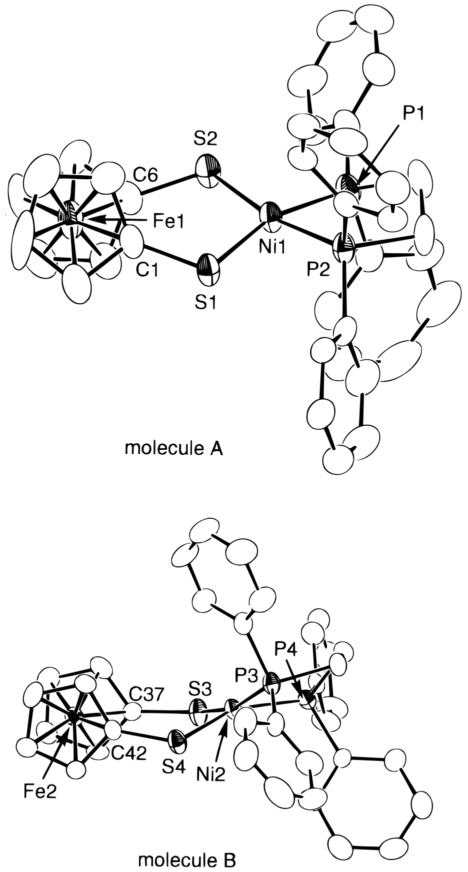


Figure 2. ORTEP drawings for the staggered (molecule A) and eclipsed (molecule B) conformers of **2a**. Hydrogen atoms are omitted for clarity.

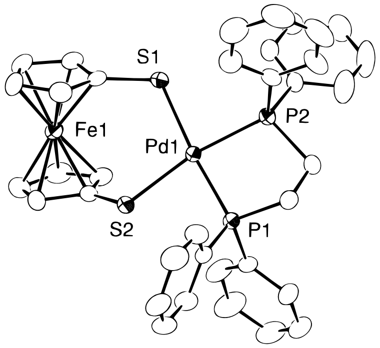
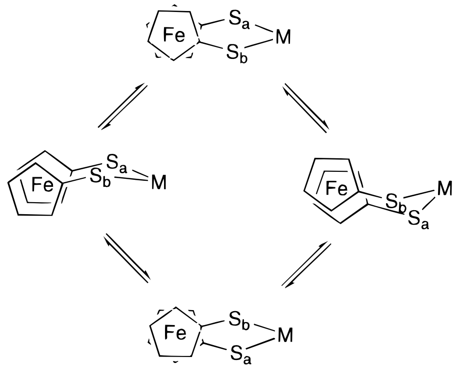


Figure 3. ORTEP drawing for **2b**·CH$_2$Cl$_2$. Hydrogen atoms as well as solvating molecule are omitted for clarity.

Table 2. Selected Interatomic Distances (Å) and Angles (deg) for **2a** and **2b**·CH$_2$Cl$_2$

	2a (M = Ni)		**2b**·CH$_2$Cl$_2$ (M = Pd)
	molecule A	molecule B	
M(1)−S(1)	2.207(4)	2.196(4)	2.370(2)
M(1)−S(2)	2.207(4)	2.199(4)	2.356(2)
M(1)−P(1)	2.186(4)	2.178(4)	2.272(2)
M(1)−P(2)	2.186(4)	2.179(4)	2.313(2)
M(1)···Fe(1)	4.246(3)	4.222(2)	4.269(1)
S(1)−M(1)−S(2)	105.2(1)	106.1(1)	102.11(5)
S(1)−M(1)−P(1)	170.0(2)	163.7(2)	174.66(6)
S(1)−M(1)−P(2)	86.5(1)	88.6(1)	89.43(6)
S(2)−M(1)−P(1)	83.2(1)	84.6(1)	82.89(5)
S(2)−M(1)−P(2)	163.8(2)	156.7(1)	167.95(6)
P(1)−M(1)−P(2)	86.5(1)	85.4(1)	85.47(6)

Scheme 1



Complexes **2a**,**b** have been fully characterized by X-ray analyses; the molecular structures are shown in Figures 2 and 3, and selected interatomic distances and angles are collected in Table 2. The asymmetric unit of **2a** consists of two crystallographically independent molecules. Interestingly, these two molecules differ in the conformation of the cyclopentadienyl rings: one is staggered (molecule A) and the other eclipsed (molecule B). However, only two triplets are observed for the cyclopentadienyl ring protons in the ^{1}H NMR spectrum of **2a** even at −50 °C, suggesting rapid interconversion between these conformers through the sulfur inversion (Scheme 1).[11] The two cyclopentadienyl rings in each molecule are almost parallel with the dihedral angles of 7.7° (molecule A) and 4.1° (molecule B), and the Ni−S−C angles are normal (115.9(5)−117.8(5)°), which sharply contrasts with **1**. The long Ni−Fe distances of 4.222(2) and 4.246(3) Å preclude any direct metal−metal bonding. The coordination geometry around the nickel atoms in both molecules is distorted square planar. The Ni−S distances (2.196(4)−2.207(4) Å) and Ni−P distances (2.178(4)−2.186(4) Å) are comparable to those in the related *cis*-bis(thiolato)nickel(II) complex [Ni(SC$_6$F$_5$)$_2$(dppe)] (Ni−S, 2.217; Ni−P, 2.188 Å (mean)).[12]

On the other hand, the palladium complex **2b** contains two parallel cyclopentadienyl rings with a staggered conformation in the solid state and is isostructural with the staggered conformer of **2a** (molecule A). The bond distances around the square planar palladium atom (Pd−S, 2.356(2) and 2.370(2); Pd−P, 2.272(2) and 2.313(2) Å) are common with the related (diphosphine)bis(thiolato)palladium(II) complex [Pd(SC$_5$H$_9$-NMe$_2$)$_2$(dppe)] (Pd−S, 2.358; Pd−P, 2.268 Å (mean)).[13] A staggered conformation of the two cyclopentadienyl rings as well as a square planar geometry around the platinum atom in **2c** has also been confirmed by a preliminary X-ray analysis.[14]

Oxidation of 2 To Give Trinuclear Complexes [{M(dppe)}$_2$(μ-S$_2$fc)][PF$_6$]$_2$ (3; M = Ni, Pd, Pt). Redox properties of the 1,1′-ferrocenedithiolato complexes **1** and **2** are of interest because they contain an electrochemically active ferrocene moiety. The cyclic voltammogram of **1** exhibits one irreversible oxidation wave at 0.28 V, whereas complexes **2** show one reversible oxidation wave around 0.2 V and a successive irreversible one at 1.0−1.1 V (Table 3). Chemical oxidation of

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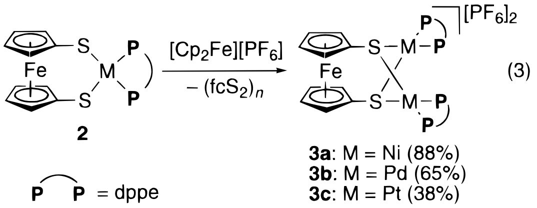
(14) Unit cell parameters for **2c**·CH$_2$Cl$_2$: orthorhombic, space group $P2_12_12_1$ with $a = 9.492$, $b = 13.758$, $c = 26.979$ Å, and $V = 3523.2$ Å^3.

Table 3. Redox Potentials of Complexes 1 and 2[a]

complex	E^{red}, V	E^{ox}, V	
1	−1.9 (ir)	0.28 (ir)	
2a	−1.6 (ir)	0.23 (r)	1.1 (ir)
2b	−1.3 (ir)	0.19 (r)	1.0 (ir)
2c	not obsd	0.21 (r)	1.1 (ir)

[a] All potentials are measured in CH_2Cl_2 solution with 0.1 M $[Bu_4N][BF_4]$, V vs SCE; r = reversible where $E = E_{1/2}$, and ir = irreversible where $E = E_p$. Scan rate = 200 mV s^{-1}.

1 by using $[Cp_2Fe][PF_6]$ (Cp = η^5-C_5H_5) did not afford any characterizable products. On the other hand, when 1 equiv of $[Cp_2Fe][PF_6]$ was added to a dichloromethane solution of **2a**, the color of the solution immediately changed from dark violet to dark red at −78 °C and finally turned to dark brown at room temperature concurrent with the formation of a yellow precipitate. From the filtrate was isolated the 1,1′-ferrocenedithiolato-bridged dinickel complex $[\{Ni(dppe)\}_2(\mu\text{-}S_2fc)][PF_6]_2$ (**3a**) in 88% yield (eq 3). Similar treatment of the palladium and platinum complexes **2b**,**c** with ferrocenium cation also afforded the corresponding trinuclear complexes $[\{M(dppe)\}_2(\mu\text{-}S_2fc)][PF_6]_2$ (**3b**, M = Pd; **3c**, M = Pt) in moderate yields, although the formation of these complexes was slower than that of **3a**. The ^1H NMR spectra of **3** resemble those of the parent complex **2** except that two dppe ligands are now present per one ferrocenedithiolato ligand. The $^{31}P\{^1H\}$ NMR spectra show only one singlet along with a septet arising from the hexafluorophosphate anion; the singlet is further accompanied by the ^{195}Pt satellites in **3c**. These spectra are consistent with the trinuclear structure where the two M(dppe) units are symmetrically bridged by a 1,1′-ferrocenedithiolato ligand.



An NMR-tube reaction of **2a** with $[Cp_2Fe][PF_6]$ at −78 °C indicated the presence of a paramagnetic species, presumably $[Ni(S_2fc)(dppe)]^+$ ($\mathbf{2a}^+$), in the initial stage of the reaction; signals assignable to this species disappeared upon warming. On the other hand, the yellow precipitate concurrently formed along with **3** has been characterized as poly(1,1′-ferrocenylene disulfide), $(fcS_2)_n$,[15] by electron-probe microanalysis (EPMA) and IR spectroscopy. These observations lead to the following mechanism for the formation of **3**. Upon treatment with $[Cp_2Fe][PF_6]$, **2** is oxidized to give $\mathbf{2}^+$, which disproportionates to **2** and $\mathbf{2}^{2+}$; the latter species liberates a coordinatively unsaturated $M(dppe)^{2+}$ fragment with concurrent formation of $(fcS_2)_n$. The fragment then reacts with **2** to afford **3**. Hembre and co-workers have recently demonstrated that the Ru−Fe bimetallic complex containing a ferrocene moiety $[Cp^*RuH\{(Ph_2PC_5H_4)_2Fe\}]$ catalyzes the reduction of ferrocenium cation by H_2, which closely relates to the hydrogenase catalysis.[2e] Stimulated by this finding, oxidation of **1** and **2a** under H_2 was attempted; however, the products were the same as those obtained under N_2.

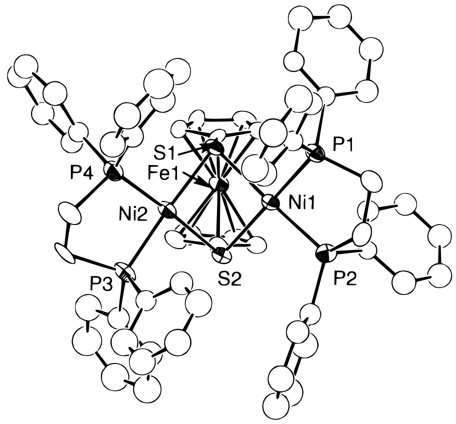


Figure 4. Molecular structure of the cationic part of **3a·**THF. Hydrogen atoms are omitted for clarity.

Table 4. Selected Interatomic Distances (Å) and Angles (deg) for **3a·**THF

Ni(1)−S(1)	2.250(4)	Ni(2)−S(1)	2.251(4)
Ni(1)−S(2)	2.229(4)	Ni(2)−S(2)	2.229(4)
Ni(1)−P(1)	2.183(4)	Ni(2)−P(3)	2.180(4)
Ni(1)−P(2)	2.174(4)	Ni(2)−P(4)	2.216(5)
Ni(1)···Ni(2)	2.972(3)	Ni(1)···Fe(1)	3.872(3)
Ni(2)···Fe(1)	3.958(3)		
P(1)−Ni(1)−P(2)	86.4(2)	P(3)−Ni(2)−P(4)	86.0(2)
P(1)−Ni(1)−S(1)	92.8(2)	S(1)−Ni(2)−P(4)	96.2(2)
S(1)−Ni(1)−S(2)	88.2(2)	S(1)−Ni(2)−S(2)	88.1(2)
S(2)−Ni(1)−P(2)	92.8(2)	S(2)−Ni(2)−P(3)	89.3(2)
Ni(1)−S(1)−Ni(2)	82.6(1)	Ni(1)−S(2)−Ni(2)	83.6(1)
S(1)−Ni(1)−P(2)	178.6(2)	S(1)−Ni(2)−P(3)	176.3(2)
P(1)−Ni(1)−S(2)	172.2(2)	S(2)−Ni(2)−P(4)	171.8(2)

An X-ray analysis of **3a** disclosed the 1,1′-ferrocenedithiolato-bridged dinickel core structure. An ORTEP drawing of the cationic part of **3a** is depicted in Figure 4, and selected interatomic distances and angles are listed in Table 4. The coordination geometry around the two nickel atoms is square planar, which is common with related thiolato-bridged dinickel(II) complexes.[16] The Ni−S and Ni−P distances are also unexceptional. Thiolato-bridged dinickel complexes reported so far are put into two categories: one comprises complexes containing a puckered Ni_2S_2 ring with *syn*-equatorial thiolato groups and relatively short Ni−Ni distances (2.73−2.76 Å), and the other a planar Ni_2S_2 ring with *anti*-thiolato groups and large Ni−Ni separations (3.31−3.35 Å).[16] The four-membered Ni_2S_2 ring in **3a** is folded with a dihedral angle of 129.5° along with the S(1)−S(2) vector, yet the two thiolato substituents are in *syn*-axial orientation due to the chelating nature of the 1,1′-ferrocenedithiolato ligand. Complex **3a** falls in the middle of the two categories in the term of the Ni−Ni distance (2.972(3) Å). A similar dinickel center bridged by a *syn*-axial dithiolato ligand is involved in the triangular complex $[Ni(\mu_2\text{-}S_2C_{10}Cl_6)(PPh_3)]_3$, although the Ni−Ni distances in this complex are relatively short (2.641 Å (mean)).[17] The two parallel cyclopentadienyl rings in **3a** are almost eclipsed.

Syntheses and Structures of Fe−Ru−M Heterotrimetallic Complexes [(*p*-cymene)RuCl(μ-S$_2$fc)M(dppe)][PF$_6$] (4; M = Ni, Pd, Pt). Formation of **3** upon oxidation of **2** suggests that complexes **2** can serve as potential precursors for the syntheses of the 1,1′-ferrocenedithiolato-bridged multinuclear complexes similarly to the related bis(thiolato) complexes $[M(SPh)_2(dppe)]$ (M = Ni, Pd) and $[Pt(SPh)_2(PPh_3)_2]$.[18] In fact, addition of **2** to

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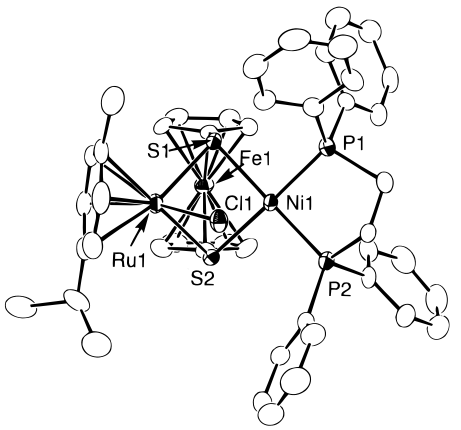
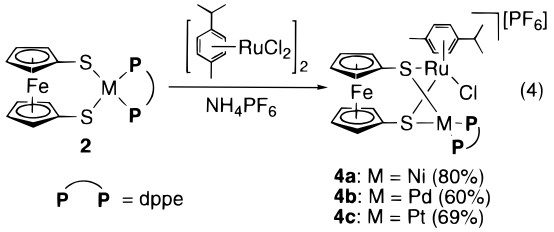


Figure 5. Molecular structure of the cationic part of **4a**. Hydrogen atoms are omitted for clarity.

Table 5. Selected Interatomic Distances (Å) and Angles (deg) for **4a**

Ru(1)−Cl(1)	2.449(2)	Ni(1)−S(1)	2.254(2)
Ru(1)−S(1)	2.416(2)	Ni(1)−S(2)	2.286(3)
Ru(1)−S(2)	2.415(2)	Ni(1)−P(1)	2.195(3)
Ni(1)−P(2)	2.192(2)	Ni(1)···Cl(1)	2.625(3)
Ru(1)···Fe(1)	4.259(2)	Ni(1)···Fe(1)	4.000(2)
Ni(1)···Ru(1)	3.131(2)		
Ru(1)−S(1)−Ni(1)	84.14(8)	Cl(1)−Ru(1)−S(1)	85.29(8)
Ru(1)−S(2)−Ni(1)	83.48(8)	Cl(1)−Ru(1)−S(2)	79.07(7)
S(1)−Ni(1)−S(2)	85.91(9)	S(1)−Ni(1)−P(1)	92.0(1)
P(1)−Ni(1)−P(2)	87.0(1)	S(2)−Ni(1)−P(2)	95.2(1)
S(1)−Ni(1)−P(2)	177.3(1)	S(2)−Ni(1)−P(1)	177.38(10)

the mixture of [(*p*-cymene)$RuCl_2$]$_2$ and NH_4PF_6 in acetonitrile afforded a series of heterometallic complexes [(*p*-cymene)RuCl(μ-S_2fc)M(dppe)][PF_6] (**4a**, M = Ni; **4b**, M = Pd, **4c**, M = Pt) in moderate yields (eq 4). The ^{1}H NMR spectra of **4** exhibit four multiplets assignable to the ferrocene ring protons, suggesting that there no longer exists a mirror plane containing the iron and the two sulfur atoms. The ^{1}H and ^{31}P{^{1}H} spectra indicate the presence of both *p*-cymene and dppe ligands in **4**.



To elucidate the detailed structure of **4**, an X-ray diffraction study of **4a** has been undertaken. An ORTEP drawing of the cationic part of **4a** is depicted in Figure 5, and selected interatomic distances and angles are listed in Table 5. As expected, complex **4a** has both (*p*-cymene)RuCl and Ni(dppe) fragments, which are bridged by a 1,1′-ferrocenedithiolato ligand. The dihedral angle between the RuS_2 and NiS_2 planes is 125.7°, and the two thiolato substituents are in *syn*-axial orientation as in the dinickel complex **3a**. The folding of the RuS_2Ni four-membered ring brings the chloro ligand bound to the ruthenium atom close to the apical position of the square planar nickel atom. The resultant Ni−Cl distance of 2.625(3) Å suggests some interaction between these atoms, although it is significantly longer than the Ni−Cl bond length in, e.g., [NiCl{(*o*-$MeSC_6H_4$)$_3$P}][ClO_4] (2.227(7) Å).[19] On the other hand, the distances between the metals (3.131(2)−4.259(2) Å) indicate the absence of direct metal−metal interactions.

In summary, we have demonstrated that the reaction of dichloronickel(II) phosphine complexes with 1,1′-ferrocenedithiolate affords the Ni−Fe heterobimetallic complex **1** containing an Fe→Ni dative bond or complex **2a** without any direct metal−metal interaction which depends on the phosphine ligand employed. Complex **2a** as well as the corresponding palladium and platinum complexes **2b**,**c** serves as a potential precursor for the syntheses of heterometallic complexes with higher nuclearity. The resultant trinuclear complexes **3** and **4** possess a puckered M_2S_2 core with *syn*-axial thiolato substituents owing to the unique cylindrical shape of the 1,1′-ferrocenedithiolato moiety.

Experimental Section

General Methods. All manipulations were performed under an atmosphere of nitrogen using standard Schlenk-tube techniques unless otherwise specified. Solvents were dried and distilled before use. Reagents were commercially obtained and used as received. The following compounds were prepared according to the literature: fc(SH)$_2$,[20] [$NiCl_2$(dppe)],[21] [$NiCl_2$(PMe_2Ph)$_2$],[22] [$PdCl_2$(dppe)],[23] [$PtCl_2$(dppe)]·H_2O,[23] and [(*p*-cymene)$RuCl_2$]$_2$.[24]

NMR spectra were recorded on a JEOL JNM-EX-270 or JEOL JNM-LA400 spectrometers, while IR spectra were recorded on a Shimadzu FTIR-8100 spectrometer. Elemental analyses were performed on a Perkin-Elmer 2400 series II CHN analyzer. Amounts of the solvent molecules were determined not only by elemental analyses but also by ^{1}H NMR spectroscopy. Electrochemical measurements were made with Hokuto Denko instrumentation (HA-501 potentiostat and HB-105 function generator) using a glassy carbon working electrode; potentials were measured in CH_2Cl_2−0.1 M $Bu^n{}_4NBF_4$ vs saturated calomel electrode as reference. EPMA was performed on a Kevex μX 7000 energy dispersive-type X-ray analyzer.

[Ni(S_2fc)(PMe_2Ph)] (1). To a solution of [$NiCl_2$(PMe_2Ph)$_2$] (203 mg, 0.500 mmol) and fc(SH)$_2$ (138 mg, 0.550 mmol) in dichloromethane (7 mL) was added 5% aqueous potassium hydroxide solution (5 mL). After stirring of the mixture for 2 h at room temperature, the organic layer was dried by $MgSO_4$ and filtered. Addition of hexanes to the concentrated filtrate afforded dark red crystals of **1** (133 mg, 60%). ^{1}H NMR ($CDCl_3$): δ 7.80−7.43 (m, 5 H, Ph), 4.99, 2.89 (t, 4 H each, J = 2.0 Hz, C_5H_4), 1.96 (d, 6 H, J = 9.6 Hz, Me). ^{31}P{^{1}H} NMR ($CDCl_3$): δ 15.3 (s). Anal. Calcd for $C_{18}H_{19}PS_2FeNi$: C, 48.58; H, 4.30. Found: C, 48.90; H, 4.27.

[Ni(S_2fc)(dppe)] (2a). To a suspension of [$NiCl_2$(dppe)] (1.06 g, 2.01 mmol) and fc(SH)$_2$ (500 mg, 2.00 mmol) in dichloromethane (40 mL) was added 10% aqueous potassium hydroxide solution (40 mL). After stirring of the mixture for 1.5 h at room temperature, the organic layer was dried by $MgSO_4$ and filtered. Addition of hexanes (100 mL) to the concentrated filtrate (ca. 20 mL) afforded dark violet crystals of **2a** (814 mg, 58%). Crystals suitable for the X-ray analysis were obtained by recrystallization from toluene−diethyl ether. ^{1}H NMR ($CDCl_3$): δ 7.94−7.44 (m, 20 H, Ph), 4.11, 3.88 (t, 4 H each, J = 1.7 Hz, C_5H_4), 2.18 (br d, 4 H, CH_2). ^{31}P{^{1}H} NMR ($CDCl_3$): δ 53.3 (s). Anal. Calcd for $C_{36}H_{32}P_2S_2FeNi$: C, 61.31; H, 4.57. Found: C, 61.30; H, 4.72.

[Pd(S_2fc)(dppe)]·CH_2Cl_2 (2b·CH_2Cl_2). To a THF (6 mL) solution of fc(SH)$_2$ (113 mg, 0.450 mmol) was added Bu^nLi (1.6 M in *n*-hexane, 0.6 mL, 0.96 mmol) and [$PdCl_2$(dppe)] (260 mg, 0.450 mmol) at room temperature. The dark violet mixture was stirred overnight. All volatiles were removed in vacuo, and the residue was extracted with dichloromethane (12 mL). Addition of hexanes to the concentrated extract

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Table 6. Crystallographic Data for **1**, **2a**, **2b**·CH_2Cl_2, **3a**·THF, and **4a**

	1	**2a**	**2b**·CH_2Cl_2	**3a**·THF	**4a**
formula	$C_{18}H_{19}PS_2FeNi$	$C_{36}H_{32}P_2S_2FeNi$	$C_{37}H_{34}Cl_2P_2S_2FePd$	$C_{66}H_{64}F_{12}OP_6S_2FeNi_2$	$C_{46}H_{46}F_6P_3S_2FeNiRu$
fw	444.99	705.26	837.90	1524.42	1120.97
space group	$P2_1$	$P\bar{1}$	$P2_12_12_1$	$P2_1/a$	$P2_1/c$
a, Å	5.985(3)	14.061(3)	13.761(6)	14.994(6)	15.546(6)
b, Å	12.476(3)	24.510(6)	27.019(6)	28.130(9)	15.108(8)
c, Å	11.876(3)	10.423(2)	9.475(6)	15.667(9)	20.001(10)
α, deg	90	100.66(2)	90	90	90
β, deg	94.09(4)	95.45(2)	90	95.24(4)	94.05(5)
γ, deg	90	74.78(2)	90	90	90
V, Å^3	884.5(6)	3402(1)	3523(2)	6580(4)	4685(3)
Z	2	4	4	4	4
ρ_{calcd}, g cm^{-3}	1.671	1.377	1.580	1.539	1.589
μ(Mo Kα), cm^{-1}	22.05	12.20	13.10	10.70	13.26
R^a	0.030	0.059	0.030	0.078	0.047
$R_w{}^a$	0.021	0.078	0.022	0.060	0.034

[a] $R = \sum||F_o| - |F_c||/\sum|F_o|$; $R_w = [\sum w(|F_o| - |F_c|)^2/\sum wF_o{}^2]^{1/2}$.

gave dark violet crystals of **2b**·CH_2Cl_2 (240 mg, 64%). ^{1}H NMR ($CDCl_3$): δ 7.87−7.45 (m, 20 H, Ph), 4.18, 3.84 (t, 4 H each, J = 2.0 Hz, C_5H_4), 2.40 (br d, 4 H, CH_2). ^{31}P{^{1}H} NMR ($CDCl_3$): δ 51.2 (s). Anal. Calcd for $C_{37}H_{34}Cl_2P_2S_2FePd$: C, 53.04; H, 4.09. Found: C, 53.31; H, 4.16.

[Pt(S_2fc)(dppe)]·CH_2Cl_2 (2c·CH_2Cl_2). To a THF (20 mL) solution of fc$(SH)_2$ (198 mg, 0.792 mmol) was added Bu^{n}Li (1.6 M in *n*-hexane, 1.1 mL, 1.8 mmol) and [$PtCl_2$(dppe)]·H_2O (540 mg, 0.792 mmol) at room temperature. The orange mixture was stirred overnight. All volatiles were removed in vacuo, and the residue was extracted with benzene (20 mL). Removal of the solvent from the extract gave an orange solid, which was washed with diethyl ether. Recrystallization from dichloromethane−hexanes gave **2c**·CH_2Cl_2 as orange crystals (470 mg, 64%). ^{1}H NMR ($CDCl_3$): δ 7.90−7.46 (m, 20 H, Ph), 4.06, 3.82 (t, 4 H each, J = 1.8 Hz, C_5H_4), 2.36 (m, 4 H, CH_2). ^{31}P{^{1}H} NMR ($CDCl_3$): δ 45.5 (s, $^1J_{\text{Pt-P}}$ = 2792 Hz). Anal. Calcd for $C_{37}H_{34}Cl_2P_2S_2FePt$: C, 47.96; H, 3.70. Found: C, 48.22; H, 3.62.

[{Ni(dppe)}$_2$(μ-S_2fc)][PF_6]$_2$ (3a). To a solution of **2a** (705 mg, 1.00 mmol) in dichloromethane (15 mL) was added [Cp_2Fe][PF_6] (331 mg, 1.00 mmol) at −78 °C, and the mixture was slowly warmed to room temperature with stirring over the period of 16 h. The mixture was then filtered. Addition of hexanes to the concentrated filtrate gave **3a** as brown plates (640 mg, 88%). An analytically pure sample was obtained by recrystallization from THF−hexanes as **3a**·THF. ^{1}H NMR (CD_2Cl_2): δ 7.77−7.37 (m, 40 H, Ph), 4.23, 3.91 (t, 4 H each, J = 2.0 Hz, C_5H_4), 2.75−2.20 (m, 8 H, CH_2). ^{31}P{^{1}H} NMR (CD_2Cl_2): δ 55.5 (s). Anal. Calcd for $C_{66}H_{64}F_{12}OP_6S_2FeNi_2$: C, 52.00; H, 4.23. Found: C, 51.61; H, 4.41. The yellow precipitate deposited from the reaction mixture was washed with dichloromethane and dried in vacuo to give $(fcS_2)_n$ as a yellow solid (46 mg, 37%). The IR spectrum of this material is identical to that of the authentic sample prepared according to the literature.[15] The EPMA data have also confirmed the presence of nearly two S atoms per Fe atoms and the absence of Ni and P atoms.

In a separate run, onto a mixture of **2a** and an equimolar amount of [Cp_2Fe][PF_6] in an NMR tube was condensed CD_2Cl_2 at −196 °C. The ^{1}H NMR spectrum of the mixture warmed to −78 °C showed broad resonances ascribed to the intermediary paramagnetic species **2a**$^+$: δ 8.1−7.4 (br m, 20 H, Ph), 6.59 (br s, 8 H, C_5H_4), 0.05 (br s, 4 H, CH_2).

[{M(dppe)}$_2$(μ-S_2fc)][PF_6]$_2$ (3b, M = Pd; 3c, M = Pt). These complexes were obtained from **2b**·CH_2Cl_2 and **2c**·CH_2Cl_2 in a similar mannar for **3a**, respectively, except that the reaction mixtures were stirred for 2 days at room temperature.

3b·$ClCH_2CH_2Cl$: brown crystals from 1,2-dichloroethane−hexanes (65%). ^{1}H NMR (acetone-d_6): δ 7.84−7.44 (m, 40 H, Ph), 4.15, 3.82 (t, 4 H each, J = 1.8 Hz, C_5H_4), 3.47−3.17, 3.10−2.90 (m, 4 H each, CH_2). ^{31}P{^{1}H} NMR (acetone-d_6): δ 61.2 (s). Anal. Calcd for $C_{64}H_{60}Cl_2F_{12}P_6S_2FePd_2$: C, 46.68; H, 3.67. Found: C, 46.88; H, 3.71.

3c·0.5CH_2Cl_2: yellow crystalline solid from dichloromethane−hexanes (38%). ^{1}H NMR (CD_3CN): δ 7.77−7.37 (m, 40 H, Ph), 4.23, 3.91 (t, 4 H each, J = 2.0 Hz, C_5H_4), 3.12−2.72, 2.70−2.38 (m, 4 H each, CH_2). ^{31}P{^{1}H} NMR (CD_3CN): δ 45.5 (s, $^1J_{\text{Pt-P}}$ = 2978 Hz). Anal. Calcd for $C_{62.5}H_{57}ClF_{12}P_6S_2FePt_2$: C, 42.47; H, 3.25. Found: C, 42.18; H, 3.28.

[(*p*-cymene)RuCl(μ-S_2fc)M(dppe)][PF_6] (4). The following procedure for the preparation of [(*p*-cymene)RuCl(μ-S_2fc)Ni(dppe)][PF_6] (**4a**) is representative. A mixture of [(*p*-cymene)$RuCl_2$]$_2$ (263 mg, 0.430 mmol) and NH_4PF_6 (152 mg, 0.933 mmol) in acetonitrile (50 mL) was stirred for 3 h at room temperature. To the suspension was added **1a** (600 mg, 0.851 mmol), and the mixture was stirred for additional 2 h. The solvent was removed in vacuo, and the residue was extracted with acetone and chromatographed on activated alumina. The brown band eluted with acetone was recrystallized from dichloromethane−hexanes to give **4a** as dark brown crystals (767 mg, 80%). ^{1}H NMR (CD_3CN): δ 7.82−7.41 (m, 20 H, Ph), 5.82, 5.52 (d, 2 H each, J = 6.2 Hz, *p*-MeC$_6$*H*$_4$Pr^i), 4.50−4.48, 4.12−4.11, 3.92−3.90, 3.81−3.79 (m, 2 H each, C_5H_4), 2.84 (sep, 1 H, J = 6.7 Hz, C*H*Me$_2$), 2.52−2.45 (m, 4 H, CH_2), 2.33(s, 3 H, *Me*C$_6$H$_4$Pr^i), 1.26 (d, 6 H, J = 6.7 Hz, CH*Me*$_2$). ^{31}P{^{1}H} NMR (CD_3CN): δ 45.7 (s). Anal. Calcd for $C_{46}H_{46}F_6ClP_3S_2FeNiRu$: C, 49.29; H, 4.14. Found: C, 48.93; H, 4.59.

4b·CH_2Cl_2: light brown needles from dichloromethane−hexanes (60%). ^{1}H NMR (CD_3CN): δ 8.01−7.38 (m, 20 H, Ph), 6.04, 5.61 (d, 2 H each, J = 6.3 Hz, *p*-MeC$_6$*H*$_4$Pr^i), 4.55−4.52, 3.85−3.82, 3.59−3.57, 3.56−3.54 (m, 2 H each, C_5H_4), 2.97 (sep, 1 H, J = 6.9 Hz, C*H*Me$_2$), 3.25−3.13, 2.46−2.36 (m, 2 H each, CH_2), 2.34 (s, 3 H, *Me*C$_6$H$_4$Pr^i), 1.41 (d, 6 H, J = 6.9 Hz, CH*Me*$_2$). ^{31}P{^{1}H} NMR (CD_3CN): δ 51.2 (s). Anal. Calcd for $C_{47}H_{48}Cl_3F_6P_3S_2FePdRu$: C, 45.03; H, 3.86. Found: C, 44.95; H, 3.90.

4c·0.5CH_2Cl_2: orange needles from dichloromethane−hexanes (69%). ^{1}H NMR (CD_3CN): δ 8.08−7.38 (m, 20 H, Ph), 6.05, 5.62 (d, 2 H each, J = 6.3 Hz, *p*-MeC$_6$*H*$_4$Pr^i), 4.44−4.43, 3.90−3.88, 3.58−3.56, 3.40−3.39 (m, 2 H each, C_5H_4), 2.96 (sep, 1 H, J = 6.9 Hz, C*H*Me$_2$), 3.15−2.90, 2.39−2.14 (m, 2 H each, CH_2), 2.34 (s, 3 H, *Me*C$_6$H$_4$Pr^i), 1.42 (d, 6 H, J = 6.9 Hz, CH*Me*$_2$). ^{31}P{^{1}H} NMR (CD_3CN): δ 36.2 (s, $^1J_{\text{Pt-P}}$ = 3090 Hz). Anal. Calcd for $C_{46.5}H_{47}Cl_2F_6P_3S_2FePtRu$: C, 42.97; H, 3.64. Found: C, 43.07; H, 3.62.

X-ray Diffraction Studies. Crystals were sealed in glass capillaries under an argon atmosphere and used for data collection. Diffraction data were collected on a Rigaku AFC-7R four-circle automated diffractometer equipped with a graphite-monochromatized Mo Kα (λ = 0.710 69 Å) source at room temperature using the $\omega-2\theta$ (for **1**, **2a**, and **4a**) or ω (for **2b**·CH_2Cl_2 and **3a**·THF) scan technique ($5° < 2\theta < 50°$ for **2a** and **4a**, $5° < 2\theta < 55°$ for **1**, **2b**·CH_2Cl_2, and **3a**·THF). Accurate cell dimensions of each crystal were determined by least-squares refinement of 25 machine-centered reflections. Empirical absorption correction based on ψ scan and Lorentz−polarization corrections were applied. The intensities of three check reflections were monitored every 150 reflections for each crystal, which showed no significant decay for **1**, **2b**·CH_2Cl_2, and **4a** but a steady decrease in intensities for **2a** and **3a**·THF during data collections (average 31.4% (**2a**) and 8.6% (**3a**·THF) decrease for the three check reflections at the final stage). Thus a decay correction was applied for **2a** and **3a**·THF. Details of the X-ray diffraction study are summarized in Table 6.

The structure solution and refinement were performed by using the TEXSAN[25] program package. The structures were solved by a combination of heavy atom Patterson methods (PATTY)[26] for **2a**, **2b**·CH_2Cl_2, **3a**·THF, and **4a** or direct methods (SIR92)[27] for **1** and subsequent Fourier techniques. All non-hydrogen atoms were found from the difference Fourier maps and refined by full-matrix least-squares techniques with anisotropic thermal parameters except for the atoms in the hexaflurophosphate anions and phenyl groups in **3a**·THF, which were refined isotropically. All hydrogen atoms were placed at calculated positions and included in the final stage of refinements with fixed parameters. The absolute structures of **1** and **2b**·CH_2Cl_2 were determined by comparison of the R and R_w values as well as the goodness of fit factors of the enantiomorphs.

Acknowledgment. Dr. Hiroyuki Matsuzaka of Tokyo Metropolitan University is gratefully acknowledged for helping us to solve the crystal structure of **1**. This work was supported by a Grant-in-Aid for Specially Promoted Research (09102004) from the Ministry of Education, Science, Sports, and Culture of Japan.

Supporting Information Available: X-ray crystallographic files, in CIF format, for the structure determinations of **1**, **2a**, **2b**·CH_2Cl_2, **3a**·THF, and **4a** are available on the Internet only. Access information is given on any current masthead page.

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