New Synthetic Methods for η^5-Cyclopentadienyl Nickel(III) Dithiolene Complexes Derived from Nickelocene

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The reactions of nickelocene with the neutral square-planar metal dithiolene complexes $[M(S_2C_2(R^1)(R^2))_2]$ gave the η^5-cyclopentadienyl nickel(III) dithiolene complexes $[CpNi(S_2C_2(R^1)(R^2))]$ (R^1, R^2 = Ph (**2**); R^1 = Ph, R^2 = H (**3**); R^1, R^2 = Me (**4**)) in 58−62% yields. The monoanions of the square-planar dithiolene complexes $[M(S_2C_2(R^1)(R^2))_2]^-$ reacted with nickelocenium to form $[CpNi(S_2C_2(R^1)(R^2))]$ (R^1, R^2 = COOMe (**5**) or CN (**6**)) in 67% or 68% yield, respectively, when the R^1 and R^2 substituents are electron-withdrawing groups. The CpNi dithiolene complexes **3** and **5** were also obtained by the thermal reactions or photoreactions of nickelocene with 1,3-dithiol-2-one or 1,3-dithiol-2-thione derivatives, $[E{=}C(S_2C_2(R^1)(R^2))]$ (E = O, S; R^1 = Ph, R^2 = H; R^1, R^2 = COOMe). The most efficient synthetic method for the CpNi dithiolene complex was the reaction of the hexacoordinated platinum dithiolene complex $[Pt(S_2C_2Ph_2)_2(dppe)]$ (dppe = bis(diphenylphosphino)ethane) with nickelocene (96% yield for complex **2**). The structure of complex **6** was determined by X-ray crystal structure analysis. The electronic and ESR properties of the CpNi dithiolene complexes **2**−**6** were investigated.

Introduction

Metal dithiolene complexes are unique complexes with an interesting π-electron system; such complexes have various optical,[1] magnetic,[2] and conductive properties.[3] The five-membered metalladithiolene ring is a metal chelate ring that exhibits aromaticity,[4] because there are delocalized 6π electrons in the chelate ring. This chemical property induces electrophilic and radical substitution reactions[5] and ring currents.[6]

The metal dithiolene complexes can be classified into two main categories. One includes the metal dithiolene complexes that consist of only dithiolate ligands (homoleptic metal dithiolene complexes).[7] Such metal complexes are well-known as the square-planar type of bisdithiolene complexes (metal = Ni, Pd, Pt)[8] and trisdithiolene complexes (metal = V, Cr, Mo, W, Re).[9] Quite recently, the trisdithiolene complexes of Nd and Ce metals[10] and the tris- or tetrakisdithiolene complexes of U metal[11] have also been reported by Fourmigué et al. The other category includes the metal dithiolene complexes that consist of dithiolate ligands and some other ligands (heteroleptic metal dithiolene complexes). For example, Eisenberg et al. reported diimine-dithiolate complexes (metal = Pt) that emit light due to an intramolecular charge transfer.[12]

As one example of heteroleptic metal dithiolene complexes, the η^5-cyclopentadienyl (Cp) metal dithiolene complexes are also well-known:[13] the Cp/dithiolene ratio 2:1 complexes of general formula $[Cp_2M(dithiolene)]^{0,+1}$ (M = group 4−6 metals), the Cp/dithiolene ratio 1:2 complexes of general formula $[CpM(dithiolene)_2]^{-1,0}$ (M = group 4−7 metals), the Cp/dithiolene ratio 1:1 complexes of general formula [CpM(dithiolene)] (M = group 9 metals), and the bimetallic 1:1 complexes of general

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[1] (a) Cummings, S. D.; Eisenberg, R. *Prog. Inorg. Chem.* **2003**, *52*, 315. (b) Kisch, H. *Coord. Chem. Rev.* **1993**, *125*, 155.

[2] (a) Fourmigué, M. *Acc. Chem. Res.* **2004**, *37*, 179. (b) Coomber, A. T.; Beljonne, D.; Friend, R. H.; Bredas, J. L.; Charlton, A.; Robertson, N.; Underhill, A. E.; Kurmoo, M.; Day, P. *Nature* **1996**, *380*, 144. (c) Faulmann, C.; Cassoux, P. *Prog. Inorg. Chem.* **2003**, *52*, 399.

[3] (a) Cassoux, P.; Valade, L.; Kobayashi, H.; Kobayashi, A.; Clark, R. A.; Underhill, A. E. *Coord. Chem. Rev.* **1991**, *91*, 115. (b) Olk, R.-M.; Olk, B.; Dietzsch, W.; Kirmse, R.; Hoyer, E. *Coord. Chem. Rev.* **1992**, *117*, *99*.

[4] (a) McCleverty, J. A. *Prog. Inorg. Chem.* **1969**, *10*, 49. (b) Sugimori, A. *Yuki Gosei Kagaku Kyokai Shi* **1990**, *48*, 788.

[5] (a) Kajitani, M.; Hagino, G.; Tamada, M.; Fujita, T.; Sakurada, M.; Akiyama, T.; Sugimori, A. *J. Am. Chem. Soc.* **1996**, *118*, 489. (b) Sugimori, A.; Tachiya, N.; Kajitani, M.; Akiyama, T. *Organometallics* **1996**, *15*, 5664.

[6] Boyde, S.; Garner, C. D.; Joule, J. A.; Rowe, D. J. *J. Chem. Soc., Chem. Commun.* **1987**, 800.

[7] Wang, K. *Prog. Inorg. Chem.* **2003**, *52*, 267.

[8] Schrauzer, G. N. *Acc. Chem. Res.* **1969**, *2*, 72, and references therein.

[9] (a) King, R. B. *J. Organomet. Chem.* **2001**, *623*, 95. (b) Falaras, P.; Mitsopoulou, C.-A.; Argyropoulos, D.; Lyris, E.; Psaroudakis, N.; Vrachnou, E.; Katakis, D. *Inorg. Chem.* **1995**, *34*, 4536. (c) Eisenberg, R.; Stiefel, E. I.; Rosenberg, R. C.; Gray, H. B. *J. Am. Chem. Chem.* **1966**, *88*, 2874. (d) Schrauzer, G. N.; Mayweg, V. P. *J. Am. Chem. Chem.* **1966**, *88*, 3235.

[10] Roger, M.; Arliguie, T.; Thuery, P.; Fourmigué, M.; Ephritikhine, M. *Inorg. Chem.* **2005**, *44*, 584.

[11] Roger, M.; Arliguie, T.; Thuery, P.; Fourmigué, M.; Ephritikhine, M. *Inorg. Chem.* **2005**, *44*, 594.

[12] (a) Paw, W.; Cummings, S. D.; Mansour, M. A.; Connick, W. B.; Geiger, D. K.; Eisenberg, R. *Coord. Chem. Rev.* **1998**, *171*, 125. (b) Zuleta, J. A.; Bevilacqua, J. M.; Eisenberg, R. *Coord. Chem. Rev.* **1991**, *111*, 237. (c) Zuleta, J. A.; Burberry, M. S.; Eisenberg, R. *Coord. Chem. Rev.* **1990**, *97*, 47.

[13] Cp metal dithiolene complexes are summarized and classified in the following review: Fourmigué, M. *Coord. Chem. Rev.* **1998**, *178*, 823, and references therein.

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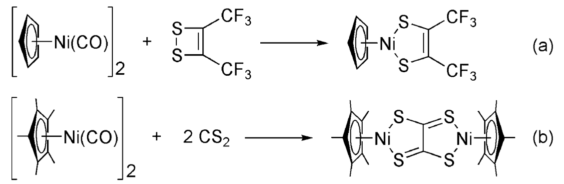
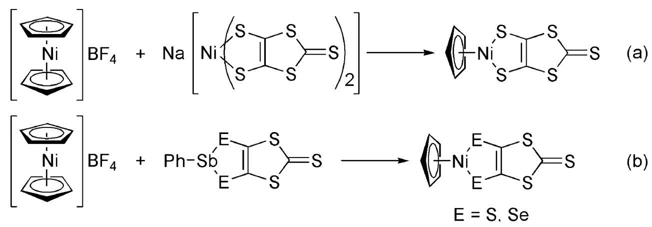
Scheme 1



Scheme 2

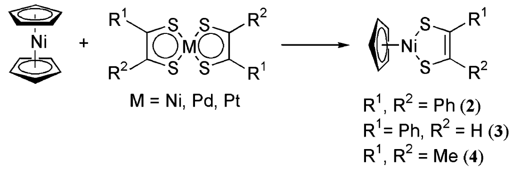


formula [CpM(dithiolene)]$_2$ (M = group 5, 6, and 8 metals). In other cases, [(η^6-arene)M(dithiolene)] (M = Ru)[14] and [(η^4-cyclobutadiene)M(dithiolene)] (M = Ni, Pd)[15] have been reported as half-sandwich metal dithiolene complexes.

However, the Cp dithiolene complexes of group 10 metals have been reported in only a few cases: King first reported the synthesis of the CpNi dithiolene complex with CF$_3$ groups, [CpNi(S$_2$C$_2$(CF$_3$)$_2$)], by the reaction of [CpNi(CO)]$_2$ with bis(trifluoromethyl)dithiete [S$_2$C$_2$(CF$_3$)$_2$] (Scheme 1(a)).[16] Dahl et al. reported the dimeric type of the η^5-pentamethylcyclopentadienyl (Cp*) nickel dithiolene complex, [Cp*Ni(C$_2$S$_4$)NiCp*], which was obtained by the reaction of [Cp*Ni(CO)]$_2$ with carbon disulfide (Scheme 1(b)).[17] Faulmann et al. attempted the reaction of nickelocenium with the monoanion of square-planar dithiolene complex [Ni(dmit)$_2$]$^-$ (dmit = 1,3-dithiol-2-thione-4,5-dithiolate), and they succeeded in the isolation and the characterization of an unexpected product, [CpNi(dmit)] (Scheme 2(a)).[18] Quite recently, Fourmigué et al. reported the improved synthetic methods of [CpNi(dmit)] and [CpNi(dsit)] from the reaction of nickelocenium with [PhSb(dmit)] or [PhSb(dsit)] (dsit = 1,3-dithiol-2-thione-4,5-diselenolate), respectively (Scheme 2(b)).[19] However, these reactions using nickelocenium are not efficient enough to synthesize a CpNi dithiolene complex because the yield of product is low.

The most paramagnetic species of Ni dithiolene complexes is the monoanion of the square-planar complex [Ni(dithiolene)$_2$]$^-$, which is air-stable and can easily be isolated in many cases. The neutral radical of a square-planar Ni dithiolene complex has also been reported as the *S*-benzyl nickel dithiolene adduct formulated as [Ni(S$_2$C$_2$Ph$_2$)(S(SCH$_2$Ph)C$_2$Ph$_2$)]. This is formed by the photoreaction[20] or the electrochemical redox reactions[21] of the *S,S'*-dibenzyl adduct [Ni(S(SCH$_2$Ph)C$_2$Ph$_2$)$_2$].[22] However, this neutral radical complex is not isolable because the lifetime is too short (10^3 s).[20] On the other hand, the CpNi dithiolene complexes form a stable and isolable species of a neutral paramagnetic complex,[18,19] but efficient synthetic methods for these complexes have not been reported yet.

Scheme 3



We report here on the convenient syntheses of the CpNi dithiolene complexes by using the reactions of nickelocene and some dithiolene transfer sources: (1) the neutral square-planar dithiolene complexes [M(S$_2$C$_2$(R^1)(R^2))$_2$] (M = Ni, Pd, Pt), (2) the 1,3-dithiol-2-one or 1,3-dithiol-2-thione derivatives [E=C(S$_2$C$_2$(R^1)(R^2))] (E = O, S), and (3) the hexacoordinated platinum dithiolene complex [Pt(S$_2$C$_2$Ph$_2$)$_2$(dppe)] (dppe = bis(diphenylphosphino)ethane). In addition, we tried to expand Faulmann's ionic reaction (Scheme 2(a)),[18] and we discuss the effects of the R^1 and R^2 substituents in the reactions of nickelocenium with the monoanions of square-planar complexes [M(S$_2$C$_2$(R^1)(R^2))$_2$]$^-$. This paper also reports on the electronic and ESR properties of the CpNi dithiolene complexes.

Results and Discussion

1. Reactions of Nickelocene with the Neutral Square-Planar Dithiolene Complexes [M(S$_2$C$_2$(R^1)(R^2))$_2$] (M = Ni, Pd, Pt). A dichloromethane solution of nickelocene (0.53 mmol) and the neutral square-planar nickel dithiolene complex [Ni(S$_2$C$_2$Ph$_2$)$_2$] (**1a**, 0.53 mmol) were stirred at room temperature. The green color of the initial solution changed to greenish-brown. When the reaction mixture was separated by column chromatography, the CpNi dithiolene complex [CpNi(S$_2$C$_2$Ph$_2$)] (**2**) was isolated as a greenish-brown product in 62% yield (Scheme 3). Complex **2** was also obtained in other organic solvents and under other conditions, but a lower yield of product was always found (Table 1). A polar solvent cannot be used for this reaction because of the low solubility of the neutral square-planar complexes (**1a**–**e** in Table 1). In addition, the reaction of nickelocene with [Ni(S$_2$C$_2$(Ph)(H))$_2$] (**1d**) gave the CpNi dithiolene complex [CpNi(S$_2$C$_2$(Ph)(H))] (**3**) with monophenyl substituent in 58% yield. The corresponding dimethyl complex [CpNi(S$_2$C$_2$Me$_2$)] (**4**) was obtained in 58% yield from nickelocene and [Ni(S$_2$C$_2$Me$_2$)$_2$] (**1e**).

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(14) (a) Mashima, K.; Kaneyoshi, H.; Kaneko, S.; Tani, K.; Nakamura, A. *Chem. Lett.* **1997**, 569. (b) Mashima, K.; Kaneyoshi, H.; Kaneko, S.; Mikami, A.; Tani, K.; Nakamura, A. *Organometallics* **1997**, *16*, 1016. (c) Nomura, M.; Fujii, M.; Fukuda, K.; Sugiyama, T.; Yokoyama, Y.; Kajitani, M. *J. Organomet. Chem.* **2005**, *690*, 1627.

(15) (a) Wharton, E. J. *Inorg. Nucl. Chem. Lett.* **1971**, *7*, 307. (b) Mashima, K.; Kaneko, S.; Tani, K. *Chem. Lett.* **1997**, 347.

(16) King, R. B. *J. Am. Chem. Soc.* **1963**, *85*, 1587.

(17) Maj, J. J.; Rae, A. D.; Dahl, L. F. *J. Am. Chem. Soc.* **1982**, *104*, 4278.

(18) Faulmann, C.; Delpech, F.; Malfant, I.; Cassoux, P. *J. Chem. Soc., Dalton Trans.* **1996**, 2261.

(19) Fourmigué, M.; Avarvari, N. *Dalton Trans.* **2005**, 1365.

(20) (a) Ohtani, M.; Ohkoshi, S.; Kajitani, M.; Akiyama, T.; Sugimori, A.; Yamauchi, S.; Ohba, Y.; Iwaizumi, M. *Inorg. Chem.* **1992**, *31*, 3873. (b) Ohkoshi, S.; Ohba, Y.; Iwaizumi, M.; Yamauchi, S.; Ohkoshi, M.; Tokuhisa, K.; Kajitani, M.; Akiyama, T.; Sugimori, A. *Inorg. Chem.* **1996**, *35*, 4569. (c) Sugimori, A. *Coord. Chem. Rev.* **1997**, *159*, 397.

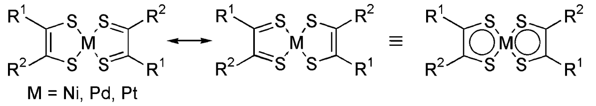
(21) Nomura, M.; Takayama, C.; Kajitani, M. *Inorg. Chem.* **2003**, *42*, 6441.

(22) (a) Schrauzer, G. N.; Rabinowiz, H. N. *J. Am. Chem. Soc.* **1968**, *90*, 4297. (b) Zhang, C.; Reddy, H. K.; Schlemper, E. O.; Schrauzer, G. N. *Inorg. Chem.* **1990**, *29*, 4100.

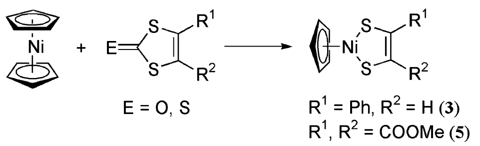
Table 1. Reactions of Nickelocene with the Neutral Square-Planar Dithiolene Complexes $[M(S_2C_2(R^1)(R^2))_2]$

M	R^1	R^2	solvent	temp	time/h	yield of **2**−**4**/%
Ni	Ph	Ph	CH_2Cl_2	rt	19	62 (**2**)
Ni	Ph	Ph	CH_2Cl_2	reflux	4	50 (**2**)
Ni	Ph	Ph	benzene	rt	3	54 (**2**)
Ni	Ph	Ph	benzene	reflux	3	56 (**2**)
Ni	Ph	H	benzene	reflux	3	58 (**3**)
Ni	Me	Me	CH_2Cl_2	rt	19	58 (**4**)
Pd	Ph	Ph	CH_2Cl_2	rt	19	36 (**2**)
Pt	Ph	Ph	CH_2Cl_2	rt	19	13 (**2**)
Pt	Ph	Ph	toluene	reflux	2	32 (**2**)

Scheme 4



Scheme 5



The reactions of nickelocene with the square-planar palladium complex $[Pd(S_2C_2Ph_2)_2]$ (**1b**) or the platinum complex $[Pt(S_2C_2Ph_2)_2]$ (**1c**) also gave the CpNi complex **2** in 36% or 13% yield, respectively (Table 1), but no product such as the CpPd or the CpPt dithiolene complex was obtained. This result suggests that the central metal (M) in the square-planar complex $[M(S_2C_2(R^1)(R^2))_2]$ is not used for the formation of the CpM dithiolene complex. Therefore, we can recognize that this is a dithiolene transfer reaction from the square-planar dithiolene complex to nickelocene. Schrauzer, Holm, and Morris have reported the dithiolene transfer reaction from complex **1a** to the molybdenum or tungsten carbonyl complexes.[23−25] In their reactions, the 1,2-dithioketone ligand of complex **1a** reacts with them to give the molybdenum or tungsten dithiolene complexes, and then the nickel dithiolene oligomer $[Ni(S_2C_2Ph_2)]_n$ is also produced. Because our reaction also gave such oligomers,[26,27] it can be explained by a reaction of the 1,2-dithioketone moiety in complex **1a**. In general, the square-planar metal dithiolene complexes $[M(S_2C_2(R^1)(R^2))_2]$ (M = Ni, Pd, Pt) can be drawn by stable "dithiolato" and reactive "dithioketone" resonance structures (Scheme 4).

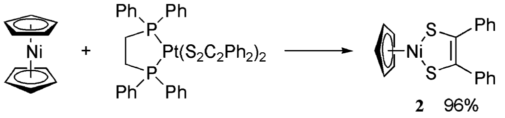
2. Reactions of Nickelocene with $[E{=}C(S_2C_2(R^1)(R^2))]$ (E = O, S) or $[Pt(S_2C_2Ph_2)_2(dppe)]$. The reactions of nickelocene with 1,3-dithiol-2-one or 1,3-dithiol-2-thione derivatives $[E{=}C(S_2C_2(R^1)(R^2))]$ (E = O, S) were carried out (Scheme 5). Our results are summarized in Table 2. When the 4-phenyl derivative of 1,3-dithiol-2-one $[O{=}C(S_2C_2(Ph)(H))]$ reacted with nickelocene under the UV-irradiation of a high-pressure Hg lamp, complex **3** was formed in 32% yield. The reactions of nickelocene with dimethyl 1,3-dithiol-2-one-4,5-dicarboxylate $[O{=}C(S_2C_2(COOMe)_2)]$ and its S=C analogue compound also gave the CpNi dithiolene complex having dimethoxycarbonyl substituents $[CpNi(S_2C_2(COOMe)_2)]$ (**5**) by heating or UV-irradiation. De Mayo et al. have reported that the photolysis or thermolysis of 1,3-dithiol-2-one derivatives produces a reactive compound such as a 1,2-dithioketone or a 1,2-dithiete.[28] In our case, we assume that the CpNi dithiolene complexes are produced by the reaction of nickelocene with a free 1,2-dithioketone or 1,2-dithiete.

Table 2. Reactions of Nickelocene with $[E{=}C(S_2C_2(R^1)(R^2))]$ (E = O, S)

R^1	R^2	E	solvent	condition	time/h	yield of **3** or **5**/%
Ph	H	O	benzene	hν	12	32 (**3**)[a]
Ph	H	O	xylene	reflux	3	0 (**3**)
COOMe	COOMe	O	benzene	hν	4	31 (**5**)[a]
COOMe	COOMe	O	xylene	reflux	3	7 (**5**)[b]
COOMe	COOMe	S	xylene	reflux	0.5	16 (**5**)[b]

[a] Analytical yield monitored by UV−vis−NIR spectrum. [b] Isolated yield.

Scheme 6



The reaction of the hexacoordinated platinum complex $[Pt(S_2C_2Ph_2)_2(dppe)]$ (**1f**) with nickelocene was attempted. In our investigation, complex **1f** was quantitatively converted to the square-planar complex $[Pt(S_2C_2Ph_2)(dppe)]$ under heating (110 °C for 30 min in toluene). We expected that a highly reactive free 1,2-dithioketone would be generated (but would not be isolable). When complex **1f** reacted with nickelocene in refluxing toluene, the CpNi complex **2** was obtained in 96% yield (Scheme 6). In this reaction, the free 1,2-dithioketone eliminated from complex **1f** efficiently reacts with nickelocene. On the other hand, the reaction of the neutral square-planar platinum complex **1c** with nickelocene in refluxing toluene resulted in a low yield of complex **2** (32% in Table 1). Therefore, most of the 1,2-dithioketone ligands are released when DPPE coordinates to complex **1c**, whereas the Pt complex **1c** was less reactive with nickelocene to form the CpNi dithiolene complex **2** than the corresponding Ni and Pd complexes **1a**,**b** (Table 1).

3. Reactions of Nickelocenium with the Monoanions of Square-Planar Dithiolene Complex $[Ni(S_2C_2(R^1)(R^2))_2]^-$. Faulmann et al. have reported the synthesis of [CpNi(dmit)] from nickelocenium and the monoanion of the square-planar dithiolene complex $[Ni(dmit)_2]^-$.[18] We can use a polar solvent for such ionic reactions (e.g., methanol or acetone). In this work, we tried to expand their ionic reactions.

The reactions of nickelocenium with the monoanions of the nickel dithiolene complexes $[Ni(S_2C_2(R^1)(R^2))_2]^-$

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(23) Schrauzer, G. N.; Mayweg, V.; Heinrich, W. *J. Am. Chem. Soc.* **1966**, *88*, 5174.

(24) (a) Lim, B. S.; Donahue, J. P.; Holm, R. H. *Inorg. Chem.* **2000**, *39*, 263. (b) Goddard, C. A.; Holm, R. H. *Inorg. Chem.* **1999**, *38*, 5389.

(25) Adams, H.; Morris, M. J.; Morris, S. A.; Motley, J. C. *J. Organomet. Chem.* **2004**, *689*, 522.

(26) This oligomer was detected by TOF-mass (no matrix): 1806 ($[Ni(S_2C_2Ph_2)]_6^+$, 100), 902 ($[Ni(S_2C_2Ph_2)]_3^+$, 23).

(27) The palladium dithiolene hexamer $[Pd(S_2C_2(COOMe)_2)]_6^n$ (n = 0, −1, −2, −3, −4) has been reported: Beswick, C. L.; Terroba, R.; Greaney, M. A.; Stiefel, E. I. *J. Am. Chem. Soc.* **2002**, *124*, 9664.

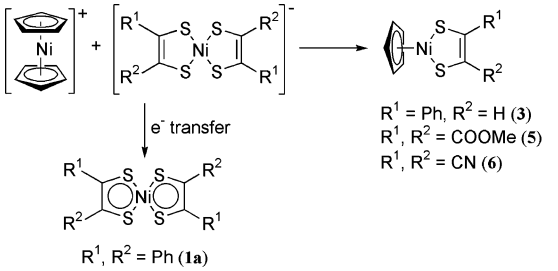
(28) (a) Kusters, W.; De Mayo, P. *J. Am. Chem. Soc.* **1974**, *96*, 3502. (b) Schroth, W.; Bahn, H.; Zschernitz, R. *Z. Chem.* **1973**, *13*, 424. (c) Schulz, R.; Schweig, A.; Hartke, K.; Koester, J. *J. Am. Chem. Soc.* **1983**, *105*, 4519.

Table 3. Reactions of Nickelocenium with the Monoanions of Square-Planar Dithiolene Complex $[M(S_2C_2(R^1)(R^2))_2]^-$

M	R^1	R^2	$E_{1/2}$(ox)/ V	solvent	temp	time/ h	yield of **2**−**6**/%^{a}
Ni	Ph	Ph	-0.49	methanol	rt	2	29 (**2**)^b
Ni	Ph	H	-0.43	methanol	rt	2	47 (**3**)
Pd	Ph	Ph	-0.39	methanol	rt	2	72 (**2**)
Ni	COOMe	COOMe	0.11	methanol	rt	2	67 (**5**)
Ni	CN	CN	0.69	methanol	reflux	1	68 (**6**)

^{a} Isolated yield. ^{b} The neutral complex $[Ni(S_2C_2Ph_2)_2]$ (**1a**) was also obtained in 70% yield.

Scheme 7



(R^1, R^2 = COOMe (**1g**$^-$) or CN (**1h**$^-$)) having electron-withdrawing substituents afforded complex **5** or the corresponding dicyano complex $[CpNi(S_2C_2(CN)_2)]$ (**6**) in moderate yields (Table 3 and Scheme 7). In addition, the reactions of nickelocenium with the monoanion $[Ni(S_2C_2(Ph)(H))_2]^-$ (**1d**$^-$) or $[Pd(S_2C_2Ph_2)_2]^-$ (**1b**$^-$) gave complex **3** or **2**, respectively (Table 3). However, when the monoanion $[Ni(S_2C_2Ph_2)_2]^-$ (**1a**$^-$) reacted with nickelocenium in methanol, the corresponding neutral square-planar complex **1a** was formed as a main product in 70% yield[29] (Scheme 7) and only a low yield of the CpNi complex **2** was found (29% yield). In this case, we assume that the monoanion **1a**$^-$ was oxidized by nickelocenium, and then the generated neutral species were inert because of their low solubility in polar solvents.

The oxidation potentials of the monoanions $[M(S_2C_2(R^1)(R^2))_2]^-$, which were measured by cyclic voltammetry (CV), are shown in Table 3. Whereas the monoanion **1a**$^-$ is easily oxidized by nickelocenium ($E_{1/2}(Cp_2Ni/Cp_2Ni^+)$ = −0.42 V vs Fc/Fc$^+$), the monoanions **1b**$^-$, **1d**$^-$, **1g**$^-$, and **1h**$^-$ are not oxidized by it. Particularly, the neutral complex $[Ni(S_2C_2(CN)_2)_2]$ (**1h**) is a difficult one to isolate,[30] because the neutral species are unstable or they rapidly oligomerize. In such cases, Faulmann's ionic reactions are especially useful for the synthesis of the CpNi dithiolene complexes (e.g., R^1, R^2 = COOMe or CN).

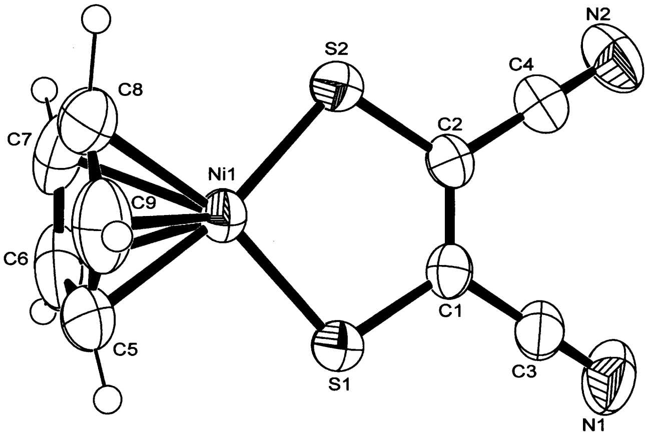


Figure 1. ORTEP drawing of $[CpNi(S_2C_2(CN)_2)]$ (**6**). Selected bond lengths (Å): Ni1−S1 = 2.1255(8), Ni1−S2 = 2.1282(8), S1−C1 = 1.715(3), S2−C2 = 1.725(3), C1−C2 = 1.354(4), N1−C3 = 1.135(4), N2−C4 = 1.136(5). Selected bond angles (deg): S1−Ni1−S2 = 94.61(3), Ni1−S1−C1 = 101.7(1), Ni1−S2−C2 = 101.7(1), S1−C1−C2 = 121.4(2), S2−C2−C1 = 120.6(2).

Table 4. Bond Lengths of the Nickeladithiolene Ring in the CpNi Dithiolene Complexes

	$[CpNi(S_2C_2(CN)_2)]$ (**6**)	[CpNi(dmit)]^a	[CpNi(dmid)]^b
Ni1−S1	2.1255(8)	2.138(2)	2.138(1)
Ni1−S2	2.1282(8)	2.133(2)	2.145(1)
S1−C1	1.715(3)	1.706(8)	1.718(3)
S2−C2	1.725(3)	1.716(7)	1.712(3)
C1−C2	1.354(4)	1.36(1)	1.352(4)

^{a} Reference 18. ^{b} Reference 19.

Table 5. CV, Electronic Absorption, and ESR Data of the CpNi Dithiolene Complexes

complex	$E_{1/2}$(red)/ V^a	$E_{1/2}$(ox)/ V^a	λ_{max}/ nm	g
$[CpNi(S_2C_2Ph_2)]$ (**2**)	-1.16^{r}	0.04^{r}	846	2.0440
$[CpNi(S_2C_2(Ph)(H))]$ (**3**)	-1.15^{r}	0.07^{r}	843	2.0412
$[CpNi(S_2C_2Me_2)]$ (**4**)	-1.38^{r}	-0.04^{r}	835	2.0430
$[CpNi(S_2C_2(COOMe)_2)]$ (**5**)	-0.86^{r}	0.48^{r}	695	2.0460
$[CpNi(S_2C_2(CN)_2]$ (**6**)	-0.64^{r}	0.79^{ir}	698	2.0487
[CpNi(dmit)]^b	-0.71^{r}	0.28^{r}		
[CpNi(dsit)]^b	-0.72^{r}	0.28^{r}		
[CpNi(dmid)]^b	-0.80^{r}	0.26^{r}		

^{a} $E_{1/2}$ (vs Fc/Fc$^+$) = $|E_p - E_{p/2}|/2$, potential scan rate = 100 mV·s^{-1}. r: reversible, ir: irreversible. ^{b} Reference 19.

4. Structure and Electronic and Magnetic Properties of CpNi Dithiolene Complexes. The structure of complex **6** was determined by X-ray crystal structure analysis. Figure 1 shows the ORTEP drawing of complex **6** together with selected bond lengths and angles. The Ni−S bond length is slightly longer than the Co−S bond length of CpCo dithiolene complexes $[CpCo(S_2C_2R_2)]$ (R = CN, COOMe, Ph)[31] previously reported (2.108−2.110 Å). According to Table 4, the bond lengths of complex **6** are similar to those of [CpNi(dmit)][18] and [CpNi(dmid)][19] (dmid = 1,3-dithiol-2-one-4,5-dithiolate). The mean deviation from the five-membered nickeladithiolene plane is 0.0124 Å; namely, this five-membered metallacycle is extremely planar. The Cp ring is located at a position almost perpendicular to the nickeladithiolene plane (the dihedral angle of nickeladithiolene/Cp = 89.908°). The packing diagram of complex **6** is given in the Supporting Information. All molecules were placed at parallel positions in the unit cell, and nickeladithiolene planes were stacked on each other. In the nickeladithiolene ring of complex **6**, there are short intermolecular distances: S···C = 3.804(3) and 3.587(3) Å.

The CVs of the CpNi dithiolene complexes **2**−**6** were measured. The redox potentials (vs Fc/Fc$^+$) and reversibilities of complexes **2**−**6** are shown in Table 5. In addition, the CV data of [CpNi(dmit)], [CpNi(dsit)], and [CpNi(dmid)] are also described in Table 5 for compari-

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[29] The neutral complex **1a** was precipitated because of low solubility for methanol.

[30] The neutral complex **1h** is electrochemically generated from the dilute solution of monoanion **1h**$^-$: (a) Geiger, W. E.; Barrière, F.; LeSuer, R. J.; Trupia, S. *Inorg. Chem.* **2001**, *40*, 2472. (b) Geiger, W. E.; Mines, T. E.; Senftleber, F. C. *Inorg. Chem.* **1975**, *14*, 2141.

[31] Takayama, C.; Kajitani, M.; Sugiyama, T.; Sugimori, A. *J. Organomet. Chem.* **1998**, *563*, 161.

son.[19] One reduction and one oxidation wave were found in the potential window of the TBAP−CH_2Cl_2 solution. This result is similar to the CV data of [CpNi(dmit)] and its analogues. From the redox potentials, the substituent effect of an electron-withdrawing or -donating group was confirmed. In complexes **2**−**4**, the potential gap ($\Delta E_{1/2} = |E_{1/2}(\text{ox}) - E_{1/2}(\text{red})|$) between the first oxidation and reduction waves is analogous to that of the square-planar complex **1a** ($\Delta E_{1/2}$ = 1.29 V in TBAP−CH_2Cl_2). This result explains why the electronic absorption wavelengths of complexes **2**−**4** (835−846 nm described in Table 5) are similar to that of complex **1a** (858 nm in CH_2Cl_2). These are low-energy electronic absorptions in the near-IR region. A blue shift of the absorption was confirmed in complexes **5** (695 nm) and **6** (698 nm) as compared with complexes **2**−**4**. The redox waves of complexes **2**−**5** were reversible, and this result suggests that the reduced or oxidized species of complexes **2**−**5** were stable on the CV time scale, but only the oxidation wave of complex **6** exhibited an irreversible response (v = 100 mV·s^{-1}).

The ESR data of the CpNi dithiolene complexes are shown in Table 5. In toluene solution at room temperature, isotropic ESR signals (g = 2.041−2.048) were observed in complexes **2**−**6**. These g values are similar to that of $[CpNi(S_2C_2(CF_3)_2)]$ (g = 2.0479) previously reported.[32] However, the g values of CpNi dithiolene complexes are very different from those of the one-electron-reduced species of CpCo dithiolene complexes, $[CpCo^{II}(S_2C_2(CF_3)_2)]^-$ (g = 2.454)[32] and $[CpCo^{II}(S_2C_2(CN)_2)]^-$ (g = ca. 2.5).[33] The DFT theoretical calculations of CpNi dithiolene complexes have been reported: the SOMO (singly occupied molecular orbital) of [CpNi(dmit)] is essentially localized on the dithiolene moiety with little metal contribution.[19] In contrast, a strong spin localization on the central metal is given in $[CpCo(dithiolene)]^-$ complexes.

Conclusion

We developed the convenient syntheses of the CpNi dithiolene complexes by the reactions of nickelocene with the neutral square-planar metal dithiolene complexes $[M(S_2C_2(R^1)(R^2))_2]$ (M = Ni, Pd, Pt). In the previous method reported by Faulmann et al., the ionic complexes (nickelocenium and $[Ni(dmit)_2]^-$) have been used (Scheme 2(a)),[18] and Fourmigué et al. have used nickelocenium and [PhSb(dmit)] or [PhSb(dsit)] (Scheme 2(b)),[19] but our procedures represent a novel synthetic method. Since we use only neutral species, syntheses are also available in a nonpolar solvent.

On the other hand, if we use the square-planar dithiolene complex having electron-withdrawing substituents (e.g., R^1, R^2 = CN, COOMe), the monoanion $[M(S_2C_2(R^1)(R^2))_2]^-$ reacts with nickelocenium to produce the CpNi dithiolene complexes, because this type of neutral square-planar dithiolene complex is unstable or is difficult to synthesize.[30] This ionic reaction can be applied when the oxidation potentials of the monoanion $[M(S_2C_2(R^1)(R^2))_2]^-$ (Table 3) are more positive than the potential of nickelocene/nickelocenium ($E_{1/2}$ = −0.42 V vs Fc/Fc^+). When the oxidation potential is more negative than −0.42 V, the monoanions $[M(S_2C_2(R^1)(R^2))_2]^-$ (e.g., M = Ni; R^1, R^2 = Ph) are oxidized by nickelocenium, and then the reaction is not efficient in a polar solvent. In such cases, the reactions of the neutral complexes can be performed in a nonpolar solvent (e.g., dichloromethane or benzene).

The nickelocene reacts with a 1,2-dithioketone ligand or with a highly reactive free 1,2-dithioketone. In this work, we found that the hexacoordinated platinum complex $[Pt(S_2C_2Ph_2)_2(dppe)]$ (**1f**) is the most efficient dithioketone source for the synthesis of the CpNi dithiolene complex (96% yield). In this paper, we reported a novel dithiolene transfer reaction that uses complex **1f**.

Experimental Section

General Remarks. All reactions were carried out under an argon atmosphere by means of standard Schlenk techniques. All solvents were dried and distilled by Na-benzophenone (for benzene, toluene, and xylene) or CaH_2 (for dichloromethane and methanol) before use. The neutral complexes $[M(S_2C_2Ph_2)_2]$ (M = Ni (**1a**), Pd (**1b**), and Pt (**1c**)),[34] $[Ni(S_2C_2(Ph)(H))_2]$ (**1d**),[5b] and $[Ni(S_2C_2Me_2)_2]$ (**1e**),[35] $[Pt(S_2C_2Ph_2)_2(dppe)]$ (**1f**),[36] the monoanions $(NBu_4)[Ni(S_2C_2Ph_2)_2]$ (**1a**$^-$),[37] $(NBu_4)[Ni(S_2C_2(Ph)(H))_2]$ (**1d**$^-$),[37] $(PPh_4)_2[Ni(S_2C_2(COOMe)_2)_2](I)$ (**1g**$^-$),[38] and $(NBu_4)[Ni(S_2C_2(CN)_2)_2]$ (**1h**$^-$),[37] and $[Cp_2Ni](BF_4)$[39] were synthesized by literature methods. The monoanion **1d**$^-$ was a novel product, and its tetrabutylammonium salt ((NBu_4^+)[**1d**$^-$]) was identified by elemental analysis (Anal. Calcd for $C_{32}H_{48}N_1Ni_1S_4$: C, 60.65; H, 7.63; N, 2.21; Found: C, 60.66; H, 7.78; N, 2.27). Nickelocene, which was stored in an inert gas, was obtained from Strem Chemicals. Dimethyl 1,3-dithiol-2-one-4,5-dicarboxylate $[O{=}C(S_2C_2(COOMe)_2)]$[40] and 4-phenyl-1,3-dithiol-2-one $[O{=}C(S_2C_2(Ph)(H))]$[41] were obtained by literature methods. Dimethyl 1,3-dithiol-2-thione-4,5-dicarboxylate $[S{=}C(S_2C_2(COOMe)_2)]$ was produced by Tokyo Kasei Kogyo Co., Ltd. Silica gel (Wakogel C-300) was obtained from Wako Pure Chemical Industries, Ltd. Mass and IR spectra were recorded on a JEOL JMS-D300 and a Shimadzu Model FTIR 8600PC instrument, respectively. UV−vis spectra were recorded on a Hitachi Model UV-2500PC spectrometer. Elemental analyses were determined by using a Shimadzu PE2400-II instrument.

Reaction of Nickelocene with the Neutral Square-Planar Metal Dithiolene Complexes $[M(S_2C_2(R^1)(R^2))_2]$. A dichloromethane solution of nickelocene (100 mg, 0.53 mmol) and the square-planar dithiolene complex $[M(S_2C_2Ph_2)_2]$ (M = Ni (**1a**), Pd (**1b**), or Pt (**1c**), 0.53 mmol) was reacted at room temperature. After the solvent was removed under reduced pressure, the residue was separated by column chromatography (silica gel, eluent = dichloromethane). The greenish-brown residue was purified by recrystallization (n-hexane/dichloromethane). Complex **2** was obtained as a greenish-brown crystal in 62% (from **1a**), 36% (from **1b**), or 13% (from **1c**) yield,

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(32) Dessy, R. E.; Stary, F. E.; King, R. B.; Waldrop, M. *J. Am. Chem. Soc.* **1966**, *88*, 471.

(33) McCleverty, J. A.; James, T. A.; Wharton, E. J. *Inorg. Chem.* **1969**, *8*, 1340.

(34) Schrauzer, G. N.; Meyweg, V. P. *J. Am. Chem. Soc.* **1965**, *87*, 1483.

(35) Ahmad, M. M.; Underhill, A. E. *J. Chem. Soc., Dalton Trans.* **1983**, 165.

(36) Bowmaker, G. A.; Boyd, P. D. W.; Campbell, G. K. *Inorg. Chem.* **1983**, *22*, 1208.

(37) Davison, A.; Edelstein, N.; Holm, R. H.; Maki, A. H. *Inorg. Chem.* **1963**, *2*, 1227.

(38) Baudron, S. A.; Batail, P. *Acta Crystallogr. Sect. C* **2002**, *C58*, m575.

(39) Miller, J. S.; Calabrese, J. C.; Rommelmann, H.; Chittipeddi, S. R.; Zhang, J. H.; Reiff, W. M.; Epstein, A. J. *J. Am. Chem. Soc.* **1987**, *109*, 769.

(40) Challenger, F.; Mason, E. A.; Holdsworth, E. C.; Emmott, R. *J. Chem. Soc.* **1953**, 292.

(41) Bhattahcharya, A. K.; Hortmann, A. G. *J. Org. Chem.* **1974**, *39*, 95.

respectively. This type of reaction was performed using various reactants and under various conditions. Results are summarized in Table 1.

Addition: If a large quantity of nickelocene remained in the reaction mixture, silica gel was added into the solution before doing the column chromatography. The nickelocene immediately reacted and was absorbed on the silica gel, and it was not eluted.

Thermal Reactions of Nickelocene with 1,3-Dithiol-2-one or 1,3-Dithiol-2-thione Derivatives. A solution of nickelocene (100 mg, 0.53 mmol) and $[E{=}C(S_2C_2(R^1)(R^2))]$ (E = O, S; R^1 = Ph, R^2 = H; R^1, R^2 = COOMe, 0.53 mmol) was reacted under heating. Silica gel was added into the solution of the reaction mixture. After the solvent was removed under reduced pressure, the residue was separated by column chromatography (silica gel, eluent = dichloromethane). Reaction conditions and results are summarized in Table 2.

Photoreactions of Nickelocene with 1,3-Dithiol-2-one or 1,3-Dithiol-2-thione Derivatives. A benzene solution of nickelocene ($c = 5 \times 10^{-5}$ mol·dm^{-3}) and $[E{=}C(S_2C_2(R^1)(R^2))]$ (E = O, S; R^1 = Ph, R^2 = H; R^1, R^2 = COOMe, $c = 5 \times 10^{-5}$ mol·dm^{-3}) was reacted by UV-irradiation of a high-pressure Hg lamp. Product yield was analyzed by using the UV−vis−NIR spectrum (843 or 695 nm absorptions were used for complex **3** or **5**, respectively.). Reaction conditions and results are summarized in Table 2.

Reaction of Nickelocene with the Hexacoordinated Platinum Dithiolene Complex $[Pt(S_2C_2Ph_2)_2(dppe)]$ (1f). A toluene solution of nickelocene (36 mg, 0.19 mmol) and complex **1f** (179 mg, 0.19 mmol) was refluxed for 0.5 h. After the solvent was removed under reduced pressure, the residue was separated by column chromatography (silica gel, eluent = dichloromethane). Complex **2** was obtained in 96% yield, and the square-planar complex $[Pt(S_2C_2Ph_2)(dppe)]$ was formed in 51% yield.

Reaction of Nickelocenium with the Monoanions of Metal Dithiolene Complex $[M(S_2C_2(R^1)(R^2))_2]^-$. A solution of nickelocenium (83 mg, 0.30 mmol) and the monoanion $[M(S_2C_2(R^1)(R^2))_2]^-$ (M = Ni or Pd, 0.30 mmol) in methanol (100 mL) was reacted at room temperature or under refluxing. After the solvent was removed under reduced pressure, the residue was separated by column chromatography (silica gel, eluent = dichloromethane). The product was further purified by recrystallization (*n*-hexane/dichloromethane). Complex **5** or **6** was obtained as a dark green crystal in 67% and 68% yield, respectively. Results of these reactions are summarized in Table 3.

$[CpNi(S_2C_2Ph_2)]$ (2). Mass (EI$^+$, 70 eV): *m/z* (relative intensity) 365 ($[M^+]$, 100), 187 ($[M^+ - C_2Ph_2]$, 36), 123 ($[CpNi^+]$, 12). UV−vis (CH_2Cl_2): λ_{max}/nm (ϵ) 846 (2900), 406 (4700), 333 (22 000), 281 (14 000). Anal. Calcd for $C_{19}H_{15}Ni_1S_2$: C, 62.33; H, 4.13. Found: C, 61.92; H, 4.00.

$[CpNi(S_2C_2(Ph)(H))]$ (3). Mass (EI$^+$, 70 eV): *m/z* (relative intensity) 289 ($[M^+]$, 100), 187 ($[M^+ - C_2(Ph)(H)]$, 28), 123 ($[CpNi^+]$, 12). UV−vis (CH_2Cl_2): λ_{max}/nm (ϵ) 843 (3300), 402 (4900), 328 (26 000), 276 (16 000). Anal. Calcd for $C_{13}H_{11}Ni_1S_2$: C, 53.83; H, 3.82. Found: C, 53.57; H, 3.66.

$[CpNi(S_2C_2Me_2)]$ (4). Mass (EI$^+$, 1.3 kV): *m/z* (relative intensity) 241 ($[M^+]$, 100), 187 ($[M^+ - C_2Me_2]$, 47), 123 ($[CpNi^+]$, 38). UV−vis (CH_2Cl_2): λ_{max}/nm (ϵ) 835 (2600), 396 (3300), 328 (16 000). HR-Mass (EI$^+$, 70 eV): calcd for $C_9H_{11}Ni_1S_2$, 240.9656; found, 240.9660.

$[CpNi(S_2C_2(COOMe)_2)]$ (5). Mass (EI$^+$, 1.3 kV): *m/z* (relative intensity) 329 ($[M^+]$, 100), 187 ($[M^+ - C_2(COOMe)_2]$, 30), 123 ($[CpNi^+]$, 30). UV−vis (CH_2Cl_2): λ_{max}/nm (ϵ) 695 (1500), 393 (4000), 329 (15 000), 269 (12 000). IR (KBr disk): 1726, 1705, 1497, 1433, 1252, 1080, 1024, 822, 766 cm^{-1}. HR-Mass (EI$^+$, 70 eV): calcd for $C_{11}H_{11}Ni_1O_4S_2$, 328.9452; found, 328.9455.

$[CpNi(S_2C_2(CN)_2)]$ (6). Mass (EI$^+$, 1.3 kV): *m/z* (relative intensity) 263 ($[M^+]$, 62), 187 ($[M^+ - C_2(CN)_2]$, 16), 123 ($[CpNi^+]$, 100). UV−vis (CH_2Cl_2): λ_{max}/nm (ϵ) 698 (2000), 394 (3400), 321 (24 000), 255 (11 000). IR (KBr disk): 2208, 1157, 820 cm^{-1}. Anal. Calcd for $C_9H_5N_2Ni_1S_2$: C, 40.95; H, 1.91; N, 10.61. Found: C, 40.85; H, 1.74; N, 10.18.

Table 6. Crystallographic Data of $[CpNi(S_2C_2(CN)_2)]$ (6)

formula	$C_9H_5N_2Ni_1S_2$
fw (g mol^{-1})	263.97
cryst color	dark green
cryst habit	block
cryst size (nm)	0.12 x 0.06 x 0.06
cryst syst	monoclinic
space group	*C*2/*c*(#15)
a (Å)	17.2403(13)
b (Å)	8.4805(4)
c (Å)	14.7512(11)
β (deg)	109.8361(10)
V (Å^3)	2028.8(2)
Z	8
D_{calc} (g cm^{-3})	1.728
μ(Mo Kα) (cm^{-1})	22.79
$2\theta_{max}$ (deg)	55.0
no. of unique data (R_{int})	2276 (0.026)
no. of observations	1386
no. of variables	132
R_1, wR_2 ($I > 3.00\sigma(I)$)	0.026, 0.037
goodness-of-fit on F^2	0.920

X-ray Diffraction Study. A single crystal of complex **6** was obtained by recrystallization from the dichloromethane solutions and then vapor diffusion of *n*-hexane into those solutions. The measurement was made on a Rigaku Mercury diffractometer with graphite-monochromated Mo Kα radiation. Each structure was solved by direct methods and expanded Fourier techniques. The non-hydrogen atoms were refined anisotropically. Idealized positions of complexes were used for the Crystal Structure crystallographic software package of Molecular Structure Corp. Crystallographic data of complex **6** are summarized in Table 6.

CV Measurements. All electrochemical measurements were performed under an argon atmosphere. Solvents for electrochemical measurements were dried by 4 Å molecular sieve before use. A platinum wire served as a counter electrode, and the reference electrode Ag/AgCl was corrected for junction potentials by being referenced internally to the ferrocene/ferrocenium (Fc/Fc$^+$) couple. A stationary platinum disk (1.6 mm in diameter) was used as a working electrode. The Model CV-50W instrument from BAS Co. was used for cyclic voltammetry (CV) measurements. CVs were measured in 1 mmol·dm^{-3} dichloromethane solutions of complexes containing 0.1 mol·dm^{-3} tetrabutylammonium perchlorate (TBAP) at 25 °C.

ESR Measurements. ESR spectra were recorded on a JEOL X-band JES-3X ESR spectrometer. Microwave frequencies, and the magnetic field were directly determined by using a microwave counter, ADVANTEST TR5212, and a field measurement unit, JEOL NMR field meter ES-FC-5, respectively. Toluene solutions (5 mmol·dm^{-3}) of complexes were used for ESR measurements.

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Note Added after ASAP Publication. In the version of this paper posted on the Web on August 25, 2005, the references that follow reference 13 were incorrectly numbered in the reference list. The numbering that now appears is correct.

Supporting Information Available: CIF files giving crystallographic data for complex **6** and the packing diagram of complex **6**. This material is available free of charge via the Internet at http://pubs.acs.org.

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