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Article

Platinum Dithiolene Complexes of π-Coordinating and π-Interacting η^4-Cyclobutadiene Ligands

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Five new organometallic platinum dithiolene complexes of the η^4-cyclobutadiene ligand [(η^4-C_4Me_4)Pt(dithiolene)] (dithiolene = mnt (**2**), dcmedt (**3**), tdt (**4**), dddt (**5**), dmit (**6**)) and one platinum diselenolene complex, [(η^4-C_4Me_4)Pt(dsit)] (**7**), were prepared from [(η^4-C_4Me_4)Pt(Cl)-(μ-Cl)]$_2$ (**1**) and Na_2(mnt), O=C(dcmedt), H_2tdt, O=C(dddt), $(NBu_4)_2$[Zn(dmit)$_2$], or $(NEt_4)_2$-[Zn(dsit)$_2$], respectively. The (η^4-C_4Me_4)Pt complexes **2**−**7** were characterized by NMR, UV−vis spectra, and CV. Those ^{1}H and ^{13}C NMR spectra showed ^{195}Pt satellite coupling at the $C_4\mathit{Me_4}$ (J_{Pt-H} = 13−15 Hz), at the $\mathit{C_4}Me_4$ (J_{Pt-C} = ca. 100 Hz), and at the dithiolene carbons. The complexes having an electron-rich dichalcogenolene ligand (**5**−**7**) resulted in lower energy electronic absorption compared with the electron-poor series **2**−**4**. The η^4-C_4Me_4 ligand was replaced by the nucleophilic substitution of bis(diphenylphosphino)ethane (DPPE) to form the square-planar [Pt(dithiolene)(dppe)] complex. **2**, **3**, and **5**−**7** were structurally determined by X-ray diffraction studies. All the molecules were monomeric, had two-legged piano-stool geometries, and were formal 16-electron complexes with the Pt^{II} (d^8) center. The crystal structure of **2** showed an inversion-centered dyad. **5** had η^4-$C_4Me_4\cdots$dithiolene plane-to-plane interaction in the crystal to form a zigzag chain. **6** and **7** were isostructural to each other and had intermolecular interactions through η^4-$C_4Me_4\cdots$trithiocarbonate contacts to form a zigzag chain. The η^4-C_4Me_4 group behaves as a π-coordinating ligand and a π-interacting ligand as well. Dithiolene and diselenolene ligands used in this work were as follows: mnt = maleonitrile-1,2-dithiolate, dcmedt = 1,2-dimethoxycarbonylethylene-1,2-dithiolate, tdt = toluene-3,4-dithiolate, dddt = 5,6-dihydro-1,4-dithiine-2,3-dithiolate, dmit = 1,3-dithiol-2-thione-4,5-dithiolate, and dsit = 1,3-dithiol-2-thione-4,5-diselenolate.

Introduction

Metal dithiolene complexes have an interesting π-electron system because of π-electron delocalization for the low-energy HOMO−LUMO gap,[1] $(4n+2)\pi$-conjugation for aromaticity (the Hückel's rule),[2] three-dimensional π-electron delocalization (nonplanar aromaticity),[3] π-electron-based magnetic interaction,[4] π-electron-induced electrical conductivity,[5] thermally driven valence tautomerism due to the M/L-CT,[6] photoexcited charge transfer due to the π-electron,[7] new olefin binding reactions derived from the low-energy LUMO,[8] and dithiolene-based "noninnocent behavior".[9] Especially, homoleptic dithiolene complexes such as square-planar bisdithiolene complexes and trigonal prismatic trisdithiolene complexes,[10] which include dithiolene ligands only, exhibit a well-delocalized π-electron system.

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(1) (a) Kobayashi, A.; Sasa, M.; Suzuki, W.; Fujiwara, E.; Tanaka, H.; Tokumoto, M.; Okano, Y.; Fujiwara, H.; Kobayashi, H. *J. Am. Chem. Soc.* **2004**, *126*, 426. (b) Tanaka, H.; Kobayashi, H.; Kobayashi, A. *J. Am. Chem. Soc.* **2002**, *124*, 10002. (c) Suzuki, W.; Fujiwara, E.; Kobayashi, A.; Fujishiro, Y.; Nishibori, E.; Takata, M.; Sakata, M.; Fujiwara, H.; Kobayashi, H. *J. Am. Chem. Soc.* **2003**, *125*, 1486.

(2) (a) Sugimori, A.; Akiyama, T.; Kajitani, M.; Sugiyama, T. *Bull. Chem. Soc. Jpn.* **1999**, *72*, 879. (b) Schrauzer, G. N. *Acc. Chem. Res.* **1969**, *2*, 72. (c) McCleverty, J. A. *Prog. Inorg. Chem.* **1968**, *10*, 49. (d) Boyde, S.; Garner, C. D.; Joule, J. A.; Rowe, D. J. *J. Chem. Soc., Chem. Commun.* **1987**, 800.

(3) Argyropoulos, D.; Lyris, E.; Mitsopoulou, C. A.; Katakis, D. *J. Chem. Soc., Dalton Trans.* **1997**, 615.

(4) (a) Fourmigué, M. *Acc. Chem. Res.* **2004**, *37*, 179. (b) Faulmann, C.; Cassoux, P. *Prog. Inorg. Chem.* **2003**, *52*, 399.

(5) (a) Kato, R. *Chem. Rev.* **2004**, *104*, 5319. (b) Kobayashi, A.; Fujiwara, E.; Kobayashi, H. *Chem. Rev.* **2004**, *104*, 5243. (c) Matsubayashi, G.; Nakano, M.; Tamura, H. *Cood. Chem. Rev.* **2002**, *226*, 143.

(6) Helton, M. E.; Gebhart, N. L.; Davies, E. S.; McMaster, J.; Garner, C. D.; Kirk, M. L. *J. Am. Chem. Soc.* **2001**, *123*, 10389.

(7) (a) Cummings, S. D.; Eisenberg, R. *Prog. Inorg. Chem.* **2003**, *52*, 315. (b) Mueller-Westerhoff, U. T.; Yoon, D. I.; Plourde, K. *Mol. Cryst. Liq. Cryst.* **1990**, *183*, 291.

(8) (a) Wang, K.; Stiefel, E. I. *Science* **2001**, *291*, 106. (b) Fan, Y.; Hall, M. B. *J. Am. Chem. Soc.* **2002**, *124*, 12076. (c) Harrison, D. J.; Nguyen, N.; Lough, A. J.; Fekl, U. *J. Am. Chem. Soc.* **2006**, *128*, 11026. (d) Harrison, D. J.; Lough, A. J.; Nguyen, N.; Fekl, U. *Angew. Chem., Int. Ed.* **2007**, *46*, 7644. (e) Han, Q.-Z.; Zhao, Y.-H.; Wen, H. *Mol. Simul.* **2008**, *34*, 631.

(9) (a) Periyasamy, G.; Burton, N. A.; Hillier, I. H.; Vincent, M. A.; Disley, H.; McMaster, J.; Garner, C. D. *Faraday Discuss.* **2007**, *135*, 469. (b) Ward, M. D.; McCleverty, J. A. *J. Chem. Soc., Dalton Trans.* **2002**, 275.

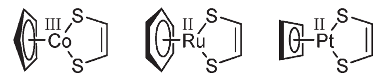
(10) Beswick, C. L.; Schulman, J. M.; Stiefel, E. I. *Prog. Inorg. Chem.* **2003**, *52*, 55.

Recently, novel tetrakisdithiolene complexes of uranium and cerium have been reported as well.[11]

In addition, heteroleptic dithiolene complexes, which have a dithiolene ligand and some other ligands, are also attractive compounds. Especially, photophysical and optical studies have been extensively investigated. Eisenberg et al. reported the photoluminescence of [Pt(dithiolene)(N^N)] (N^N = 2,2′-bipyridines, 1,10-phenanthrolines) and proved the nature of the photoexcited state in 1990s.[12] The [Pt(dithiolene)(N^N)] complex with a TiO_2 system can be a photocatalyst to generate molecular hydrogen from water,[13] can also be one component of a dye-sensitized solar cell,[14] and can exhibit nonlinear optical properties (NLO).[15] Recently, Noh et al. reported [Pt(dithiolene)(P^P)] (P^P = diphosphines) and their redox and photoluminescent properties.[16] Furthermore, some conducting molecules have been reported in the heteroleptic dithiolene complexes. The partially oxidized [M(dithiolene)(C^N)] (M = Au[17] and Pt,[18] C^N = 2-phenylpyridine) complexes show electrical conductivities.

On the other hand, organometallic dithiolene complexes having η^5-cyclopentadienyl (Cp) and η^6-arene (η^6-C_6R_6) ligands are another category of dithiolene complexes. Among them, the Cp/dithiolene complexes are further classified into four main categories:[19] Cp/dithiolene ratio 2:1 complexes of general formula $[Cp_2M(dithiolene)]^{0,+1}$ (M = group 4−6 metals), Cp/dithiolene ratio 1:2 complexes $[CpM(dithiolene)_2]^{-1,0}$ (M = group 4−7 metals), Cp/dithiolene ratio 1:1 complexes [CpM(dithiolene)] (M = group 9 and 10 metals, Chart 1), and bimetallic 1:1 complexes $[CpM(dithiolene)]_2$ (M = group 5, 6, and 8 metals). In the η^6-arene/dithiolene category, only group 8 metal complexes have been reported (Chart 1).[20−24]

Chart 1. 16-Electron Organometallic Dithiolene Complexes with π-Coordinating Organic Ligand



Introducing these planar π-coordinating organic ligands, Cp and η^6-arene, is plausibly interesting for the structural chemistry of dithiolenes because the complexes have intermolecular π-interactions through the π-coordinating organic ligand but show strong magnetic interactions in the solid state while the complexes are paramagnetic. Recently, the paramagnetic $[CpNi(dithiolene)]^{\bullet}$ ($S = 1/2$) complexes have been investigated from combined structural and magnetic properties.[25] For example, the Cp ligand of these complexes exhibits a Cp···dithiolene zigzag chain interaction in [CpNi(tfd)] (tfd = 1,2-bis(trifluoromethyl)ethene-1,2-dithiolate),[26] a Cp···S═C interaction in [CpNi(dmit)] (dmit = 1,3-dithiol-2-thione-4,5-dithiolate),[25,27] and a Cp···Cp dimeric interaction in [CpNi(adt)] (adt = acrylonitrile-1,2-dithiolate),[26] [CpNi(bdt)] (bdt = benzene-1,2-dithiolate),[28] and [CpNi(bds)] (bds = benzene-1,2-diselenolate).[28] A theoretical study on [CpNi(dithiolene)] has indicated the existence of some spin densities on the Cp ligand.[25,26,28,29] In addition, the diamagnetic [Cp*Co(dithiolene)] (Cp* = η^5-pentamethylcyclopentadienyl) complexes exhibit Cp*··· benzene interactions in the mononuclear Cp*Co with benzene-1,2-dithiolate (bdt),[30] the dinuclear $(Cp^*Co)_2$ with benzene-1,2,4,5-tetrathiolate,[30] and the trinuclear $(Cp^*Co)_3$ with benzenehexathiolate complexes.[31] According to reasons noted above, these planar π-coordinating organic ligands behave also as intermolecular *π-interacting* ligands.

In this work, we attempted to introduce another planar π-coordinating and probable π-interacting organic ligand, η^4-cyclobutadiene (η^4-C_4R_4),[32] to form a new organometallic dithiolene complex. The dithiolene complex of the η^4-C_4R_4 ligand has been much less investigated compared with the Cp and η^6-C_6R_6 dithiolene complexes, because there

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(11) (a) Roger, M.; Arliguie, T.; Thuery, P.; Fourmigué, M.; Ephritikhine, M. *Inorg. Chem.* **2005**, *44*, 594. (b) Weis, E. M.; Barnes, C. L.; Duval, P. B. *Inorg. Chem.* **2006**, *45*, 10126.

(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. (d) Hissler, M.; McGarrah, J. E.; Connick, W. B.; Geiger, D. K.; Cummings, S. D.; Eisenberg, R. *Coord. Chem. Rev.* **2000**, *208*, 115.

(13) Zhang, J.; Du, P.; Schneider, J.; Jarosz, P.; Eisenberg, R. *J. Am. Chem. Soc.* **2007**, *129*, 7726.

(14) (a) Moorcraft, L. P.; Morandeira, A.; Durrant, J. R.; Jennings, J. R.; Peter, L. M.; Parsons, S.; Turner, A.; Yellowlees, L. J.; Robertson, N. *Dalton Trans.* **2008**, 6940. (b) Geary, E. A. M.; Yellowlees, L. J.; Jack, L. A.; Oswald, I. D. H.; Parsons, S.; Hirata, N.; Durrant, J. R.; Robertson, N. *Inorg. Chem.* **2005**, *44*, 242. (c) Geary, E. A. M.; Hirata, N.; Clifford, J.; Durrant, J. R.; Parsons, S.; Dawson, A.; Yellowlees, L. J.; Robertson, N. *Dalton Trans.* **2003**, 3757. (d) Islam, A.; Sugihara, H.; Hara, K.; Singh, L. P.; Katoh, R.; Yanagida, M.; Takahashi, Y.; Murata, S.; Arakawa, H. *Inorg. Chem.* **2001**, *40*, 5371.

(15) Cummings, S. D.; Cheng, L.-T.; Eisenberg, R. *Chem. Mater.* **1997**, *9*, 440.

(16) (a) Shin, K.-S.; Jung, Y. J.; Lee, S.-K.; Fourmigué, M.; Barrière, F.; Bergamini, J.-F.; Noh, D.-Y. *Dalton Trans.* **2008**, 5869. (b) Shin, K.-S.; Son, K.-I.; Kim, J. I.; Hong, C. S.; Suh, M.; Noh, D.-Y. *Dalton Trans.* **2009**, 1767.

(17) (a) Kubo, K.; Nakao, A.; Ishii, Y.; Tamura, M.; Kato, R.; Matsubayashi, G. *J. Low Temp. Phys.* **2006**, *142*, 413. (b) Kubo, K.; Nakao, A.; Ishii, Y.; Kato, R.; Matsubayashi, G. *Synth. Met.* **2005**, *153*, 425. (c) Kubo, K.; Nakao, A.; Ishii, Y.; Yamamoto, T.; Tamura, M.; Kato, R.; Yakushi, K.; Matsubayashi, G. *Inorg. Chem.* **2008**, *47*, 5495. (d) Kubo, K.; Nakano, M.; Tamura, H.; Matsubayashi, G. *Eur. J. Inorg. Chem.* **2003**, *22*, 4093. (e) Kubo, K.; Nakano, M.; Tamura, H.; Matsubayashi, G.; Nakamoto, M. *J. Organomet. Chem.* **2003**, *669*, 141.

(18) (a) Suga, Y.; Nakano, M.; Tamura, H.; Matsubayashi, G. *Bull. Chem. Soc. Jpn.* **2004**, *77*, 1877.

(19) Cp metal dithiolene complexes are classified in the review: Fourmigué, M. *Coord. Chem. Rev.* **1998**, *178*, 823. and references therein.

(20) (a) Mashima, K.; Kaneyoshi, H.; Kaneko, S.; Mikami, A.; Tani, K.; Nakamura, A. *Organometallics* **1997**, *16*, 1016. (b) Mashima, K.; Kaneyoshi, H.; Kaneko, S.; Tani, K.; Nakamura, A. *Chem. Lett.* **1997**, 569.

(21) Szczepura, L. F.; Galloway, C. P.; Zheng, Y.; Han, P.; Rheingold, A. L.; Wilson, S. R.; Rauchfuss, T. B. *Angew. Chem., Int. Ed.* **1995**, *34*, 1890.

(22) Nomura, M.; Fujii, M.; Fukuda, K.; Sugiyama, T.; Yokoyama, Y.; Kajitani, M. *J. Organomet. Chem.* **2005**, *690*, 1627.

(23) (a) Jia, W.-G.; Han, Y.-F.; Zhang, J.-S.; Jin, G.-X. *Inorg. Chem. Commun.* **2007**, *10*, 1222.

(24) (a) Takemoto, S.; Shimadzu, D.; Kamikawa, K.; Matsuzaka, H.; Nomura, R. *Organometallics* **2006**, *25*, 982. (b) Nakagawa, N.; Murata, M.; Sugimoto, M.; Nishihara, H. *Eur. J. Inorg. Chem.* **2006**, 2129. (c) Nakagawa, N.; Yamada, T.; Murata, M.; Sugimoto, M.; Nishihara, H. *Inorg. Chem.* **2006**, *45*, 14.

(25) Fourmigué, M.; Cauchy, T.; Nomura, M. *CrystEngComm* **2009**, in press.

(26) Cauchy, T.; Ruiz, E.; Jeannin, O.; Nomura, M.; Fourmigué, M. *Chem.—Eur. J.* **2007**, *13*, 8858.

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

(28) Nomura, M.; Cauchy, T.; Geoffroy, M.; Adkine, P.; Fourmigué, M. *Inorg. Chem.* **2006**, *45*, 8194.

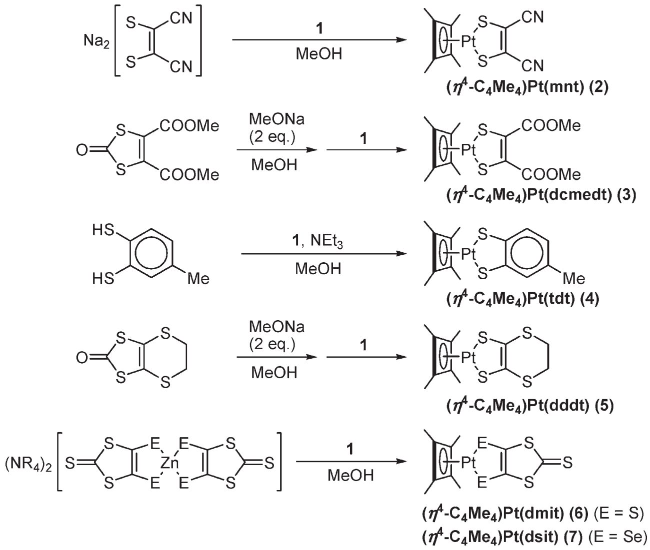
(29) Grosshans, P.; Adkine, P.; Sidorenkova, H.; Nomura, M.; Fourmigué, M.; Geoffroy, M. *J. Phys. Chem. A* **2008**, *112*, 4067.

(30) Nomura, M.; Fourmigué, M. *Inorg. Chem.* **2008**, *47*, 1301.

(31) Shibata, Y.; Zhu, B.; Kume, S.; Nishihara, H. *Dalton Trans.* **2009**, 1939.

(32) Maitlis, P. M. *Adv. Organomet. Chem.* **1966**, *4*, 95.

Scheme 1



are some difficulties in the synthetic procedure. One possible species is a η^4-C$_4$R$_4$ complex of the group 10 metals. The neutral η^4-C$_4$R$_4$ ligand with its 4π-electron donation makes formal M^{II} (d^8) dithiolene complexes, which are formulated as [(η^4-C$_4$R$_4$)M^{IV}(dithiolene)] (Chart 1). They become 16-electron half-sandwich dithiolene complexes and are well comparable with other 16-electron dithiolene complexes such as [CpM^{III}(dithiolene)] (M^{III} = group 9 metals)[19] and [(η^6-C$_6$R$_6$)M^{II}(dithiolene)] (M^{II} = group 8 metals) (Chart 1).[20−24]

Some nickel and palladium complexes of the η^4-C$_4$R$_4$ ligand have been reported as follows: [(η^4-C$_4$Me$_4$)Ni(mnt)] (mnt = maleonitrile-1,2-dithiolate),[33,34] [(η^4-C$_4$Ph$_4$)Pd(mnt)],[33] and [(η^4-C$_4$(Me)$_2$(*t*Bu)$_2$)Pd(bdt)].[35] However, the highly toxic [Ni(CO)$_4$][36] is required for the (η^4-C$_4$R$_4$)Ni complexes,[37] and the Pd complex requires an expensive asymmetric alkyne as a precursor.[38] We noted that no platinum dithiolene complex of the η^4-C$_4$R$_4$ ligand has been reported, and the possible starting material [(η^4-C$_4$Me$_4$)Pt(Cl)(μ-Cl)]$_2$ (**1**) is relatively easy to prepare compared with the Ni and Pd precursors. The synthetic procedure of **1** has been developed by Maitlis et al.[39,40] Here we report on the syntheses of five new [(η^4-C$_4$Me$_4$)Pt(dithiolene)] (dithiolene = dcmedt, mnt, tdt, dddt, dmit; see Scheme 1) complexes from **1** and one [(η^4-C$_4$Me$_4$)Pt(diselenolene)] (diselenolene = dsit) complex as well. These new products were characterized by NMR and UV−vis spectra and CV measurements. Especially, we discuss their crystal structures and review the intermolecular π-interaction based on the π-interacting η^4-C$_4$Me$_4$ ligand.

Results and Discussion

1. Preparations, Characterizations, and Reactivity of [(η^4-C$_4$Me$_4$)Pt(dithiolene)] and [(η^4-C$_4$Me$_4$)Pt(diselenolene)] Complexes. Maitlis et al. have reported the facile preparation of **1** by the reaction of [Pt(NCMe)$_2$(Cl)$_2$] with 2-butyne in the presence of SnCl$_2$, and the produced intermediate [(η^4-C$_4$Me$_4$)$_2$Pt$_2$(μ-Cl)$_3$][(η^4-C$_4$Me$_4$)Pt(SnCl$_3$)$_3$], when treated with aqueous HCl, forms **1**.[39] As shown in Scheme 1, disodium maleonitrile-1,2-dithiolate (Na$_2$mnt) reacted with **1** in MeOH solution at room temperature to form [(η^4-C$_4$Me$_4$)Pt(mnt)] (**2**) in 63% yield. The treatment of dimethyl 1,3-dithiol-2-one-4,5-dicarboxylate (O=C(dcmedt)) with 2 equiv of sodium methoxide in MeOH affords the corresponding dithiolate dianion (dcmedt^{2-}), and then successive addition of **1** gave [(η^4-C$_4$Me$_4$)Pt(dcmedt)] (**3**) in 42% yield. **1** reacted with toluene-3,4-dithiol (H$_2$tdt) in the presence of excess NEt$_3$ to produce [(η^4-C$_4$Me$_4$)Pt(tdt)] (**4**) in 59% yield. [(η^4-C$_4$Me$_4$)Pt(dddt)] (**5**) was prepared in 17% yield from O=C(dddt) by a similar synthetic procedure to that of **3**. [(η^4-C$_4$Me$_4$)Pt(dmit)] (**6**, 64% yield) and [(η^4-C$_4$Me$_4$)Pt(dsit)] (**7**, 48% yield) were obtained from **1** and (NBu$_4$)$_2$[Zn(dmit)$_2$] or (NEt$_4$)$_2$[Zn(dsit)$_2$] without any base, respectively (Scheme 1). The products **2**−**7** were air stable and could be separated by column chromatography on silica gel. **2**−**7** were soluble in dichloromethane, chloroform, acetone, and benzene. However, **6** and **7** were not soluble enough in CDCl$_3$ and CD$_2$Cl$_2$ for ^{13}C NMR measurements. The diselenolene complex **7** was less soluble than the others. **2**−**7** were characterized by spectroscopic data and elemental analyses.

The ^{1}H NMR spectra of **2**−**7** showed four equivalent Me groups around 1.9−2.1 ppm (vs TMS) and also resulted in coupling effects due to the Pt satellite (^{195}Pt natural abundance = 33.80% (I = 1/2)), whose $J_{\mathrm{Pt-H}}$ values were 13−15 Hz (Table 1). The ^{13}C NMR spectra showed equivalent cyclobutadiene carbons (C_4Me$_4$) around 100 ppm (vs TMS), which are an aromatic region, and also suggested Pt satellite coupling with $J_{\mathrm{Pt-C}}$ = ca. 100 Hz (Table 1). These results indicated an equivalent π-coordination by four carbons of the η^4-cyclobutadiene ligand to the Pt center. Furthermore, the ^{13}C NMR spectra of **2**−**5** exhibited a $J_{\mathrm{Pt-C}}$ at the dithiolene carbons, and the toluene-3,4-dithiolate complex **4** showed a $J_{\mathrm{Pt-C}}$ at 2,5-carbons on the toluene moiety as well, but the $J_{\mathrm{Pt-C}}$ values ($J_{\mathrm{Pt-C}}$ = 8.4, 8.8 Hz) were relatively small because of the long distances between the carbons and the Pt center. In previous papers, [Pt(cod)(dithiolene)] (cod = 1,5-cyclooctadiene) complexes have shown a similar Pt satellite coupling at the dithiolene and cod carbons, which have been reported by Bereman[41] and Eisenberg[42] et al.

The UV−vis spectra of **2**−**7** were obtained, and the absorption maxima (λ_{max}/nm) appeared as follows: **2** (430 nm), **3** (439 nm), **4** (449 nm), **5** (535 nm), **6** (512 nm), and **7** (503 nm) as lowest energy absorption bands (Table 2). These results may indicate that the complex with the more electron-rich dithiolene ligand shows lower energy absorption. In fact, these results correlate with those of

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(33) Wharton, E. J. *Inorg. Nucl. Chem. Lett.* **1971**, *7*, 307.

(34) Hemmer, R.; Brune, H. A.; Thewalt, U. *Z. Naturforsch.* **1981**, *36B*, 78.

(35) Mashima, K.; Kaneko, S.; Tani, K. *Chem. Lett.* **1997**, 347.

(36) (a) Schroeder, W.; Poerschke, K. R.; Tsay, Y. H.; Krueger, C. *Angew. Chem.* **1987**, *99*, 953. (b) Schroeder, W.; Poerschke, K. R. *J. Organomet. Chem.* **1987**, *322*, 385. (c) Kaschube, W.; Poerschke, K. R.; Seevogel, K.; Krueger, C. *J. Organomet. Chem.* **1989**, *367*, 233.

(37) Criegee, R.; Schroder, G. *Angew. Chem.* **1959**, *71*, 70.

(38) Kelley, E. A.; Maitlis, P. M. *J. Chem. Soc., Dalton Trans.* **1979**, 167.

(39) Moreto, J.; Maitlis, P. M. *J. Chem. Soc., Dalton Trans.* **1980**, 1368.

(40) Maitlis, P. M. *Acc. Chem. Res.* **1976**, *9*, 93.

(41) (a) Keefer, C. E.; Bereman, R. D.; Purrington, S. T.; Knight, B. W.; Boyle, P. D. *Inorg. Chem.* **1999**, *38*, 2294. (b) Keefer, C. E.; Purrington, S. T.; Bereman, R. D.; Boyle, P. D. *Inorg. Chem.* **1999**, *38*, 5437.

(42) (a) Cummings, S. D.; Eisenberg, R. *Inorg. Chem.* **1995**, *34*, 2007. (b) Bevilacqua, J. M.; Eisenberg, R. *Inorg. Chem.* **1994**, *33*, 2913.

Table 1. ^{1}H NMR and ^{13}C NMR Chemical Shifts^b (δ/ppm vs TMS) and Coupling Constants ($J_{\mathrm{Pt-H}}$, $J_{\mathrm{Pt-C}}$/Hz) by ^{195}Pt Satellite in CDCl$_3$

	^{1}H NMR $C_4(CH_3)_4$	$J_{\mathrm{Pt-H}}$	^{13}C NMR $C_4(CH_3)_4$	$J_{\mathrm{Pt-C}}$	dithiolene-C	$J_{\mathrm{Pt-C}}$	others	$J_{\mathrm{Pt-C}}$
2	2.11	13.2	104.8	99.7	131.8	38.3		
3	2.06	13.2	102.0	98.4	167.7	80.3		
4	2.06	13.2	100.2	98.4	130.3, 129.8	92.4, 93.6	132.6, 124.3	8.4, 8.8
5	2.02	13.7	100.3	100.6	129.5	9.6		
6	2.08	14.3	102.4	102.0	^{a}			
7	1.91	15.1	^{a}		^{a}			

^{a} No ^{13}C NMR signals were found due to poor solubility. ^{b} Only δ values having ^{195}Pt satellite coupling are shown.

Table 2. UV−Vis Spectral Data ($\lambda_{\max}$/nm (ε/M$^{-1}\cdot$cm^{-1})) in Dichloromethane Solution

ligand	(η^4-C$_4$Me$_4$)Pt complex	CpNi complex	ref
mnt	430 (4800) (**2**)	698 (2000)	43
dcmedt	439 (5200) (**3**)	695 (1500)	43
tdt	449 (9200) (**4**)	722^a (2600)	28
dddt	535 (5300) (**5**)	1012 (4700)	28
dmit	512 (8000) (**6**)	967 (6000)	28
dsit	503 (7000) (**7**)	948 (3200)	28

^{a} Benzene-1,2-dithiolate (bdt) ligand was used instead of tdt.

Table 3. Redox Potentials (vs Fc/Fc$^+$) of 2−7 Obtained from CV^a

	E_p(red)/V	E_p(ox)/V	$\lvert E_{pa} - E_{pc}\rvert$/mV	i_{pa}/i_{pc}	E_p(2ox)/V
2	−1.74 (ir)	+ 1.08 (ir)	(ir)	(ir)	^{b}
3	−2.06 (ir)	+ 0.74 (ir)	(ir)	(ir)	^{b}
4	−2.11 (ir)	+ 0.45 (ir)	(ir)	(ir)	^{b}
5	−2.12 (ir)	0^c (qr)	165	1	0.88 (ir)
6	−1.88 (ir)	+ 0.35^c (qr)	177	0.65	+ 1.02 (ir)
7	−1.85 (ir)	+ 0.26^c (qr)	156	0.50	+ 1.04 (ir)

^{a} E_p = peak potentials. $\lvert E_{pa} - E_{pc}\rvert$ = peak-to-peak separation. i_{pa}/i_{pc} = ratio of peak current. ^{b} Not observed in the potential window of dichloromethane-TBAP. ^{c} Half-wave potentials ($E_{1/2}$/V) were used. (qr) and (ir): quasi-reversible and irreversible waves, respectively.

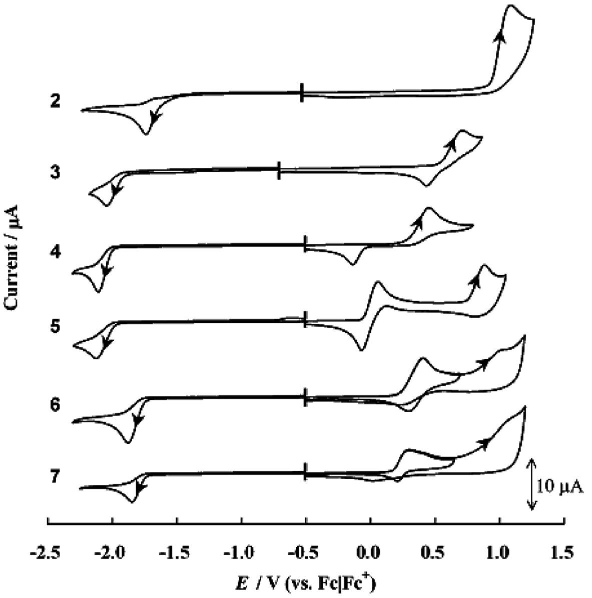

Figure 1. Cyclic voltammograms of **2**−**7** in dichloromethane solution containing 0.1 M TBAP (c = 1.0 mmol·dm^{-3}, Φ = 1.6 mm Pt disk as a working electrode, v = 100 mV·s^{-1}).

[CpNi(dithiolene)] and [CpNi(diselenolene)] complexes as follows (Table 2): [CpNi(mnt)] (698 nm), [CpNi(dcmedt)] (695 nm),[43] [CpNi(bdt)] (722 nm), [CpNi(dmit)] (967 nm), [CpNi(dsit)] (948 nm), and [CpNi(dddt)] (1012 nm).[28] In the square-planar complexes of bisdithiolene, the electron-rich complexes [M(dddt)$_2$],[44] [M(dmit)$_2$],[44] [M(S$_2$C$_2$Fc$_2$)$_2$] (Fc = ferrocenyl),[45] and [M(R,R′timdt)$_2$] (R,R′timdt = *N*,*N*′-disubstituted imidazolidine-2,4,5-trithione)[46] indicated strong NIR absorption. The low-energy absorption of the neutral or monoanionic [M(dithiolene)$_2$]$^{n-}$ complexes can be attributed to the ligand-to-ligand charge transfer,[10] and that of [Pt(dithiolene)(N$\widehat{\;}$N)] (N$\widehat{\;}$N = 2,2’-bipyridines, 1,10-phenanthrolines) can be assigned also to ligand(dithiolene)-to-ligand(N N).[12] The latter absorption is usually solvatochromic, and it depends on the polarity of the solvent.[12b]

The redox potentials (vs Fc/Fc$^+$) taken from CV measurement are described in Table 3. These cyclic voltammograms are shown in Figure 1. Their reduction waves were completely irreversible, and the first oxidation waves of **2**−**4** were also irreversible. These results explain that the reduced or oxidized species are unstable on the CV time scale. In contrast, the first oxidation waves of **5**, **6**, and **7** looked quasi-reversible (Figure 1), because the peak-to-peak separation $\lvert E_{pa} - E_{pc}\rvert$ values are 156−177 mV (Table 3). These facts indicate that an electron-rich dithiolene ligand stabilizes the oxidized complex. According to the i_{pa}/i_{pc} ratios, the oxidized species of **5** is stable enough on the CV time scale (i_{pa}/i_{pc} = 1), but those of **6** and **7** are less stable than that of **5** (i_{pa}/i_{pc} = 0.65 and 0.50, respectively). The reduction potential of **2**−**7** appeared in the range between −1.74 (mnt) and −2.12 V (dddt). In contrast, the CVs indicated a wide range of first oxidation potentials (Table 3). Although **2** (mnt) was oxidized at + 1.08 V, **5** (dddt) was oxidized at 0 V (Table 3).

These results supported that modification of the dithiolene ligand has a greater effect on oxidation potentials than reduction potentials. Namely, the complexes of electron-rich dithiolene ligands such as dddt, dmit, and dsit (**5**−**7**) have higher energy HOMO levels, and eventually the HOMO−LUMO gaps of **5**−**7** (503−535 nm) are much lower than those of the others (430−449 nm). We may conclude that the first oxidation of the [(η^4-C$_4$Me$_4$)Pt(dithiolene)] complex is based on the dithiolene ligand, and the first reduction is due to the Pt center, because ligand modification does not well contribute to the reduction potential. Normally, the

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(43) Nomura, M.; Okuyama, R.; Fujita-Takayama, C.; Kajitani, M. *Organometallics* **2005**, *24*, 5110.

(44) (a) Mueller-Westerhoff, U. T.; Yoon, D. I.; Plourde, K. *Mol. Cryst. Liq. Cryst.* **1990**, *183*, 291. (b) Mueller-Westerhoff, U. T.; Vance, B.; Yoon, D. I. *Tetrahedron* **1991**, *47*, 909.

(45) Mueller-Westerhoff, U. T.; Sanders, R. W. *Organometallics* **2003**, *22*, 4778.

(46) (a) Aragoni, M. C.; Arca, M.; Demartin, F.; Devillanova, F. A.; Garau, A.; Isaia, F.; Lelj, F.; Lippolis, V.; Verani, G. *J. Am. Chem. Soc.* **1999**, *121*, 7098. (b) Arca, M.; Demartin, F.; Devillanova, F. A.; Garau, A.; Isaia, F.; Lelj, F.; Lippolis, V.; Pedraglio, S.; Verani, G. *J. Chem. Soc., Dalton Trans.* **1998**, 3731.

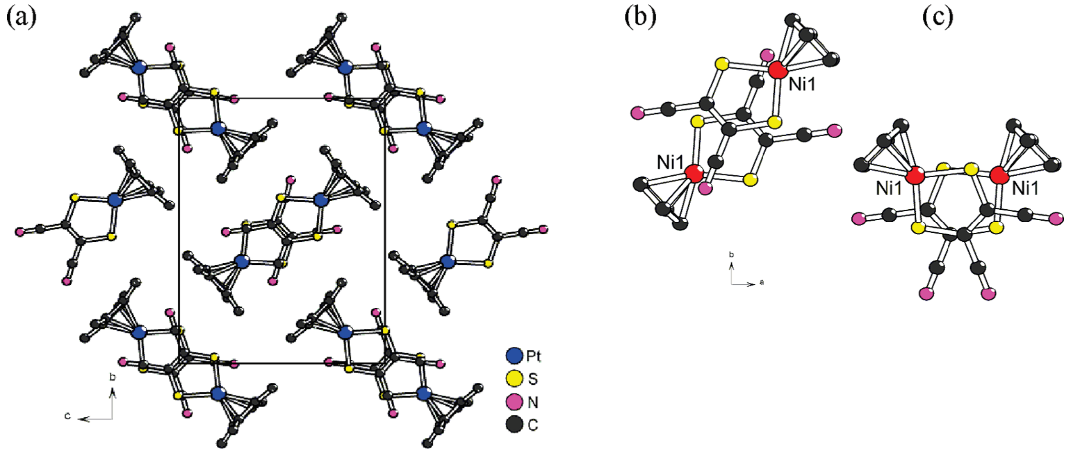
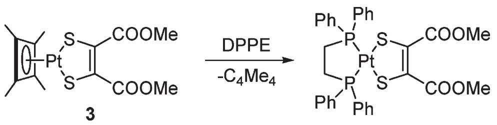


Figure 2. (a) Projection view along the *a* axis of **2** showing an inversion-centered dyad arrangement, (b) inversion-centered dyad of [CpNi(mnt)], and (c) crisscross dyad of [CpNi(mnt)].[43] Both (b) and (c) dyads are observed in the same unit cell.

Scheme 2



3

homoleptic dithiolene complexes [M(dithiolene)$_2$] (M = Ni, Pd, Pt) have a dithiolene ligand-based HOMO and LUMO. In total, five different oxidation states (−2, −1, 0, +1, +2) have been observed, because the dithiolene ligand itself involves dithiolate (−2), dithiosemiquinone (−1), and dithioketone (0).[10] In addition, the heteroleptic dithiolene complexes [Pt(dithiolene)(N^N)] can be reduced at the N^N moiety and oxidized at the dithiolene ligand. Eventually, four different oxidation states (−2, −1, 0, +1) were observed.[12]

The reactivity of [(η^4-C$_4$Me$_4$)Pt(dithiolene)] complexes was investigated. The reaction of **3** with bis(diphenylphosphino)ethane (DPPE) at room temperature gave the square-planar Pt dithiolene complex that was formulated as [Pt(dcmedt)(dppe)][47] in quantitative yield (Scheme 2). This result suggests a ligand exchange reaction between DPPE and the η^4-C$_4$Me$_4$ ligand, followed by nucleophilic attack of DPPE to the Pt center. Mashima et al. have reported the synthesis of [(η^4-C$_4$(Me)$_2$(*t*Bu)$_2$)Pd(bdt)][35] and also its reactivity with PEt$_3$ or isocyanide (CNR) to form the corresponding square-planar Pd complex [Pd(bdt)(PEt$_3$)$_2$] or [Pd(bdt)(CNR)$_2$], respectively.[35] Additionally, the cod ligand in [Pt(cod)(dithiolene)] has also been substituted by diphosphines or monophosphines to obtain the luminescent [Pt(dithiolene)(P$_2$)] complexes.[42,48] Here we propose that [(η^4-C$_4$Me$_4$)Pt(dithiolene)] is also an important precursor of the luminescent Pt dithiolene complexes and asymmetric dithiolene complexes.

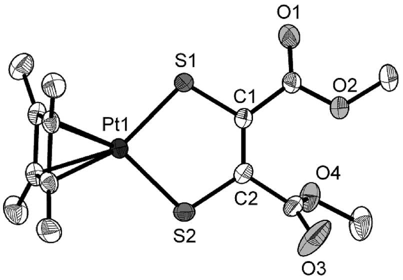


Figure 3. ORTEP drawing of **3**. Thermal ellipsoids are drawn at the 30% probability level. All hydrogen atoms are omitted for simplicity.

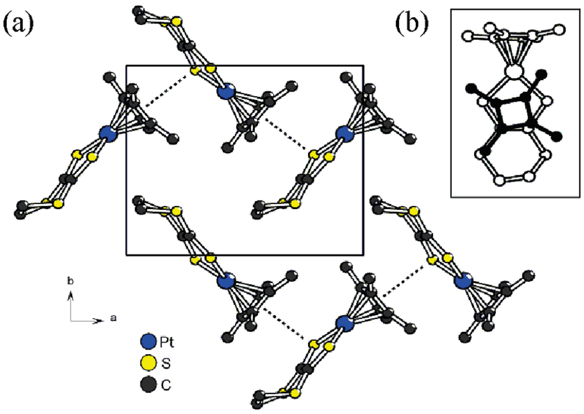


Figure 4. (a) Projection view along the *c* axis of **5** and the zigzag-shaped intermolecular interaction running along the *a* axis through the η^4-C$_4$Me$_4$···dithiolene interaction. (b) Overlap pattern of η^4-C$_4$Me$_4$···dithiolene stacking from the top view.

2. X-ray Crystal Structure Analyses of [(η^4-C$_4$Me$_4$)Pt(dithiolene)] and [(η^4-C$_4$Me$_4$)Pt(diselenolene)] Complexes. Single crystals of the products except for **4** were obtained from recrystallization of dichloromethane/*n*-hexane solution. The ORTEP drawings and packing diagrams are shown in Figures 2−6. Table 4 exhibits selected bond lengths, bond angles, and dihedral angles. These crystal data are summarized in Table 5. All molecules **2**, **3**, and **5**−**7** are monomeric at room temperature, and each η^4-C$_4$Me$_4$ ligand is located in a perpendicular position with respect to the Pt-dithiolene or Pt-diselenolene ring because the dihedral angles of η^4-C$_4$Me$_4$/PtE$_2$ (E = S, Se) are almost 90°. Thus, they have typical two-legged piano-stool geometries. As shown in Table 4 for mean planes, the η^4-C$_4$Me$_4$ and PtE$_2$C$_2$ (E = S, Se) rings are extremely planar. Some dimeric [CpM(dichalcogenolene)]$_2$ and [Cp*M(dichalcogenolene)]$_2$ with group 9 metal complexes have been reported in

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(47) Ford, S.; Lewtas, M. R.; Morley, C. P.; Vaira, M. D. *Eur. J. Inorg. Chem.* **2000**, 933.

(48) Bevilacqua, J. M.; Zuleta, J. A.; Eisenberg, R. *Inorg. Chem.* **1994**, *33*, 258.

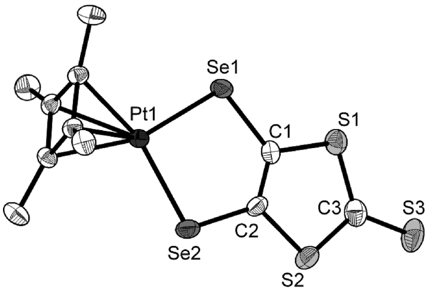

Figure 5. ORTEP drawing of **7**. Thermal ellipsoids are drawn at the 30% probability level. All hydrogen atoms are omitted for simplicity.

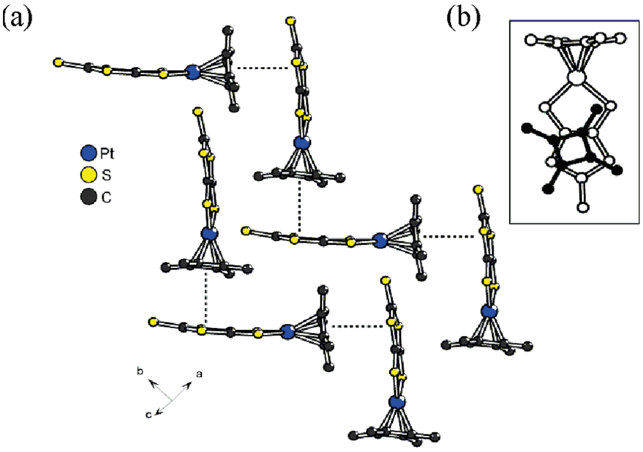

Figure 6. (a) Crystal-packing diagram of **6** showing the zigzag-shaped interaction running along the *b* axis through the η^4-C$_4$Me$_4\cdots$trithiocarbonate interaction. (b) Overlap pattern of η^4-C$_4$Me$_4\cdots$trithiocarbonate stacking from the top view.

Table 4. Selected Bond Lengths (Å), Bond Angles (deg), and Dihedral Angles (deg) in the PtE$_2$C$_2$ Metallacycle (E = S, Se)

	2	**3**	**5**	**6**	**7**
			Bond Lengths		
Pt1−E1	2.277(3)	2.2594(10)	2.2714(9)	2.2856(17)	2.3955(7)
Pt1−E2	2.265(3)	2.2742(10)	2.2735(9)	2.2793(19)	2.3871(6)
E1−C1	1.724(11)	1.741(3)	1.735(4)	1.737(7)	1.895(6)
E2−C2	1.732(10)	1.733(4)	1.741(4)	1.719(7)	1.878(6)
C1−C2	1.343(15)	1.350(5)	1.355(5)	1.347(8)	1.330(7)
			Bond Angles		
E1−Pt1−E2	89.71(10)	89.22(3)	89.00(3)	90.81(6)	92.83(2)
Pt1−E1−C1	102.4(3)	103.82(13)	103.05(12)	101.1(2)	98.80(18)
Pt1−E2−C2	102.7(3)	103.24(14)	103.00(14)	101.1(2)	99.16(17)
E1−C1−C2	122.9(8)	121.3(3)	121.9(3)	122.6(5)	124.1(5)
E2−C2−C1	122.3(8)	122.4(3)	121.7(3)	124.3(5)	124.8(5)
			Dihedral Angle		
η^4-C$_4$Me$_4$/PtE$_2$	91.805	89.254	96.083	92.539	87.027
			Mean Plane		
η^4-C$_4$Me$_4$	0.0088	0.0012	0.0064	0.0057	0.0108
PtE$_2$C$_2$	0.0051	0.0068	0.1049	0.0375	0.0594

[CpCo(bdt)]$_2$,[49] [CpCo(bds)]$_2$ (bds = benzene-1,2-diselenolate),[50] [Cp*Rh(mnt)]$_2$,[51] [Cp*Rh(bdt)]$_2$,[52] and [Cp*Rh(dmit)]$_2$.[53] In the group 10 metal complexes of Cp and η^4-C$_4$R$_4$ ligands, no dimeric species has been observed.

The bond lengths in the metallacycle of [(η^4-C$_4$Me$_4$)Pt(dithiolene)] complexes are 2.26−2.28 Å for Pt−S, 1.72−1.74 Å for S−C, and 1.34−1.35 Å for C=C bonds (Table 4). These bond lengths are similar to those of the corresponding square-planar Pt bisdithiolene complexes such as [Pt(mnt)$_2$]$^-$,[54] [Pt(dddt)$_2$]$^-$,[55] and [Pt(dmit)$_2$]$^-$,[56] and slightly different from that of the diselenolene complex **7** (Table 4). The difference of bond length between dithiolene and diselenolene complexes is due to the atomic radius between S^{2-} (1.70 Å) and Se^{2-} (1.84 Å).[57] Each cyclobutadiene ring is rectangular as normally well-known in any η^4-cyclobutadiene metal complex. For example, the C−C bond lengths in the cyclobutadiene carbons (C5−C8) in **2** are as follows: C5−C6 = 1.493(17), C5−C8 = 1.429(18), C6−C7 = 1.42(2), C7−C8 = 1.492(18) Å.

The dmit complex **6** is crystallographically isostructural to the corresponding selenium complex **7** (Table 5). Both complexes crystallized as a monoclinic system, space group $P2_1/n$, with one independent molecule in general position in the unit cell. Such crystallographic similarity between dithiolene and diselenolene complexes has been found as follows: [CpNi(dmit)] vs [CpNi(dsit)],[27] [CpNi(bdt)] vs [CpNi(bds)],[28] [CpNi(dddt)] vs [CpNi(ddds)] (ddds = 5,6-dihydro-1,4-dithiin-2,3-diselenolate),[28] and [CpCo(bdt)]$_2$[49] vs [CpCo(bds)]$_2$.[50]

The packing diagram of **2** demonstrated an inversion-centered dyad in the unit cell. Two molecules are stacked along the *a* axis (Figure 2a). The intermolecular distance between two molecules is ca. 3.8 Å. According to early studies, the monomeric [CpM(mnt)] complexes have tended to show an intermolecular dimeric interaction. In the CpCo and CpNi complexes of mnt,[43,58] there are two different dyads. One is an inversion-centered dyad type as displayed in Figure 2b, and the other is a crisscross type whose two molecules are shifted at 90° (Figure 2c).[43,58] In addition, the monomeric [Cp*Ir(mnt)] complex has been reported. There are two crystallographically independent molecules in the unit cell. The same molecules interact as an inversion-centered dyad.[59] On the other hand, **3** does not have any specific intermolecular interactions due to bulkiness of the two ester groups. **5** crystallized as a monoclinic system, space group $P2_1/a$, with one molecule in the unit cell. Figure 4 indicates an intermolecular η^4-C$_4$Me$_4\cdots$dithiolene interaction whose plane-to-plane distance is ca. 3.7 Å. The whole packing diagram exhibited a zigzag-shaped intermolecular chain along the *a* axis in the unit cell. Some early papers have

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(49) Miller, E. J.; Brill, T. B.; Rheingold, A. L.; Fultz, W. C. *J. Am. Chem. Soc.* **1983**, *105*, 7580.

(50) Habe, S.; Yamada, T.; Nankawa, T.; Mizutani, J.; Murata, M.; Nishihara, H. *Inorg. Chem.* **2003**, *42*, 1952.

(51) Don, M.-J.; Yang, K.; Bott, S. G.; Richmond, M. G. *J. Organomet. Chem.* **1997**, *544*, 15.

(52) Xi, R.; Abe, M.; Suzuki, T.; Nishioka, T.; Isobe, K. *J. Organomet. Chem.* **1997**, *549*, 117.

(53) Kawabata, K.; Nakano, M.; Tamura, H.; Matsubayashi, G. *J. Organomet. Chem.* **2004**, *689*, 405.

(54) (a) Guentner, W.; Gliemann, G.; Klement, U.; Zabel, M. *Inorg. Chim. Acta* **1989**, *165*, 51. (b) Clemenson, P. I.; Underhill, A. E.; Hursthouse, M. B.; Short, R. L. *J. Chem. Soc., Dalton Trans.* **1989**, 61.

(55) Welch, J. H.; Bereman, R. D.; Singh, P. *Inorg. Chim. Acta* **1989**, *163*, 93.

(56) Mentzafos, D.; Hountas, A.; Terzis, A. *Acta Crystallogr.* **1988**, *C44*, 1550.

(57) Fujiwara, H.; Ojima, E.; Kobayashi, H.; Courcet, T.; Malfant, I.; Cassoux, P. *Eur. J. Inorg. Chem.* **1998**, 1631.

(58) Takayama, C.; Kajitani, M.; Sugiyama, T.; Sugimori, A. *J. Organomet. Chem.* **1998**, *563*, 161.

(59) Ren, C.-X.; Ding, Y.-Q. *Acta Crystallogr.* **2007**, *E63*, m249.

Table 5. Crystallographic Data

	2	3	5	6	7
formula	$C_{12}H_{12}N_2PtS_2$	$C_{14}H_{18}O_4PtS_2$	$C_{12}H_{16}PtS_4$	$C_{11}H_{12}PtS_5$	$C_{11}H_{12}PtS_3Se_2$
fw (g·mol^{-1})	443.45	509.50	483.59	499.61	593.41
cryst color	orange	orange	dark red	red	red
cryst shape	needle	block	block	block	block
cryst size (mm)	0.30 × 0.05 × 0.05	0.16 × 0.10 × 0.10	0.21 × 0.21 × 0.18	0.07 × 0.05 × 0.03	0.15 × 0.10 × 0.05
cryst syst	monoclinic	monoclinic	monoclinic	monoclinic	monoclinic
space group	$P2_1/n$ (No. 14)	$P2_1/a$ (No. 14)	$P2_1/a$ (No. 14)	$P2_1/n$ (No. 14)	$P2_1/n$ (No. 14)
T (K)	298	298	298	298	298
a (Å)	7.8569(7)	13.3701(19)	11.429(2)	8.489(2)	8.588(2)
b (Å)	16.0720(13)	9.6363(14)	9.9809(19)	14.062(4)	14.183(4)
c (Å)	11.4186(10)	13.491(2)	13.087(3)	12.994(3)	13.174(4)
β (deg)	94.1190(15)	90.8299(5)	96.6553(7)	102.6420(9)	102.3993(11)
V (Å^3)	1438.2(2)	1737.9(4)	1482.8(5)	1513.5(7)	1567.3(7)
Z	4	4	4	4	4
D_{calc} (g·cm^{-3})	2.048	1.947	2.166	2.192	2.515
μ (mm^{-1})	9.987	8.292	9.964	9.898	13.938
total reflns	10 963	12 779	11 231	11 771	12 036
unique reflns (R_{int})	3223 (0.042)	3933 (0.032)	3393 (0.029)	3344 (0.035)	3500 (0.040)
unique reflns ($I > 2\sigma(I)$)	2788	3397	2908	2486	2743
R ($I > 2\sigma(I)$)^a	0.0572	0.0284	0.0232	0.0276	0.0288
wR ($I > 2\sigma(I)$)^a	0.1656	0.0783	0.0706	0.0826	0.0822
goodness-of-fit	1.036	1.025	1.014	1.022	1.067

reported that the dithiolene ring interacts with other organic aromatic rings, which involves Cp···dithiolene[26] and benzene···dithiolene interactions.[60] In addition, a dithiolene···dithiolene interaction has been reported as well.[61] Most probably, these π-interactions are due to the aromaticity and good planarity of the dithiolene ring.[2] In the dmit complex **6**, the η^4-C_4Me_4 ligand interacts with the trithiocarbonate moiety ($C_2S_2C{=}S$). The packing diagram of **6** (Figure 6) displays a zigzag-shaped intermolecular chain whose plane-to-plane distance is ca. 3.7 Å. The dsit complex **7** also showed a similar interaction to **6** because they are isostructural with each other. The η^4-C_4Me_4···$C_2S_2C{=}S$ plane-to-plane distance is 3.7 Å.

Conclusion

In this work, we reported the preparation, spectroscopic characterization, electrochemical behavior, chemical reactivity, and crystal structures of the [(η^4-C_4Me_4)Pt(dithiolene)] and [(η^4-C_4Me_4)Pt(diselenolene)] complexes. Although rich organometallic dithiolene complexes of Cp and η^6-arene ligands have been reported, this work has described an introduction of the new planar organic η^4-C_4Me_4 ligand to prepare organometallic dithiolene complexes (Chart 1). In conclusion, the η^4-C_4Me_4 ligand behaves as a π-coordinating ligand to form the 16-electron dithiolene complexes of group 10 metals (Ni^{II}, Pd^{II}, Pt^{II}), but also behaves as a π-interacting ligand to form some intermolecular plane-to-plane interactions in the crystal. However, the π-coordination of the η^4-C_4Me_4 ligand to the metal was not enough strong, because it was replaced by other nucleophiles (Scheme 2).

Here we have reported only basic studies for [(η^4-C_4Me_4)-Pt(dithiolene)] and [(η^4-C_4Me_4)Pt(diselenolene)] complexes. However, these complexes will be interesting for other chemical, photophysical, and solid state properties for the following reasons: (1) Heteronuclear cluster complexes of [{CpM(dithiolene)}$_2$M′(CO)$_n$] (M = group 9 metals) or [{(η^6-arene)M(dithiolene)}$_2$M′(CO)$_n$] (M = group 8 metals) have been reported.[62] The η^4-C_4Me_4 ligand with group 10 metals can be used instead of Cp and η^6-arene complexes. (2) Introduction of the η^4-Si_4Me_4 ligand is possible instead of the η^4-cyclobutadiene ligand,[63] although η^5-Si_5R_5 and η^6-Si_6R_6 π-coordination is not possible yet. They will be new heteroleptic dithiolene complexes. (3) Electron-rich complexes **5** (dddt) and **6** (dmit) are electrochemically and reversibly oxidized (Figure 1). The oxidized species can be paramagnetic and might be conductive. An intermolecular magnetic interaction through plane-to-plane interaction by the π-interacting η^4-C_4Me_4 ligand and conducting behavior through the zigzag interaction (Figures 4 and 6) can be expected. (4) The [(η^4-C_4Me_4)Pt(dithiolene)] and [(η^4-C_4Me_4)Pt(diselenolene)] complexes are useful precursors for luminescent Pt complexes[12,42,48] through ligand exchange reaction of η^4-C_4Me_4 ligand with nucleophiles such as $N^\wedge N$, $P^\wedge P$, $As^\wedge As$, and $S^\wedge S$ bidentate (or two monodentate) ligands. This reactivity indicates the formation of new asymmetric dithiolene complexes.

Experimental Section

General Remarks. All reactions were carried out under an argon atmosphere by means of standard Schlenk techniques. All solvents for reactions were purified by using CaH_2 for MeOH and dichloromethane before use. [Pt(NCMe)$_2$(Cl)$_2$],[64] [(η^4-C_4Me_4)Pt(Cl)(μ-Cl)]$_2$ (**1**),[39] disodium maleonitrile-1,2-dithiolate

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[60] Nomura, M.; Kajitani, M. *J. Organomet. Chem.* **2006**, *691*, 2691.

[61] Nomura, M.; Geoffroy, M.; Adkine, P.; Fourmigué, M. *Eur. J. Inorg. Chem.* **2006**, 5012.

[62] (a) Muratsugu, S.; Sodeyama, K.; Kitamura, F.; Sugimoto, M.; Tsuneyuki, S.; Miyashita, S.; Kato, T.; Nishihara, H. *J. Am. Chem. Soc.* **2009**, *131*, 1388. (b) Nakagawa, N.; Murata, M.; Sugimoto, M.; Nishihara, H. *Eur. J. Inorg. Chem.* **2006**, 2129. (c) Murata, M.; Habe, S.; Araki, S.; Namiki, K.; Yamada, T.; Nakagawa, N.; Nankawa, T.; Nihei, M.; Mizutani, J.; Kurihara, M.; Nishihara, H. *Inorg. Chem.* **2006**, *45*, 1108. (d) Nakagawa, N.; Yamada, T.; Murata, M.; Sugimoto, M.; Nishihara, H. *Inorg. Chem.* **2006**, *45*, 14. (e) Nihei, M.; Nankawa, T.; Kuribara, M.; Nishihara, H. *Angew. Chem., Int. Ed.* **1999**, *38*, 1098.

[63] (a) Takanashi, K.; Lee, V. Y.; Sekiguchi, A. *Organometallics* **2009**, *28*, 1248. (b) Takanashi, K.; Lee, V. Y.; Ichinohe, M.; Sekiguchi, A. *Eur. J. Inorg. Chem.* **2007**, 5471. (c) Takanashi, K.; Lee, V. Y.; Ichinohe, M.; Sekiguchi, A. *Angew. Chem., Int. Ed.* **2006**, *45*, 3269. (d) Takanashi, K.; Lee, V. Y.; Matsuno, T.; Ichinohe, M.; Sekiguchi, A. *J. Am. Chem. Soc.* **2005**, *127*, 5768.

[64] Bailey, P. M.; Mann, B. E.; Brown, I. D.; Maitlis, P. M. *J. Chem. Soc., Chem. Commun.* **1976**, 238.

(Na_2mnt),[65] dimethyl 1,3-dithiol-2-one-4,5-dicarboxylate (O=C(dcmedt)),[66] O=C(dddt),[67] $(NBu_4)_2$[Zn(dmit)$_2$],[68] and $(NEt_4)_2$[Zn(dsit)$_2$][69] were prepared by literature methods. 2-Butyne, $SnCl_2$ (for **1**), toluene-3,4-dithiol, NEt_3, and silica gel (Wakogel C-300) were obtained from Wako Pure Chemical Industries, Ltd. Sodium methoxide in MeOH solution was prepared from dry MeOH and fresh sodium metal. Mass spectra were recorded on a JEOL JMS-D300. NMR spectra were measured with a JEOL LA500 spectrometer. The ^{1}H and ^{13}C chemical shifts (δ in ppm) are referenced using chemical shifts of TMS at δ 0 ppm. Chloroform-*d* was purchased from Aldrich Chemicals. UV−vis spectra were recorded on a Hitachi model UV-2500PC. Elemental analyses were determined by using a Shimadzu PE2400-II instrument.

Preparation of [(η^4-C_4Me_4)Pt(mnt)] (2). A mixture of **1** (187 mg, 0.25 mmol) and Na_2(mnt) (93 mg, 0.5 mmol) was stirred in MeOH (20 mL) at room temperature for 3 h. An orange cloudy solution was obtained. After the reaction, the solvent was removed under reduced pressure. The mixture was separated by column chromatography on silica gel (eluent: dichloromethane). The resulting orange solid was further purified by recrystallization from dichloromethane/*n*-hexane (1:1). The orange product **2** was obtained in 63% yield.

[(η^4-C_4Me_4)Pt(mnt)] (2). Mass (EI$^+$, 70 eV): *m*/*z* (rel intensity) 443 ([M$^+$], 100), 428 ([M$^+$ − Me], 15), 335 ([M$^+$ − C_4Me_4], 48). ^{1}H NMR ($CDCl_3$, 500 MHz, vs TMS): δ 2.11 (s with Pt satellites, J_{Pt-H} = 13.2 Hz, 12H, Me). ^{13}C NMR ($CDCl_3$, 125 MHz, vs TMS): δ 131.8 (s, dithiolene-C), 117.5 (s, CN), 104.8 (s with Pt satellites, J_{C-Pt} = 99.7 Hz, *C_4*Me$_4$), 9.3 (C_4*Me$_4$*). UV−vis (CH_2Cl_2): λ_{max}/nm (ε/M$^{-1}\cdot$cm^{-1}) 267 (34 700), 430 (4800). Anal. Calcd for $C_{12}H_{12}N_2PtS_2$: C, 32.50; H, 2.73; N, 6.32. Found: C, 32.39; H, 2.46; N, 6.38.

Preparation of [(η^4-C_4Me_4)Pt(dcmedt)] (3). Dimethyl 1,3-dithiole-2-one-4,5-dicarboxylate, O=C(dcmedt) (380 mg, 1.62 mmol), was treated with 2 equiv of sodium methoxide in methanol solution (50 mL) at room temperature. The colorless solution changed to yellow after 1 h. When **1** (464 mg, 0.62 mmol) was added to this solution, the yellow solution changed to brown. The reaction mixture was stirred at room temperature for 24 h. After the solvent was removed under reduced pressure, the residue was extracted and the organic layer was purified by column chromatography on silica gel (eluent: dichloromethane). The product **3** was recrystallized with dichloromethane/*n*-hexane (1:1) and obtained as an orange solid in 42% yield.

[(η^4-C_4Me_4)Pt(dcmedt)] (3). Mp: 219−221 °C. Mass (EI$^+$, 70 eV): *m*/*z* (rel intensity) 509 ([M$^+$], 100), 478 ([M$^+$ −OMe], 22.3), 450 ([M$^+$ − COOMe], 15), 391 ([M$^+$ − (COOMe)$_2$], 23). ^{1}H NMR ($CDCl_3$, 500 MHz, vs TMS): δ 3.98 (s, 6H, OMe), 2.06 (s with Pt satellites, J_{Pt-H} = 13.2 Hz, 12H, Me). ^{13}C NMR ($CDCl_3$, 125 MHz, vs TMS): δ 167.7 (s, dithiolene-C), 167.7 (d, J_{C-Pt} = 80.3 Hz, dithiolene-C), 146.7 (s, C=O), 102.0 (s with Pt satellites, J_{C-Pt} = 98.4 Hz, *C_4*Me$_4$), 52.8 (s, OMe), 9.1 (s, C_4*Me$_4$*). IR (KBr disk): 2945, 1719, 1701, 1508, 1425, 1254, 1240, 1072, 1022 cm^{-1}. UV−vis (CH_2Cl_2): λ_{max}/nm (ε/M$^{-1}\cdot$cm^{-1}) 263 (29 000), 439 (5200). Anal. Calcd for $C_{14}H_{18}O_4PtS_2$: C, 33.00; H, 3.56 Found: C, 32.87; H, 3.28.

Preparation of [(η^4-C_4Me_4)Pt(tdt)] (4). Two drops of NEt_3 (excess) was added into the stirring solution of **1** (187 mg, 0.25 mmol) and toluene-3,4-dithiol (78 mg, 0.5 mmol) in MeOH (20 mL). An orange solution was rapidly obtained, and the reaction mixture was further stirred for 3 h. After the reaction, the solvent was removed under reduced pressure. The residue was separated by column chromatography on silica gel with dichloromethane eluent. The resulting orange solid was recrystallized from dichloromethane and *n*-hexane (1:1). **4** was obtained in 59% yield.

[(η^4-C_4Me_4)Pt(tdt)] (4). Mass (EI$^+$, 70 eV): *m*/*z* (rel intensity) 457 ([M$^+$], 100), 442 ([M$^+$ − Me], 38), 349 ([M$^+$ −C_4Me_4], 25). ^{1}H NMR ($CDCl_3$, 500 MHz, vs TMS): δ 7.80 (d, *J* = 8.0 Hz, 1H, benzene), 7.74 (d, *J* = 1.7 Hz, 1H, benzene), 6.83 (dd, *J* = 8.0, 1.7 Hz, 1H, benzene), 2.37 (s, 3H, Me), 2.06 (s with Pt satellites, J_{Pt-H} = 13.2 Hz, 12H, Me). ^{13}C NMR ($CDCl_3$, 125 MHz, vs TMS): δ 149.2 (s, benzene), 146.0 (s, benzene), 132.6 (s with Pt satellites, J_{C-Pt} = 8.4 Hz, benzene), 130.3 (s with Pt satellites, J_{C-Pt} = 92.4 Hz, benzene), 129.8 (s with Pt satellites, J_{C-Pt} = 93.6 Hz, benzene), 124.3 (s with Pt satellites, J_{C-Pt} = 8.8 Hz, benzene), 100.2 (s with Pt satellites, J_{C-Pt} = 97.8 Hz, *C_4*Me$_4$), 20.6 (s, Me), 9.0 (s, C_4*Me$_4$*). UV−vis (CH_2Cl_2): λ_{max}/nm (ε/M$^{-1}\cdot$cm^{-1}) 449 (9200). Anal. Calcd for $C_{15}H_{18}PtS_2$: C, 39.38; H, 3.97. Found: C, 39.53; H, 3.84.

Preparation of [(η^4-C_4Me_4)Pt(dddt)] (5). Sodium methoxide (1.1 mmol) was added into a methanol solution (20 mL) of O=C (dddt) (104 mg, 0.5 mmol) for 1 h at room temperature. The initial colorless solution changed to yellow. **1** (187 mg, 0.25 mmol) was successively added to the reaction mixture and further stirred for 3 h at room temperature. After the solvent was removed under reduced pressure, the resulting mixture was separated by column chromatography on silica gel. A red fraction was extracted with dichloromethane. The resulting red solid was further purified by recrystallization from dichloromethane/*n*-hexane (1:1). The dark red crystal **5** was obtained in 17% yield.

[(η^4-C_4Me_4)Pt(dddt)] (5). Mass (EI$^+$, 70 eV): *m*/*z* (rel intensity) 483 ([M$^+$], 100), 468 ([M$^+$ − Me], 3), 303 ([(C_4Me_4)Pt$^+$], 38). ^{1}H NMR ($CDCl_3$, 500 MHz, vs TMS): δ 3.18 (s, 4H, CH_2), 2.02 (s with Pt satellites, J_{Pt-H} = 13.7 Hz, 12H, Me). ^{13}C NMR ($CDCl_3$, 125 MHz, vs TMS): δ 129.5 (s with Pt satellites, J_{C-Pt} = 9.6 Hz, dithiolene-C), 100.3 (s with Pt satellites, J_{C-Pt} = 100.8 Hz, *C_4*Me$_4$), 31.3 (s, CH_2), 9.0 (s, C_4*Me$_4$*). UV−vis (CH_2Cl_2): λ_{max}/nm (ε/M$^{-1}\cdot$cm^{-1}) 414 (1900), 535 (5300). Anal. Calcd for $C_{12}H_{16}PtS_4$: C, 29.80; H, 3.33. Found: C, 29.70; H, 3.13.

Preparations of [(η^4-C_4Me_4)Pt(dmit)] (6) and [(η^4-C_4Me_4)Pt(dsit)] (7). A mixture of **1** (187 mg, 0.25 mmol) and $(NBu_4)_2$[Zn(dmit)$_2$] (236 mg, 0.25 mmol) was stirred in MeOH (20 mL) at room temperature for 3 h. After the solvent was removed, the mixture was separated by column chromatography on silica gel with dichloromethane eluent. The resulting red solid was recrystallized from dichloromethane/*n*-hexane (1:1) to obtain **6** as a red crystal in 64% yield. **7** (red crystal, 48% yield) was obtained from $(NEt_4)_2$[Zn(dsit)$_2$] by using a similar method to that for **6**.

[(η^4-C_4Me_4)Pt(dmit)] (6). Mass (EI$^+$, 70 eV): *m*/*z* (rel intensity) 499 ([M$^+$], 100), 484 ([M$^+$ −Me], 4), 391 ([M$^+$ − C_4Me_4], 4). ^{1}H NMR ($CDCl_3$, 500 MHz, vs TMS): δ 2.08 (s with Pt satellites, J_{Pt-H} = 14.3 Hz, 12H, Me). ^{13}C NMR ($CDCl_3$, 125 MHz, vs TMS): δ 144.6 (s, dithiolene-C), 102.4 (s with Pt satellites, J_{C-Pt} = 102.0 Hz, *C_4*Me$_4$), 9.2 (s, C_4*Me$_4$*), doublet signal at 144.6 ppm and signal for C=S are not observed due to poor solubility of the sample. UV−vis (CH_2Cl_2): λ_{max}/nm (ε/M$^{-1}\cdot$cm^{-1}) 267 (26 300), 433 (15 200), 512 (8000). Anal. Calcd for $C_{11}H_{12}PtS_5$: C, 26.44; H, 2.42. Found: C, 26.19; H, 2.21.

[(η^4-C_4Me_4)Pt(dsit)] (7). Mass (EI$^+$, 70 eV): *m*/*z* (rel intensity) 594 ([M$^+$], 100). ^{1}H NMR ($CDCl_3$, 500 MHz, vs TMS): δ 1.91 (s with Pt satellites, J_{Pt-H} = 15.1 Hz, 12H, Me). The ^{13}C NMR was not obtained due to poor solubility of the sample. UV−vis (CH_2Cl_2): λ_{max}/nm (ε/M$^{-1}\cdot$cm^{-1}) 274 (30 200), 424 (17 100), 503 (7000). Anal. Calcd for $C_{11}H_{12}PtS_3Se_2$: C, 22.26; H, 2.04. Found: C, 22.34; H, 2.15.

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(65) Holm, R. H.; Davison, A. *Inorg. Synth.* **1967**, *10*, 8.

(66) (a) Nakayama, J.; Kimata, A.; Taniguchi, H.; Takahashi, F. *Chem. Commun.* **1996**, 205. (b) Challenger, F.; Mason, E. A.; Holdsworth, E. C.; Emmott, R. *J. Chem. Soc.* **1953**, 292.

(67) Liu, S.-G.; Wu, P.-J.; Liu, Y.-Q.; Zhu, D.-B. *Phosphorus, Sulfur Silicon Relat. Elem.* **1995**, *106*, 145.

(68) Steimecke, G.; Sieler, H.; Kirmse, R.; Hoyer, E. *Phosphorus, Sulfur Silicon Relat. Elem.* **1979**, *7*, 49.

(69) Poleschner, H.; Radeglia, R.; Fuchs, J. *J. Organomet. Chem.* **1992**, *427*, 213.

Reaction of 3 with DPPE. A dichloromethane solution (10 mL) of **3** (51 mg, 0.1 mmol) and DPPE (40 mg, 0.1 mmol) was stirred at room temperature for 1 h. An orange product was separated by column chromatography on silica gel with dichloromethane. The orange product [Pt(dcmedt)(dppe)] was obtained in quantitative yield. The [Pt(dcmedt)(dppe)] was identified with the same product in the literature.[47]

Electrochemical Measurements. All electrochemical measurements were performed under an argon atmosphere. Solvents for electrochemical measurements were dried by molecular sieves 4A before use. A platinum wire served as a counter electrode, and the reference electrode is Ag/AgCl corrected for junction potentials by referencing internally to the ferrocene/ferrocenium (Fc/Fc$^+$) couple. Cyclic voltammetry was measured with model CV-50W of BAS Co. Sample complexes were done in 1 mmol·dm^{-3} dichloromethane solutions of complexes containing 0.1 mol·dm^{-3} tetra-*n*-butylammonium perchlorate (TBAP) at 25 °C. A stationary platinum disk (1.6 mm in diameter) was used as a working electrode.

X-ray Diffraction Study. Single crystals of **2**, **3**, and **5**−**7** were obtained by recrystallization from dichloromethane solutions and then vapor diffusion of *n*-hexane into those solutions. Crystals were mounted on top of a thin glass fiber. Measurements were made on a Rigaku Mercury CCD diffractometer with graphite-monochromated Mo Kα radiation (λ = 0.71073 Å). Each structure was solved by direct methods and expanded using Fourier techniques.[70] The non-hydrogen atoms were refined anisotropically. Hydrogen atoms were introduced at calculated positions (riding model) and included in structure factor calculations, and these were not refined. Absorption corrections were applied. All calculations were performed using the Crystal Structure software package.[71] Crystallographic data are summarized in Table 5.

Supporting Information Available: Crystallographic data, atomic coordinates, bond distances, bond angles, and anisotropic displacement parameters for **2**, **3**, and **5**−**7** in CIF format. These materials are available free of charge via the Internet at http://pubs.acs.org.

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(70) Beurstkens, P. T.; Admiraal, G.; Beurskens, G.; Bosman, W. P.; Garcia-Granda, S.; Gould, R. O.; Smits, J. M. M.; Smykala, C. *The DIRDIF Program System, Technical Report of the Crystallography Laboratory*; University of Nijmegen: Nijmegen, The Netherlands, 1992.

(71) *Crystal Structure 3.6.0, Single Crystal Structure Analysis Software*; Molecular Structure Corp. and Rigaku Corp.: The Woodlands, TX, and Tokyo, Japan, 2004.