Inorg. Chem. **2009**, *48*, 2215−2223

Inorganic Chemistry
Article

Synthesis and Reactions of Mono- and Dinuclear Ni(I) Thiolate Complexes

Mikinao Ito, Tsuyoshi Matsumoto, and Kazuyuki Tatsumi*

Research Center for Materials Science and Department of Chemistry, Graduate School of Science,
Nagoya University, Furo-cho, Chikusa-ku, Nagoya 464-8602, Japan

Received November 27, 2008

The dinuclear and mononuclear nickel(I) thiolates, $[Ni(PPh_3)(\mu\text{-SR})]_2$ (**1a**: R is 2,4,6-triisopropylphenyl (Tip), **1b**: R is 1-adamantyl (Ad)), $(DxpS)Ni(\mu\text{-SDxp})Ni(PPh_3)$ (**2**) (Dxp is 2,6-dixylylphenyl), and $Ni(SDmp)(PPh_3)$ (**3**) (Dmp is 2,6-dimesitylphenyl), have been synthesized by the reaction of the nickel(I) amide $Ni\{N(SiMe_3)_2\}(PPh_3)_2$ with the corresponding thiols. The two nickel centers of **1a** and **1b** are equivalent, and are linked by two thiolato sulfurs and a Ni−Ni bond, whereas the two inequivalent nickels of **2** are connected by a SDxp sulfur, a η^2/η^3-xylyl group of the other SDxp ligand, and a Ni−Ni bond. A slightly bulkier *m*-terphenyl thiolate, SDmp, prevents its nickel complex from forming a Ni−Ni bond, and the mononuclear nickel(I) center of **3** is bound to PPh_3 and SDmp through interactions with the sulfur and a η^2-mesityl. The coordinatively unsaturated nickel(I) complex **3** is reactive, and the reaction of **3** with TEMPO generated diamagnetic $Ni(SDmp)(PPh_3)(O,N{:}\eta^2\text{-TEMPO})$ (**4**). *N*-Heterocyclic carbenes, 1,3,4,5-tetramethylimidazolin-2-ylidene (IMe′) and 1,3-bis-(2,4,6-trimethylphenyl)imidazolin-2-ylidene (IMes), also react with **3** to afford a dinuclear nickel(I) complex, $[Ni(IMe')(\mu\text{-SDmp})]_2$ (**5**), and a mononuclear nickel(I) complex, Ni(SDmp)(IMes) (**6**), respectively. The reaction of **3** with 1 equiv of ${}^tBuNC$ afforded the dinuclear complex $[Ni(CN{}^tBu)(\mu\text{-SDmp})]_2$ (**7**), whereas the analogous reaction with 1 equiv of CO resulted in a mixture of $Ni(PPh_3)_2(CO)_2$ and $Ni(CO)(SDmp)_2(PPh_3)$ (**8**).

Introduction

Nickel is recognized as an important element in nature, and so far, six nickel-containing enzymes have been identified, which include CO-dehydrogenase, acetyl-CoA synthase, [NiFe] hydrogenase, methyl-CoM reductase, urease, and Ni-SOD.[1] The protein structures of these nickel enzymes are available, and various nickel complexes have been synthesized to model the active site structures. Nickel(I) complexes have attracted attention as potential models for the active states/forms of some of these nickel enzymes. Whereas there is a good number of Ni(I) complexes carrying nitrogen and phosphorus ligands such as porphyrins,[2] tetraaza macrocycles,[3] tetradentate aminopyridines,[4] anilidoamines,[5] diketiminates,[6] and phosphines,[7] those with sulfur ligands that could be used for the synthesis of active site models of nickel enzymes such as acetyl-CoA synthase[8] and [NiFe] hydrogenase are scarce.[9] Structurally characterized thioether-coordinated Ni(I) complexes are limited to $[Ni(psnet)]^+$ (psnet

---

* To whom correspondence should be addressed. E-mail: i45100a@nucc.cc.nagoya-u.ac.jp.

[1] *Nickel and Its Surprising Impact in Nature*; Sigel, A., Sigel, H., Sigel, R. K. O., Eds.; John Wiley & Sons, Ltd.: Chichester, U.K., 2007; Metal Ions in Life Science, Vol. 2.

[2] Arai, T.; Kashitani, K.; Kondo, H.; Sakaki, S. *Bull. Chem. Soc. Jpn.* **1994**, *67*, 705–709.

[3] (a) Stile, M. *J. Org. Chem.* **1994**, *59*, 5381–5385. (b) Stolzenberg, A. M.; Zhang, Z. *Inorg. Chem.* **1997**, *36*, 593–600.

[4] Kryatov, S. V.; Mohanraj, B. S.; Tarasov, V. V.; Kryatova, O. P.; Rybak-Akimova, E. V.; Nuthakki, B.; Rusling, J. F.; Staples, R. J.; Nazarenko, A. Y. *Inorg. Chem.* **2002**, *41*, 923–930.

[5] Wang, H.-Y.; Meng, X.; Jin, G.-X. *Dalton Trans.* **2006**, 2579–2585.

[6] (a) Kogut, E.; Wiencko, H. L.; Zhang, L.; Cordeau, D. E.; Warren, T. H. *J. Am. Chem. Soc.* **2005**, *127*, 11248–11249. (b) Eckert, N. A.; Dinescu, A.; Cundari, T. R.; Holland, P. L. *Inorg. Chem.* **2005**, *44*, 7702–7704. (c) Bai, G.; Wei, P.; Stephan, D. W. *Organometallics* **2005**, *24*, 5901–5908.

[7] (a) Bradley, D. C.; Hursthouse, M. B.; Smallwood, R. J.; Welch, A. J. *J. Chem. Soc., Chem. Commun.* **1972**, 872–873. (b) Mindiola, D. J.; Hillhouse, G. L. *J. Am. Chem. Soc.* **2001**, *123*, 4623–4624. (c) Melenkivitz, R.; Mindiola, D. J.; Hillhouse, G. L. *J. Am. Chem. Soc.* **2002**, *124*, 3846–3847. (d) Kitiachvili, K. D.; Mindiola, D. J.; Hillhouse, G. L. *J. Am. Chem. Soc.* **2004**, *126*, 10554–10555. (e) Adhikari, D.; Mossin, S.; Basuli, F.; Dible, B. R.; Chipara, M.; Fan, H.; Huffman, J. C.; Meyer, K.; Mindiola, D. J. *Inorg. Chem.* **2008**, *47*, 10479–10490. (f) Weng, Z.; Teo, S.; Koh, L. L.; Hor, T. S. A. *Angew. Chem., Int. Ed.* **2005**, *44*, 7560–7564.

[8] (a) Riordan, C. G. *J. Biol. Inorg. Chem.* **2004**, *9*, 509–510. (b) Ragsdale, S. W. *Crit. Rev. Biochem. Mol. Biol.* **2004**, *39*, 165–195. (c) Evans, D. J. *Coord. Chem. Rev.* **2005**, *249*, 1582–1595.

10.1021/ic802276w CCC: $40.75

is bis(5-(diphenylphosphino)-3-thiapentamethyl)amine)[10] and [PhTt^{tBu}]Ni(CO) ([PhTt^{tBu}] is phenyltris((*tert*-butylthio)methyl)borate).[11] Reports of nickel(I) thiolates are also rare. The formation of a Ni(I) thiolate was postulated in the photolysis of $(Ph_2P(o\text{-}C_6H_4)SCH_3)_2Ni$, via C−S cleavage of the thioether ligand.[12] Thiolato-bridged dinuclear Ni(I) complexes, [Ni(dadt^{Et})Ni(dppe)][PF_6] (dadt^{Et} is *N*,*N*′-diethyl-3,7-diazanonane-1,9-dithiolate)[13] and [Et_4N][Ni(PhPepS)Ni(dppe)(CO)] (PhPepS is *N*,*N*′-phenylenebis(*o*-mercaptobenzamide)) were synthesized in situ.[14]

We report herein the synthesis and structures of a series of mono- and dinuclear nickel(I) thiolate complexes, where the nickel(I) amide, $Ni\{N(SiMe_3)_2\}(PPh_3)_2$, was used as a synthon.[7a] We have also combined the mononuclear Ni(I) thiolates with such σ donors as *N*-heterocyclic carbenes, ^tBuNC, and CO to synthesize the various Ni(I) thiolates.

Experimental Section

General Procedures. All reactions and manipulation were conducted using standard Schlenk and vacuum line techniques or in a glovebox under nitrogen atmosphere. Hexane, pentane, ether, THF, acetonitrile, and toluene were purified according to the method described by Grubbs, in which the solvents were passed over columns of activated alumina and a copper catalyst supplied by Hansen. DME was dried over 4 Å molecular sieves under nitrogen. Deuterated solvents were dried over potassium (THF-d_8) or sodium (benzene-d_6, toluene-d_8) under nitrogen. ^1H NMR spectra were recorded on a JEOL ECA-600 apparatus. UV/vis spectra were recorded in 10 mm quartz glass cells on a JASCO V-560 spectrometer. IR spectra were recorded on a JASCO FT/IR-410 spectrometer or a Perkin-Elmer 2000 FT/IR spectrometer. EPR spectra were collected on a Bruker EMX-plus spectrometer at X-band frequencies with liquid helium cryostat. Cyclic voltammograms were recorded on a BSA-660B electrochemical analyzer using a glassy carbon working electrode and 0.2 M $n\text{-}Bu_4NPF_6$ as the supporting electrolyte; potentials are referred to the Ag/$AgNO_3$ electrode. Elemental analyses were performed on a LECO-CHNS-932 elemental analyzer, where the crystalline samples were sealed in silver capsules under nitrogen. $Ni\{N(SiMe_3)_2\}(PPh_3)_2$,[7a] HSTip (Tip is 2,4,6-triisopropylphenyl),[15] HSAd (Ad is 1-adamantly),[16] HSDxp (Dxp is 2,6-dixylylphenyl),[17] HSDmp (Dmp is 2,6-dimesitylphenyl),[18] IMe′ (1,3,4,5-tetramethylimidazole-2-ylidene),[19] and IMes (1,3-bis-(2,4,6-trimethylphenyl)imidazolin-2-ylidene)[20] were prepared according to the literature procedures.

Synthesis of [Ni(PPh_3)(μ-STip)]$_2$ (1a). At room temperature, HSTip (32 mg, 0.14 mmol) in toluene (5 mL) was added to a toluene solution (10 mL) of $Ni\{N(SiMe_3)_2\}(PPh_3)_2$ (100 mg, 0.134 mmol). A yellowish green precipitate immediately formed. After being stirred for 2 h, the precipitate was filtrated, washed with hexane (10 mL), and dried in vacuo to produce **1a** (72 mg, 96% yield) as a yellowish green powder. By layering a hexane solution of HSTip on a THF solution of $Ni\{N(SiMe_3)_2\}(PPh_3)_2$, crystals suitable for X-ray structural analysis grew within 3 days. Anal. Calcd for $C_{66}H_{76}Ni_2P_2S_2$: C, 71.24; H, 6.884. Found: C, 71.08; H, 6.509.

Synthesis of [Ni(PPh_3)(μ-SAd)]$_2$ (1b). At room temperature, a solution of HSAd (21 mg, 0.13 mmol) in THF (5 mL) was added to a THF solution (10 mL) of $Ni\{N(SiMe_3)_2\}(PPh_3)_2$ (100 mg, 0.134 mmol). The green solution was stirred for 12 h and then evaporated to dryness to produce a green powder. The product was recrystallized from THF/hexane to produce 28 mg (44% yield) of **1b** as green crystals. Anal. Calcd for $C_{56}H_{60}Ni_2P_2S_2$: C, 68.88; H, 6.193. Found: C, 69.12; H, 6.494. ^1H NMR (THF-d_8, δ): 7.77−7.60 (m, 12H, PPh_3), 7.36−7.27 (m, 18H, PPh_3), 1.54−1.45 (m, 12H, adamantyl), 1.45−1.39 (m, 6H, adamantyl), 1.32−1.20 (m, 6H, adamantyl), 1.18−1.09 (m, 6H, adamantyl).

Synthesis of Ni(SDxp)(μ-SDxp)Ni(PPh_3) (2). At room temperature, a THF solution (10 mL) of HSDxp (47 mg, 0.15 mmol) was added to a THF solution (10 mL) of $Ni\{N(SiMe_3)_2\}(PPh_3)_2$ (100 mg, 0.135 mmol)). The green solution was stirred overnight and then evaporated to dryness to produce a green solid. This material was washed with hexane (10 mL) and recrystallized from THF/hexane to produce 95 mg (70% yield) of **2** as green crystals. Anal. Calcd for $C_{66}H_{65}Ni_2OPS_2$: C, 72.95; H, 6.029. Found: C, 72.85; H, 6.438. ^1H NMR (Tol-d_8, δ): 7.35−6.66 (30H, PPh_3+Dxp), 4.80 (br s, 2H, *m*-H of Xyl), 3.73 (br s, 1H, *p*-H of Xyl), 2.29 (s, 6H, Me of Xyl), 2.17 (s, 6H, Me of Xyl), 1.86 (s, 6H, Me of Xyl), 1.78 (s, 6H, Me of Xyl).

Synthesis of Ni(SDmp)(PPh_3) (3). At room temperature, a toluene solution (5 mL) of HSDmp (75 mg, 0.22 mmol) was added to a toluene solution (5 mL) of $Ni\{N(SiMe_3)_2\}(PPh_3)_2$ (160 mg, 0.215 mmol). The red-brown solution was stirred for 1 h and then evaporated to dryness to produce a red solid. This material was washed with pentane (10 mL) and extracted with ether (30 mL). The solution was concentrated to 2 mL and kept at −30 °C to produce 99 mg (69% yield) of **3** as orange crystals. Anal. Calcd for $C_{42}H_{40}NiPS$: C, 75.69; H, 6.409. Found: C, 76.00; H, 6.010. $\mu_{eff} = 1.93\mu_B$ in C_6D_6 at 25 °C (Evans NMR method). λ_{max}/nm (ε) = 314 (sh, 7.9 × 10^3), 272 (1.6 × 10^4).

Synthesis of Ni(SDmp)(PPh_3)(*O*,*N*:η^2-TEMPO) (4). At room temperature, a toluene solution (5 mL) of TEMPO (23 mg, 0.150 mmol) was added to a toluene solution (5 mL) of Ni(SDmp)(PPh_3) (100 mg, 0.150 mmol). The purple solution was stirred for 3 h, centrifuged, and evaporated to dryness to produce a purple powder. The product was recrystallized from THF/hexane to produce 67 mg (54% yield) of **4** as pink-purple crystals. Anal. Calcd for $C_{51}H_{58}NNiOPS$: C, 74.45; H, 7.105; N, 1.702. Found: C, 74.29; H, 6.875; N, 1.741. ^1H NMR (C_6D_6, δ): 7.83−7.72 (m, 6H, PPh_3), 7.24−7.19 (m, 16H, Dmp+PPh_3), 2.59 (s, 6H, *p*-Me of Mes), 2.50 (s, 12H, *o*-Me of Mes), 2.01 (s, 6H, Me of TEMPO), 1.12 (s, 6H,

---

[9] (a) Volbeda, A.; Fontecilla-Camps, J. C. *Coord. Chem. Rev.* **2005**, *249*, 1609–1619. (b) Stein, M.; Lubitz, W. *J. Inorg. Biochem.* **2004**, *98*, 862–877.

[10] James, T. L.; Cai, L.; Muetterties, M. C.; Holm, R. H. *Inorg. Chem.* **1996**, *35*, 4148–4161.

[11] The ν_{CO} band of the Ni(I)−CO complex, [PhTt^{tBu}]Ni(CO), was observed at 1995 cm^{-1}. See: (a) Craft, J. L.; Mandimutsira, B. S.; Fujita, K.; Riordan, C. G.; Brunold, T. C. *Inorg. Chem.* **2003**, *42*, 859–867. (b) Fujita, K.; Rheingold, A. L.; Riordan, C. G. *Dalton Trans.* **2003**, 2004–2008.

[12] Kim, J. S.; Reibenspies, J. H.; Darensbourg, M. Y. *J. Am. Chem. Soc.* **1996**, *118*, 4115–4123.

[13] Wang, Q.; Blake, A. J.; Davies, E. S.; McInnes, E. J. L.; Wilson, C.; Schröder, M. *Chem. Commun.* **2003**, 3012–3013.

[14] (a) Harrop, T. C.; Olmstead, M. M.; Mascharak, P. K. *J. Am. Chem. Soc.* **2004**, *126*, 14714–14715. (b) Harrop, T. C.; Olmstead, M. M.; Mascharak, P. K. *Inorg. Chem.* **2006**, *45*, 3424–3436.

[15] Blower, P. J.; Dilworth, J. R.; Hutchinson, J. P.; Zubieta, J. A. *J. Chem. Soc., Dalton Trans.* **1985**, 1533–1541.

[16] Khullar, H. K.; Bauer, L. *J. Org. Chem.* **1971**, *36*, 3038–3040.

[17] Luening, U.; Baumgartner, H. *Synlett* **1993**, *8*, 571–572.

[18] Ellison, J. J.; Rhulandt-Senge, K.; Power, P. P. *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 1178–1180.

[19] Hanasaka, F.; Fujita, K.; Yamaguchi, R. *Organometallics* **2005**, *24*, 3422–3433.

[20] Arduengo, A. J., III; Krafczyk, R.; Schmutzler, R. *Tetrahedron* **1999**, *55*, 14523–14534.

Me of TEMPO), 0.88−0.84 (m, 2H, TEMPO), 0.58−0.52 (m, 2H, TEMPO), 0.18−0.12 (m, 2H, TEMPO).

Synthesis of [Ni(IMe′)(μ-SDmp)]$_2$ (5). At room temperature, a toluene solution (5 mL) of IMe′ (20 mg, 0.161 mmol) was added to a toluene solution (10 mL) of Ni(SDmp)(PPh$_3$) (107 mg, 0.161 mmol). After being stirred for 4 h, the reaction mixture was centrifuged. The supernatant was evaporated to dryness, and the residue was washed with hexane (20 mL) to produce 42 mg (49% yield) of **5** as a dark-yellow powder. Crystallization from THF/hexane produced crystals suitable for X-ray structural analysis. ^{1}H NMR (C$_6$D$_6$, δ): 6.92 (t, *J* = 7.6 Hz, 2H, *p*-H of Dmp), 6.74 (d, *J* = 7.6 Hz, 4H, *m*-H of Dmp), 6.71 (s, 8H, *m*-H of Mes), 3.34 (s, 12H, N-*Me*), 2.26 (s, 12H, *p*-Me of Mes), 2.24 (s, 24H, *o*-Me of Mes), 1.77 (s, 12H, Me).

Synthesis of Ni(SDmp)(IMes) (6). At room temperature, a toluene solution (15 mL) of IMes (320 mg, 1.05 mmol) was added to a toluene solution (50 mL) of Ni(SDmp)(PPh$_3$) (700 mg, 1.05 mmol). After being stirred for 3 h, the reaction mixture was centrifuged, and the supernatant was evaporated to dryness. The residue was washed with pentane (70 mL) to produce 450 mg (44% yield) of **6** as an orange powder. Crystallization from hexane produced crystals suitable for X-ray structural analysis. Anal. Calcd for C$_{45}$H$_{49}$N$_2$NiS: C, 76.27; H, 6.970; N, 3.953. Found: C, 75.84; H, 6.593; N, 3.989.

Synthesis of [Ni(CN^{t}Bu)(μ-SDmp)]$_2$ (7). At −80 °C, ^{t}BuNC (0.5 M toluene solution, 0.15 mL, 0.075 mmol) was added to a toluene solution (5 mL) of Ni(SDmp)(PPh$_3$) (50 mg, 0.075 mmol). The solution became reddish purple and then orange-yellow upon warming to r.t. After being stirred for 30 min at r.t., the solution was evaporated to dryness, and the residue was washed with hexane (5 mL) to produce 23 mg (63% yield) of **7** as a yellow-brown powder. Crystallization from THF/hexane produced crystals suitable for X-ray structural analysis. Anal. Calcd for C$_{58}$H$_{68}$N$_2$Ni$_2$S$_2$: C, 71.47; H, 7.032; N, 2.874. Found: C, 71.45; H, 6.477; N, 2.478. ^{1}H NMR (C$_6$D$_6$, δ): 7.84−7.76 (m, 2H, *p*-H of Dmp), 7.01 (s, 8H, *m*-H of Mes), 6.95−6.86 (m, 4H, *m*-H of Dmp), 2.45 (s, 12H, *p*-Me of Mes), 2.30 (s, 24H, *o*-Me of Mes), 0.86 (s, 18H, ^{t}Bu). IR (Tol): ν(CN)/cm^{-1} 2180.

Reaction of Ni(SDmp)(PPh$_3$) with CO. At −80 °C, CO gas (2.0 mL, 0.090 mmol) was injected by syringe into the head space above a toluene solution (3 mL) of Ni(SDmp)(PPh$_3$) (60 mg, 0.090 mmol). The solution became bright purple. An IR spectrum of this solution displayed a band at 2000 cm^{-1}. The purple solution turned reddish brown within 15 min at −80 °C with ν_{CO} bands in the IR spectrum at 1943 and 2001 cm^{-1} [Ni(PPh$_3$)$_2$(CO)$_2$] and at 2069 cm^{-1} [Ni(CO)(SDmp)$_2$(PPh$_3$) (**8**)]. The solution was covered by a hexane layer to produce Ni(PPh$_3$)$_2$(CO)$_2$ and **8** as colorless and reddish brown crystals, respectively. For **8**: Anal. Calcd for C$_{67}$H$_{65}$NiOPS$_2$: C, 77.37; H, 6.300. Found: C, 77.32; H, 6.185. ^{1}H NMR (C$_6$D$_6$, δ): 7.83−7.76 (m, 6H, PPh$_3$), 7.46−7.42 (m, 2H, *p*-H of Dmp), 7.11−7.02 (m, 10H, *m*-H of Dmp + PPh$_3$), 6.84−6.77 (m, 3H, PPh$_3$), 6.71 (s, 8H, *m*-H of Mes), 2.22 (s, 24H, *o*-Me of Mes), 2.06 (s, 12H, *p*-Me of Mes). IR (KBr): ν(CO)/cm^{-1} 2069.

Synthesis of Ni(SDmp)$_2$ (9). At 0 °C, a DME solution (50 mL) of LiSDmp, prepared from HSDmp (1.00 g, 2.89 mmol) and *n*-BuLi (1.8 mL of a 1.65 M solution in hexane), was added to a DME suspension (50 mL) of Ni(dme)Cl$_2$ (317 mg, 1.44 mmol). After being stirred for 2 h at room temperature, the red solution was evaporated to dryness, extracted with toluene (100 mL), and concentrated to 10 mL. The solution was kept at −30 °C to produce 510 mg (47% yield) of **9** as red crystals. Anal. Calcd for C$_{55}$H$_{58}$NiS$_2$: C, 78.47; H, 6.94. Found: C, 78.82; H, 7.18. ^{1}H NMR (C$_6$D$_6$, δ): 6.91 (d, *J* = 7.5 Hz, 4H, *m*-H of Dmp), 6.74 (s, 8H, *m*-H of Mes), 6.66 (t, *J* = 7.5 Hz, 2H, *p*-H of Dmp), 2.26 (s, 24H, *o*-Me of Mes), 2.15 (s, 12H, *p*-Me of Mes).

Synthesis of Ni(CO)(SDmp)$_2$(PPh$_3$) (8). At room temperature, a hexane solution (8 mL) of PPh$_3$ (70 mg, 0.27 mmol) was added to a hexane suspension (10 mL) of Ni(SDmp)$_2$ (200 mg, 0.267 mmol). The reddish brown suspension was stirred for 2 h and then purged for 5 min with CO at 1 atm. The suspended material dissolved to produce a reddish brown solution that slowly yielded a precipitate. After being stirred for 1 h, the precipitate was filtrated, washed with hexane (10 mL), and dried in vacuo to produce 216 mg (77% yield) of **8** as a reddish brown powder.

X-ray Structure Determinations. Crystal data and refinement parameters for the structurally characterized complexes are summarized in Table 1. Single crystals were mounted on a loop using oil (CryoLoop, immersion oil type B: code 1248, Hampton Laboratories). Diffraction data were collected at −100 °C under a cold nitrogen stream on a Rigaku AFC8 apparatus equipped with a Mercury CCD area detector (for **4**, **8**, and **9**), on a Rigaku AFC8 apparatus equipped with a Saturn 70 CCD area detector (for **1a**, **1b**, **2**, **3**, **5**, and **6**), or on a Rigaku RA-Micro007 apparatus with a Saturn 70 CCD area detector (for **7**) equipped with a graphite-monochromatized Mo Kα source (λ = 0.71070 Å). Data were collected for 1200 images with an oscillation range of 0.3° (for **1a**, **1b**, **2**, **3**, **4**, and **6**) or for 720 images with an oscillation range of 0.5° (for **5**, **7**, **8**, and **9**). The data were integrated and corrected for absorption using the Rigaku/MSC CrystalClear program package. The structures were solved by a direct method (SIR-92 or SIR-97) and were refined by full-matrix least-squares on F^2 using SHELXL-97[21] in the Rigaku/MSC CrystalStructure program package. Anisotropic refinement was applied to all non-hydrogen atoms except for disordered atoms, and all hydrogen atoms were put at the calculated positions. An adamantyl group of **1b** was disordered over two positions in a 1:1 ratio, and two THF crystal solvents of **1b** were disordered over two or four positions in 1:1 or 1:1:2:4 ratios, respectively. A xylyl group of **2** was disordered over two positions in a 55:45 ratio, and the THF crystal solvent of **2** was disordered over two positions in a 65:35 ratio. A phenyl group of **3** was disordered over two positions in a 1:1 ratio. A THF crystal solvent of **4** was disordered over three positions in 4:3:3 ratio. A mesityl group interacting with nickel in **6** was disordered over two positions in a 1:1 ratio and two methyl groups of an *N*-heterocyclic carbene were disordered over two positions in a 1:1 ratio. A tertiary butyl group of **7** was disordered over two positions in a 60:40 ratio. A Dmp group of **8** was disordered over two positions in a 1:1 ratio, and the hexane crystal solvent of **8** was disordered over two positions in a 1:1 ratio. Additional crystallographic data are given in the Supporting Information.

Results and Discussion

Dinuclear Nickel(I) Bis-μ-thiolate Complexes. The reaction of transition-metal amides with thiols has been recognized as a convenient route to the corresponding metal thiolate complexes.[22,23] Our strategy to synthesize Ni(I) thiolate complexes follows this line, and the nickel(I) amide complex, Ni{N(SiMe$_3$)$_2$}(PPh$_3$)$_2$,[7a] was reacted with sterically demanding arene- and alkanethiols.

When 2,4,6-triisopropylbenzenethiol (HSTip) was added to Ni{N(SiMe$_3$)$_2$}(PPh$_3$)$_2$ in toluene, a large amount of a yellow-green powder immediately precipitated. Although

---

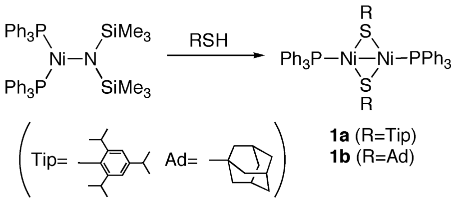
(21) Sheldrick, G. M. *SHELX97*; University of Göttingen: Göttingen, Germany, 1997.

Table 1. Crystallographic Data

	1a	**1b·3THF**	**2·THF**	**3**	**4·0.5THF**	**5**	**6**	**7**	**8·Hex**	**9·2Tol**
formula	$C_{66}H_{76}P_2S_2Ni_2$	$C_{56}H_{45}P_2S_2Ni_2\cdot 3THF$	$C_{62}H_{57}PS_2Ni_2\cdot THF$	$C_{42}H_{35}PSNi$	$C_{51}H_{58}NOPSNi\cdot 0.5THF$	$C_{31}H_{37}N_2SNi$	$C_{45}H_{32}N_2SNi$	$C_{58}H_{59}N_2S_2Ni_2$	$C_{67}H_{51}OPS_2Ni\cdot Hex$	$C_{48}H_{50}S_2Ni\cdot 2Tol$
fw	1112.80	1161.63	1069.60	661.47	854.78	528.41	691.52	965.64	1098.00	934.02
cryst syst	monoclinic	monoclinic	monoclinic	triclinic	monoclinic	monoclinic	orthorhombic	monoclinic	triclinic	triclinic
space group	$P2_1/c$	$P2_1/n$	$P2_1/n$	P-1	$C2/c$	$C2/c$	$Pbca$	$P2_1/n$	P-1	P-1
a, Å	11.896(3)	12.9760(14)	17.538(4)	10.600(4)	39.992 (10)	16.047(5)	12.5951(16)	12.107(2)	14.739(2)	12.445(2)
b, Å	25.328(6)	23.768(3)	17.614(3)	13.289(4)	12.637(3)	23.127(6)	19.079(2)	19.868(3)	14.871(3)	14.829(2)
c, Å	9.995(3)	19.638(2)	18.475(4)	13.354(4)	19.189(5)	16.194(5)	32.223(4)	22.859(4)	17.573(3)	15.151(3)
α, deg				65.334(13)					69.649(14)	74.185(7)
β, deg	109.086(3)	97.1760(11)	108.320(3)	85.557(18)	100.963(3)	100.628(5)		103.178(4)	71.411(15)	79.903(7)
γ, deg				80.478(16)					63.879(12)	70.441(6)
V, Å^3	2846.2(13)	6009.2(11)	5417.8(19)	1685.7(9)	9521(4)	5624(3)	5353.9(16)	5353.9(16)	3178.9(10)	2524.0(7)
Z	2	4	4	2	8	8	8	4	2	2
D_{calcd}, g/cm^3	1.298	1.284	1.311	1.303	1.193	1.248	1.198	1.198	1.147	1.229
$2\theta_{max}$, deg	54.96	54.96	54.96	54.96	54.96	54.96	54.96	54.96	54.96	54.96
no. of unique rflns	6471	13 722	12 369	7566	10 884	6445	8867	12 248	14 503	11 507
no. of obsd rflns	22864	46 750	42 228	14 978	37 918	22 875	60 023	43 275	39 324	29 907
no. of params	326	774	699	431	546	319	442	595	671	587
GOF (F^2)	1.158	1.047	1.085	1.081	1.183	1.033	1.122	1.017	1.048	1.129
$R_1{}^a$	0.0458	0.0470	0.0443	0.0495	0.0633	0.0819	0.0659	0.0816	0.0755	0.0567
$wR_2{}^b$	0.1357	0.1402	0.1121	0.1272	0.1818	0.2350	0.1403	0.2645	0.2208	0.1549

[a] $R_1 = \Sigma[(F_o - F_c)]/\Sigma(F_o)$. [b] $wR_2 = \{\Sigma[w(F_o{}^2 - F_c{}^2)^2/\Sigma[w(F_o{}^2)^2]\}^{1/2}$.

Scheme 1



spectroscopic characterization of the product was not possible because of its insolubility in common organic solvents, slow diffusion between two layers of a hexane solution of HSTip and a THF solution of Ni{N(SiMe$_3$)$_2$}(PPh$_3$)$_2$ produced crystals suitable for X-ray analysis, which revealed a dinuclear structure for [Ni(PPh$_3$)(μ-STip)]$_2$ (**1a**). A similar reaction of Ni{N(SiMe$_3$)$_2$}(PPh$_3$)$_2$ with 1-adamantanethiol (HSAd) afforded [Ni(PPh$_3$)(μ-SAd)]$_2$ (**1b**). Better solubility of **1b** allowed us to characterize it by ^{1}H NMR in THF-d_8, and the crystal structure was determined by X-ray analysis. The spectrum indicates that the complex is diamagnetic, and thus the two Ni(I) centers are magnetically coupled through the Ni–Ni bond.

The molecular structures of **1a** and **1b** are very much alike, and Figure 1 shows a perspective view of **1a**. Selected metric parameters are compared in Table 1. With crystallographic C_i symmetry, complex **1a** has an inversion center at the center of the Ni$_2$S$_2$ rhombus. Although **1b** has no crystallographic inversion center, the Ni$_2$S$_2$ ring is also nearly planar, as indicated by the sum of the four interior angles of 358.3°. Each nickel assumes a trigonal-planar coordination geometry with two thiolato sulfurs and one phosphorus, and the sum of the bond angles at nickel is 359.6° for **1a** and 358.5 and 358.9° for **1b**. The Tip groups of the two μ-thiolates of **1a** orient above and below the Ni$_2$S$_2$ plane, whereas the Ad groups of **1b** are both on the same side of the Ni$_2$S$_2$ plane. The four Ni–S bond distances in each Ni$_2$S$_2$ rhombus are approximately the same, where the mean values are 2.179 Å for **1a** and 2.183 Å for **1b**. The short metal–metal distances are consistent with strong Ni(I)–Ni(I) bonding. These distances are somewhat shorter than those for the analogous dinuclear Ni(I) complexes such as [Ni(μ-PCy$_2$)(PCy$_2$Me)]$_2$ (2.3910(8) Å)[24a] and [Ni(μ-Cl)(*I*iPr)]$_2$ (2.5194(5) Å) (*Ii*Pr is 1,3-bis(2,6-diisopropylphenyl)imidazol-2-ylidene).[24b]

Unsymmetric Dinuclear Nickel(I) Thiolate Complex. A similar reaction of Ni{N(SiMe$_3$)$_2$}(PPh$_3$)$_2$ with 2,6-dixylylbenzenethiol (HSDxp) in THF resulted in isolation of the dinuclear nickel(I) complex Ni(SDxp)(μ-SDxp)Ni(PPh$_3$) (**2**) in 70% yield as green crystals (Scheme 2). The X-ray derived structure of **2** is shown in Figure 2. Interestingly, this dinuclear Ni(I) complex with bulkier SDxp ligands has a structure that is quite different from those of **1a**,**b**. Complex **2** consists of two inequivalent nickel centers, one bound to a SDxp sulfur and the other bound to a PPh$_3$ ligand, and

---

(22) Ellison, J. J.; Ruhlandt-Senge, K.; Power, P. P. *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 1178–1180.

(23) (a) Ohki, Y.; Ikagawa, Y.; Tatsumi, K. *J. Am. Chem. Soc.* **2007**, *129*, 10457–10465. (b) Ohta, S.; Ohki, Y.; Ikagawa, Y.; Suizu, R.; Tatsumi, K. *J. Organomet. Chem.* **2007**, *692*, 4792–4799.

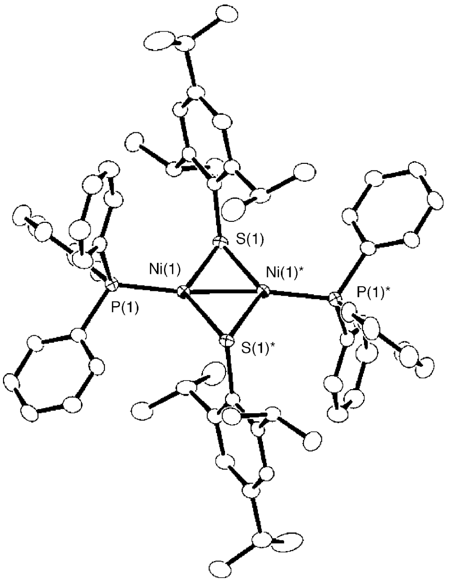


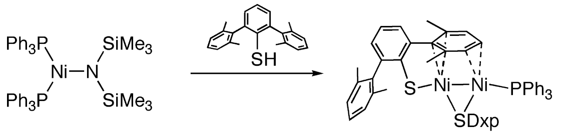
Figure 1. ORTEP drawing of [Ni(PPh$_3$)(μ-STip)$_2$]$_2$ (**1a**). Thermal ellipsoids are shown at 50% probability.

Table 2. Selected Bond Lengths (Å) and Angles (deg) for **1a** and **1b**

	1a^{a}	**1b**
Ni(1)−Ni(2)	2.3353(4)	2.3510(3)
Ni(1)−S(1)	2.1784(6)	2.1821(5)
Ni(1)−S(2)	2.1793(5)	2.1881(6)
Ni(2)−S(1)		2.1859(6)
Ni(2)−S(2)		2.1766(5)
Ni(1)−P(1)	2.1392(6)	2.1432(6)
Ni(2)−P(2)		2.1481(6)
S(1)−Ni(1)−S(2)	115.19(2)	113.85(2)
S(1)−Ni(1)−P(1)	126.08(2)	124.82(2)
S(2)−Ni(1)−P(1)	118.36(2)	119.85(2)
S(1)−Ni(2)−S(2)		114.16(2)
S(1)−Ni(2)−P(2)		121.33(2)
S(2)−Ni(2)−P(2)		123.45(2)
Ni(1)−S(1)−Ni(2)	64.810(19)	65.127(17)
Ni(1)−S(2)−Ni(2)		65.184(17)

^{a} For **1a**, Ni(2), S(2), and P(2) correspond to Ni(1)*, S(1)*, and P(1)*, respectively.

Scheme 2



2

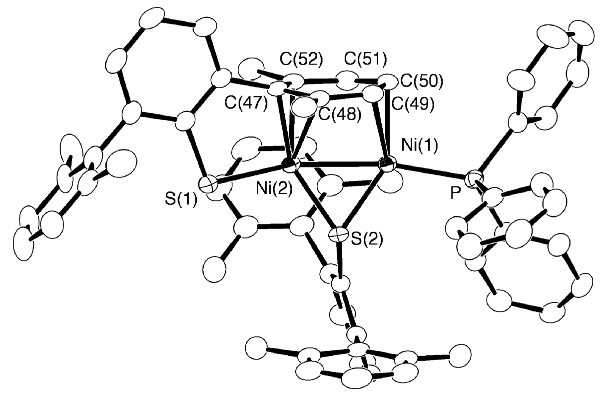
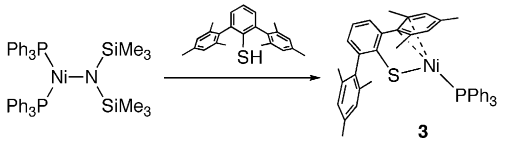


Figure 2. ORTEP drawing of Ni(SDxp)(μ-SDxp)Ni(PPh$_3$) (**2**). Thermal ellipsoids are shown at 50% probability. The xylyl ring that does not coordinate to the nickels was modeled with two disordered components in a 55:45 ratio, and the major component is shown. Distances (Å) and angles (deg): Ni(1)−Ni(2) 2.4238(4), Ni(1)−P 2.2043(6), Ni(1)−S(2) 2.1666(5), Ni(2)−S(1) 2.1718(6), Ni(2)−S(2) 2.1276(5), Ni(1)−C(49) 2.217(2), Ni(1)−C(50) 2.0489(19), Ni(2)−C(47) 1.9979(19), Ni(2)−C(48) 2.328(6), Ni(2)−C(52) 2.2342(19), C(47)−C(48) 1.441(3), C(48)−C(49) 1.402(3), C(49)−C(50) 1.420(3), C(50)−C(51) 1.403(3), C(51)−C(52) 1.399(3), C(47)−C(52) 1.432(3), P−Ni(1)−S(2) 113.99(2), Ni(2)−Ni(1)−P 167.159(17), S(1)−Ni(2)−S(2) 110.23(2), Ni(1)−Ni(2)−S(1) 165.403(18), Ni(2)−Ni(1)−S(2) 54.879(16), Ni(1)−Ni(2)−S(2) 56.399(18), Ni(1)−S(2)−Ni(2) 68.721(17).

Scheme 3



3

they are bridged by a μ-SDxp sulfur and a μ-η^2:η^3-xylyl group of the terminal SDxp. The μ-η^2:η^3-xylyl coordination mode can be seen in the Ni−C(η-xylyl) distances, namely, Ni(1)−C(49) = 2.217(2), Ni(1)−C(50) = 2.0489(19), Ni(2)−C(47) = 1.9979(19), Ni(2)−C(48) = 2.328(6), and Ni(2)−C(52) = 2.2342(19). This coordination mode is further evident in the significant bond localization of the xylyl C−C bonds. Three C−C bonds coordinating to Ni(1) and Ni(2), C(47)−C(48), C(49)−C(50), and C(47)−C(52), are longer (1.420(3) to 1.441(3) Å) than the other three C−C bonds (1.399(3) to 1.402(3) Å). Ni(1) sits in a trigonal plane composed of μ-sulfur, phosphorus, and the midpoint of the η^2-arene carbons C(49) and C(50). Ni(2) also assumes a trigonal planar geometry coordinated by two thiolato sulfurs and the η^3-xylyl at C(47), C(52), C(48). The Ni−Ni distance 2.4240(5) Å compares well to the reported Ni(I)−Ni(I) bond distances described above and is slightly longer than those of **1a** and **1b**.

The ^{1}H NMR spectrum confirms the diamagnetism of **2**, consistent with the formation of a Ni−Ni bond. Two broad signals observed at δ 4.80 and 3.73 in a 2:1 intensity ratio are assignable to the *m*- and *p*-protons of the η^2:η^3-coordinated xylyl group, respectively. These signals are shifted upfield by more than 2 to 3 ppm from those of HSDxp, which is consistent with the bonding of the xylyl group to the nickels. Because the broadness of the *m*-proton signal at δ 4.80 suggests a fluxional process, and considering the attachment of Ni(1) to only the C(49) meta site observed in the crystalline state, we carried out a variable temperature ^{1}H NMR analysis. At −60 °C, the signal at δ 4.80 splits into two broad signals at δ 5.14 and 4.48, and the two signals further broaden as the temperature rises to coalesce at −25 °C. We attribute this fluxional process to Ni(1) migration between the η^2-C(49)−C(50) and η^2-C(50)−C(51) bonds of the xylyl group, which accompanies the synchronous shift of the Ni(2) position that is asymmetrically η^3-coordinated to C(48)−C(47)−C(52).

Mononuclear Nickel(I) Complex with SDmp. The mononuclear nickel(I) thiolate complex Ni(SDmp)(PPh$_3$) (**3**) was synthesized by the reaction of the nickel(I) amide (vide

---

(24) (a) Kriley, C. E.; Woolley, C. J.; Krepps, M. K.; Popa, E. M.; Fanwick, P. E.; Rothwell, I. P. *Inorg. Chim. Acta* **2000**, *300*, 200–205. (b) Dible, B. R.; Sigman, M. S.; Arif, A. M. *Inorg. Chem.* **2005**, *44*, 3774–3776.

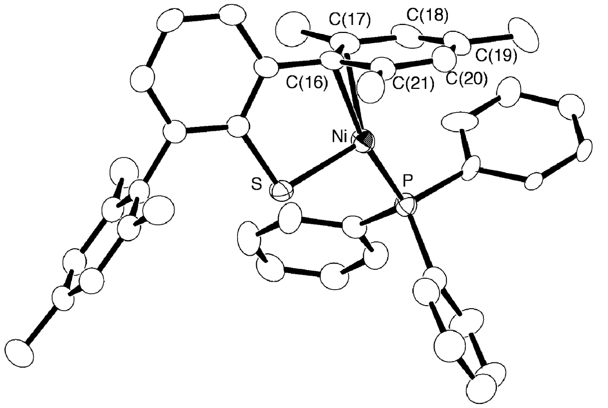


Figure 3. ORTEP drawing of Ni(SDmp)(PPh$_3$) (**3**). Thermal ellipsoids are shown at 50% probability. One phenyl group of the PPh$_3$ was modeled with two disordered components in a 1:1 ratio, and only one component is shown. Distances (Å) and angles (deg): Ni−S 2.2378(7), Ni−P 2.2034(9), Ni−C(16) 2.129(3), Ni−C(17) 2.147(2), C(16)−C(17) 1.418(4), C(17)−C(18) 1.404(4), C(18)−C(19) 1.392(4), C(19)−C(20) 1.382(4), C(20)−C(21) 1.391(3), C(16)−C(21) 1.419(3), S−Ni−P 107.30(3), P−Ni−C(16) 164.38(7), P−Ni−C(17) 126.50(9).

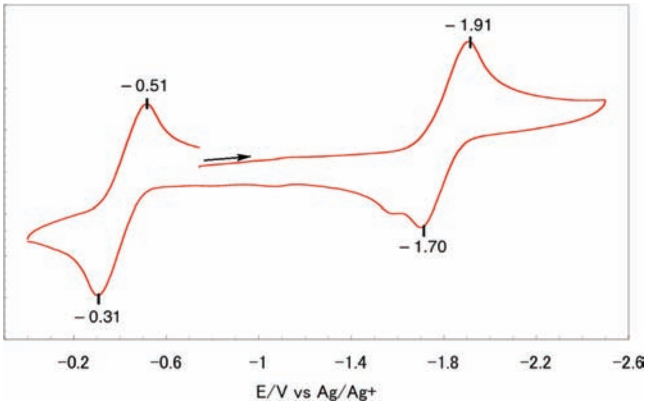
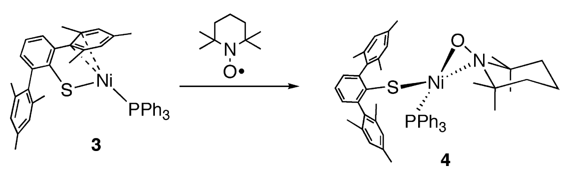


Figure 4. Cyclic voltammogram of a 2 mM THF solution of **3** and 0.2 M *n*-Bu$_4$NPF$_6$ at a scan rate of 100 mV/s.

Scheme 4



supra) with 2,6-dimesitylbenzenethiol (HSDmp) (Scheme 3). Although Dmp has just one additional methyl group on each of the two xylyl groups of Dxp at the *p*-position, it prevents the molecule from dimerizing interaction. Complex **3** was obtained in 69% yield as orange crystals, and the mononuclearity of **3** was confirmed by X-ray crystallography, as shown in Figure 3. The nickel is coordinated by PPh$_3$, the thiolate, and an η^2-mesityl of Dmp to form a considerably distorted trigonal planar geometry. The mesityl coordination can be described as η^2 because the Ni−C(16) and Ni−C(17) distances, 2.129(3) and 2.147(2) Å, respectively, are notably shorter than the other four Ni−C(mesityl) distances ranging from 2.529 to 2.907 Å.[25] Note that the C(16)−C(17) bond distance of 1.418(4) Å is slightly longer than those of the other C−C bonds in the mesityl ring because of the nickel coordination.

Electron Paramagnetic Resonance and Cyclic Voltammogram of Ni(SDmp)(PPh$_3$) (3). Complex **3** is paramagnetic ($\mu_{\mathrm{eff}} = 1.93\mu_{\mathrm{B}}$ in C$_6$D$_6$ at 25 °C), and the EPR spectrum in toluene exhibits a broad isotropic signal with $g_{\mathrm{iso}} = 2.18$ at 298 K attributable to the nickel unpaired electron.[26]

The cyclic voltammogram of **3** exhibits two quasi-reversible redox waves with peak separations of 0.2 V, a reductive Ni$^{\mathrm{I}}$/Ni^0 wave at $E_{1/2} = -1.80$, and an oxidative Ni$^{\mathrm{II}}$/Ni$^{\mathrm{I}}$ wave at $E_{1/2} = -0.41$ V (vs Ag/Ag$^+$) (Figure 4). These values exhibit an understandable negative shift compared with those of thioether-coordinated nickel(II) complexes such as [(Ph$_2$PCH$_2$CH$_2$SEt)$_2$Ni]$^{2+}$ ($E_{1/2} = -0.78$ for Ni$^{\mathrm{I}}$/Ni^0, −0.09 V for Ni$^{\mathrm{II}}$/Ni$^{\mathrm{I}}$) and [(Ph$_2$P(*o*-C$_6$H$_4$)-SMe)$_2$Ni]$^{2+}$ ($E_{1/2} = -0.90$ for Ni$^{\mathrm{I}}$/Ni^0, −0.35 V for Ni$^{\mathrm{II}}$/Ni$^{\mathrm{I}}$)[12] because these complexes are cationic, whereas **3** is charge neutral. Greater electron donation of the thiolate ligand of **3** compared with that of thioethers also may contribute.

Reaction of 3 with TEMPO. Hillhouse et al. reported that the Ni(I) dimer [(dtbpe)Ni(μ-Cl)]$_2$ reacted with TEMPO to afford the diamagnetic adduct (dtbpe)Ni(Cl)(*O*,*N*:η^2-TEMPO) (dtbpe is 1,2-bis(di-*tert*-butylphosphino)ethane, TEMPO is 2,2,6,6-tetramethyl-1-piperidine-*N*-oxyl).[27] Treatment of **3** with 1 equiv of TEMPO in toluene produced a similar mononuclear Ni(II) complex, Ni(SDmp)(PPh$_3$)(*O*,*N*:η^2-TEMPO) (**4**), in 54% yield (Scheme 4). The ^{1}H NMR spectrum confirms the diamagnetism of **4**, in which all of the aromatic protons of Dmp resonate in the normal region δ 7.14 to 7.09, suggesting the absence of π coordination of

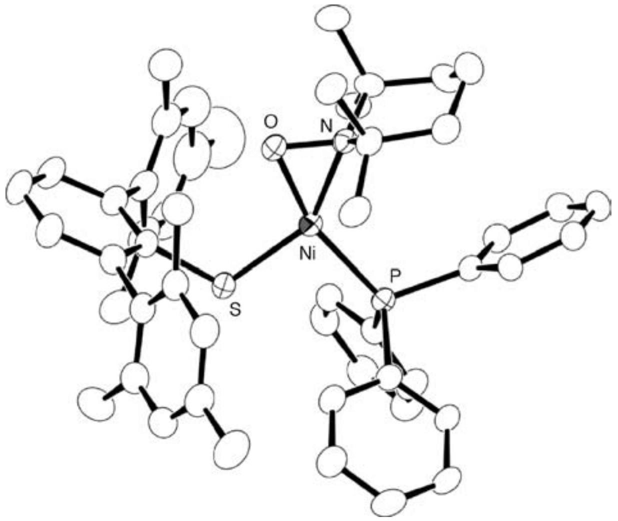


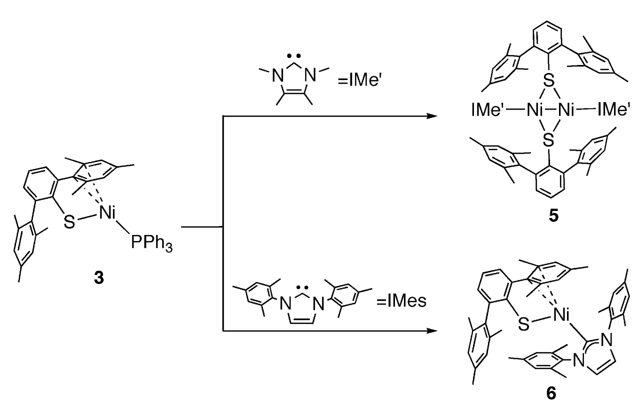
Figure 5. ORTEP drawing of Ni(SDmp)(PPh$_3$)(*O*,*N*:η^2-TEMPO) (**4**). Thermal ellipsoids are shown at 50% probability. Distances (Å) and angles (deg): Ni−S 2.1780(8), Ni−P 2.1697(7), Ni−N 1.949(2), Ni−O 1.832(2), P−Ni−S 93.51(3), P−Ni−N 118.41(7), S−Ni−O 104.84(6), N−Ni−O 43.24(8).

---

(25) The Ni−C(18) and Ni−C(21) distances, 2.529(2) and 2.538(2) Å, are substantially longer than those of the Ni−C(16) and Ni−C(17) bonds.

(26) Only a poor simulation for the complicated hyperfine coupling appearing at 77 K could be attained, even considering the interactions of the unpaired electron with only the other nuclei of the ligands including the phosphorous and the protons in the η-mesityl group. It may suggest substantial delocalization of the unpaired Ni d electron over the ligands. The EPR spectrum is shown in the Supporting Information.

Scheme 5



the mesityl group to the nickel, as was observed for **3**. The X-ray-derived structure of **4** shown in Figure 5 confirms that nickel is not bound to the mesityl group that resides in a plane composed of *O*,*N*:η^2-TEMPO, phosphorus, and the thiolato sulfur. The respective Ni−N and Ni−O bond distances compare well to those of the reported (dtbpe)Ni(Cl)(*O*,*N*:η^2-TEMPO).[27]

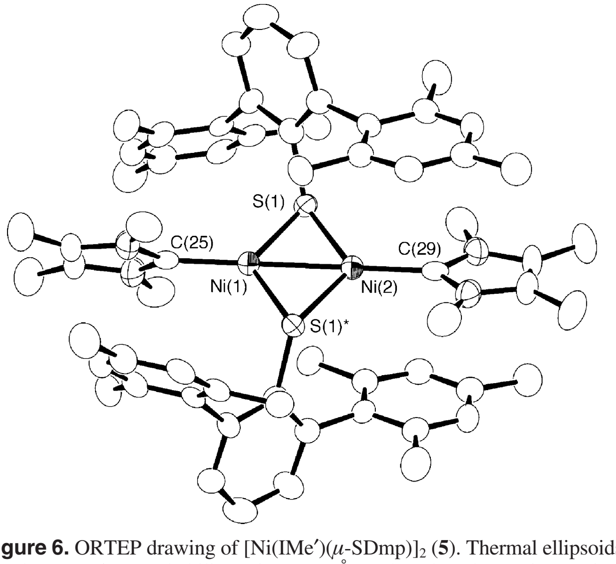


Figure 6. ORTEP drawing of [Ni(IMe′)(μ-SDmp)]$_2$ (**5**). Thermal ellipsoids are shown at 50% probability. Distances (Å) and angles (deg): Ni(1)−Ni(2) 2.3941(13), Ni(1)−S(1) 2.1663(16), Ni(2)−S(1) 2.1935(16), Ni(1)−C(25) 1.912(6), Ni(2)−C(29) 1.920(9), S(1)−Ni(1)−S(1)* 114.48(6), S(1)−Ni(2)−S(1)* 112.30(6), Ni(1)−S(1)−Ni(2) 66.61(5), S(1)−Ni(1)−C(25) 122.76(4), S(1)−Ni(2)−C(29) 123.85(4).

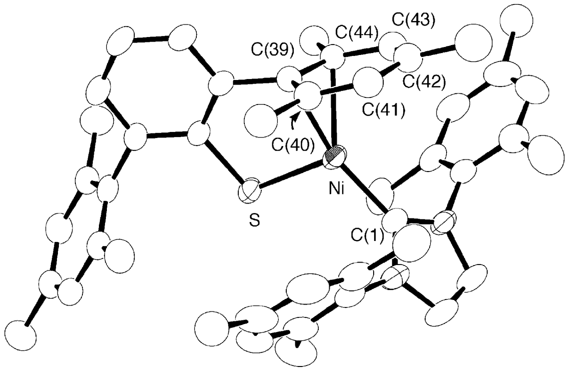
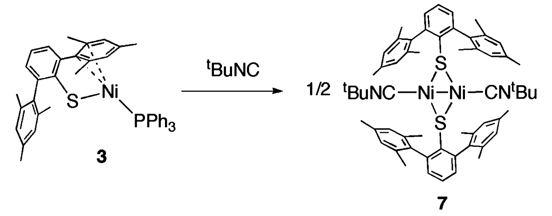


Figure 7. ORTEP drawing of [Ni(IMes)(SDmp)] (**6**). Thermal ellipsoids are shown at 50% probability. A mesityl ring interacting with nickel was modeled with two disordered components in a 1:1 ratio, and only one position of the disordered atoms is shown here. Distances (Å) and angles (deg): Ni−S 2.2424(7), Ni−C(1) 1.935(2), Ni−C(39) 2.090(5), Ni−C(44) 2.098(5), S−Ni−C(1) 106.55(7), C(1)−Ni-C(39) 163.27(16), C(1)−Ni-C(44) 136.98(15).

Scheme 6



Reactions of 3 with *N*-Heterocyclic Carbenes. Complex **3** smoothly reacts with σ donors to afford the corresponding adducts via ligand substitution. The addition of 1,3,4,5-tetramethylimidazolin-2-ylidene (denoted as IMe′) to **3** at room temperature afforded the dinuclear Ni(I) complex [Ni(IMe′)(μ-SDmp)]$_2$ (**5**) similar to **1a** and **1b** (Scheme 5). The short Ni−Ni distance of 2.3941(13) Å confirms Ni−Ni bond formation (Figure 6). The formation of the dinuclear complex **5** suggests that the IMe′ ligand is too small to prevent dimerization. Accordingly, the employment of the bulkier *N*-heterocyclic carbene, 1,3-bis-(2,4,6-trimethylphenyl)imidazolin-2-ylidene (IMes), afforded the mononuclear Ni(IMes)(SDmp) (**6**) in 60% yield. The structure of **6** revealed by X-ray analysis is shown in Figure 7. The mesityl group capping the nickel is disordered over two positions in a 1:1 ratio, and only one set is depicted here.[28] The nickel assumes a similar coordination geometry to that of **3**, and the Ni−S distance of 2.2424(7) Å also compares well to that of **3**.

Reaction of 3 with ^{t}BuNC or CO. Similarly, treatment of **3** with 1 equiv of ^{t}BuNC at room temperature produced the thiolato-bridged dinuclear Ni(I) complex [Ni(CN^{t}Bu)(μ-SDmp)]$_2$ (**7**) in 63% yield as a yellow-brown powder (Scheme 6). The substitution of PPh$_3$ with the sterically less demanding ^{t}BuNC allows the formation of the thiolato-bridged dimer **7** with a Ni−Ni bond. Note that the dinuclear Ni(I) complex **7** again has a Ni−Ni bond of 2.3354(8) Å (Figure 8), and the ^{1}H NMR spectrum in C$_6$D$_6$ confirms its diamagnetism, as was observed for **1a**, **1b**, and **5**. The IR spectrum of **7** displays a CN stretching band at 2180 cm^{-1}.

The reaction of **3** with CO produced a somewhat different adduct from those described above for *N*-heterocyclic carbenes and ^{t}BuNC. When 1 equiv of CO gas was charged to the toluene solution of **3**, the reddish orange solution immediately turned reddish brown, and the IR spectrum of this solution shows three ν_{CO} bands at 1943 (s), 2001 (s), and 2069 (m) cm^{-1}. The bands at 1943 and 2001 cm^{-1} are coincident with those of Ni^0(PPh$_3$)$_2$(CO)$_2$, and recrystallization of the products from hexane produced Ni^0(PPh$_3$)$_2$(CO)$_2$

---

(27) Mindiola, D. J.; Waterman, R.; Jenkins, D. M.; Hillhouse, G. L. *Inorg. Chim. Acta* **2003**, *345*, 299–308.

(28) See the Supporting Information for the structural details of **6**.

(29) (a) Chen, J.; Huang, S.; Seravalli, J.; Gutzman, H.; Swartz, D. J.; Ragsdale, S.; Bagley, K. A. *Biochemistry* **2003**, *42*, 14822–14830. (b) Seravalli, J.; Kumar, M.; Ragsdale, S. W. *Biochemistry* **2002**, *41*, 1807–1819. (c) George, S. J.; Seravalli, J.; Ragsdale, S. W. *J. Am. Chem. Soc.* **2005**, *127*, 13500–13501.

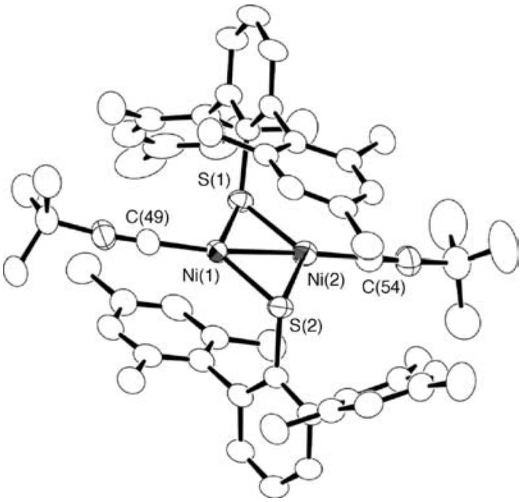
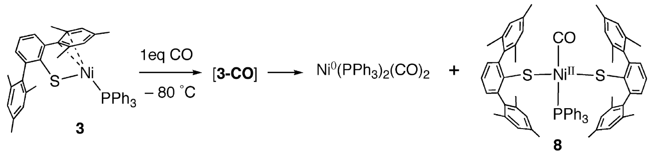
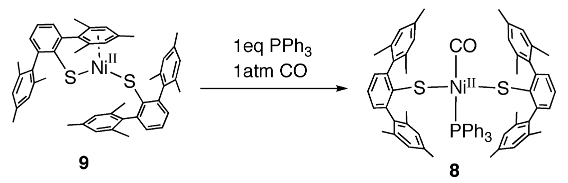


Figure 8. ORTEP drawing of $[Ni(CN^tBu)(\mu\text{-}SDmp)]_2$ (**7**). Thermal ellipsoids are shown at 50% probability. One *tert*-butyl group was modeled with two disordered components in a 6:4 ratio, and the major component is shown. Distances (Å): Ni(1)−Ni(2) 2.3354(8), Ni(1)−S(1) 2.2047(16), Ni(1)−S(2) 2.1775(12), Ni(1)−C(49) 1.817(5), Ni(2)−S(1) 2.2070(14), Ni(2)−S(2) 2.1810(15), Ni(1)−C(54) 1.815(5).

Scheme 7



Scheme 8



as a major product. The recrystallization also produced a small amount of $Ni^{II}(CO)(SDmp)_2(PPh_3)$ (**8**) in crystalline form, which has a ν_{CO} band at 2069 cm^{-1} (Scheme 7). To provide insight into this reaction that affords both Ni(0) and Ni(II) carbonyl complexes, the reaction of **3** with 1 equiv of CO was conducted at −80 °C in toluene. The red-orange solution of **3** immediately turned bright purple, and the IR spectrum of the solution shows only one strong ν_{CO} band at 2000 cm^{-1}. Because this value is reasonable for a Ni(I)-CO species, the formation of a CO adduct of **3** (**3-CO**) is indicated. However, IR analysis also shows the formation of a significant amount of $Ni^0(PPh_3)_2(CO)_2$ and **8** within 15 min, even at −80 °C, and thus the characterization of the **3-CO** is limited by its instability.

Here the chemical significance of **8** is worth mentioning. Although the Ni(II)-CO complexes carrying thiolato ligands have been found in the active sites of nickel enzymes such as CO-dehydrogenase[29a,30] and [NiFe] hydrogenase,[31] Ni(II)-CO complexes are rather rare.[33,34] Whereas complex **8** was obtained as a minor product in the former reaction, it can be synthesized in a good yield via an alternative pathway; $Ni(SDmp)_2$ (**9**), synthesized from $Ni(dme)Cl_2$ and 2 equiv of LiSDmp,[32] reacts with PPh_3 under a CO atmosphere to produce **8** in 77% yield (Scheme 8). As shown in Figure 9, the nickel sits in a square plane composed of the two thiolates, CO, and PPh_3. The two Dmp groups of the thiolates occupy positions that are cis to the CO and are tipped toward the CO side because of steric repulsion with the PPh_3 located trans to the CO. As a result, the CO is completely covered by the Dmp groups, which stabilizes the CO adduct **8**. The Ni−C(78) distance (1.761(3) Å) is within the range of reported Ni(II)-CO complexes (1.728 to 1.80 Å),[33] and the ν_{CO} band of **8** at 2069 cm^{-1} is comparable to those of Ni(II)-CO complexes ranging from 2003 to 2162 cm^{-1}.[33]

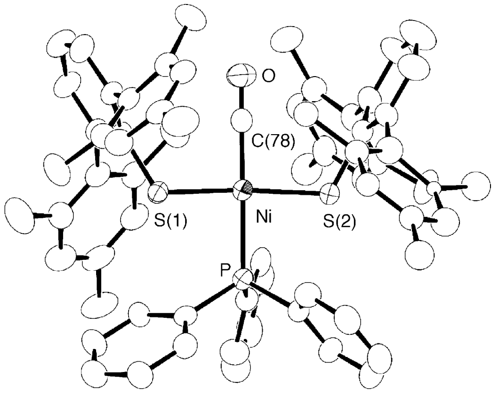


Figure 9. ORTEP drawing of $Ni(CO)(SDmp)_2(PPh_3)$ (**8**). Thermal ellipsoids are shown at 50% probability. One phenyl and one mesityl ring of a Dmp group were modeled with two disordered components in a 1:1 ratio, and only one set of disordered atoms is shown here. Distances (Å) and angles (deg): Ni−S(1) 2.2087(14), Ni−S(2) 2.2009(14), Ni−P 2.2480(10), Ni−C(78) 1.761(3), C(78)−O 1.123(4), S(1)−Ni−P 90.36(4), S(2)−Ni−P 86.59(4), S(1)−Ni−C(78) 91.14(19), S(2)−Ni−C(78) 92.91(19), Ni−C(78)−O 178.4(3).

Conclusions

Mono- and dinuclear nickel(I) thiolates have been synthesized by acid−base reactions of the Ni(I) amide, $Ni\{N(SiMe_3)_2\}(PPh_3)_2$, and the corresponding thiols. Whereas

---

(30) (a) Darnault, C.; Volbeda, A.; Kim, E. J.; Legrand, P.; Vernede, X.; Lindahl, P. A.; Fontecilla-Camps, J. C. *Nat. Struct. Biol.* **2003**, *10*, 271–279. (b) Jeoung, J.-H.; Dobbek, H. *Science* **2007**, *318*, 1461–1464.

(31) Ogata, H.; Mizoguchi, Y.; Mizuno, N.; Miki, K.; Adachi, S.; Yasuoka, N.; Yagi, T.; Yamauchi, O.; Hirota, S.; Higuchi, Y. *J. Am. Chem. Soc.* **2002**, *126*, 11628–11635.

(32) (a) The structure of $Ni(SDmp)_2$ (**9**) was confirmed by X-ray structural analysis. The structural details are described in the Supporting Information. Power and coworkers have reported a similar Ni(II) thiolate. See: (b) Nguyen, T.; Panda, A.; Olmstead, M. M.; Richards, A. F.; Stender, M.; Brynda, M.; Power, P. P. *J. Am. Chem. Soc.* **2005**, *127*, 8545–8552.

(33) (a) Saint-Joly, C.; Mari, A.; Gleizes, A.; Dartiguenave, M.; Dartiguenave, Y.; Galy, J. *Inorg. Chem.* **1980**, *19*, 2403–2410. (b) Miedanger, A.; Curtis, C. J.; Wander, S. A.; Goodson, P. A.; DuBois, D. L. *Organometallics* **1996**, *15*, 5185–5190. (c) Nguyen, D. H.; Hsu, H. F.; Millar, M.; Koch, S. A. *J. Am. Chem. Soc.* **1996**, *118*, 8963–8964. (d) Liaw, W.-F.; Horng, Y.-C.; Ou, D.-S.; Ching, C.-Y.; Lee, G.-H.; Peng, S.-M. *J. Am. Chem. Soc.* **1997**, *119*, 9299–9300. (e) Liaw, W.-F.; Chen, C.-H.; Lee, C.-M.; Lee, G.-H.; Peng, S.-M. *J. Chem. Soc., Dalton Trans.* **2001**, 138–143. (f) Forniés, J.; Martín, A.; Martín, L. F.; Menjón, B.; Kalamarides, H. A.; Rhodes, L. F.; Day, C. S.; Day, V. W. *Chem.—Eur. J.* **2002**, *8*, 4925–4934. (g) Wilson, A. D.; Fraze, K.; Twamley, B.; Miller, S. M.; DuBois, D. L.; Rakowsky DuBois, M. *J. Am. Chem. Soc.* **2008**, *130*, 1061–1068.

(34) Macgregor, S. A.; Lu, Z.; Eisenstein, O.; Crabtree, R. H. *Inorg. Chem.* **1994**, *33*, 3616–3618.

the reaction with each of HSTip, HSAd, and HSDxp results in each case in the formation of a dinuclear Ni(I) thiolate with a Ni−Ni bond, the bulkier Dmp ligand prevents the molecule from being dimerized to afford the mononuclear Ni(I) thiolate, Ni(SDmp)(PPh_3) (**3**). Complex **3** smoothly reacts with σ donors such as *N*-heterocyclic carbenes and ^{t}BuNC to form the mono- and dinuclear Ni(I) complexes in which the nuclearity depends on the steric bulk of the donors. The reaction of **3** with CO produced the corresponding Ni(I)-CO adduct of **3**, which is further converted to Ni(0) and Ni(II) carbonyl complexes because of the thermodynamic instability of the CO adduct of **3**. The complexes reported here are rare examples of Ni(I) thiolates and are expected to be useful precursors of active site models of nickel enzymes.

Acknowledgment. This research was financially supported by Grant-in-Aids for Scientific Research (nos. 18GS0207 and 18065013) from the Ministry of Education, Culture, Sports, Science, and Technology, Japan. We are grateful to Prof. Ryo Miyamoto (Hirosaki University) for discussions on EPR spectra. We also thank Prof. Roger E. Cramer for discussions and careful reading of the manuscript.

Supporting Information Available: EPR spectra for **3**, molecular structures for **6** and **9**, and X-ray crystallographic data for **1a**,**1b**, and **2**−**9** in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

IC802276W