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Synthesis and Reactivity of Dinuclear Ni(II) Azido Complexes Containing Bithienylene or Terthienylene Bridging Ligands

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Dinuclear Ni(II)–thiophene halides, which contain linear bridging thienylenes, *trans*,*trans*-[$(PR_3)_2(X)Ni–Y–Ni(X)(PR_3)_2$] {X = Cl, Br; H_2Y = 5,5'-dichloro-2,2'-bithiophene (H_2bth); H_2tth = 5,5"-dichloro-2,2':5',2"-terthiophene (H_2tth)} were prepared by the oxidative addition of dihalobithiophene (H_2bth) or dihaloterthiophene (H_2tth) to [$Ni(COD)_2$] in the presence of tertiary phosphines. Subsequent reactions of NaN_3 with the dinuclear Ni(II)–thiophene chlorides gave the corresponding Ni(II)–azido complexes, *trans*,*trans*-[$(PR_3)_2(N_3)Ni–Y–Ni(N_3)(PR_3)_2$], whose reactivity toward trimethylsilyl pseudohalides such as trimethylsilyl isothiocyanates and cyanides was investigated. In addition, the reaction of *trans*-[$BrNi(PEt_3)_2–C_4H_2S–C_4H_2S–CHO$], a thienyl Ni(II) complex containing a terminal aldehyde group, with phosphonium ylide was examined.

Key Words : Azido, Thienylene, Trimethylsilyl isothiocyanate, Trimethylsilyl cyanide, Nickel

Introduction

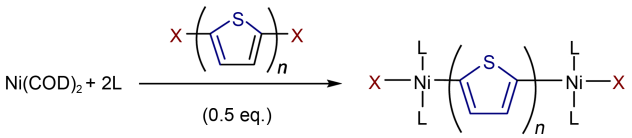
Molecular thiophene or polythiophene compounds have been intensively studied because of their interesting luminescent properties, electro- or conductive polymerization, and various coordination behaviors such as cyclometallation of the linear thiophene backbones.[1-10] In particular, group 10 metal dinuclear complexes with linear thiophene arrays are known to be catalytic intermediates in the regioselective reduction of organic thiophenes and are considered as potential materials for electronic or optical molecules.[11-15] Those dinuclear complexes having bridging thienylene ligands are typically prepared by the oxidative addition of dihalothienylene compounds to zerovalent metal complexes, but the scope of their synthesis is still limited.

We previously prepared dinuclear Pd(II) complexes containing bridging thienylene ligands by the double oxidative addition of dihalothienylene compounds to Pd(0) complexes.[14,15] Those complexes exhibited interesting reactivity toward organic isocyanides or isothiocyanates. However, Ni(II) analogues are still unknown, which are believed to be useful precursors or intermediates in Ni-catalyzed syntheses of oligomeric thienylene or polymeric thienylenes.[16-18] In this work, we prepared such dinuclear Ni(II) compounds and investigated their reactivity toward trimethylsilyl pseudohalides such as trimethylsilyl isothiocyanate ($Me_3Si–NCS$) and cyanides ($Me_3Si–CN$).

Results and Discussion

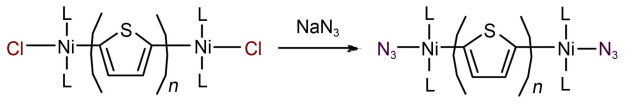
Reactions of [$Ni(COD)_2$] with dihalothiophenes {H_2Y = 5,5'-dichloro-2,2'-bithiophene (H_2bth); H_2tth = 5,5"-dichloro-2,2':5',2"-terthiophene (H_2tth)} in the presence of PR_3 in the 2:1 mole ratio gave double oxidative-addition products, [$(PR_3)_2(X)Ni–Y–Ni(X)(PR_3)_2$] (X = Cl, **1-3**; X= Br, **4**) (Scheme 1). The subsequent treatment of complexes **1-3** with excess NaN_3 produced the corresponding dinuclear Ni(II)–azido complexes [$(PR_3)_2(N_3)Ni–Y–Ni(N_3)(PR_3)_2$] (**5-7**) (Scheme 2). In contrast, such reactivity was not observed for the bromo analogues [$L_2(Br)Ni–Y–Ni(Br)L_2$], may be because of the similar nucleophilicity of the N_3 and Br groups. A triplet (J_{CP} = 39 Hz) at 137-140 ppm due to the Ni–C bond in the ^{13}C NMR spectra of complexes **1-7** supports the formation of the thienylene-bridged dinuclear Ni(II) complexes. A singlet in the ^{31}P-NMR spectra of the complexes indicates their symmetric structures. The IR spectra of the azido complexes (**5-7**) display a characteristic absorption band at 2054-2060 cm^{-1} due to the $\nu(N_3)$ band.

In order to investigate the reactivity of the Ni–azido bond



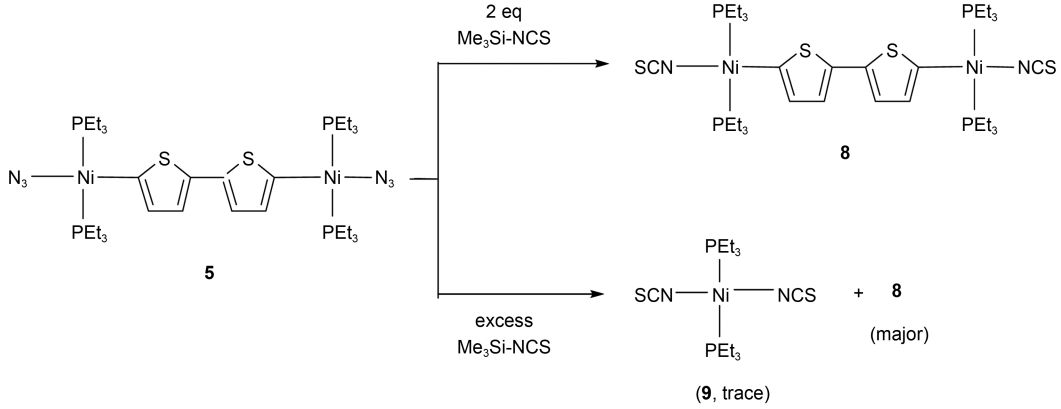
X=Cl, *n*=2; L=PEt_3 **1**, 90%
L=P(*n*-Pr)$_3$ **2**, 70%
n=3; L=PEt_3 **3**, 65%
X=Br, *n*=2; L=PEt_3 **4**, 90%

Scheme 1



n=2; L=PEt_3 **5**, 90%
L=P(*n*-Pr)$_3$ **6**, 87%
n=3; L=PEt_3 **7**, 60%

Scheme 2



Scheme 3

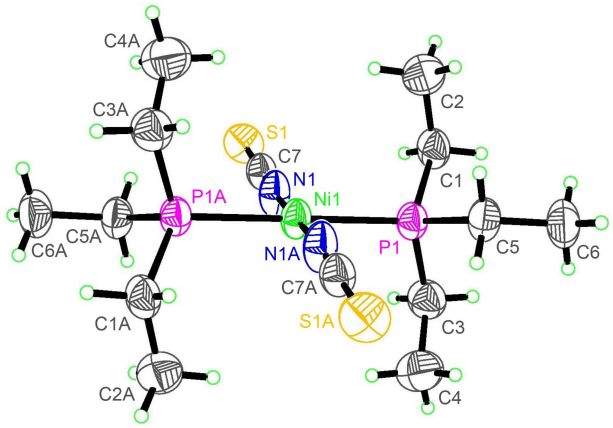


Figure 1. *ORTEP* drawing of complex **9** showing the atom-labelling scheme and 50% probability thermal ellipsoids. Selected bond lengths (Å) and angles (°): Ni1–N 11.822(3), Ni1–P 12.2422(9), S1–C7 1.614(3), N1–C7 1.160(5); N1–Ni1–P1 88.76(8), C7–N1–Ni1 172.54, N1–C7–S1 179.3(3).

in complexes **5-7**, they were treated with trimethylsilyl isothiocyanate (TMS–NCS). Complex **5** underwent ligand exchange with two equivalents of TMS–NCS to produce the *trans,trans*-bis(isothiocyanato) Ni(II) complex (**8**) in 63% yield as a brown solid (Scheme 3). On the other hand, the same reaction with excess TMS–NCS gave a mixture of **8** (major) and a trace amount of *trans*-[Ni(NCS)$_2$(PEt$_3$)$_2$] (**9**). Suitable amounts of other organic compounds for characterization could not be obtained. The IR spectrum of complex **8** displays a strong absorption at 2091 cm^{-1} due to the NCS bond. A singlet in the ^{31}P-NMR of the complex reflects the symmetric structure of **8**. The molecular structure of complex **9** (Figure 1) was determined by X-ray diffraction. The crystal and refinements data for complex **9** are summarized in Table 1.

In contrast, similar reactions with trimethylsilyl cyanide (TMS–CN) gave quite different results. Treatments of complexes **5** and **7** with the two equiv TMS–CN afforded the expected products, *trans,trans*-bis(cyano) Ni(II) (**10** and **11**) by ligand substitution (Scheme 4). However, in the presence of excess TMS–CN, those reactions led to the formation of organic cyanides, bi(cyano)bithiophene (**12**) or bi(cyano)-terthiophene (**13**), by the Ni–C bond cleavage as well as the bis(cyano) Ni(II) compound (**14**).

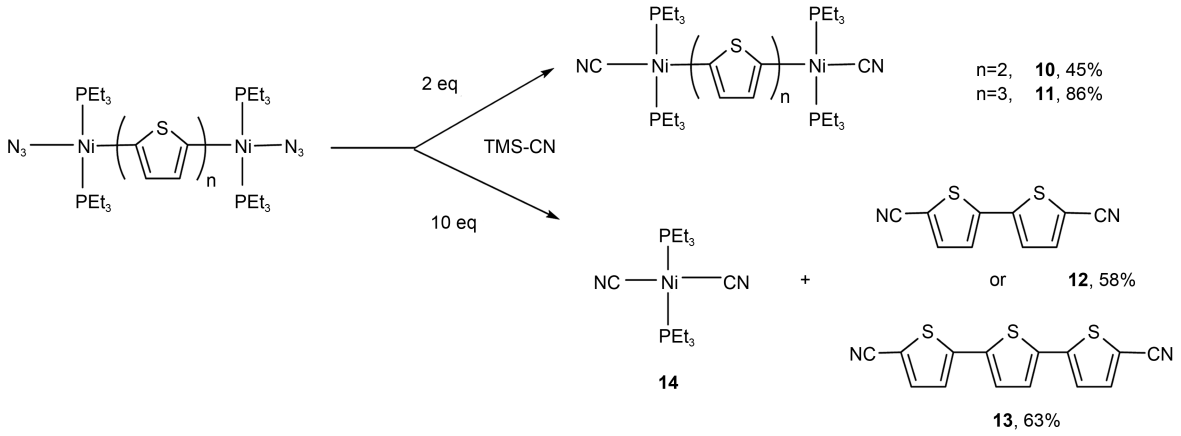
Table 1. X-ray data collection and structure refinement for complexes **9** and **15**

Empirical formula	$C_{14}H_{30}N_2NiP_2S_2$	$C_{21}H_{35}BrNiOP_2S_2$
Formula weight	411.17	568.17
Temperature, K	293(2)	296(2) K
Crystal system	monoclinic	monoclinic
Space group	$P2_1/n$	$P2_1/c$
a, Å	7.4329(14)	6.8986(3)
b, Å	11.512(2)	11.7145(5)
c, Å	12.406(2)	32.6642(14)
α, (°)	90°	90°
β, (°)	95.002(14)	94.051(2)
γ, (°)	90°	90°
V, Å^3	1057.5(4)	2633.1(2)
Z	2	4
d_{cal}, g cm^{-3}	1.291	1.433
μ, mm^{-1}	1.262	2.544
F(000)	436	1176
T_{max}	0.8597	0.7499
T_{min}	0.5461	0.4293
θ range (°)	3.5-50	1.85-28.38
No. of reflnscollected	1900	39116
No. of reflnsindependent	1748	6202
No. of reflns with $I > 2\sigma(I)$	1408	3098
No. of parameters	97	253
Max., in $\Delta\rho$ (e Å^{-3})	0.217	0.996
Min., in $\Delta\rho$ (e Å^{-3})	–0.231	–0.792
GOF on F^2	1.078	0.947
R^a	0.0368	0.0657
$wR2^b$	0.0943	0.1492

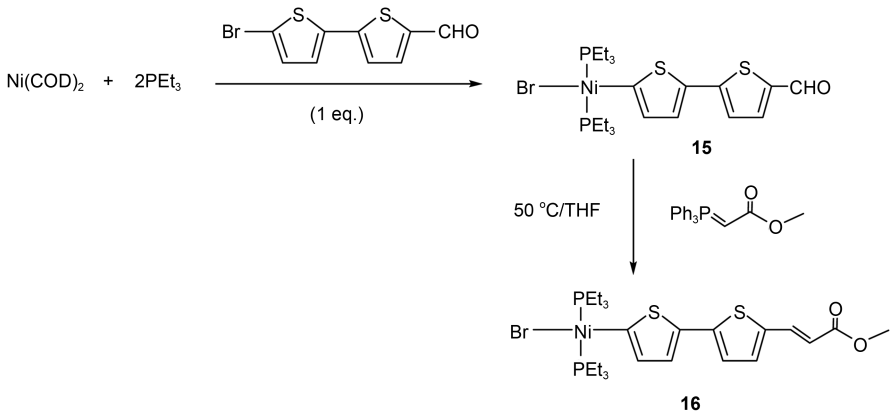
$^aR = \Sigma[|F_o| - |F_c|]/\Sigma|F_o|]$, $^bwR2 = \Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]^{1/2}$

The organic thiophenes could be readily separated by using the solubility difference from the final reaction mixtures. The above results indicate that the ability of nucleophilic attack of TMS–CN (CN$^-$) at the bridged-thienylene ligand is higher than that of TMS–NCS (NCS$^-$) and therefore eliminates organic bi(cyano) thiophenes.

We also attempted to investigate the reactivity of Sono-



Scheme 4



Scheme 5

gashira coupling, a reaction between phenyl acetylene (a π-conjugated molecule) and the dinucelar Ni(II) halides [$(PR_3)_2$(X)Ni–Y–Ni(X)$(PR_3)_2$] in the presence of Et_3N and a Pd catalyst. However, our attempts to obtain desired products failed. So, we decided to examine the following oxidative addition (Scheme 5) with a halobithiophene derivative. This reaction gave the thienyl Ni(II) complex containing a terminal active group, whose π system can be extended over the entire molecule. [$Ni(COD)_2$] was treated with 5-bromo-2,2'-bithiophene-5'-carboxaldehyde and 2 equiv. PEt_3 to produce a complex, *trans*-[BrNi$(PEt_3)_2$–C_4H_2S–C_4H_2S–CHO] (**15**), an oxidative-addition product. Complex **15** was then treated with phosphonium ylides, Ph_3P=N–Ph or Ph_3P=CH–C(O)OCH_3. In the case of Ph_3P=N–Ph, no reaction occurred, probably because of its poor reactivity under our reaction conditions. However, Ph_3P=CH–C(O)OCH_3 reacted with the terminal aldehyde group in complex **15** to form *trans*-[BrNi$(PEt_3)_2$–C_4H_2S–C_4H_2S–CH=CH–C(O)OMe] (**16**) in 38% yield as yellowish orange crystals as well as Ph_3P=O. Complexes **15** and **16** were isolated and characterized by NMR spectroscopy and elemental analyses. Molecular structure of **15** (Figure 2) clearly demonstrates the proposed formation.

In summary, we prepared the dinuclear Ni(II)–thiophene azides, *trans,trans*-[$(PR_3)_2(N_3)$Ni–Y–Ni$(N_3)(PR_3)_2$] (H_2Y = 5,5'-dichloro-2,2'-bithiophene or H_2tth = 5,5"-dichloro-2,2':5',2"-terthiophene). Treatments of these complexes with two equivalents of trimethylsilyl pseudohalides (Me_3S–NCS or Me_3Si–CN) produced the corresponding dinuclear Ni(II) isothiocyanate or cyanides. Similar reactions with excess

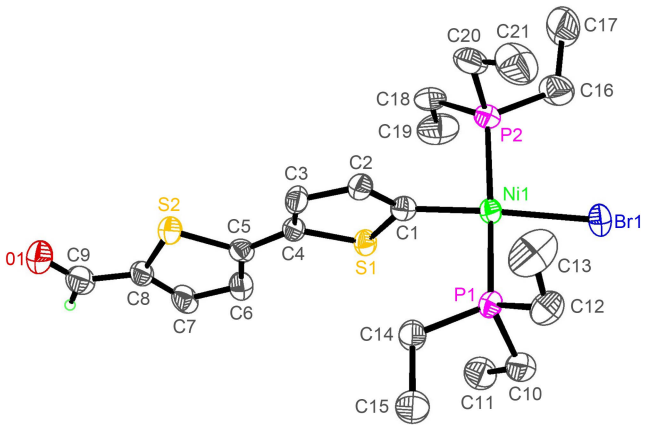


Figure 2. *ORTEP* drawing of complex **15**. Selected bond lengths (Å) and angles (°): Ni1–Br 12.3473(9), Ni1–C1 1.872(5), Ni1–P2 2.218(2), Ni1–P1 2.228(2), O1–C9 1.210(9), S1–C4 1.733(6), S1–C1 1.742(5), S2–C5 1.724(6), S2–C8 1.732(6); C1–Ni1–P2 87.6(2), P2–Ni1–P1 170.39(7), C1–Ni1–Br1 176.7(2), C1–Ni1–P1 90.0(2), C5–S2–C8 91.2(3), C4–S1–C1 93.8(3).

amounts of Me_3Si–CN gave bi(cyano)bithiophene or bi(cyano)terthiophenes as an organic product by the Ni–C bond cleavage. In addition, the reaction of the thienyl Ni(II) complex containing a terminal aldehyde group, *trans*-[BrNi(PEt_3)$_2$–C_4H_2S–C_4H_2S–CHO], with phosphonium ylide (PPh_3P=CH–C(O)OCH_3) produced a π-bond extended molecule, *trans*-[BrNi(PEt_3)$_2$–C_4H_2S–C_4H_2S–CH=CH–C(O)OMe].

Experimental Sections

General, Materials and Measurements. All manipulations of air-sensitive compounds were performed under N_2 or Ar by standard Schlenk techniques. Solvents were distilled from Na–benzophenone. The analytical laboratories at Kangnung–Wonju National University carried out elemental analyses with CE instruments EA1110. IR spectra were recorded on a Perkin Elmer BX spectrophotometer. NMR (^{1}H, ^{13}C{^{1}H}, and ^{31}P{^{1}H}) spectra were obtained on a JEOL Lamda 300 and ECA 600 MHz spectrometer. Chemical shifts were referenced to internal Me_4Si or to external 85% H_3PO_4. Mass spectra were obtained at Korea Basic Science Institute (Seoul) and the analytical laboratories of Kangnung–Wonju National University. 5,5'-Dichloro-2,2'-bithiophene and 5,5''-dichloro-2,2':5',2''-terthiophene were prepared according to the literature methods.[19-21] 5-Bromo-2,2'-bithiophene-5'-carboxaldehyde and methyl(triphenyl phosphoranylidene)acetate were purchased.

Preparation of [(PR_3)$_2$(X)Ni–Y–Ni(X)(PR_3)$_2$] (Y = bth-*C*^{5},*C*$^{5'}$or tth-*C*^{5},*C*$^{5''}$) (1-3). PEt_3 (0.593 mL, 4.02 mmol) and 5,5'-dichloro-2,2'-bithiophene (1.00 mmol) were added to a diethyl ether (8 mL) solution that contained Ni(COD)$_2$ (0.553 g, 2.01 mmol) in that order. The initial yellow suspension turned to a brown solution. After stirring for 3 h at room temperature, the reaction mixture was concentrated to half the original solution and stored at –30 °C to give brown solids, which were washed with *n*-hexane. Recrystallization from CH_2Cl_2/hexane gave brown solids of [(PEt_3)$_2$(Cl)Ni–Y–Ni(Cl)(PEt_3)$_2$] (Y = bth-*C*^{5},*C*$^{5'}$) (**1**, 0.792 g, 96%). ^{1}H NMR (300 MHz, $CDCl_3$, δ): 1.23 (qu, 36H, *J* = 7.8 Hz, P(CH_2CH_3)$_3$), 1.46 (m, 24H, P(CH_2CH_3)$_3$), 6.33 (br, 2H, Th), 6.84 (d, 2H, *J* = 3.0 Hz, Th).^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$, δ): 8.21 (s, P(CH_2CH_3)$_3$), 13.2 (t, J_{CP} = 13 Hz, P(CH_2CH_3)$_3$), 122.2, 130.7 (t, J_{CP} = 3.8 Hz, Th), 138.2 (t, J_{CP} = 39 Hz, Ni–*C*), 142.2 (t, J_{CP} = 1.9 Hz, Th). ^{31}P{^{1}H} NMR (120 MHz, $CDCl_3$, δ): 11.4 (s).

Complexes [(P(*n*-Pr_3)$_2$(Cl)Ni–Y–Ni(Cl)(P(*n*-Pr_3)$_2$)] (Y = bth-*C*^{5},*C*$^{5'}$) (**2**, 70%), [(PEt_3)$_2$(Cl)Ni–Y–Ni(Cl)(PEt_3)$_2$] (Y = tth-*C*^{5},*C*$^{5''}$) (**3**, 65%), and [(PEt_3)$_2$(Br)Ni–Y–Ni(Br)(PEt_3)$_2$] (Y = bth-*C*^{5},*C*$^{5'}$) (**4**, 95%) were prepared analogously.

Complex 2: ^{1}H NMR (C_6D_6 in 300 MHz, δ): 0.69 (t, 36H, *J* = 7.0 Hz, P($CH_2CH_2CH_3$)$_3$), 1.19 (m, 24H, P($CH_2CH_2CH_3$)$_3$), 1.33 (m, 24H, P($CH_2CH_2CH_3$)$_3$), 6.29 (br, 2H, Th), 6.97 (d, 2H, *J* = 3.3 Hz, Th). ^{13}C{^{1}H} NMR (75 MHz, C_6D_6, δ): 16.3 (t, J_{CP} = 6.8 Hz, P($CH_2CH_2CH_3$)$_3$), 18.3 (s, P($CH_2CH_2CH_3$)$_3$), 24.4 (t, J_{CP} = 12 Hz, P($CH_2CH_2CH_3$)$_3$), 123.0 (t, J_{CP} = 3.7 Hz, Th), 131.5 (t, J_{CP} = 3.7 Hz, Th), 139.9 (t, J_{CP} = 39 Hz, Ni–*C*), 143.7 (t,J_{CP} = 1.9 Hz, Th). ^{31}P{^{1}H} NMR (120 MHz, C_6D_6, δ): 2.7 (s).

Complex 3: ^{1}H NMR (300 MHz, C_6D_6, δ): 1.03 (qu, 36H, *J* = 7.9 Hz, P(CH_2CH_3)$_3$), 1.38 (m, 24H, P(CH_2CH_3)$_3$), 6.50 (br, 2H, Th), 6.98 (s, 2H, Th), 7.22 (d, 2H, *J* = 3.3 Hz, Th). ^{13}C{^{1}H} NMR (75 MHz, C_6D_6, δ): 8.38 (s, P(CH_2CH_3)$_3$), 13.8 (t, J_{CP} = 12 Hz, P(CH_2CH_3)$_3$), 122.2, 124.4, 131.7, 136.3, 141.9, 144.8 (s, Th). ^{31}P{^{1}H} NMR (120 MHz, C_6D_6, δ): 12.4 (s).

Complex 4: ^{1}H NMR (300 MHz, $CDCl_3$, δ): 1.19 (qu, 36H, *J* = 7.87 Hz, P(CH_2CH_3)$_3$), 1.55 (m, 24H, P(CH_2CH_3)$_3$), 6.34 (br, 2H, Th), 6.86 (d, 2H, *J* = 3.3 Hz, Th). ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$, δ): 8.23 (s, P(CH_2CH_3)$_3$),13.8 (t, J_{CP} = 13 Hz, P(CH_2CH_3)$_3$), 122.3, 130.8 (t, J_{CP} = 3.8 Hz, Th), 140.2 (t, J_{CP} = 39 Hz, Ni–*C*), 143.0 (t, J_{CP} = 1.9 Hz, Th). ^{31}P{^{1}H} NMR (120 MHz, $CDCl_3$, δ): 11.5 (s).

Preparation of [(PR_3)$_2$(N_3)Ni–Y–Ni(N_3)(PR_3)$_2$] (Y = bth-*C*^{5},*C*$^{5'}$or tth-*C*^{5},*C*$^{5''}$) (5-7). To a Schlenk flask containing **1** (0.245 g, 0.30 mmol) were added sequentially CH_2Cl_2 (3 mL) and a solution of NaN_3 (0.058 g, 0.89 mmol) in H_2O (1 mL). The initial red solution turned to a dark yellow suspension. After stirring for 18 h at room temperature, the solvent was completely removed under vacuum, and the resulting crude solids were washed with *n*-hexane. Recrystallization from CH_2Cl_2/hexane gave yellow crystals of [(PEt_3)$_2$(N_3)Pd–Y–Pd(N_3)(PEt_3)$_2$] (Y = bth-*C*^{5},*C*$^{5'}$) (**5**, 0.223 g, 91%). Anal. Calcd. for $C_{32}H_{64}N_6P_4S_2Ni_2$: C, 46.98; H, 7.23; N, 9.13. Found: C, 46.83; H, 7.36; N, 8.61. IR (KBr, cm^{-1}): ν(N_3) 2054. ^{1}H NMR (300 MHz, $CDCl_3$, δ): 1.19 (qu, 36H, *J* = 7.7 Hz, P(CH_2CH_3)$_3$), 1.48 (m, 24H, P(CH_2CH_3)$_3$), 6.34 (d, 2H, *J* = 2.0 Hz, Th), 6.84 (d, 2H, *J* = 3.0 Hz, Th). ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$, δ): 8.11 (s, P(CH_2CH_3)$_3$), 13.3 (t, J_{CP} = 12 Hz, P(CH_2CH_3)$_3$), 122.5 (t, J_{CP} = 3.1 Hz, Th), 130.6 (t, J_{CP} = 3.8 Hz, Th), 137.0 (t, J_{CP} = 39 Hz, Ni–*C*), 142.9 (t, J_{CP} = 1.9 Hz, Th). ^{31}P{^{1}H} NMR (120 MHz, $CDCl_3$, δ): 13.9 (s).

Complexes [(P(*n*-Pr_3)$_2$(N_3)Ni–Y–Ni(N_3)(P(*n*-Pr_3)$_2$)] (Y = bth-*C*^{5},*C*$^{5'}$) (**6**, 87%) and [(PEt_3)$_2$(N_3)Ni–Y–Ni(N_3)(PEt_3)$_2$] (Y = tth-*C*^{5},*C*$^{5''}$) (**7**, 60%) were prepared analogously.

Complex 6: Anal. Calcd. for $C_{32}H_{64}N_6P_4S_2Ni_2$: C, 52.50; H, 8.81; N, 8.35. Found: C, 52.80; H, 9.23; N, 8.42. IR (KBr, cm^{-1}): ν(N_3) 2060. ^{1}H NMR (300 MHz, acetone-d_6, δ): 1.07 (t, 36H, *J* = 7.3 Hz, P($CH_2CH_2CH_3$)$_3$), 1.45 (m, 24H, P($CH_2CH_2CH_3$)$_3$), 1.69 (m, 24H, P($CH_2CH_2CH_3$)$_3$), 6.39 (dt, 2H, *J* = 2.2, 3.3 Hz, Th), 6.87 (d, 2H, *J* = 3.3 Hz, Th). ^{13}C{^{1}H} NMR (75 MHz, acetone-d_6, δ): 16.4 (t, J_{CP} = 6.8 Hz, P($CH_2CH_2CH_3$)$_3$), 18.5 (s, P($CH_2CH_2CH_3$)$_3$), 24.6 (t, J_{CP} = 12 Hz, P($CH_2CH_2CH_3$)$_3$), 123.2 (t, J_{CP} = 2.5 Hz, Th), 131.8 (t, J_{CP} = 4.6 Hz, Th), 138.7 (t, J_{CP} = 39 Hz, Ni–*C*), 143.9 (t, J_{CP} = 2.2 Hz, Th). ^{31}P{^{1}H} NMR (120 MHz, acetone-d_6, δ): 4.9 (s).

Complex 7: Anal. Calcd. for $C_{36}H_{66}N_6P_4S_3Ni_2$: C, 46.98; H, 7.23; N, 9.13. Found: C, 47.05; H, 7.45; N, 8.57. IR (KBr, cm^{-1}): ν(N_3) 2055. ^{1}H NMR (300 MHz, C_6D_6, δ): 0.99 (qu, 36H, *J* = 7.9 Hz, P(CH_2CH_3)$_3$), 1.25 (m, 24H, P(CH_2CH_3)$_3$), 6.42 (dt, 2H, *J* = 2.2, 3.1 Hz, Th), 6.90 (s, 2H, Th), 7.17 (m, 2H, Th). ^{13}C{^{1}H} NMR (75 MHz, C_6D_6, δ): 8.16 (s,

$P(CH_2CH_3)_3$), 13.7 (t, J_{CP} = 12 Hz, $P(CH_2CH_3)_3$), 122.3, 124.4 (t, J_{CP} = 3.7 Hz, Th), 131.4 (t, J_{CP} = 3.7 Hz, Th), 136.1, 141.9 (t, J_{CP} = 2.5 Hz, Th), 143.3 (t, J_{CP} = 39 Hz, Th). $^{31}P\{^1H\}$ NMR (120 MHz, C_6D_6, δ): 13.8 (s).

Reactions of 5 and 7 with Me_3SiX (X = NCS, CN). To a Schlenk flask containing **5** (0.275 g, 0.33 mmol) were added CH_2Cl_2 (4 mL) and Me_3Si–NCS (0.464 mL, 3.28 mmol) in that order. The initial red solution turned to a brown one. After stirring for 18 h at room temperature, the solvent was completely removed under vacuum, and the resulting solids were extracted with diethyl ether (2 mL × 3). The collected solution was evaporated to give crude compounds of *trans*-$[Ni(NCS)_2(PEt_3)_2]$ (**9**). The suitable crystals for X-ray determination was obtained from the diethyl ether solution at –35 °C. The remaining solids were crystallized from CH_2Cl_2/hexane to give brown crystals of $[(PEt_3)_2(SCN)Ni$–Y–$Ni(NCS)(PEt_3)_2]$ (Y = bth-C^5,$C^{5'}$) (**8**, 0.157 g, 83%). Anal. Calcd. for $C_{34}H_{64}N_2P_4S_4Ni_2$: C, 46.92; H, 7.41; N, 3.22. Found: C, 46.81; H, 7.91; N, 3.20. IR (KBr, cm^{-1}): ν(NCS) 2091. ^1H NMR (300 MHz, $CDCl_3$, δ): 1.21 (qu, 36H, J = 7.9 Hz, $P(CH_2CH_3)_3$), 1.46 (m, 24H, $P(CH_2CH_3)_3$), 6.32 (dt, 2H, J = 2.2, 3.3 Hz, Th), 6.84 (d, 2H, J = 3.0 Hz, Th). $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$, δ): 8.13 (s, $P(CH_2CH_3)_3$), 13.6 (t, J_{CP} = 12 Hz, $P(CH_2CH_3)_3$), 122.8 (t, J_{CP} = 1.9 Hz, Th), 130.5, 136.7, 139.5, 142.9 (t, J_{CP} = 39 Hz, Ni–*C*). $^{31}P\{^1H\}$ NMR (120 MHz, $CDCl_3$, δ): 15.3 (s).

The same reaction with two equiv Me_3Si–NCS also gave the compound **8** in 93% yield. *Trans*-$[Ni(NCS)_2(PEt_3)_2]$ (**9**) was identified by comparing their spectral data with those of the product from the reaction of $[Ni(N_3)_2(PEt_3)_2]$ with 2 equiv Me_3Si–NCS.[22] Complex **9** was also previously obtained from $Ni(NO_3)_2{\cdot}6H_2O$, KSCN, and PEt_3.[23]

To a Schlenk flask containing **5** (0.150 g, 0.18 mmol) were added CH_2Cl_2 (1 mL) and Me_3Si–CN (0.050 mL, 0.38 mmol). The initial dark red solution slowly turned to a brown suspension. After stirring for 5 h at room temperature, the solvent was completely removed under vacuum, and the resulting solids were washed with *n*-hexane. The crude solids were crystallized from CH_2Cl_2/hexane to give brown crystals of $[(PEt_3)_2(NC)Ni$–Y–$Ni(CN)(PEt_3)_2]$ (Y = bth-C^5,$C^{5'}$) (**10**, 0.067 g, 46%). Anal. Calcd. for $C_{34}H_{64}N_2P_4S_2Ni_2$: C, 50.73; H, 8.02; N, 3.48. Found: C, 50.64; H, 7.91; N, 3.21. IR (KBr, cm^{-1}): ν(CN) 2106. ^1H NMR (300 MHz, $CDCl_3$, δ): 1.18 (qu, 36H, J = 7.8 Hz, $P(CH_2CH_3)_3$), 1.64 (m, 24H, $P(CH_2CH_3)_3$), 6.36 (dt, 2H, J = 2.2, 3.3 Hz, Th), 6.95 (d, 2H, J = 3.3 Hz, Th). $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$, δ): 8.40 (s, $P(CH_2CH_3)_3$), 15.2 (t, J_{CP} = 14 Hz, $P(CH_2CH_3)_3$), 122.9, 130.6 (t, J_{CP} = 3.7 Hz, Th), 140.7, 142.9 (t, J_{CP} = 1.9 Hz, Th), 147.3 (t, J_{CP} = 34 Hz, Ni–*C*). $^{31}P\{^1H\}$ NMR (120 MHz, $CDCl_3$, δ): 18.9 (s).

Similar reaction of **5** with two equiv Me_3Si–CN gave the complex, $[(PEt_3)_2(NC)Ni$–Y–$Ni(CN)(PEt_3)_2]$ (Y = tth-C^5,$C^{5''}$) (**11**, 86%). Anal. Calcd. for $C_{38}H_{66}N_2P_4S_3Ni_2$: C, 51.76; H, 7.51; N, 3.16. Found: C, 51.59; H, 7.83; N, 3.26. IR (KBr, cm^{-1}): ν(CN) 2103. ^1H NMR (300 MHz, C_6D_6, δ): 1.17 (qu, 36H, J = 7.8 Hz, $P(CH_2CH_3)_3$), 1.62 (m, 24H, $P(CH_2CH_3)_3$), 6.42 (dt, 2H, J = 2.2, 3.3 Hz, Th), 6.87 (s, 2H, Th), 7.07 (d, 2H, J = 3.3 Hz, Th). $^{13}C\{^1H\}$ NMR (75 MHz, C_6D_6, δ): 8.36 (s, $P(CH_2CH_3)_3$), 15.3 (t, J_{CP} = 14 Hz, $P(CH_2CH_3)_3$), 121.7, 124.3 (t, J_{CP} = 3.7 Hz, Th), 131.0 (t, J_{CP} = 3.7 Hz, Th), 135.7, 140.3 (t, J_{CP} = 3.7 Hz, Th), 141.1 (t, J_{CP} = 2.5 Hz, Th), 151.4 (t, J_{CP} = 34 Hz, Th). $^{31}P\{^1H\}$ NMR (120 MHz, C_6D_6, δ): 19.1 (s).

To a Schlenk flask containing **5** (0.340 g, 0.41 mmol) were added CH_2Cl_2 (3 mL) and Me_3Si–CN (0.542 mL, 4.06 mmol) in that order. The initial dark red solution slowly turned to a brown suspension. After stirring for 5 h at room temperature, the reaction mixture was filtered and then the remaining solids were washed with CH_2Cl_2 (0.5 mL × 2) to give pale yellow solids of 1,4-bi(cyano) -C^5,$C^{5'}$-bithiophene (**12**, 0.074 g, 85%). The filtrate was evaporated to give yellow residues and then crystallized from CH_2Cl_2/hexane to give pale yellow solids of $[Ni(CN)_2(PEt_3)_2]$ (**14**). Compound **14** was also identified by comparing their spectral data with those of the product from the reaction of $[Ni(N_3)_2((PEt_3)_2]$ with 2 equiv Me_3Si–CN.[24] Complex **14** was also previously obtained from $[NiBr_2(PEt_3)_2]$ and AgCN.[25]

12 (58%): Anal. Calcd. for $C_{10}H_4N_2S_2$: C, 55.56; H, 1.87; N, 12.97. Found: C, 55.36; H, 1.85; N, 12.66.IR (KBr, cm^{-1}): ν(CN) 2220. ^1H NMR (300 MHz, $CDCl_3$, δ): 7.26 (d, 2H, J = 4.0 Hz, Th), 7.58 (d, 2H, J = 4.0 Hz, Th). $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$, δ): 113.3, 125.7, 138.3, 141.4, 145.0 (s, Th). MS (*m*/*e*): 216 (M^+).

1,4-Bi(cyano)-C^5,$C^{5''}$-terthiophene (**13**) was prepared analogously (63%). Anal. Calcd. for $C_{14}H_6N_2S_3$: C, 56.38; H, 2.03; N, 9.40. Found: C, 56.80; H, 2.18; N, 9.20. IR (KBr, cm^{-1}): ν(CN) 2219. ^1H NMR (300 MHz, DMSO-d_6, δ): 7.57 (d, 2H, J = 4.0 Hz, Th), 7.61 (s, 2H, Th), 7.97 (d, 2H, J = 4.0 Hz, Th). $^{13}C\{^1H\}$ NMR (75 MHz, DMSO-d_6, δ): 106.8, 114.0, 125.3, 128.2, 135.1, 140.3, 142.8 (s, Th). MS (*m*/*e*): 298 (M^+).

Preparation of *trans*-[BrNi(PEt_3)$_2$–C_4H_2S–C_4H_2S–CHO] (15) and *trans*-[BrNi(PEt_3)$_2$–C_4H_2S-C_4H_2S–CH=CH–C(O)OMe] (16). PEt_3 (0.334 mL, 1.13 mmol) and 5-bromo-2,2'-bithiophene-5'-carboxaldehyde (0.309 g, 1.13 mmol) were added to a THF (3 mL) solution containing $[Ni(COD)_2]$ (0.311 g, 1.13 mmol) at 0 °C. The initial yellow solution turned to a dark orange one. After stirring for 2 h at room temperature, the solvent was removed completely under vacuum, and the resulting solids were washed with *n*-hexane. Recrystallization from THF/hexane (1:4) gave brown solids of *trans*-[BrNi(PEt_3)$_2$–C_4H_2S–C_4H_2S–CHO] (**15**, 0.567 g, 88%). Anal. Calcd. for $C_{21}H_{35}BrP_2S_2Ni$: C, 44.39; H, 6.21. Found: C, 44.59; H, 6.67. IR (KBr, cm^{-1}): ν(CO) 1651. ^1H NMR (300 MHz, $CDCl_3$, δ): 1.19 (qu, 18H, J = 7.8 Hz, $P(CH_2CH_3)_3$), 1.53 (m, 12H, $P(CH_2CH_3)_3$), 6.56 (dt, 1H, J = 3.7 Hz, Th), 7.06 (d, 1H, J = 4.0 Hz, Th), 7.26 (d, 1H, J = 3.3 Hz, Th), 7.60 (d, 1H, J = 4.0 Hz, Th), 9.80 (s, 1H, CHO). $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$, δ): 8.24 (s, $P(CH_2CH_3)_3$), 14.0 (t, J_{CP} = 13 Hz, $P(CH_2CH_3)_3$), 121.7, 127.7 (t, J_{CP} = 3.1 Hz, Th), 132.4 (t, J_{CP} = 3.7 Hz, Th), 137.9, 138.9, 139.6, 149.0, 154.8 (t, J_{CP} = 36 Hz, Ni-*C*), 182.2 (s, CO). $^{31}P\{^1H\}$ NMR (120 MHz, $CDCl_3$, δ): 12.2 (s).

To a Schlenk flask containing **15** (0.153 g, 0.27 mmol)

were added methyl(triphenyl phosphoranylidene)acetate (0.099 g, 0.29 mmol) and THF (4 mL). The initial reddish orange solution slowly turned to a dark red one. After stirring for 5 h at 50 °C, the solvent was removed, and the resulting residues were extracted with excess diethyl ether. The collected extracts were evaporated to give crude solids which were repeatedly crystallized from a diethyl ether/hexane to remove white crystals of triphenyl phosphine oxide. The final solution was fully evaporated and recrystallized from a diethyl ether/hexane to give yellowish orange crystals of *trans*-[BrNi(PEt_3)$_2$–C_4H_2S–C_4H_2S–CH=CH–C(O)OMe] (**16**, 0.063 g, 38%). Anal. Calcd. for $C_{24}H_{39}BrO_2P_2S_2Ni$: C, 46.18; H, 6.30. Found: C, 46.22; H, 6.61. IR (KBr, cm^{-1}): ν(CO) 1708, ν(C=C) 1610. ^{1}H NMR (600 MHz, CD_2Cl_2, δ, 10 °C): 1.10 (qu, 18H, J = 7.8 Hz, P(CH_2CH_3)$_3$), 1.44 (m, 12H, P(CH_2CH_3)$_3$), 3.66 (s, 3H, Me)), 6.00 (d, 1H, J = 15 Hz, C*H*=), 6.45 (dt, 1H, J = 2.2, 3.3 Hz, Th), 6.85 (d, 1H, J = 3.7 Hz, Th), 7.05 (dd, 2H, J = 3.7, 10 Hz, Th), 7.62 (d, 1H, J = 15 Hz, C*H*=). ^{13}C{^{1}H} NMR (151 MHz, CD_2Cl_2, δ, 10 °C): 8.12 (s, P(CH_2CH_3)$_3$), 13.9 (t, J_{CP} = 13 Hz, P(CH_2CH_3)$_3$), 51.5 (s, Me), 114.3, 121.6, 125.8, 132.2, 133.0, 135.3, 137.3, 140.0, 142.3, 151.4 (t, J_{CP} = 36 Hz, Ni-*C*), 167.3 (s, CO). ^{31}P{^{1}H} NMR (120 MHz, CD_2Cl_2, δ): 12.2 (s).

X-ray Structure Determination. All X-ray data were collected with a Bruker Smart APEX2 diffractometer equipped with a Mo X-ray tube. Collected data were corrected for absorption with SADABS based upon the Laue symmetry by using equivalent reflections.[25] All calculations were carried out with the SHELXTL programs.[26] All structures were solved by direct methods. All non-hydrogen atoms were refined anisotropically, and all hydrogen atoms were generated in ideal positions and refined in a riding model.

CCDC 832223 and 832224 contain the supplementary crystallographic data for this paper. Copies of this information may be obtained free of charge from: The director, CCDC, 12 Union Road, Cambridge, CB21EZ, UK (Fax: +44-1223-336-033; email: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

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