Dinuclear palladium–azido complexes containing thiophene derivatives: reactivity toward organic isocyanides and isothiocyanates†

Xiaohong Chang,[a,b] Mi-Young Kim,[a] Yong-Joo Kim,*[a] Hyun Sue Huh[c] and Soon W. Lee[c]

Received 21st November 2006, Accepted 8th January 2007
First published as an Advance Article on the web 18th January 2007
DOI: 10.1039/b616901e

Cyclopalladated tetranuclear Pd(II) complexes, $[Pd_2(\mu\text{-}Cl)_2(Y)]_2$ (Y = $\mathbf{L}^1$ or $\mathbf{L}^2$; $H_2\mathbf{L}^1$ = di(2-pyridyl)-2,2′-bithiophene; $H_2\mathbf{L}^2$ = 5,5″-di(2-pyridyl)-2,2′:5′,2″-terthiophene), containing two pyridyl-α, α′-disubstituted derivatives of thiophene were prepared. Treating these products with PR_3 and subsequently with NaN_3 produced the dinuclear Pd–azido complexes $[(PR_3)_2(N_3)Pd\text{–}Y\text{–}Pd(N_3)(PR_3)_2]$ (Y = $\mathbf{L}^1$ or $\mathbf{L}^2$) or a cyclometallated complex $[(PR_3)(N_3)Pd\text{–}Y'\text{–}Pd(N_3)(PR_3)]$ (Y′ = *C*,*N*-$\mathbf{L}^2$). Reactions of these Pd–azido complexes with CN–Ar (Ar = 2,6-$Me_2C_6H_3$, 2,6-*i*-$Pr_2C_6H_3$) or R–NCS (R = *i*-Pr, Et, allyl) led to the complexes containing end-on carbodiimido groups $[(PMe_3)_2(N{=}C{=}N\text{–}Ar)Pd\text{–}Y\text{–}Pd(N{=}C{=}N\text{–}Ar)(PMe_3)_2]$ or *S*-coordinated tetrazole-thiolato groups $\{(PMe_3)_2[CN_4(R)]S\text{–}Pd\text{–}Y\text{–}Pd\text{–}S[CN_4)(R)](PMe_3)_2\}$. Interestingly, when treated with elemental sulfur, the carbodiimido complexes transformed into the cyclometallated derivatives, $[(PMe_3)(N{=}C{=}N\text{–}Ar)Pd\text{–}Y'\text{–}Pd(N{=}C{=}N\text{–}Ar)(PMe_3)]$ (Y′ = *C*,*N*-$\mathbf{L}^1$, *C*,*N*-$\mathbf{L}^2$). We also report the preparation of linear, thienylene-bridged dinuclear Pd complexes $[L_2(N_3)Pd\text{–}X(\text{or } X')\text{–}Pd(N_3)L_2]$ (L = PMe_3 or PMe_2Ph; H_2X = 2,2′-bithiophene or H_2X' = 2,2′:5′,2″-terthiophene) and their reactivity toward organic isocyanide and isothiocyanates.

Introduction

π-Conjugated thiophene compounds have been intensively studied because of their intriguing electronic or optical properties.[1–6] In particular, pyridine-substituted thiophene (thienyl pyridine) compounds with extended π-electron bonds have been focused on because of their potential use in the construction of molecular wires, electronic, or chemical devices.[7,8] For transition metal complexes containing a 2-(2′-thienyl)pyridine unit, four coordination types (I–IV in Chart 1), chelate (*C*,*N*) or monodentate, are observed. For example, cyclometallated or non-cyclometallated (σ-bond) Pd, Pt, Ru, and Au complexes containing this type of ligand are known.[9–12]

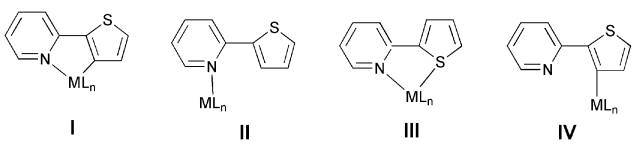
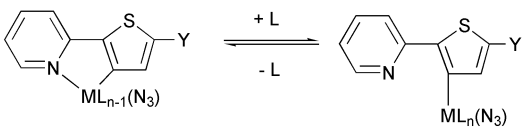


Chart 1

We have recently reported the preparation of cyclometallated Pd(II) complexes containing *C*,*N*- or *C*,*N*,*N*-donor ligands such as 2-phenylpyridyl or 6-phenyl-2,2′-bipyridyl.[13] In that study, we introduced the azido group to the cyclometallated system, because the azido ligand may undergo thermal or nucleophilic cycloaddition or imido-compound formation with unsaturated organic molecules. While the cyclometallated Pd and Pt complexes containing phenyl pyridyl derivatives as *C*,*N*-donor ligands are now relatively common, those containing thienyl pyridyl derivatives are rare.[9–12,14] Moreover, dinuclear azido complexes containing pyridyl thiophene units of type I (*C*,*N*-coordinated) or type IV (non-cyclometallated or σ-bonded thienyl derivatives) have not been reported yet.

In this work, we describe the preparation and properties of the dinuclear Pd(II)–azido complexes bridged by pyridyl thiophene derivatives, $[(PR_3)_2Pd(N_3)\text{–}Y\text{–}Pd(N_3)(PR_3)_2]$, in which "Y" denotes a di(2-pyridyl) bithienyl ($\mathbf{L}^1$) or terthienyl ligand ($\mathbf{L}^2$) acting as a *C*,*N*-donor chelate ligand (type I) or just a *C*-donor ligand (type IV), along with their interconversion between a cyclometallated and non-cyclometallated form (Scheme 1).



(Y = Pyridyl thienyl or bithienyl ML$_n$)

Scheme 1

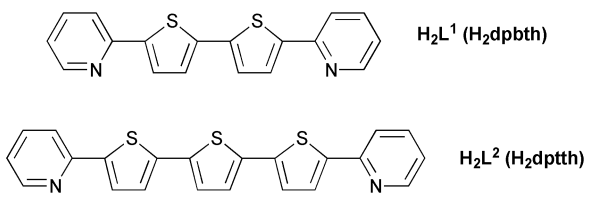


Chart 2

[a]*Department of Chemistry, Kangnung National University, Kangnung, 210-702, Korea. E-mail: yjkim@kangnung.ac.kr; Fax: Int + 82 + 33-647-1183; Tel: Int + 82 + 33-640-2308*
[b]*Department of Chemistry, Liaoning University, Shenyang, 110036, PR China*
[c]*Department of Chemistry, Sungkyunkwan University, Natural Science Campus, Suwon, 440-746, Korea*
† Electronic supplementary information (ESI) available: NMR data. See DOI: 10.1039/b616901e

As a comparative work, we also prepared the dinuclear Pd(II)–azido complexes by empolying linear thienylene ligands, $[(PR_3)_2Pd(N_3)–X(\text{or } X')–Pd(N_3)(PR_3)_2]$ (X = bth-$C^5,C^{5'}$ or X′ = tth-$C^5,C^{5'}$), and examined their reactivity toward organic isocyanides or isothiocyanates.

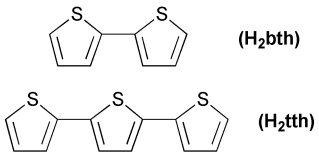
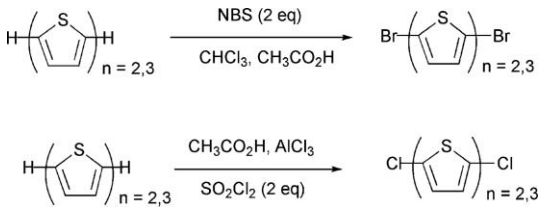


Chart 3

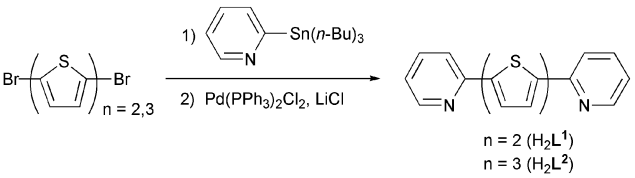
Results and discussion

Synthesis of pyridyl-α,α′-disubstituted derivatives of thiophene

For the preparation of pyridyl-α,α′-disubstituted derivatives of thiophene ($H_2\mathbf{L}^1$ and $H_2\mathbf{L}^2$), we first synthesized halo-α,α′-disubstituted derivatives of thiophene by employing NBS or $AlCl_3$(cat.)–SO_2Cl_2 (Scheme 2).[15–17] In the subsequent step, the pyridyl groups were introduced to the α positions of the thiophene by the Pd-catalyzed Stille coupling reactions (Scheme 3).[18–19] The reactions yielded a mixture of a disubstituted thiophene (major) and a monosubstituted thiophene (minor), which could be readily separated by column chromatography.



Scheme 2



Scheme 3

Synthesis of dinuclear Pd–azido complexes containing pyridyl-α,α′-disubstituted derivatives of thiophene

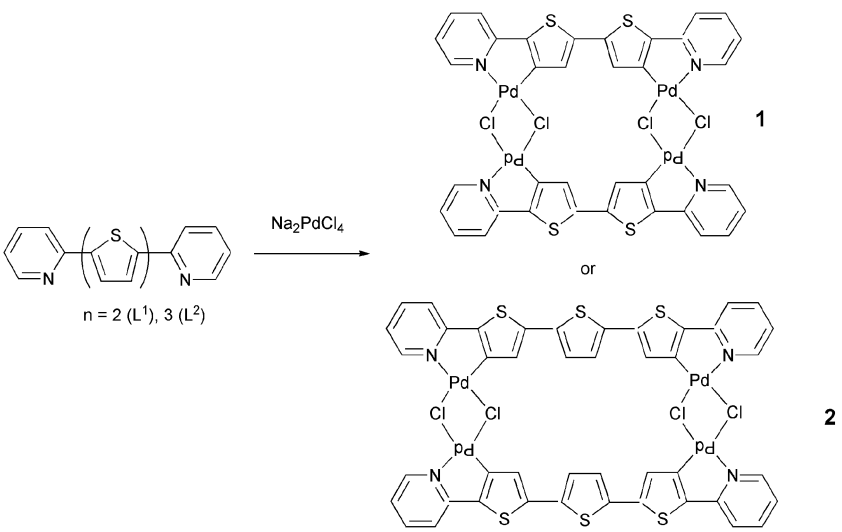
Cyclopalladated tetranuclear Pd complexes (**1** and **2**) containing two pyridyl-α,α′-disubstituted derivatives of thiophene ($\mathbf{L}^1$ and $\mathbf{L}^2$), which are the starting materials for the corresponding dinuclear chlorides or azides, were prepared from $H_2\mathbf{L}^1$ or $H_2\mathbf{L}^2$ and Na_2PdCl_4 (Scheme 4).

The products are slightly soluble in common organic solvents. Addition of excess PR_3 (8 equiv.) to the tetranuclear chloro-bridged Pd complexes **1** and **2** cleaved the Cl–Pd–Cl bridges to give the dinuclear Pd chlorides (**3**, **4**, and **7**) containing a single bridging $\mathbf{L}^1$ or $\mathbf{L}^2$ (Y), and then metathesis with NaN_3 gave the dinuclear Pd–azido complexes, $[(PR_3)_2(N_3)Pd–Y–Pd(N_3)(PR_3)_2]$ (**5**, **6**, and **8**), as shown in Scheme 5.

On the other hand, treating complex **2** with 4 equiv. of PR_3 produced a cyclometallated Pd chloride (**9**) with the thiophene derivative, a *C*,*N*-coordinated $\mathbf{L}^2$ (*C*,*N*-$\mathbf{L}^2$). Subsequent treatment of **9** with NaN_3 produced another cyclometallated Pd–azido complex (**10**).

The IR spectra of these complexes display a strong N_3 absorption band at 2036–2037 cm^{-1}. Crystallographic data of **5** are given in Table 1. Despite severe disorder of the PMe_3 ligand, the ORTEP[36] drawing of **5** (Fig. 1) clearly exhibits the geometry of the dinuclear Pd–azido complex bridged by $\mathbf{L}^1$. The coordination sphere of each Pd can be described as square planar. The crystallographic inversion center is located in the middle of the central C–C bond joining two thiophene rings, which explains why the crystal of complex **5** has the *Z* value of 4 instead of 8.

Several cyclometallated complexes containing terthienyl-based ligands and dinuclear complexes bridged by polythiophene or

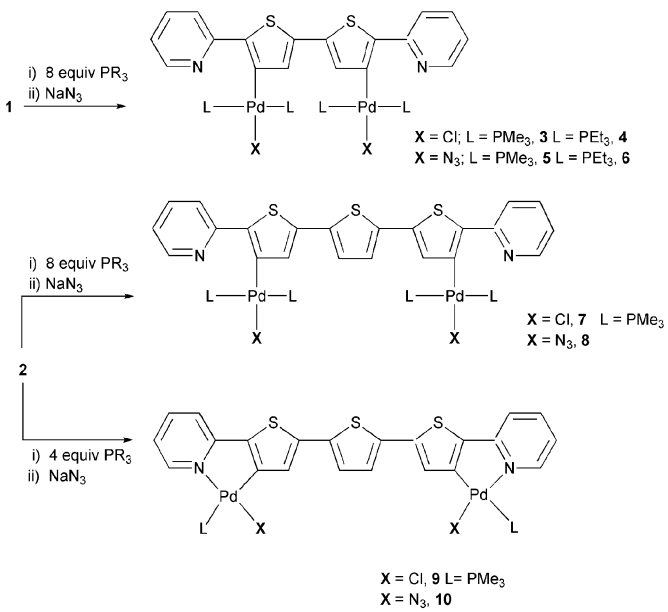


Scheme 4

Table 1 X-Ray data collection and structure refinement for **5**, **15** and **26**

	5	**15**	**26**·$2CH_2Cl_2$
Formula	$C_{30}H_{46}N_8P_4Pd_2S_2$	$C_{50}H_{62}N_6P_2Pd_2S_2$	$C_{40}H_{62}Cl_4N_4P_4Pd_2S_2$
FW	919.55	1085.92	1141.54
Temperature/K	293(2)	293(2)	293(2)
Crystal size/mm^3	0.24 × 0.18 × 0.12	0.46 × 0.24 × 0.24	0.24 × 0.20 × 0.20
Crystal system	Monoclinic	Orthorhombic	Triclinic
Space group	*C*2/*c*	*Pbca*	*P*-1
a/Å	28.363(4)	39.276(8)	8.5056(17)
b/Å	11.025(1)	8.758(2)	12.325(2)
c/Å	15.054(3)	14.875(3)	13.107(4)
α/°	—	—	87.887(17)
β/°	98.08(1)	—	76.69(2)
γ/°	—	—	81.063(16)
V/Å^3	4660(1)	5117(2)	1320.9(5)
Z	4	4	1
d_{cal}/g cm^{-3}	1.310	0.410	1.435
μ/mm^{-1}	1.026	0.886	1.114
F(000)	1864	2232	582
T_{min}	0.6863	0.4390	0.4721
T_{max}	0.9102	0.4970	0.8289
Scan type	ω	ω	ω
No. of reflns measured	4109	4485	4962
No. of reflns unique	4025	4485	4624
No. of reflns with $I > 2\sigma(I)$	2884	3323	3598
No. of parameters refined	194	281	255
Max., in $\Delta\rho$/e Å^{-3}	0.987	0.372	0.666
Min., in $\Delta\rho$/e Å^{-3}	−0.606	−0.824	−0.772
GOF on F^2	1.025	1.003	1.019
R	0.0697	0.0389	0.0463
w*R*2[a]	0.1747	0.0917	0.1135

[a] $wR2 = \Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]^1$



Scheme 5

phosphinothiophene ligands were reported.[20–27] However, examples of the complexes containing pyridyl-substituted thiophene derivatives are quite rare.[9] Furthermore, the reactivity of these complexes toward organic isocyanide and isothiocyanates has never been reported.

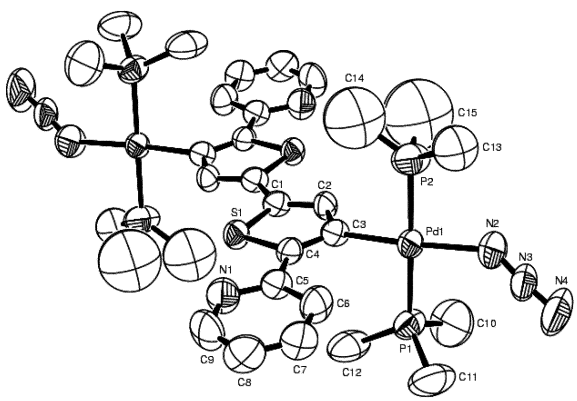
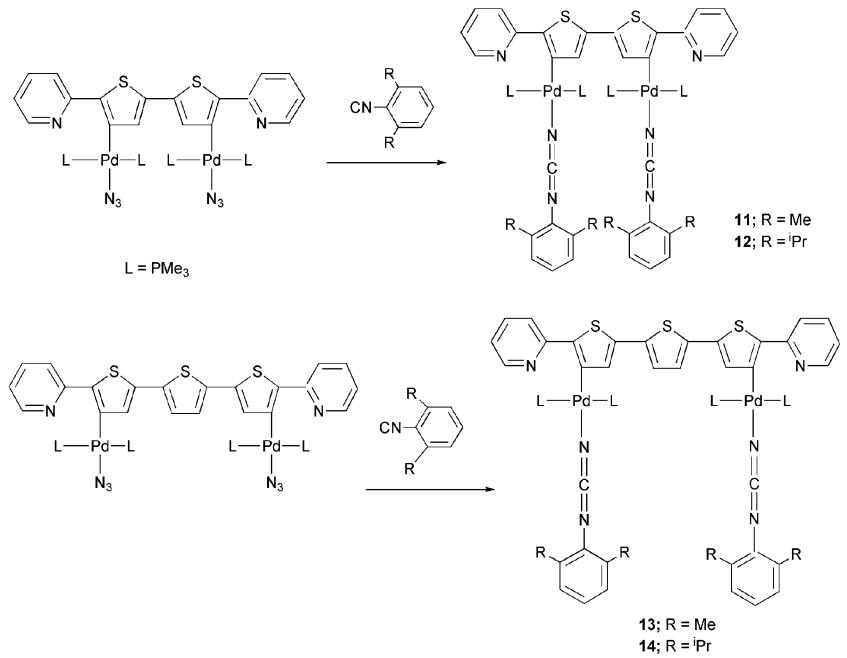


Fig. 1 ORTEP drawing[36] of compound **5** with 50% probability thermal ellipsoids. Selected bond lengths (Å) and angles (°): Pd1–C3 2.019(8), Pd1–N2 2.093(9), Pd1–P2 2.293(3), Pd1–P1 2.319(3), N2–N3 1.11(1), N3–N4 1.09(1); C3–Pd1–N2 175.7(4), C3–Pd1–P2 89.4(2), N2–Pd1–P2 88.2(3), C3–Pd1–P1 89.4(2), N2–Pd1–P1 93.0(3), P2–Pd1–P1 177.4(1), C1–S1–C4 90.8(4), N3–N2–Pd1 138.2(9), N4–N3–N2 174(2).

Reactivity towards organic isocyanide

We recently reported that treatments of late transition-metal–azides with organic isocyanides gave *C*-coordinated tetrazolato or carbodiimido compounds, depending on the nature of the isocyanides used.[28] On the basis of these results, we decided to employ the same synthetic strategy to prepare novel complexes. Reactions of the dinuclear Pd–azido complexes **5** and **8** with CN–Ar (Ar = 2,6-$Me_2C_6H_3$, 2,6-*i*-$Pr_2C_6H_3$) afforded the dinuclear



Scheme 6

Pd complexes (**11–14**) containing end-on carbodiimido ligands in high yield (Scheme 6). The formation of the products could readily be monitored by IR spectra, which show the disappearance of an asymmetric stretching band $\nu(N_3)$ of the starting material and the appearance of a new strong band at 2115–2147 cm^{-1} due to the carbodiimido group (N=C=N) of the products. A singlet in the ^{31}P NMR spectra of the complexes strongly supports the formation of the symmetric dinuclear Pd–carbodiimido complexes.

In contrast, the same reaction of **10** with two or more equiv. of isocyanide (CN–Ar) gave a mixture of three products whose NMR spectra indicate the presence of a carbodiimido complex (**16**, isolated), a new imidoyl complex [(PMe_3)(N=C=N–Ar)(–C=N–Ar)Pd–Y′–Pd(–C=N–Ar)(N=C=N–Ar)(PMe_3)] (Y′ = *C*,*N*-**L**^{2}, Ar = C_6H_3-2,6-*i*-Pr_2), and an unidentified compound. Several attempts to separate the mixture were unsuccessful.

However, when treated with elemental sulfur (slight excess) at room temperature, the dinuclear Pd–carbodiimido complexes **12** and **14** slowly transformed into the dinuclear Pd–carbodiimido complexes containing *C*,*N*-**L**^{1} (**15**) or *C*,*N*-**L**^{2} (**16**), which is accompanied by dissociation of one PMe_3 from each Pd (Scheme 7). On addition of a slight excess of PMe_3, complexes **15** and **16** go back to the starting materials, which indicates a hemilabile character of the ligands *C*,*N*-**L**^{1} and *C*,*N*-**L**^{2}.

The formation of the cyclometallated Pd–carbodiimido complexes can be readily followed by ^1H NMR, which exhibits the appearance of a doublet due to one PMe_3 ligand per Pd in the products. The molecular structure of orange-red complex **15** was determined by X-ray diffraction. The dinuclear Pd complex **15** (Fig. 2) can be regarded as having two equal halves, each of which consists of one half of *C*,*N*-**L**^{1}, a carbodiimido group, and a PMe_3 ligand in a square-planar geometry. The molecule lies about an inversion center, which is at the midpoint of the C–C bond linking the two thiophene moieties.

Recently, we prepared the cyclometallated Pd–azido complexes [$Pd(N_3)(PR_3)$L] (L = 2-phenylpyridine derivatives), in which the ligands are *C*, *N* or σ-donors, and investigated their reactivity toward isocyanides.[13] In the present work, we have also obtained novel Pd–azido complexes containing the *C*,*N*-coordinated (*C*,*N*-**L**^{2}) or *C*-coordinated (*C*-**L**^{1} and *C*-**L**^{2}) pyridyl thiophene derivatives and observed their transformation to the corresponding carbodiimido complexes. The addition of elemental sulfur to the Pd complexes possessing *C*,*N*-donor ligands may be a useful synthetic strategy for the preparation of other interesting cyclometallated Pd compounds.

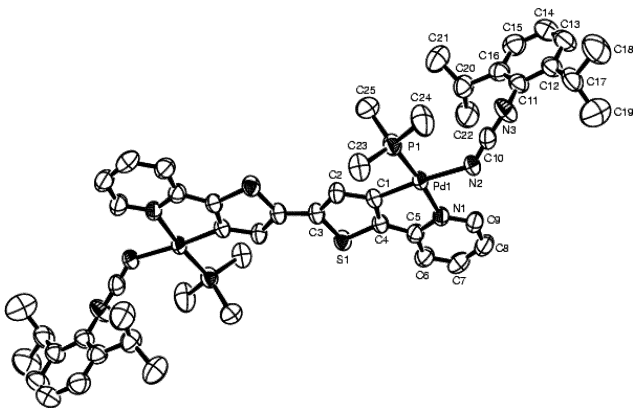
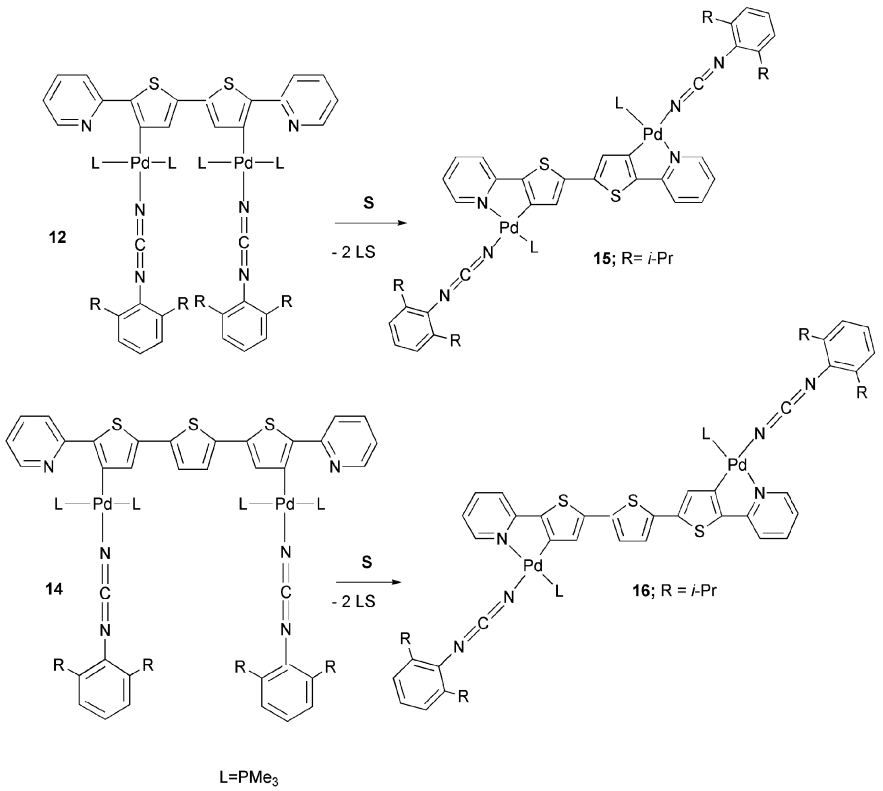


Fig. 2 ORTEP drawing of compound **15** with 50% probability thermal ellipsoids. Selected bond lengths (Å) and angles (°): Pd1–C1 1.995(4), Pd1–N2 2.078(3), Pd1–N1 2.122(3), Pd1–P1 2.224(1), N2–C10 1.155(5), N3–C10 1.253(6), N3–C11 1.408(6), C3–C3#1 1.450(7); C1–Pd1–N2 171.7(2), C1–Pd1–N1 81.4(1), N2–Pd1–N1 90.5(1), C1–Pd1–P1 93.1(1), N2–Pd1–P1 95.0(1), N1–Pd1–P1, 174.3(1), C10–N2–Pd1, 135.9(3), C10–N3–C11 128.6(4), N2–C10–N3 171.4(5).

Reactions toward organic isothiocyanates

We have previously reported on the dipolar cycloaddition of organic isothiocyanates (R–NCS) to a transition-metal–azido

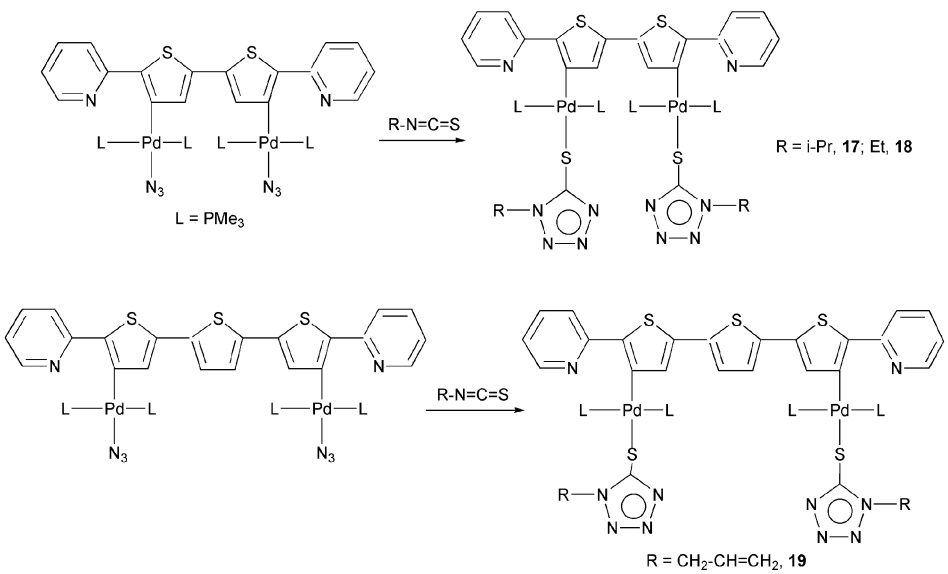


Scheme 7

bond to give *S*-coordinated tetrazole-thiolato compounds.[29] Consistent with our expectations, such reactivity was also observed in the reactions of R–NCS with the cyclometallated Pd–azido complexes containing thienylpyridine derivatives. Treating **5** and **8** with R–NCS (R = *i*-Pr, ethyl, allyl) produced tetrazole-thiolato Pd complexes (**17–19**), which were presumably formed by the dipolar cycloaddition of the isothiocyanates to the Pd–azido bond (Scheme 8).

Synthesis of dinuclear Pd–azido complexes containing linear thiophene derivatives

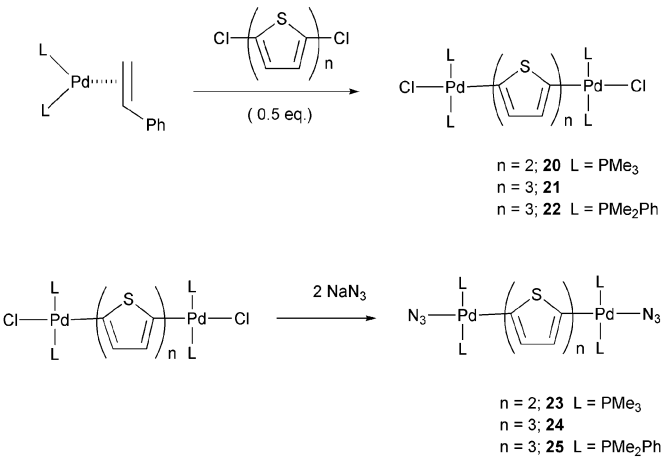
Dinuclear group 10 metal complexes containing a linear aromatic array are known and have been prepared by double oxidative addition of dihalo aromatic compounds to zerovalent metal complexes.[30–33] However, examples containing a heteroaromatic array such as thiophene are rare.[22–24] These complexes are useful



Scheme 8

for the construction of self-assembled macromolecules or as potential building blocks for electronic or optical molecules.[23] For a comparative study of cyclometallated and non-cyclometallated (σ-bonded) dinuclear Pd–azido complexes with linear thiophene derivatives, we decided to synthesize the dinuclear Pd–azido complexes containing these derivatives.

Reactions of $Pd(CH_2{=}CHPh)L_2$ (L = PMe_3 or PMe_2Ph),[34] which could be generated *in situ* from *trans*-$PdEt_2L_2$ and styrene, with a dihalo thiophene (5,5′-dichloro-2,2′-bithiophene (H_2bth) or 5,5″-dichloro-2,2′:5′,2″-terthiophene (H_2tth)) in a 2 : 1 molar ratio gave the double oxidative addition products $[L_2(Cl)Pd–X(or\ X')–Pd(Cl)L_2]$ (X = bth-C^5,$C^{5'}$ or X′ = tth-C^5,$C^{5''}$) (**20–22**) (Scheme 9). The subsequent treatment of complexes **20–22** with excess NaN_3 produced the corresponding Pd–azido complexes $[L_2(N_3)Pd–X(or\ X')–Pd(N_3)L_2]$ (**23–25**). In contrast, such reactivity was not observed for the bromo analogue $[L_2(Br)Pd–X–Pd(Br)L_2]$, probably because of the comparable nucleophilicity of the N_3 and Br groups. A singlet in the ^{31}P NMR data of the complexes supports the symmetric structure of complexes **23–25**. It is worth noting that these reactions do not proceed *via* cyclometallation that would result in the *S*,*C*-coordination of the thiophene moiety.

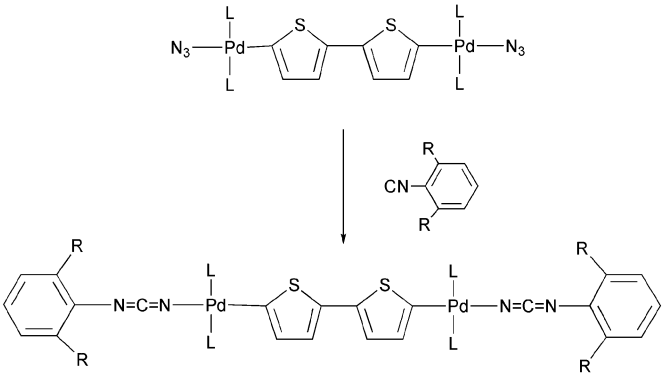


Scheme 9

Reactivity toward organic isocyanides and isothiocyanates

Sonogashira and co-workers reported that the thienylene-bridged Pt(II) halides reacted with organic isocyanides to give dinuclear Pt(II) complexes which result from the isocyanide insertion into Pt–C bonds.[22] We have also observed similar reactvities for the thienylene-bridged Pd(II) halides.[24] In this context, we have investigated the reactivity of the thienylene-bridged Pd–azido compounds toward organic isocyanides and isothiocyanates.

Treating bithienylene- or terthienylene-bridged Pd–azido complexes with aromatic isocyanides (CN–Ar) at room temperature produced π-bond-extended Pd complexes containing end-on carbodiimido groups (Scheme 10).



Scheme 10

The formation of products could be readily confirmed by the IR spectrum, which shows the disappearance of an asymmetric N_3 stretching band of the starting material and the appearance of a new strong N=C=N band at 2140 (for **26**) or 2131 cm^{-1} (for **27**) in the product. The spectral data indicate that the imido (C=N–R) compound, formed by the isocyanide insertion into the Pd–C (thiophene ring), does not exist. The molecular structure of a yellow crystalline complex **26** was determined by X-ray crystallography (Fig. 3). The molecule lies around an inversion center, which is at the midpoint of the C–C bond linking the two thiophene moieties. The coordination sphere of Pd can be described as square planar. Two sulfur atoms are oriented in a *trans* manner in the thiophene rings, which link two $[Pd(PMe_3)_2(NCN–C_6H_3\text{-}2,6\text{-}Me_2)]$ moieties to give a rod-shaped compound. The molecular plane, defined by Pd1, P1, P2, C1, and N1, is essentially planar with an average atomic displacement of 0.0297 Å, to which the thiophenyl ring is roughly perpendicular with a dihedral angle of 84.0 (1)°.

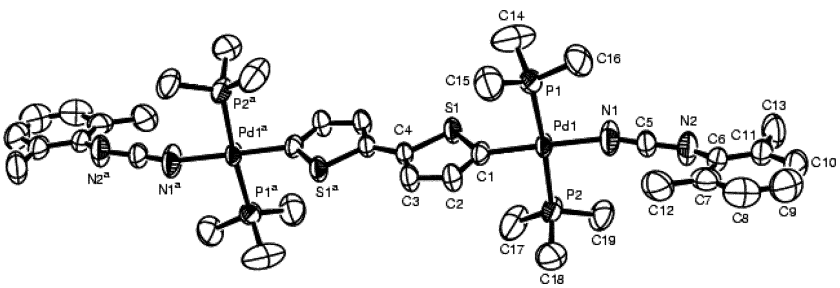
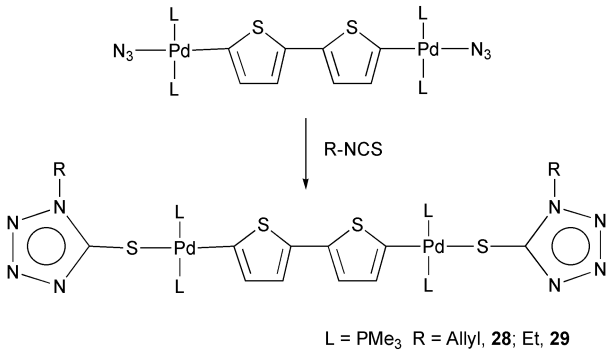


Fig. 3 ORTEP drawing of compound **26** with 50% probability thermal ellipsoids. Selected bond lengths (Å) and angles (°): atoms flagged with a superscript letter "a" are at equivalent position (1 − *x*, 1 − *y*, 1 − *z*): Pd1–C1 1.992(4), Pd1–N1 2.053(5), Pd1–P2 2.3111(15), Pd1–P1 2.3113(15), N1–C5 1.155(6), N2–C5 1.258(), N2–C6 1.387(7); N1–Pd1–P2 91.37(16), C1–Pd1–P1 88.50(14), N1–Pd1–P1 92.37(16), P2–Pd1–P1 175.11(6), N1–C5–N2 171.9(7).

The dinuclear Pd–azide compound **23** also underwent cycloaddition with R–NCS (R = ethyl, allyl) to give dinuclar Pd compounds with *S*-coordinated heterocycles as shown in Scheme 11.



Scheme 11

In summary, we prepared the novel dinuclear Pd(II)–azido complexes bridged by a pyridyl thiophene derivative (Y or Y′), $[(PR_3)_2(N_3)Pd–Y–Pd(N_3)(PR_3)_2]$ and $[(PR_3)(N_3)Pd–Y'–Pd(N_3)(PR_3)]$, in which Y or Y′ acts as either a σ-donor or a cyclometallated *C*,*N*-donor ligand. These complexes reacted with organic isocyanides (CN–Ar) and isothiocyanates (SCN–R) to give π-bond-extended Pd complexes, $[(PR_3)_2(N{=}C{=}N–Ar)Pd–Y–Pd(N{=}C{=}N–Ar)(PR_3)_2]$ containing end-on carbodiimido groups and dinuclear Pd complexes with *S*-coordinated heterocycle rings $[(PR_3)_2(SCN_4R)Pd–Y–Pd(SCN_4R)(PR_3)_2]$, respectively. Non-cyclometallated (σ-bond) forms are converted to the cyclometallated (*C*,*N*) forms and *vice versa* on addition of elemental sulfur or PR_3, which indicates the hemilabile character of the pyridyl thiophene ligands. Finally, we prepared dinuclear Pd–azido complexes with linear bithienyl (or terthienyl) ligands, which reacted with organic isocyanides or isothiocyanates to give rod-shaped dinuclear Pd compounds.

Experimental

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 National University carried out elemental analyses using CE instruments EA1110. IR spectra were recorded on a Perkin Elmer BX spectrophotometer. NMR (^1H, $^{13}C\{^1H\}$, and $^{31}P\{^1H\}$) spectra were obtained on a JEOL Lamda 300 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 National University. Complexes *trans*-$PdEt_2L_2$ (L = PMe_3 and PMe_2Ph) were prepared by the literature method.[34]

Preparations

Halo-α,α′-disubstituted derivatives of thiophene compounds. 5,5′-dibromo-2,2′-bithiophene, 5,5″-dibromo-2,2′:5′,2″-terthiophene, 5,5′-dichloro-2,2′-bithiophene, and 5,5″-dichloro-2,2′:5′,2″-terthiophene were prepared according to literature methods.[15–17]

Synthesis of pyridyl-α,α′-disubstituted derivatives of thiophene: 5,5′-di(2-pyridyl)-2,2′-bithiophene (H_2L^1) and 5,5″-di(2-pyridyl)-2,2′:5′,2″-terthiophene (H_2L^2). A mixture of 5,5′-dibromo-2,2′-bithiophene (0.609 g, 1.88 mmol), (2-pyridyl)-tri-*n*-butylstannane (1.73 g, 4.7 mmol), $Pd(PPh_3)_2Cl_2$ (0.106 g, 0.15 mmol), and LiCl (0.797 g, 18.80 mmol) in toluene (60 cm^3) was refluxed for 2 days. After cooling to room temperature, a saturated KF (20 cm^3) solution was added, and the mixture was stirred for 30 min. A large amount of CH_2Cl_2 was added to the mixture, and the solid residue was filtered off. 5% $NaHCO_3$ (150 cm^3) solution was added to the filtrate. Distilled water was added to the separated organic phase, and the organic phase was separated and dried over anhydrous Na_2SO_4. After the solvent was completely evaporated, the yellow solids were obtained. The crude product was purified by chromatography (silica gel, $CHCl_3$) to give a yellow solid product (0.374 g, 62%). H_2L^1: ESI-MS: m/z = 321.0603 (MH^+) for $C_{18}H_{12}N_2S_2$. M = 320.4334; δ_H ($CDCl_3$): 7.15 (2 H, dd, J = 1.7, 6.8 Hz), 7.26 (2 H, d, J = 3.8 Hz), 7.49 (2 H, d, J = 3.8 Hz), 7.63–7.72 (4 H, m), 8.57 (2 H, m).

H_2L^1 could also be prepared by treating pyridyl thiophene with *n*-BuLi and then $CuCl_2/O_2$.[9]

H_2L^2 was prepared in a similar manner (0.147 g, 30%). H_2L^2: (Found: C, 65.25; H, 3.82; N, 6.55%. ESI-MS: m/z = 403.1425 (MH^+). $C_{22}H_{14}N_2S_3$ (M_r = 402.5584) requires C, 65.64; H, 3.51; N, 6.96%); δ_H ($CDCl_3$): 7.15 (2 H, dd, J = 1.8, 5.0 Hz), 7.17 (2 H, S), 7.19 (2 H, d, J = 3.8 Hz), 7.49 (2 H, d, J = 4.0 Hz), 7.64–7.70 (4 H, m), 8.57 (2 H, m). ^{13}C NMR spectrum could not be obtained due to the compound's poor solubility.

Preparation of $[Pd_2(\mu\text{-}Cl)_2(C,N\text{-}L^1)]_2$ (1) and $[Pd_2(\mu\text{-}Cl)_2(C,N\text{-}L^2)]_2$ (2). Na_2PdCl_4 (0.300 g, 1.02 mmol) was dissolved in degassed ethanol (90 cm^3) and H_2L^1 (0.196 g, 0.61 mmol) was added to the resulting red solution. The yellow suspension slowly turned to a dark orange suspension. After stirring for 24 h, the dark orange solids were filtered out with a glass frit and washed with distilled water and ether. The product was dried under vacuum to give a dark red solid, complex **1** (0.498 g, 81%). Complex **1**: (Found: C, 36.34; H, 1.92; N, 4.78%. ESI-MS: m/z = 1205.6500 (MH^+). $C_{36}H_{20}Cl_4N_4Pd_4S_4$ (M_r = 1204.3284) requires: C, 35.90; H, 1.67; N, 4.65%); NMR spectra could not be obtained owing to its poor solubility.

Complex **2** was prepared in a similar way (82%). Complex **2**: ESI-MS: m/z = 1369.9897 (MH^+). $C_{44}H_{24}Cl_4N_4Pd_4S_6$ (M_r = 1368.5751); δ_H (DMF-d^7): 7.07 (4 H, dd, J = 1.1, 5.0 Hz), 7.21 (4 H, s), 7.21(4 H, d, J = 3.8 Hz), 7.60 (4 H, d, J = 3.8 Hz), 7.64 (4 H, dd, J = 1.8, 7.5 Hz), 8.33–8.35 (4 H, m). ^{13}C NMR spectrum could not be obtained due to its poor solubility.

Cleavage of complexes 1 and 2 by tertiary phosphines (PMe_3, PEt_3). To a Schlenk flask containing complex **1** (0.202 g, 0.17 mmol) were added CH_2Cl_2 (30 cm^3) and PMe_3 (0.14 cm^3, 1.36 mmol) in that order. The red suspension turned to a yellow homogeneous solution. After stirring for 2 h, the mixture was evaporated to give orange solids, which were recrystallized from CH_2Cl_2–hexane to give orange crystals of $[(PMe_3)_2(Cl)Pd–Y–Pd(Cl)(PMe_3)_2]$ (Y = L^1) (**3**, 0.200 g, 66%). Complex **3**: (Found: C, 40.18; H, 5.33; N, 2.94. $C_{30}H_{46}Cl_2N_2P_4Pd_2S_2$ requires: C, 39.75; H, 5.11; N, 3.09%).

Complexes $[(PEt_3)_2(Cl)Pd–Y–Pd(Cl)(PEt_3)_2]$ (Y = **L**[1]) (**4**, 39%) and $[(PMe_3)_2(Cl)Pd–Y–Pd(Cl)(PMe_3)_2]$ (Y = **L**[2]) (**7**, 47%) were prepared in a similar way.

The orange complex $[(PMe_3)(Cl)Pd–Y'–Pd(Cl)(PMe_3)]$ (Y′ = *C*,*N*-**L**[2]) (**9**, 42%) was prepared from complex **2** and PMe_3 in the mole ratio of 1 : 4.

Complexes **3**, **4**, **7**, and **9** were further treated with NaN_3 to prepare the corresponding azido complexes **5**, **6**, **8**, and **10** (see below).

$[(PR_3)_2(N_3)Pd–Y–Pd(N_3)(PR_3)_2]$ (Y = L[1], L[2]; R = Me, Et) (5, 6, 8) and $[(PR_3)(N_3)Pd–Y'–Pd(N_3)(PR_3)]$ (Y′ = *C*,*N*–L[2], R = Me) (10). To a Schlenk flask containing **3** (0.216 g, 0.24 mmol) were added CH_2Cl_2 (12 cm^3) and NaN_3 solution (0.0618 g, 0.96 mmol) dissolved in H_2O (2 cm^3) in that order. The initial orange solution turned to a yellow suspension. After stirring for 18 h at room temperature, the solvent was completely removed under vacuum, and the remaining solid was extracted with CH_2Cl_2. Recrystallization from CH_2Cl_2–hexane gave yellow crystals of $[(PMe_3)_2(N_3)Pd–Y–Pd(N_3)(PMe_3)_2]$ (Y = **L**[1]) (**5**, 0.189 g, 86%). Complex **5**: (Found: C, 38.92; H, 5.26; N, 12.30. $C_{30}H_{46}N_8P_4Pd_2S_2$ requires C, 39.18; H, 5.04; N, 12.18%); ν_{max}/cm^{-1} (N_3): 2036 (vs).

Complexes $[(PEt_3)_2(N_3)Pd–Y–Pd(N_3)(PEt_3)_2]$ (Y = **L**[1]) (**6**, 67%), $[(PMe_3)_2(N_3)Pd–Y–Pd(N_3)(PMe_3)_2]$ (Y = **L**[2]) (**8**, 76%), and $[(PMe_3)(N_3)Pd–Y'–Pd(N_3)(PMe_3)]$ (Y′ = *C*,*N*-**L**[2]) (**10**, 70%) were prepared in a similar manner. Complex **6**: (Found: C, 46.80; H, 6.72; N, 10.67. $C_{42}H_{70}N_8P_4Pd_2S_2$ requires C, 46.37; H, 6.49; N, 10.30%); ν_{max}/cm^{-1} (N_3): 2037 (vs). Complex **8**: (Found: C, 40.99; H, 4.88; N, 10.83. $C_{34}H_{48}N_8P_4Pd_2S_3$ requires C, 40.77; H, 4.83; N, 11.19%); ν_{max}/cm^{-1} (N_3): 2036 (vs). Complex **10**: (Found: C, 39.72; H, 3.67; N, 12.32. $C_{28}H_{30}N_8P_2Pd_2S_3$ requires C, 39.58; H, 3.56; N, 13.19%); ν_{max}/cm^{-1} (N_3): 2037 (vs).

Reaction of $[(PMe_3)_2(N_3)Pd–Y–Pd(N_3)(PMe_3)_2]$ (Y = L[1] or L[2]) (5 and 8) with CN–Ar (Ar = C_6H_3-2,6-Me_2 or C_6H_3-2,6-*i*-Pr_2). CH_2Cl_2 (6 cm^3) and 2,6-dimethylphenyl isocyanide (0.022 g, 0.17 mmol) were added sequentially to a Schlenk flask containing **5** (0.070 g, 0.076 mmol). The initial yellow solution slowly turned to a yellowish green solution. After stirring for 4 h at room temperature, the solvent was completely removed, and then the resulting residue was solidified with hexane. The solids were filtered and washed with hexanes to give crude solids, which were recrystallized from CH_2Cl_2–hexane to give dark yellow crystals of $[(PMe_3)_2(N{=}C{=}N–Ar)Pd–Y–Pd(N{=}C{=}N–Ar)(PMe_3)_2]$ (Y = **L**[1], Ar = C_6H_3-2,6-Me_2) (**11**, 0.067 g, 77%). Complex **11**: (Found: C, 50.93; H, 5.86; N, 7.04. $C_{48}H_{64}N_6P_4Pd_2S_2$ requires C, 51.20; H, 5.73; N, 7.46%); ν_{max}/cm^{-1} (N=C=N): 2147 (vs).

Complexes $[(PMe_3)_2(N{=}C{=}N–Ar)Pd–Y–Pd(N{=}C{=}N–Ar)(PMe_3)_2]$ (Y = **L**[1], Ar = C_6H_3-2,6-*i*-Pr_2) (**12**, 75%), $[(PMe_3)_2(N{=}C{=}N–Ar)Pd–Y–Pd(N{=}C{=}N–Ar)(PMe_3)_2]$ (Y = **L**[2], Ar = C_6H_3-2,6-Me_2) (**13**, 95%) and $[(PMe_3)_2(N{=}C{=}N–Ar)Pd–Y–Pd(N{=}C{=}N–Ar)(PMe_3)_2]$ (Y = **L**[2], Ar = C_6H_3-2,6-*i*-Pr_2) (**14**, 80%) were prepared in a similar way. Complex **12**: (Found: C, 54.69; H, 6.82; N, 6.61. $C_{56}H_{80}N_6P_4Pd_2S_2$ requires C, 54.32; H, 6.51; N, 6.79%); ν_{max}/cm^{-1} (N=C=N): 2129 (vs). Complex **13**; (Found: C, 51.34; H, 5.62; N, 6.71. $C_{52}H_{66}N_6P_4Pd_2S_3$ requires C, 51.70; H, 5.51; N, 6.96%); ν_{max}/cm^{-1} (N=C=N): 2137 (vs). Complex **14**: (Found: C, 54.17; H, 6.41; N, 6.05. $C_{60}H_{82}N_6P_4Pd_2S_3$ requires C, 54.58; H, 6.26; N, 6.37%); ν_{max}/cm^{-1} (N=C=N): 2115 (vs).

Reaction of $[(PMe_3)_2(N{=}C{=}N–Ar)Pd–Y–Pd(N{=}C{=}N–Ar)(PMe_3)_2]$ (Y = L[1] or L[2], Ar = C_6H_3-2,6-*i*-Pr_2) with elemental sulfur. CH_2Cl_2 (5 cm^3) and elemental sulfur (0.005 g, 0.15 mmol) were added sequentially to a Schlenk flask containing **12** (0.074 g, 0.060 mmol). The initial yellow solution slowly turned to an orange suspension. After stirring for 12 h at room temperature, the solvent was completely evaporated, and then the resulting residue was solidified with diethyl ether. The solids were filtered off and washed with hexanes to give crude solids. Recrystallization from CH_2Cl_2–ether gave orange crystals of $[(PMe_3)(N{=}C{=}N–Ar)Pd–Y'–Pd(N{=}C{=}N–Ar)(PMe_3)]$ (Y′ = *C*,*N*-**L**[1], Ar=C_6H_3-2,6-*i*-Pr_2) (**15**, 0.061 g, 93%). Complex **15** (Found: C, 54.89; H, 5.82; N, 7.60. $C_{50}H_{62}N_6P_2Pd_2S_2$ requires C, 55.30; H, 5.75; N, 7.74%); ν_{max}/cm^{-1} (N=C=N): 2098 (vs).

Complex $[(PMe_3)(N{=}C{=}N–Ar)Pd–Y'–Pd(N{=}C{=}N–Ar)(PMe_3)]$ (Y′ = *C*,*N*-**L**[2], Ar=C_6H_3-2,6-*i*-Pr_2) (**16**, 94%) was prepared in a similar way. Complex **16**: (Found: C, 55.18; H, 5.34; N, 7.11. $C_{54}H_{64}N_6P_2Pd_2S_3$ requires C, 55.52; H, 5.52; N, 7.19%); ν_{max}/cm^{-1} (N=C=N): 2138 (vs).

Reactions of $[(PMe_3)_2(N_3)Pd–Y–Pd(N_3)(PMe_3)_2]$ (Y=L[1] or L[2]) (5 and 8) with R–N=C=S (R = *i*-Pr, Et or allyl). To a Schlenk flask containing **5** (0.081 g, 0.088 mmol) were added CH_2Cl_2 (5 cm^3) and isopropyl isothiocyanate (0.031 cm^3, 0.35 mmol) in that order. After stirring for 20 h at room temperature, the solvent was completely removed, and then the resulting residue was solidified with hexane. The solids were filtered off and washed with hexane (3 cm^3 × 2) to give crude solids. Recrystallization from CH_2Cl_2–hexane gave yellow solids of $[(PMe_3)_2(SCN_4\text{-}i\text{-}Pr)Pd–Y–Pd(SCN_4\text{-}i\text{-}Pr)(PMe_3)_2]$ (Y = **L**[1]) (**17**, 0.090 g, 90%). Complex **17**: (Found: C, 40.99; H, 5.61; N, 12.24. $C_{38}H_{60}N_{10}P_4Pd_2S_4$ requires C, 40.68; H, 5.39; N, 12.48%).

Complexes $[(PMe_3)_2(SCN_4–Et)Pd–Y–Pd(SCN_4–Et)(PMe_3)_2]$ (Y = **L**[1]) (**18**, 90%) and $[(PMe_3)_2(SCN_4–R)Pd–Y–Pd(SCN_4–R)(PMe_3)_2]$ (Y = **L**[2], R = allyl) (**19**, 70%) were prepared in a similar way. Complex **18**: (Found: C, 39.68; H, 5.23; N, 12.25. $C_{36}H_{56}N_{10}P_4Pd_2S_4$ requires C, 39.53; H, 5.16; N, 12.80%). Complex **19**: (Found: C, 41.68; H, 4.92; N, 11.17. $C_{42}H_{58}N_{10}P_4Pd_2S_5$ requires C, 42.04; H, 4.87; N, 11.67%).

Preperation of $[(PMe_3)_2(Cl)Pd–X–Pd(Cl)(PMe_3)_2]$ (X = bth-*C*[5],*C*[5″]) (H_2bth = 2,2′-bithiophene) (20) and $[(PR_3)_2(Cl)Pd–X'–Pd(Cl)(PR_3)_2]$ (X′ = tth-*C*[5],*C*[5′]) (H_2tth = 2,2′:5′,2′-terthiophene) (R = Me (21), Me_2Ph (22)). To a Schlenk flask containing *trans*-$PdEt_2(PMe_3)_2$ (0.336 g, 1.06 mmol) at 0 were added styrene (0.441 g, 4.24 mmol) and THF (3 cm^3) sequentially. The mixture was heated at 55 °C for 30 min to give a yellow solution. At room temperature 5,5′-dichloro-2,2′-bithiophene (0.122 g, 0.52 mmol) was added to the mixture, and the yellow solution turned to a pale yellow suspension. After stirring for 2 h at room temperature, the solvent was completely removed under vacuum, and then the resulting residue was solidified with hexane. The solids were filtered and washed with hexane (3 cm^3 × 2) to give crude solids. Recrystallization from CH_2Cl_2–hexane gave gray solids of $[(PMe_3)_2(Cl)Pd–X–Pd(Cl)(PMe_3)_2]$ (X = bth-*C*[5],*C*[5′]) (**20**, 0.380 g, 80%). Complex **20**: (Found: C, 32.06; H, 5.56. $C_{20}H_{40}Cl_2P_4Pd_2S_2$ requires C, 31.93; H, 5.36%).

Complexes $[(PMe_3)_2(Cl)Pd–X'–Pd(Cl)(PMe_3)_2]$ (X′ = tth-*C*[5],*C*[5″]) (**21**, 45%) and $[(PMe_2Ph)_2(Cl)Pd–X'–Pd(Cl)(PMe_2Ph)_2]$ (X′ = tth-*C*[5],*C*[5″]) (**22**, 40%) were prepared in a similar way.

Complex **21**: (Found: C, 34.83; H, 5.21. $C_{24}H_{42}Cl_2P_4Pd_2S_3$ requires C, 34.55; H, 5.07%). Complex **22**: (Found: C, 48.78; H, 4.53. $C_{44}H_{50}Cl_2P_4Pd_2S_3$ requires C, 48.81; H, 4.65%).

Complexes **20–22** were treated further with NaN_3 to produce the corresponding azido complexes **23–25** (see below).

Preparation of $[(PMe_3)_2(N_3)Pd–X–Pd(N_3)(PMe_3)_2]$ (X = bth-$C^5,C^{5\prime}$; H_2bth = 2,2′-bithiophene) (23) and $[(PR_3)_2(N_3)Pd–X'–Pd(N_3)(PR_3)_2]$ (X′ = tth-$C^5,C^{5\prime\prime}$; H_2tth = 2,2′:5′,2″-terthiophene; R = Me (24), Me_2Ph (25)). To a Schlenk flask containing **20** (0.281 g, 0.37 mmol) were added CH_2Cl_2 (15 cm^3) and NaN_3 solution (0.073 g, 1.11 mmol) dissolved in H_2O (2 cm^3) in that order. The initial yellow solution turned to a yellow suspension. After stirring for 11 h at room temperature, the solvent was completely evaporated to give pale yellow solids, which were extracted with CH_2Cl_2. Recrystallization from CH_2Cl_2–hexane gave pale yellow solids of complex **23** (0.221 g, 77%). Complex **23**: (Found: C, 31.36; H, 5.45, N, 10.37. $C_{20}H_{40}N_6P_4Pd_2S_2$ requires C, 31.38; H, 5.27; N, 10.98%); ν_{max}/cm^{-1} (N_3): 2032 (vs).

Complexes $[(PMe_3)_2(N_3)Pd–X'–Pd(N_3)(PMe_3)_2]$ (X′ = tth-$C^5,C^{5\prime\prime}$) (**24**, 73%) and $[(PMe_2Ph)_2(N_3)Pd–X'–Pd(N_3)(PMe_2Ph)_2]$ (X′ = tth-$C^5,C^{5\prime\prime}$) (**25**, 98%) were prepared in a similar way. Complex **24**: (Found: C, 34.21; H, 5.32; N, 9.63. $C_{24}H_{42}N_6P_4Pd_2S_3$ requires C, 34.01; H, 4.99; N, 9.92%); ν_{max}/cm^{-1} (N_3): 2036 (vs). Complex **25**: (Found: C, 48.38; H, 4.85; N, 7.26. $C_{44}H_{50}N_6P_4Pd_2S_3$ requires C, 48.23; H, 4.60; N, 7.67); ν_{max}/cm^{-1} (N_3): 2037.

Reaction of $[(PMe_3)_2(N_3)Pd–X–Pd(N_3)(PMe_3)_2]$ (X = bth-$C^5,C^{5\prime}$) (23) with CN–Ar (Ar = C_6H_3-2,6-Me_2 or C_6H_3-2,6-*i*-Pr_2). To a Schlenk flask containing **23** (0.094 g, 0.12 mmol) were added sequentially CH_2Cl_2 (10 ml) and 2,6-dimethylphenyl isocyanide (0.034 g, 0.25 mmol). After the yellow solution was stirred for 4 h at room temperature, the solvent was removed, and then the resulting residue was solidified with hexane. The solids were filtered off and washed with hexanes to give crude solids. Recrystallization from CH_2Cl_2–hexane gave yellow crystals of $[(PMe_3)_2(N{=}C{=}N–Ar)Pd–X–Pd(N{=}C{=}N–Ar)(PMe_3)_2]$ (X = bth-$C^5,C^{5\prime}$; Ar=C_6H_3-2,6-Me_2) (**26**, 0.087 g, 73%). Complex **26**: (Found: C, 42.39; H, 5.73; N, 4.70. $C_{40}H_{62}N_4Cl_4P_4Pd_2S_2$ requires C, 42.08; H, 5.47; N, 4.91%); ν_{max}/cm^{-1} (N=C=N): 2140 (vs).

Complex $[(PMe_3)_2(N{=}C{=}N–Ar)Pd–X–Pd(N{=}C{=}N–Ar)(PMe_3)_2]$ (X = bth-$C^5,C^{5\prime}$; Ar=C_6H_3-2,6-*i*-Pr_2) (**27**, 48%) was prepared in a similar way. Complex **27**: (Found: C, 50.67; H, 6.64; N, 5.24. $C_{46}H_{74}N_4P_4Pd_2S_2$ requires C, 50.97; H, 6.88; N, 5.17%); ν_{max}/cm^{-1} (N=C=N): 2131 (vs).

Reaction of $[(PMe_3)_2(N_3)Pd–X–Pd(N_3)(PMe_3)_2]$ (X = bth-$C^5,C^{5\prime}$) (23) with R–N=C=S (R = allyl or Et). To a Schlenk flask containing **23** (0.101 g, 0.13 mmol) were added CH_2Cl_2 (8 ml) and allyl isothiocyanate (0.027 cm^3, 0.27 mmol) in that order. After stirring for 14 h at room temperature, the solvent was removed, and the resulting residue was solidified with hexane. The solids were filtered and washed with hexane (3 cm^3 × 2) to give crude solids. Recrystallization from CH_2Cl_2–hexane gave yellow solids of $[(PMe_3)_2(SCN_4–R)Pd–X–Pd(SCN_4–R)(PMe_3)_2]$ (X = bth-$C^5,C^{5\prime}$; R = allyl) (**28**, 0.079 g, 62%). Complex **28**: (Found: C, 35.03; H, 5.10; N, 11.46. $C_{28}H_{50}N_8P_4Pd_2S_4$ requires C, 34.89; H, 5.23; N, 11.63%).

Complex $[(PMe_3)_2(SCN_4–Et)Pd–X–Pd(SCN_4–Et)(PMe_3)_2]$ (X = bth-$C^5,C^{5\prime}$) (**29**, 88%) was prepared in a similar way. Complex **29**: (Found: C, 33.03; H, 5.11; N, 11.54. $C_{26}H_{50}N_8P_4Pd_2S_4$ requires C, 33.23; H, 5.36; N, 11.92%).

X-Ray structure determination

X-Ray data of complexes **5**, **15**, and **26** were collected with a Siemens P4 diffractometer equipped with a Mo X-ray tube. Intensity data were corrected for absorption with Ψ-scan data. All calculations were carried out with the SHELX-97 programs.[35] All the structures were solved by direct methods. All hydrogen atoms were generated in ideal positions and refined in a riding model and all non-hydrogen atoms were refined anisotropically, except the carbon atoms (C13–C15) in one phosphine ligand of complex **5**, which were extremely disordered and therefore refined isotropically. Details of crystal data, intensity collection, and refinement details are given in Table 1.

CCDC reference numbers 628104–628106. For crystallographic data in CIF or other electronic format see DOI: 10.1039/b616901e

Acknowledgements

This work was supported by Grant R05-2004-000-10149-0 from the Korea Research Foundation and partly from the NURI-2004-0244 and 2006-006 of Gangwon Advanced Materials

References

1 *Hand book of Oligo- and Polythiophenes*, ed. D. Fichou, WIELY-VCH, Weinheim, 1999; D. Fichou, *J. Mater. Chem.*, 2000, **3**, 571.
2 P. Bäuerle, Oligothiophenes, in *Electronic Materials: The Oligomer Approach*, ed. K. Mullen and G. Wegner, Wiley-VCH, Weinheim, 1998, pp. 105–197.
3 J. Roncali, *Chem. Rev.*, 1992, **92**, 711.
4 J. M. Tour, *Acc. Chem. Res.*, 2000, **33**, 791.
5 M. Melucci, G. Barbarella, M. Zambianchi, P. Di Pietro and A. Bongini, *J. Org. Chem.*, 2004, **69**, 4821.
6 R. D. Myrex, G. M. Gray, A. G. VanEngen Spivey and C. M. Lawson, *Organometallics*, 2006, **25**, 5045.
7 W. M. Albers, G. W. Canters and J. Reedijk, *Tetrahedron*, 1995, **51**, 3895.
8 L. Trouillet, A. D. Nicola and S. Guillerz, *Chem. Mater.*, 2000, **12**, 1611.
9 E. C. Constable and Y. A. Leese, *J. Organomet. Chem.*, 1989, **363**, 419; E. C. Constable and L. R. Sousa, *J. Organomet. Chem.*, 1992, **427**, 125; E. C. Constable, R. P. G. Henney, P. R. Raithby and L. R. Sousa, *J. Chem. Soc., Dalton Trans.*, 1992, 2251.
10 Y. Fuchida, H. Idea, S. Wada, S. Kameda and M. Mikuriya, *J. Chem. Soc., Dalton Trans.*, 1999, 4431.
11 T. J. Giordano and P. G. Rasmussen, *Inorg. Chem.*, 1975, **14**, 1628; T. J. Giordano, W. M. Butler and P. G. Rasmussen, *Inorg. Chem.*, 1978, **17**, 1917.
12 M. V. Kulikova, P.-I. Kvam, J. Songstad and K. P. Balashev, *Russ. J. Gen. Chem.*, 1997, **67**, 967; K. P. Balashev, M. V. Puzyk, O. P. Kanhukaeva, N. V. Antonov and A. Y. Ivanov, *Russ. J. Gen. Chem.*, 1998, **68**, 1670.
13 Y.-J. Kim, X. Chang, J.-T. Han, M. S. Lim and S. W. Lee, *Dalton Trans.*, 2004, 3699.
14 P. Jolliet, M. Gianini, A. von Zelewsky, G. Bernardinelli and H. Stoeckli-Evans, *Inorg. Chem.*, 1996, **35**, 4883.
15 G. Zotti, G. Schiavon, A. Berlin and G. Pagani, *Chem. Mater.*, 1993, **5**, 430.
16 J. H. Uhlenbroek and J. D. Bijloo, *Recl. Trav. Chim. Pays-Bas*, 1960, **79**, 1181.
17 M. S. Mubarak, *J. Electrochem. Soc.*, 2002, **149**, E222.
18 D. J. Cárdenas and J.-P. Sauvage, *Synlett*, 1996, 916; D. J. Cárdenas, A. M. Echavarren and M. C. R. de Arellano, *Organometallics*, 1999, **18**, 3337.
19 M. Fujita, H. Oka and K. Ogura, *Tetrahedron Lett.*, 1995, **36**, 5247.
20 B. O. Patrick, O. Clot, M. O. Wolf and B. O. Patrick, *J. Am. Chem. Soc.*, 2000, **122**, 10456; O. Clot, M. O. Wolf and B. O. Patrick, *J. Am.*

Chem. Soc., 2001, **123**, 9963; O. Clot, M. O. Wolf, G. P. A. Yap and B. O. Patrick, *J. Chem. Soc., Dalton Trans.*, 2000, 2729.
21 D. A. Weinberger, T. B. Higgins, C. A. Mirkin, L. M. Liable-Sands and A. L. Rheingold, *Angew. Chem., Int. Ed.*, 1999, **38**, 2565.
22 S. Kotani, K. Shiina and K. Sonogashira, *J. Organomet. Chem.*, 1992, **429**, 403; K. Onitsuka, K. Murakami, K. Matsukawa, K. Sonogashira, T. Adachi and T. Yoshida, *J. Organomet. Chem.*, 1995, **490**, 117.
23 Y. Xie, B.-M. Wu, F. Xue, S.-C. Ng, T. C. W. Mak and T. S. Andy Hor, *Organometallics*, 1998, **17**, 3988; P. Teo and T. S. Andy Hor, *Inorg. Chem.*, 2003, **42**, 7290.
24 Y.-J. Kim, S.-C. Lee, M. H. Cho and S. W. Lee, *J. Organomet. Chem.*, 1999, **588**, 268.
25 R. D. Myrex, C. S. Colbert and G. M. Gray, *Organometallics*, 2004, **23**, 409.
26 T. L. Stott, M. O. Wolf and A. Lam, *Dalton Trans.*, 2005, 652.
27 M. Landman, M. van Staden, H. Görls and S. Lotz, *Inorg. Chim. Acta*, 2005, **358**, 2602.
28 Y.-J. Kim, Y.-S. Kwak and S. W. Lee, *J. Organomet. Chem.*, 2000, **603**, 152; Y.-J. Kim, Y.-S. Joo, J.-T. Han, W. S. Han and S. W. Lee, *J. Chem. Soc., Dalton Trans.*, 2002, 3611; Y.-J. Kim, Y.-S. Kwak, Y.-S. Joo and S. W. Lee, *J. Chem. Soc., Dalton Trans.*, 2002, 144.
29 Y.-J. Kim, J.-T. Han, S. Kang, W. S. Han and S. W. Lee, *Dalton Trans.*, 2003, 3357.
30 J. Manna, J. A. Whiteford and P. J. Stang, *J. Am. Chem. Soc.*, 1996, **118**, 8731; J. Manna, C. J. Kuehl, J. A. Whiteford and P. J. Stang, *Organometallics*, 1997, **16**, 1897.
31 M. G. Crisp, S. M. Pyke and L. M. Rendina, *J. Organomet. Chem.*, 2000, **607**, 222.
32 H. B. Lee and P. R. Sharp, *Organometallics*, 2005, **24**, 4875.
33 Y.-J. Kim, R. Sato, T. Maruyama, K. Osakada and T. Yamamoto, *J. Chem. Soc., Dalton Trans.*, 1994, 943; Y.-J. Kim, S.-W. Song, S.-C. Lee, S. W. Lee, K. Osakada and T. Yamamoto, *J. Chem. Soc., Dalton Trans.*, 1998, 1775.
34 Y.-J. Kim, K. Osakada, A. Takenaka and A. Yamamoto, *J. Am. Chem. Soc.*, 1990, **112**, 1096.
35 G. M. Sheldrick, *SHELX-97*, University of Gőttingen: Germany, 1997.
36 L. J. Farrugia, *ORTEP-3 for Windows*, University of Glasgow, 1997.