

Synthesis and reactions of mono- and dipalladium complexes containing 2-thienyl and 2,5 (or 2,5') -bridged thienylene (or dithienylene) ligand: new dipalladium complex formation connected by thioketene part via C–S bond cleavage of thiophene

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Abstract

Oxidative addition reactions of 2-iodothiophene, 2-bromothiophene, and 2,5-dibromothiophene with equimolar Pd(CH₂=CHPh)L₂ (L = PMe₃ and PEt₃) at room temperature in THF produce mononuclear σ-thienyl palladium(II) complexes *trans*-(2-C₄H₃S)PdX(PMe₃)₂ (X = I, **1**; X = Br, **2**) and *trans*-(5-Br(2-C₄H₂S))PdBrL₂ (L = PMe₃, **3**; L = PEt₃, **4**). Reactions using 2,5-dibromothiophene, 2,5-diiodothiophene, and 5,5-dibromo-2,2'-bithiophene under 2:1 molar ratio in THF give thienylene (or dithienylene) bridged dipalladium complexes *trans,trans*-L₂XPd(μ-2,5-C₄H₂S)PdXL₂ (L = PMe₃; X = I, **5**; Br, **6**; L = PEt₃; X = Br, **7**) and *trans,trans*-(Me₃P)₂BrPd(μ-2,5'-C₄H₂S-C₄H₂S)PdBr(PMe₃)₂ (**8**), in high yields. However, the equimolar reaction of 2,5-dibromothiophene with the Pd(0) complex results in formation of a dinuclear complex *cis,trans*-[(Me₃P)₂Pd(η²-S=C-CH-CH=CBr)PdBr(PMe₃)₂] (**9**), in 56% yield via C–S bond cleavage of the thiophene ring. All the complexes provided satisfactory IR and NMR (¹H, ³¹P{¹H}, and ¹³C{¹H}) spectra as well as elemental analyses. Molecular structures of **1**, **7**, and **9** were confirmed by X-ray crystallography. Treatment of **5** and **7** with CO (1 atm) results in CO insertion into one of the Pd–C bonds to give *trans,trans*-(Me₃P)₂IPdC(O)C₄H₂SPdI(PMe₃)₂ (**10**) in 94% and *trans,trans*-(Et₃P)₂BrPdC(O)C₄H₂SPdBr(PEt₃)₂ (**11**) in 23%, respectively. Also, treatments of **5** with *n*-butyl, *tert*-butyl, and cyclohexyl isocyanides result in its insertion into both of the Pd–C bonds to form iminoacyl Pd complexes *trans,trans*-(Me₃P)₂IPd–C(=N–R)C₄H₂SC(=N–R)–PdI(PMe₃)₂ (R = *n*-Bu, **12**; *t*-Bu, **13**; cyclohexyl, **14**), respectively. © 1999 Elsevier Science S.A. All rights reserved.

Keywords: Palladium; Thienyl; Thienylene bridged; Dipalladium complex; Thioketene

1. Introduction

Thienyl group bonded Group 10 metal complexes have been studied as a model for elucidation of the d_π–p_π interactions between transition metal and π-conjugated groups and as the catalytic intermediates for regioselective reduction and/or for conducting polymerization using these metals [1–3]. Several thienyl or thienylene bridged complexes of these metals were prepared from the reactions of metal halide complexes with 2-trimethylstannylthiophene [4] or 2,5-

bis(trimethylstannyl)thiophene [1], thienylmercury chloride [5], and thienyllithium compounds [1,6] and also from the oxidative addition reactions of halothiophene compounds with Pd(PPh₃)₄ [2,5,7]. In particular, the oxidative addition of dihalothiophenes to zerovalent complexes of Group 10 metals is expected to provide a convenient synthetic route to the dinuclear metal complexes with a bridging thienylene ligand. We have recently synthesized a series of bridging arylene or diarylene dinickel(II) and dipalladium(II) complexes [8] by the oxidative addition reactions of dihaloarene with Ni(0) and Pd(0) compounds. The produced complexes possess a unique structure containing the π-conjugated ligand between two metal centers and show unique

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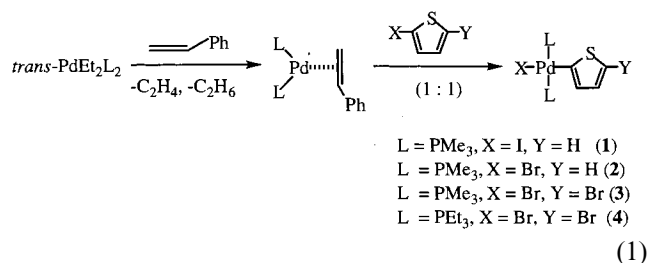
chemical properties such as the insertion of small molecules into the metal–carbon bond. This allows us to study the structure and chemical properties of other electron delocalized compounds such as thiophenes.

In this work we have focused on the preparation of dinuclear palladium complexes with a bridging thienylene and dithienylene ligand including thienyl monopalladium complexes via oxidative addition of dihalothiophene and dihalobithiophene compounds and their reaction with isocyanides and CO to result in their insertion into Pd–C bonds.

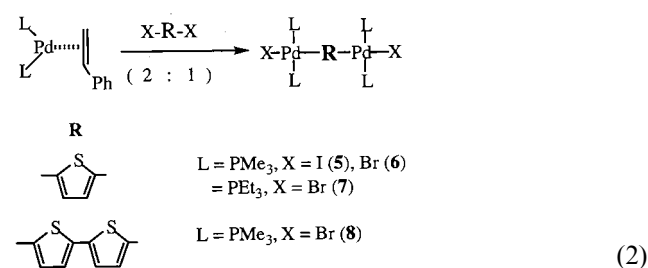
2. Results and discussion

2.1. Preparation and structure of thienyl palladium(II) or bridging thienylene dipalladium(II) complexes

Reactions of $\text{Pd}(\text{CH}_2=\text{CHPh})\text{L}_2$ ($\text{L} = \text{PMe}_3, \text{PEt}_3$) [9], which are generated in situ from the reaction of *trans*- PdEt_2L_2 with styrene, with equimolar 2-iodothiophene, 2-bromothiophene, and 2,5-dibromothiophene in THF at room temperature give mononuclear σ -thienyl palladium(II) complexes ($2\text{-C}_4\text{H}_3\text{S}$) $\text{PdX}(\text{PMe}_3)_2$ ($\text{X} = \text{I}$, **1**; Br , **2**) and $5\text{-Br}(2\text{-C}_4\text{H}_2\text{S})\text{PdBrL}_2$ ($\text{L} = \text{PMe}_3$, **3**), PEt_3 (**4**) in high yields, respectively, as shown in Eq. (1). These reactions can also be carried out in a hexane media.



Similar reactions of 2,5-dibromothiophene, 2,5-diiodothiophene, and 5,5'-dibromo-2,2'-bithiophene with $\text{Pd}(\text{CH}_2=\text{CHPh})\text{L}_2$ in a 1:2 molar ratio in THF or toluene lead to oxidative addition of C–X bonds to two Pd centers giving dinuclear palladium complexes with bridging thienylene or dithienylene ligand, $\text{L}_2\text{XPd}(\mu\text{-}2,5\text{-C}_4\text{H}_2\text{S})\text{PdXL}_2$ ($\text{L} = \text{PMe}_3$; $\text{X} = \text{I}$, **5**; Br , **6**; $\text{L} = \text{PEt}_3$; $\text{X} = \text{Br}$, **7**) and *trans,trans*- $(\text{Me}_3\text{P})_2\text{BrPd}(\mu\text{-}2,5,5'\text{-C}_4\text{H}_2\text{S}\text{-C}_4\text{H}_2\text{S})\text{PdBr}(\text{PMe}_3)_2$ (**8**), in moderately good yields, respectively, as shown in Eq. (2).



Reaction of **3** with equimolar $\text{Pd}(\text{CH}_2=\text{CHPh})(\text{PMe}_3)_2$ also causes the formation of dinuclear complex **6**, suggesting the stepwise oxidative addition of the two C–Br bonds in the substrate to the Pd(0) centers. Previously, we observed similar results on the pathway of diarylene bridged dinuclear Pd complex formation [8b].

The *trans* configuration around the Pd centers in the above complexes (**1–8**) is supported by the ^1H - and ^{13}C -NMR signals of PMe_3 or PEt_3 ligands showing apparent triplets (P–CH₃) or quintet (CH₃ of PEt_3) arising from virtual coupling [10]. The $^{31}\text{P}\{^1\text{H}\}$ -NMR spectra of **1–8** show a singlet in agreement with a *trans* configuration having two or four magnetically equivalent PR_3 ligands. Fig. 1 shows the molecular structure of **1** with the atomic numbering scheme determined by X-ray crystallography. Selected bond lengths and angles of the complex are listed in Table 1. The coordination sphere of the Pd metal in **1** can be described as a slightly distorted square plane. The molecular plane, defined by Pd, P(1), P(2), I, and C(1), is with the average atomic displacement of 0.001 Å. The thienyl ring is also nearly planar with the average atomic displacement of 0.006 Å and is almost perpendicular to the molecular plane with a dihedral angle 85.9(1)°. Fig. 2 shows an expected dinuclear form of **7**. There are two crystallographically independent molecules in the asymmetric unit. The two molecules are chemically equivalent and almost perpendicular to each other, the dihedral angle between the two thiophene rings is 87.7(2)°. The coordination sphere of each Pd can be described as a square plane. The equatorial planes (Pd(1), Br(1), P(1), P(2), C(13) and Pd(2), Br(2), P(3), P(4), C(16)) are nearly planar with the atomic displacement not exceeding 0.0665 Å. The thiophene ring (S(1), C(13), C(14), C(15), and C(16)) is essentially planar with the average atomic displacement of 0.0070 Å and this ring is almost perpendicular to the two equatorial planes with the dihedral angles of 86.0(2)° and 81.4(2)°.

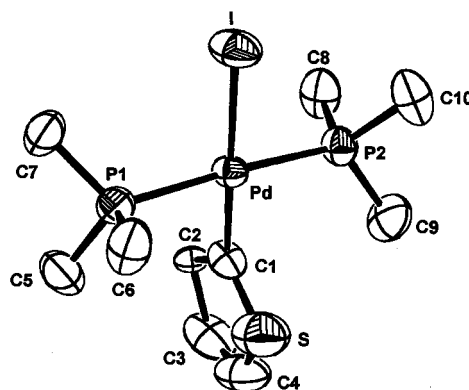


Fig. 1. ORTEP drawing of **1** showing the atomic labeling scheme and 50% probability thermal ellipsoids.

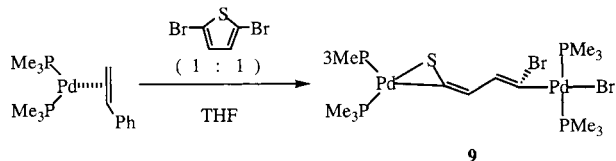
Table 1
Selected bond lengths (Å) and angles (°) for **1** and **7**^a

| Complex 1 | | | |
|-------------------|------------|-------------------|------------|
| Pd–C(1) | 2.015(6) | C(1)–Pd–P(1) | 88.5(2) |
| Pd–P(1) | 2.314(2) | C(1)–Pd–P(2) | 87.4(2) |
| Pd–P(2) | 2.324(2) | P(1)–Pd–P(2) | 175.86(5) |
| Pd–I | 2.6667(9) | C(1)–Pd–I | 179.7(2) |
| S–C(4) | 1.582(10) | C(4)–S–C(1) | 96.9(4) |
| S–C(1) | 1.622(7) | C(2)–C(1)–S | 114.0(4) |
| C(1)–C(2) | 1.589(5) | C(2)–C(1)–Pd | 123.6(4) |
| C(2)–C(3) | 1.575(7) | S–C(1)–Pd | 122.4(3) |
| C(3)–C(4) | 1.328(14) | C(3)–C(2)–C(1) | 97.9(4) |
| | | C(4)–C(3)–C(2) | 115.7(6) |
| | | C(3)–C(4)–S | 115.5(6) |
| Complex 7 | | | |
| Pd(1)–C(13) | 2.012(8) | Pd(3)–C(41) | 2.006(9) |
| Pd(1)–P(2) | 2.310(2) | Pd(3)–P(6) | 2.313(3) |
| Pd(1)–P(1) | 2.319(2) | Pd(3)–P(5) | 2.312(2) |
| Pd(1)–Br(1) | 2.4922(11) | Pd(3)–Br(3) | 2.4939(12) |
| Pd(2)–C(16) | 2.017(8) | Pd(4)–C(44) | 2.002(8) |
| Pd(2)–P(4) | 2.311(3) | Pd(4)–P(7) | 2.319(3) |
| Pd(2)–P(3) | 2.325(2) | Pd(4)–P(8) | 2.323(3) |
| Pd(2)–Br(2) | 2.4951(12) | Pd(4)–Br(4) | 2.5013(12) |
| S(1)–C(16) | 1.737(8) | S(2)–C(44) | 1.725(8) |
| S(1)–C(13) | 1.738(8) | S(2)–C(41) | 1.723(8) |
| C(13)–C(14) | 1.339(12) | C(41)–C(42) | 1.381(12) |
| C(14)–C(15) | 1.441(11) | C(42)–C(43) | 1.430(12) |
| C(15)–C(16) | 1.333(12) | C(43)–C(44) | 1.354(12) |
| C(13)–Pd(1)–P(2) | 89.8(2) | C(41)–Pd(3)–P(6) | 88.8(2) |
| C(13)–Pd(1)–P(1) | 87.6(2) | C(41)–Pd(3)–P(5) | 86.9(2) |
| P(2)–Pd(1)–P(1) | 175.66(9) | P(6)–Pd(3)–P(5) | 174.23(9) |
| C(13)–Pd(1)–Br(1) | 177.5(2) | C(41)–Pd(3)–Br(3) | 179.1(2) |
| P(2)–Pd(1)–Br(1) | 87.85(7) | P(6)–Pd(3)–Br(3) | 90.63(8) |
| C(16)–Pd(2)–P(4) | 89.2(2) | C(44)–Pd(4)–P(7) | 87.5(2) |
| C(16)–Pd(2)–P(3) | 88.2(2) | C(44)–Pd(4)–P(8) | 89.4(2) |
| P(4)–Pd(2)–P(3) | 173.57(10) | P(7)–Pd(4)–P(8) | 170.66(10) |
| C(16)–Pd(2)–Br(2) | 179.3(3) | C(44)–Pd(4)–Br(4) | 176.3(2) |
| P(3)–Pd(2)–Br(2) | 91.98(7) | P(7)–Pd(4)–Br(4) | 93.86(7) |
| C(16)–S(1)–C(13) | 94.3(4) | C(41)–S(2)–C(44) | 95.7(4) |
| C(14)–C(13)–S(1) | 107.9(6) | C(42)–C(41)–S(2) | 108.3(6) |
| C(14)–C(13)–Pd(1) | 131.3(6) | C(42)–C(41)–Pd(3) | 128.5(6) |
| S(1)–C(13)–Pd(1) | 120.7(5) | S(2)–C(41)–Pd(3) | 123.1(5) |

^a Symmetry transformations used to generate equivalent atoms.

In addition, the two equatorial planes are twisted with the dihedral angle of 35.2(1)°.

Reaction of Pd(CH₂=CHPh)(PMe₃)₂ with an equimolar amount of 2,5-dibromothiophene in THF at room temperature gives a dinuclear complex *cis,trans*-(Me₃P)₂Pd(η²-S=C=CH=CH=CBr)PdBr(PMe₃)₂ (**9**), in 56% yield, which is formed via cleavage of the C–S bond in thiophene ring as shown in Eq. (3).



(3)

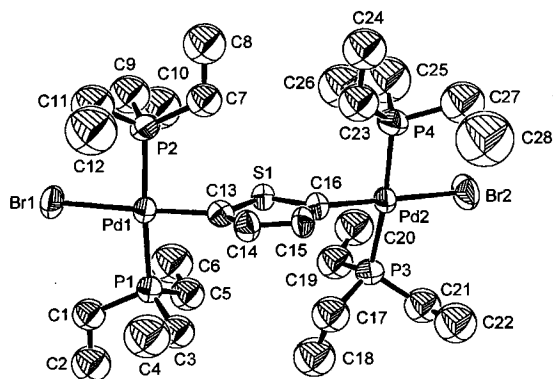


Fig. 2. ORTEP drawing of **7** showing the atomic labeling scheme and 50% probability thermal ellipsoids. One of the two crystallographically independent molecules is shown.

Fig. 3 shows the molecular structure of **9** confirmed by X-ray crystallography. The ORTEP drawing displays that one Pd(1) atom containing two mutually *trans* PMe₃ ligands and Br is coordinated to C(4) of bridging S=C=CH=CH=CBr and the other Pd(2) atom containing two mutually *cis* PMe₃ ligand is coordinated in an η²-C,S fashion to the thioketene part of S=C=CH=CH=CBr connecting two Pd centers. Two square planar planes are almost perpendicular with a dihedral angle of 88.70(9)°. The bond lengths of C(1)–C(2) (1.310 Å) and C(3)–C(4) (1.329 Å) (Table 2) are near to the bond length of normal double bonds (1.33 Å) but are slightly shorter than those (C(13)–C(14), 1.34 Å and C(15)–C(16), 1.33 Å) of bridged thienyl ring of **7**. The C(1)–S(1) bond length (1.698 Å) is close to the C–S bond lengths previously reported for C₅H₅Co(η²-S=C=CCMe₂[CH₂]₃CMe₂)-PMe₃ (1.695(7) Å) [11a], C₅H₅Rh(η²-S=C=CH₂)(PPr₃) (1.69(3) Å) [11b], and [CpRu(dppm)(η²-S=C=CHPh)]PF₆ (C–S; 1.671(4) Å) [12]. Most of the already reported thioketene complexes were obtained by ligand exchange with a stable thioketene or by the addition of elemental sulfur to a vinylidene complex [11,13,14]. Complex **9** is the first example of formation of the Pd complex containing a co-

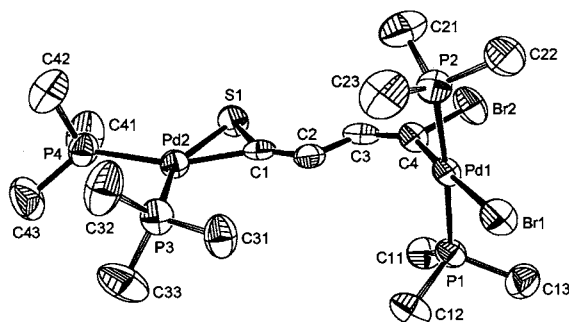


Fig. 3. ORTEP drawing of **9** showing the atomic labeling scheme and 50% probability thermal ellipsoids.

Table 2
Selected bond lengths (Å) and angles (°) for **9**

| Bond lengths (Å) | | | |
|------------------|------------|------------------|------------|
| Pd(1)–C(4) | 1.977(9) | Pd(1)–P(1) | 2.297(3) |
| Pd(1)–P(2) | 2.306(3) | Pd(1)–Br(1) | 2.5012(14) |
| Pd(2)–C(1) | 2.051(10) | Pd(2)–P(3) | 2.276(3) |
| Pd(2)–S(1) | 2.317(3) | Pd(2)–P(4) | 2.336(3) |
| Br(2)–C(4) | 1.929(9) | S(1)–C(1) | 1.698(10) |
| C(1)–C(2) | 1.310(12) | C(2)–C(3) | 1.462(13) |
| C(3)–C(4) | 1.329(13) | | |
| Bond angles (°) | | | |
| C(4)–Pd(1)–P(1) | 89.6(3) | C(4)–Pd(1)–P(2) | 90.0(3) |
| P(1)–Pd(1)–P(2) | 175.39(10) | C(4)–Pd(1)–Br(1) | 176.6(3) |
| P(1)–Pd(1)–Br(1) | 90.33(8) | P(2)–Pd(1)–Br(1) | 90.40(8) |
| C(1)–Pd(2)–P(3) | 106.4(3) | C(1)–Pd(2)–S(1) | 45.2(3) |
| P(3)–Pd(2)–S(1) | 151.57(11) | C(1)–Pd(2)–P(4) | 151.1(3) |
| P(3)–Pd(2)–P(4) | 102.39(11) | S(1)–Pd(2)–P(4) | 106.04(10) |
| C(1)–S(1)–Pd(2) | 59.1(3) | C(33)–P(3)–Pd(2) | 113.7(4) |
| C(2)–C(1)–Pd(2) | 146.1(8) | S(1)–C(1)–Pd(2) | 75.7(4) |
| C(1)–C(2)–C(3) | 122.9(9) | C(4)–C(3)–C(2) | 125.0(9) |
| C(3)–C(4)–Br(2) | 115.5(7) | C(3)–C(4)–Pd(1) | 132.7(7) |
| Br(2)–C(4)–Pd(1) | 111.9(5) | | |

ordinated thioketene ligand via C–S bond cleavage in the thiophene ring under mild conditions. Related C–S bond cleavage of thiophene or thiophene derivatives using metal complexes in low oxidation states including the Pt(0) complex have been reported [15–20]. The ¹H-NMR spectrum of the unsymmetrical dinuclear Pd complex **9** shows an apparent triplet at 1.32 ppm due to virtual coupling of PMe₃ ligands coordinated to the square-planar Pd center and two set of doublets at 0.90, 1.08 ppm due to two nonequivalent PMe₃ ligands bonded to the three-coordinated Pd center. A singlet at δ –15.6 and two sets of doublets at δ –17.0 and –26.8 (*J* = 14.6 Hz) at –30°C in the ³¹P{¹H}-spectrum also support these configurations. The ¹H-NMR signals of the bridging ligand are observed at δ 6.47 and 7.61. The former signal showing splitting due to P–H coupling (14 Hz) is assigned to S=C=CH– hydrogen. A larger *J*(HH) value of the signals (10 Hz) than the two 3, 4 hydrogens of the common thiophene ring (*J* = 3–5 Hz) [16c, 21] indicates the *s-trans* structure of the 1,3-diene unit. These signals are evidently different from those of thienylene bridged dinuclear complexes **5–7** having a singlet at δ 6.51–6.86. The ¹³C{¹H}-NMR signals of the S=C=CH–CH=CBr group are observed at δ 106.4, 128.3, 131.2, and 141.7.

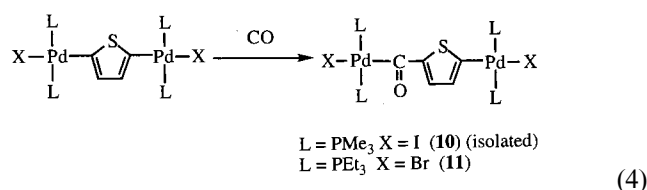
The reaction (Eq. (3)) is dependent on solvent and on the substrate to complex molar ratio. The same reaction in hexane produces a 2-thienyl complex **3**, which is separated from the solution due to its low solubility in hexane. However, the reaction in THF in a 2:1 molar ratio gives a mixture of **9** and thienylene bridged dinuclear complex **6** after 30 min stirring. On further stirring the reaction mixture changes into a mixture of **9**, **6**, and an unidentified species that may be produced due

to thermal decomposition of **9** in solution at room temperature. These reactions are monitored by ¹H- and ³¹P-NMR. It is also observed that isolated **9** is thermally unstable at room temperature in solution and changes slowly into the unidentified species. The reaction (Eq. (3)) occurs exclusively in the presence of an equimolar or excess amounts of 2,5-dibromothiophene although the detailed mechanism of C–S bond cleavage in the thiophene ring is not clear at present. As one of the possible pathways, oxidative addition of 2,5-dibromothiophene to Pd(0) complex might occur to give **3**. The complex was then rearranged to give the intermediate containing thiokene group, (S=C=CH–CH=CBr)-PdBr(PMe₃)₂ via C–S bond cleavage of the thiophene ring whose thioketene part is coordinated in an η²-C,S fashion to the other Pd(0) complex.

In order to obtain insight into the pathway of the reaction, we have examined the reaction of **3** with Pd(0) complex Pd(CH₂=CHPh)(PMe₃)₂. The reaction in THF or toluene in 1:1 molar ratio affords a thienylene bridged dipalladium complex **6** as a grayish white solid as well as unidentified species as a minor product, whereas the reaction in the presence of 2,5-dibromothiophene similarly to Eq. (3) causes formation of **3** as sole product. These results do not provide any clue to elucidate detailed mechanism of C–S bond cleavage of thiophene ring.

2.2. Reactions of CO and isocyanide with bridging thienylene dipalladium complexes

Treatment of **5** and **7** with CO (1 atm) at room temperature causes smooth CO insertion to give *trans,trans*-[L₂XPdC(O)C₄H₂SPdXL₂] (L = PMe₃, X = I (**10**), L = PEt₃, X = Br (**11**)) in 99 and 23% yields as shown in Eq. (4), respectively.



Complex **11** has quite a similar solubility to the starting material and was not isolated by fractional crystallization. Also, the lower yield of **11** than **10** may be due to a larger steric hindrance of PEt₃ than PMe₃ for CO insertion into a Pd–C bond in the thienylene bridged complex. The reaction occurs selectively at one of the Pd–C bonds and shows no further CO insertion. Previously, we also observed similar selective CO insertion into a Pd–C bond of arylene or biarylene bridged dinuclear Pd complexes [8b].

IR spectra show a strong ν(CO) absorption at 1598 cm⁻¹. The ¹³C-NMR signals at δ 220–222 support the

single CO insertion into Pd–C bond of the thienylene dipalladium complexes during the reaction. Two triplets for PMe_3 ligand (**10**) and two triplets and two singlets for PEt_3 (**11**) in the ^{13}C -NMR spectra as well as two singlets in the $^{31}\text{P}\{^1\text{H}\}$ -NMR spectra support the presence of inequivalent phosphine ligands due to the unsymmetrical molecular structure.

Reaction of **5** with two times molar butyl isocyanide at room temperature gives a complex with the symmetrical structure *trans,trans*-(Me_3P)₂IPd–C(=N-*n*-Bu)C₄H₂SC(=N-*n*-Bu)–PdI(PMe_3)₂ (**12**) in 69% yield. The IR spectrum shows a strong absorption band at 1574 cm^{-1} , which can be assigned to $\nu(\text{C}=\text{N})$ for the iminoacyl metal complex [1b, 22]. The crude product before purification shows an absorption band at 2160 cm^{-1} assigned to $\nu(\text{C}\equiv\text{N})$ of the isonitrile coordinated to a Pd centre. These results suggest that the reaction gives not only **12** but also cationic complexes such as $[(\text{Me}_3\text{P})_2(\text{CN}-\text{R})\text{Pd}-\text{C}_4\text{H}_2\text{S}-\text{Pd}(\text{CN}-\text{R})(\text{PMe}_3)_2]_2^+$ or $[(\text{Me}_3\text{P})_2\text{IPd}-\text{C}(=\text{N}-\text{R})\text{C}_4\text{H}_2\text{S}-\text{Pd}(\text{CN}-\text{R})(\text{PMe}_3)_2]^+$ ($\text{R} = n\text{-Bu}$) which may be regarded as the intermediate for formation of **12**. Other reactions with more bulky isocyanides such as *tert*-butyl or cyclohexyl isocyanides also gave the cationic adducts and the neutral complexes with the symmetrical structure *trans,trans*-(Me_3P)₂IPd–C(=N-*R*)C₄H₂SC(=N-*R*)–PdI(PMe_3)₂ ($\text{R} = t\text{-Bu}$, **13** and cyclohexyl, **14**). Complexes **13** and **14** were isolated by repeated recrystallization in the yields of 49 and 60% respectively. Previously, Sonogashira and co-workers [1b] have reported that insertion of aryl isocyanide into the Pt–C bonds of thienyl bridged diplatinum complexes occurs to give the unsymmetric or symmetric iminodiplatinum complexes at much higher temperature and their insertion is affected by the bulkiness of isocyanide and ligands on platinum. In our case using less bulky or bulky isocyanides, iminoacyl palladium complexes with symmetrical structure are easily formed under mild conditions. These results indicate that isocyanide insertion into the Pd–C bonds of thienylene bridged dipalladium complexes occurs more easily, than into the Pt–C bonds of thienylene bridged diplatinum complexes. Previous work by Mantovani et al. [23] also showed that isocyanide insertion at room temperature occurs in the Pd–C bond of 2-thienylpalladium complex.

In summary, we prepared thienyl palladium(II) and thienylene (or dithienylene) bridged dipalladium complexes from the oxidative addition of halothiophenes or dihalothiophenes with $\text{Pd}(\text{CH}_2=\text{CHPh})\text{L}_2$ ($\text{L} = \text{PMe}_3$ or PEt_3). Also, we have observed unusual C–S bond cleavage of thiophene ring to give a dipalladium complex connected by the thioketene part in the oxidative addition using equimolar or excess amounts of 2,5-dibromothiophene. The thienylene bridged dipalladium complexes undergo insertion of small molecules such as CO and isocyanide into their Pd–C bond at room temperature.

3. Experimental

3.1. General, materials, and measurement

All manipulations of air-sensitive compounds were performed under N_2 or argon atmosphere with use of standard Schlenk technique. Solvents were distilled from Na–benzophenone. PMe_3 , PEt_3 , and halothiophenes were purchased from Aldrich and used without further purification. 5,5'-Dibromo-2,2'-thiophene was prepared by the literature method [24]. *trans*-PdEt₂L₂ ($\text{L} = \text{PMe}_3$, PEt_3) [9] were prepared by the literature methods.

Elemental analyses were carried out by the analytical laboratory, Basic Science Institute of Korea and Sangji University. UV–vis and IR spectra were recorded on a Hitachi 200-20 and 270-30 spectrophotometer, respectively. NMR (^1H , $^{13}\text{C}\{^1\text{H}\}$ and $^{31}\text{P}\{^1\text{H}\}$) spectra were obtained on Jeol-Lambda-300, 400 MHz and Bruker 300 MHz spectrometers. Chemical shifts were referred to internal Me_4Si or to external 85% H_3PO_4 .

3.2. Preparation of thienyl palladium(II) complexes *trans*-[(2- $\text{C}_4\text{H}_3\text{S}$)PdX(PMe_3)₂], ($\text{X} = \text{I}$, **1**; Br , **2**), *trans*-[(2-(5- $\text{BrC}_4\text{H}_2\text{S}$)PdBr(PMe_3)₂)] (**3**), and *trans*-[(2-(5- $\text{BrC}_4\text{H}_2\text{S}$)PdBr(PEt_3)₂)] (**4**)

To a Schlenk flask containing *trans*-PdEt₂(PMe_3)₂ (0.413 g, 1.31 mmol) at 0°C were added styrene (0.544 g, 5.24 mmol) and THF (4 ml) in that order. The mixture was heated at 55°C for 3 h to give a pale yellow solution. At 0°C 2-iodothiophene (0.274 g, 1.31 mmol) was added to the solution. After stirring of the mixture for 2 h at room temperature (r.t.), the solvent was evaporated to ca. 2 ml under reduced pressure. Addition of Et₂O and storage at –30°C resulted in a white solid which was filtered off, washed with hexane and then with Et₂O and recrystallized from THF–hexane to give *trans*-[(2- $\text{C}_4\text{H}_3\text{S}$)PdI(PMe_3)₂] (**1**) as slightly gray crystals (0.577 g, 95%). UV–vis (λ_{max} nm): 302 (ϵ 3800), 250 (ϵ 14700). ^1H -NMR (300 MHz, CDCl_3 , δ): 1.03 (t, $J = 3.6$ Hz, 18H, PMe_3), 6.62 (d, $J = 3.4$ Hz, 1H, thienyl), 7.07 (dd, $J = 3.3$, 5.0 Hz, 1H, thienyl), 7.42 (dd, $J = 4.3$, 0.8 Hz, 1H, thienyl). $^{13}\text{C}\{^1\text{H}\}$ -NMR (75 MHz, CDCl_3 , δ): 15.7 (t, $J(\text{CP}) = 15.8$ Hz, PMe_3), 127.2 (t, $J(\text{CP}) = 2.6$ Hz, thienyl), 127.3 (s, thienyl), 128.2 (t, $J(\text{CP}) = 4.6$ Hz, thienyl), 146.5 (t, $J(\text{CP}) = 9.3$ Hz, thienyl). $^{31}\text{P}\{^1\text{H}\}$ -NMR (120 MHz, CDCl_3 , δ): –17.3 (s). Anal. Calc. for $\text{C}_{10}\text{H}_{21}\text{SiP}_2\text{Pd}$: C, 25.63; H, 4.52; S, 6.84. Found: C, 25.45; H, 4.29; S, 6.86.

trans-[(2- $\text{C}_4\text{H}_3\text{S}$)PdBr(PMe_3)₂] (**2**), *trans*-[(2-(5- $\text{BrC}_4\text{H}_2\text{S}$)PdBr(PMe_3)₂)] (**3**), and *trans*-[(2-(5- $\text{BrC}_4\text{H}_2\text{S}$)PdBr(PEt_3)₂)] (**4**) were obtained similarly in 95, 98, and 85% yields, respectively.

Complex **2**: UV–vis (λ_{max} nm): 298 (ϵ 9800), 250 (ϵ 37600). ^1H -NMR (300 MHz, CDCl_3 , δ): 1.26 (t, $J = 3.6$

Hz, 18H, PMe_3), 6.62 (d, $J = 3.4$ Hz, thienyl), 7.05 (dd, $J = 3.3, 5.0$ Hz, 1H, thienyl), 7.40 (dd, $J = 5.0, 0.8$ Hz, 1H, thienyl). $^{13}\text{C}\{^1\text{H}\}$ -NMR (75 MHz, CDCl_3 , δ); 14.0 (t, $J(\text{CP}) = 15.9$ Hz, PMe_3), 127.1 (t, $J(\text{CP}) = 2.8$ Hz, thienyl), 127.2 (s, thienyl), 128.2 (t, $J(\text{CP}) = 4.7$ Hz, thienyl), 143.1 (t, $J(\text{CP}) = 10$ Hz, thienyl). $^{31}\text{P}\{^1\text{H}\}$ -NMR (120 MHz, CDCl_3 , δ); -20.6 (s). Anal. Calc. for $\text{C}_{10}\text{H}_{21}\text{SBrP}_2\text{Pd}$: C, 28.49; H, 5.02; S, 7.61. Found: C, 28.62; H, 4.92; S, 7.73.

Complex 3: ^1H -NMR (300 MHz, CDCl_3 , δ); 0.86 (t, $J = 3.5$ Hz, 18H, PMe_3), 6.36 (d, $J = 3.0$ Hz, thienyl), 7.00 (dd, $J = 3.6$ Hz, 1H, thienyl). $^{13}\text{C}\{^1\text{H}\}$ -NMR (75 MHz, CDCl_3 , δ); 13.7 (t, $J(\text{CP}) = 15.4$ Hz, PMe_3), 111.0 (t, $J(\text{CP}) = 3.0$ Hz, thienyl), 129.7 (t, $J(\text{CP}) = 4.5$ Hz, thienyl), 130.9 (s, thienyl) 148.3 (t, $J(\text{CP}) = 11$ Hz, thienyl). $^{31}\text{P}\{^1\text{H}\}$ -NMR (120 MHz, CDCl_3 , δ); -16.0 (s). Anal. Calc. for $\text{C}_{10}\text{H}_{20}\text{SBr}_2\text{P}_2\text{Pd}$: C, 24.00; H, 4.03; S, 6.41. Found: C, 24.04; H, 4.10; S, 6.47.

Complex 4: ^1H -NMR (300 MHz, CDCl_3 , δ); 1.10 (apparent quintet, 18H, $\text{P}(\text{CH}_2\text{CH}_3)_3$), 1.68 (m, 12H, $\text{P}(\text{CH}_2\text{CH}_3)_3$), 6.36 (d, $J = 3.5$ Hz, 1H, thienyl), 6.91 (d, $J = 3.4$ Hz, 1H, thienyl). $^{13}\text{C}\{^1\text{H}\}$ -NMR (75 MHz, CDCl_3 , δ); 8.2 (s, $\text{P}(\text{CH}_2\text{CH}_3)_3$), 14.5 (t, $J(\text{CP}) = 13.6$ Hz, $\text{P}(\text{CH}_2\text{CH}_3)_3$), 110.7 (s, thienyl), 130.0 (t, $J(\text{CP}) = 3.8$ Hz, thienyl), 130.2 (s, thienyl) 145.7 (t, $J(\text{CP}) = 10$ Hz, thienyl). $^{31}\text{P}\{^1\text{H}\}$ -NMR (120 MHz, CDCl_3 , δ); 15.3 (s). Anal. Calc. for $\text{C}_{16}\text{H}_{32}\text{SBr}_2\text{P}_2\text{Pd}$: C, 32.87; H, 5.52; S, 5.48. Found: C, 32.92; H, 5.96; S, 5.84.

3.3. Preparation of bridging thienylene(or dithienylene) dipalladium complexes *trans,trans*- $[(\text{Me}_3\text{P})_2\text{XPd}(\mu\text{-}2,5\text{-C}_4\text{H}_2\text{S})\text{PdX}(\text{PMe}_3)_2]$ ($X = \text{I}$ (5); Br (6)), *trans,trans*- $[(\text{Et}_3\text{P})_2\text{BrPd}(\mu\text{-}2,5\text{-C}_4\text{H}_2\text{S})\text{PdBr}(\text{PEt}_3)_2]$ (7), and *trans,trans*- $[(\text{Me}_3\text{P})_2\text{BrPd}(\mu\text{-}2,5'\text{-C}_4\text{H}_2\text{S}\text{-C}_4\text{H}_2\text{S})\text{PdBr}(\text{PMe}_3)_2]$ (8)

To a Schlenk flask containing *trans*- $\text{PdEt}_2(\text{PMe}_3)_2$ (0.577 g, 1.82 mmol) at 0°C were added styrene (0.759 g, 7.36 mmol) and THF (4 ml) in this order. The mixture was heated at 55°C for 3 h to give a pale yellow solution. At 0°C 2,5-diiododothiophene (0.300 g, 0.89 mmol) was added to the mixture. After stirring the mixture for 3 h at r.t. the solvent was evaporated to ca. 2 ml under reduced pressure. Addition of Et_2O (2 ml) and storage at -30°C in a freezer resulted in a pale yellow solid which was filtered off, washed with hexane and then with Et_2O and recrystallized from THF– Et_2O to give as pale yellow crystals of *trans,trans*- $[(\text{Me}_3\text{P})_2\text{IPd}(\mu\text{-}2,5\text{-C}_4\text{H}_2\text{S})\text{PdI}(\text{PMe}_3)_2]$ (5) (0.694 g, 91%). UV–vis (λ_{max} nm): 316 (ϵ 7600), 274 (ϵ 19600). ^1H -NMR (300 MHz, CDCl_3 , δ); 1.38 (t, $J = 3.4$ Hz, 36H, PMe_3), 6.63 (s, 2H, thienylene). $^{13}\text{C}\{^1\text{H}\}$ -NMR (75 MHz, CDCl_3 , δ); 16.1 (t, $J(\text{CP}) = 16.0$ Hz, PMe_3), 129.9 (t, $J(\text{CP}) = 4.6$ Hz, thienylene), 145.0 (s, thienylene). $^{31}\text{P}\{^1\text{H}\}$ -NMR (120 MHz, CDCl_3 , δ); -20.8 (s). Anal. Calc. for $\text{C}_{16}\text{H}_{38}\text{SI}_2\text{P}_4\text{Pd}_2$: C, 22.50; H, 4.48; S, 6.41. Found: C, 22.62; H, 4.50; S, 6.39.

trans,trans- $[(\text{Me}_3\text{P})_2\text{BrPd}(\mu\text{-}2,5\text{-C}_4\text{H}_2\text{S})\text{PdBr}(\text{PMe}_3)_2]$ (6), *trans,trans*- $[(\text{Et}_3\text{P})_2\text{BrPd}(\mu\text{-}2,5\text{-C}_4\text{H}_2\text{S})\text{PdBr}(\text{PEt}_3)_2]$ (7), and *trans,trans*- $[(\text{Me}_3\text{P})_2\text{BrPd}(\mu\text{-}2,5'\text{-C}_4\text{H}_2\text{S}\text{-C}_4\text{H}_2\text{S})\text{PdBr}(\text{PMe}_3)_2]$ (8) were similarly obtained in 75, 80, and 98% yields, respectively.

Complex 6: UV–vis (λ_{max} nm): 275 (ϵ 11400). ^1H -NMR (300 MHz, CDCl_3 , δ); 1.29 (t, $J = 3.6$ Hz, 36H, PMe_3), 6.60 (s, 2H, thienylene). $^{13}\text{C}\{^1\text{H}\}$ -NMR (75 MHz, CDCl_3 , δ); 14.4 (t, $J(\text{CP}) = 15.8$ Hz, PMe_3), 129.9 (t, $J(\text{CP}) = 4.6$ Hz, thienylene), 142.1 (t, $J(\text{CP}) = 10.1$ Hz, thienylene). $^{31}\text{P}\{^1\text{H}\}$ -NMR (120 MHz, CDCl_3 , δ); -18.2 (s). Anal. Calc. for $\text{C}_{16}\text{H}_{38}\text{SBr}_2\text{P}_4\text{Pd}_2$: C, 25.32; H, 5.05; S, 4.22. Found: C, 25.40; H, 5.11; S, 4.24.

Complex 7: ^1H -NMR (300 MHz, CDCl_3 , δ); 1.11 (apparent quintet, 36H, $\text{P}(\text{CH}_2\text{CH}_3)_3$), 1.67 (m, 24H, $\text{P}(\text{CH}_2\text{CH}_3)_3$), 6.51 (s, 2H, thienylene). $^{13}\text{C}\{^1\text{H}\}$ -NMR (75 MHz, CDCl_3 , δ); 8.1 (s, $\text{P}(\text{CH}_2\text{CH}_3)_3$), 14.2 (t, $J(\text{CP}) = 13.7$ Hz, $\text{P}(\text{CH}_2\text{CH}_3)_3$), 129.6 (s, thienylene), 143.8 (t, $J(\text{CP}) = 10.2$ Hz, thienylene). $^{31}\text{P}\{^1\text{H}\}$ -NMR (120 MHz, CDCl_3 , δ); 12.8 (s). Anal. Calc. for $\text{C}_{28}\text{H}_{62}\text{SBr}_2\text{P}_4\text{Pd}_2$: C, 36.26; H, 6.74; S, 3.46. Found: C, 36.27; H, 6.76; S, 3.43.

Complex 8: UV–vis (λ_{max} nm): 346 (ϵ 26400), 275 (ϵ 20000). ^1H -NMR (300 MHz, CDCl_3 , δ); 1.32 (t, $J = 3.5$ Hz, 36H, PMe_3), 6.46 (d, $J = 3.6$ Hz, 2H, thienylene), 6.97 (d, $J = 3.3$ Hz, 2H, thienylene). $^{13}\text{C}\{^1\text{H}\}$ -NMR (75 MHz, CDCl_3 , δ); 14.2 (t, $J(\text{CP}) = 15.1$ Hz, PMe_3), 122.6 (s, thienylene), 129.2 (t, $J(\text{CP}) = 4.6$ Hz, thienylene), 141.0 (s, thienylene), 142.0 (t, $J(\text{CP}) = 10.5$ Hz, thienylene). $^{31}\text{P}\{^1\text{H}\}$ -NMR (120 MHz, CDCl_3 , δ); -21.6 (s). Anal. Calc. for $\text{C}_{20}\text{H}_{40}\text{S}_2\text{Br}_2\text{P}_4\text{Pd}_2$: C, 28.56; H, 4.79; S, 7.62. Found: C, 28.72; H, 4.97; S, 7.70.

3.4. Preparation of *cis,trans*- $[(\text{Me}_3\text{P})_2\text{Pd}(\eta^2\text{-S=C=CH-CH=CBr})\text{PdBr}(\text{PMe}_3)_2]$ (9)

To a Schlenk flask containing *trans*- $\text{PdEt}_2(\text{PMe}_3)_2$ (0.210 g, 0.662 mmol) at 0°C were added styrene (0.276 g, 2.65 mmol) and THF (2 ml) in this order. The mixture was heated at 55°C for 3 h to give a pale yellow solution. At 0°C 2,5-dibromothiophene (0.160 g, 0.662 mmol) was added to the solution. After stirring the mixture for 3 h at r.t. the solvent was evaporated to 1 ml under reduced pressure. Addition of Et_2O (3 ml) and storage at -30°C resulted in a pale yellow solid which was filtered off, washed with hexane (2×2 ml) and recrystallized from THF–hexane (3:1) to give as yellow crystals of *cis,trans*- $[(\text{Me}_3\text{P})_2\text{Pd}(\eta^2\text{-S=C=CH-CH=CBr})\text{PdBr}(\text{PMe}_3)_2]$ (9) (0.140 g, 56%). ^1H -NMR (300 MHz, C_6D_6 , δ); 0.90 d, $J = 8.2$ Hz, 9H, *cis* PMe_3). 1.08 (d, $J = 8.2$ Hz, 9H, *cis* PMe_3), 1.32 (t, $J = 3.6$ Hz, 18H, *trans* PMe_3), 6.47 (dd, $J = 9.6, 13.7$ Hz, 1H, S=C-CH-CH=CBr), 7.61 (d, $J = 9.6$ Hz, 1H, S=C-CH-CH=CBr). $^{13}\text{C}\{^1\text{H}\}$ -NMR (75 MHz, C_6D_6 ,

δ); 14.6 (t, $J(\text{CP}) = 14.8$ Hz, PMe_3), 18.0 (apparent triplet, PMe_3), 106.4 (s, $\text{S}=\text{C}=\text{CH}-\text{CH}=\text{CBr}$), 128.3 (s, $\text{S}=\text{C}=\text{CH}-\text{CH}=\text{CBr}$), 131.2 (s, $\text{S}=\text{C}=\text{CH}-\text{CH}=\text{CBr}$), 141.7 (s, $\text{S}=\text{C}=\text{CH}-\text{CH}=\text{CBr}$). $^{31}\text{P}\{^1\text{H}\}$ -NMR (160 MHz, d_8 -toluene, δ , -30°C); -15.6 (s, *trans*- PMe_3), -17.0 (d, $J = 14.6$ Hz, *cis*- PMe_3), -26.8 (d, $J = 14.6$ Hz, *cis*- PMe_3). Anal. Calc. for $\text{C}_{16}\text{H}_{38}\text{SBr}_2\text{P}_4\text{Pd}_2$: C, 25.32; H, 5.05; S, 4.22. Found: C, 25.22; H, 5.28; S, 4.31.

3.5. Reactions of CO with **5** and **7**

Complex **5** (0.194 g, 0.23 mmol) was dissolved in CH_2Cl_2 (2 ml) at r.t. After evacuation of the system CO (1 atm) was introduced and the initial pale yellow solution immediately turned to orange–yellow. After the solution was stirred for 4 h at r.t., the solvent was evaporated under a reduced pressure to give a yellow residue, which was recrystallized from THF–hexane to give a yellow solid of *trans,trans*-(Me_3P) $_2$ IPdC(O)- $\text{C}_4\text{H}_2\text{SPdI}(\text{PMe}_3)_2$ (**10**) (0.188 g, 94%). IR (KBr, $\nu(\text{C}=\text{O})$ cm^{-1}): 1598. ^1H -NMR (300 MHz, CDCl_3 , δ); 1.36 (t, $J = 3.6$ Hz, 18H, PMe_3), 1.41 (apparent triplet, 18H, PMe_3), 6.82 (d, $J = 3.7$ Hz, 1H, thienylene), 8.03 (d, $J = 3.6$ Hz, 1H, thienylene). $^{13}\text{C}\{^1\text{H}\}$ -NMR (75 MHz, CDCl_3 , δ); 15.6 (t, $J(\text{CP}) = 14.6$ Hz, PMe_3), 15.8 (apparent triplet, PMe_3), 130.2 (t, $J = 4.4$ Hz, thienylene), 135.5 (s, thienylene), 150.8 (d, $J = 18$ Hz, thienylene), 164.2 (t, $J = 9.5$ Hz, thienylene), 221.6 (s, CO). $^{31}\text{P}\{^1\text{H}\}$ -NMR (120 MHz, CDCl_3 , δ); -23.4 (s), -26.5 (s). Anal. Calc. for $\text{C}_{17}\text{H}_{38}\text{SI}_2\text{OP}_4\text{Pd}_2$: C, 23.18; H, 4.35; S, 3.64. Found: C, 23.23; H, 4.40; S, 3.76. Reaction of CO with **7** was carried out analogously to give *trans,trans*-(Et_3P) $_2$ BrPdC(O) $\text{C}_4\text{H}_2\text{SPdBr}(\text{PEt}_3)_2$, (**11**) in spectroscopic 23% yield. IR (KBr, $\nu(\text{C}=\text{O})$ cm^{-1}): 1598. ^1H -NMR (300 MHz, CDCl_3 , δ); 1.10 (m, 36H, $\text{P}(\text{CH}_2\text{CH}_3)_3$), 1.81 (m, 24H, $\text{P}(\text{CH}_2\text{CH}_3)_3$), 6.76 (d, $J = 3.6$ Hz, 1H, thienylene), 8.04 (br, 1H, thienylene). $^{13}\text{C}\{^1\text{H}\}$ -NMR (75 MHz, CDCl_3 , δ); 8.1 (s, $\text{P}(\text{CH}_2\text{CH}_3)_3$), 8.2 (s, $\text{P}(\text{CH}_2\text{CH}_3)_3$), 14.5 (apparent triplet, $\text{P}(\text{CH}_2\text{CH}_3)_3$), 15.2 (apparent triplet, $\text{P}(\text{CH}_2\text{CH}_3)_3$). Other signals could not be observed due to low intensity. $^{31}\text{P}\{^1\text{H}\}$ -NMR (120 MHz, CDCl_3 , δ); 12.2 (s), 16.9 (s).

3.6. Reactions of *n*-butyl, *t*-butyl, and cyclohexyl isocyanides with **5**

To a solution containing **5** (0.111 g, 0.13 mmol) in THF (4 ml) was added *n*-butyl isocyanide (23 mg, 0.27 mmol) at r.t. The initial dark red solution immediately turned to yellow suspension. While stirring for 3 h the mixture turned to a yellow solution. The solution was fully evaporated to give an oily residue and then Et_2O (2 ml) and hexane (7 ml) were added to give a yellow solid. The solid was dissolved in Et_2O and stored at

-30° in a freezer to afford yellow precipitates. IR spectrum of the precipitates showed the presence of $\nu(\text{C}=\text{N})$ band in isocyanide coordinated on Pd metal. The solution part was fully evaporated and washed with hexane (1 \times 2 ml) to give *trans,trans*-(Me_3P) $_2$ IPd-C(=N-*n*-Bu) $\text{C}_4\text{H}_2\text{SC}(\text{N-}n\text{-Bu})\text{-PdI}(\text{PMe}_3)_2$ (**12**) as pale yellow solids (91 mg, 69%). IR (KBr, $\nu(\text{C}=\text{N})$ cm^{-1}): 1574. ^1H -NMR (300 MHz, CDCl_3 , δ); 0.98 (t, 6H, $-\text{CH}_3$), 1.45 (t, $J = 3.6$ Hz, 18H, PMe_3), 1.46 (m, 4H, $-\text{CH}_2$), 1.71 (m, 4H, $-\text{CH}_2$), 3.75 (t, $J = 7.2$ Hz, 4H, $-\text{CH}_2$), 7.54 (s, 2H, thienylene). $^{13}\text{C}\{^1\text{H}\}$ -NMR (75 MHz, CDCl_3 , δ); 14.2 (s, CH_3), 16.7 (t, $J(\text{CP}) = 15.4$ Hz, PMe_3), 21.1 (s, $-\text{CH}_2$), 33.3 (s, $-\text{CH}_2$), 59.7 (t, $J = 6.3$ Hz, $-\text{CH}_2$), 128.0 (s, thienylene), 151.2 (s, thienylene), 180.1 (t, $J(\text{CP}) = 4.9$ Hz, C=N). $^{31}\text{P}\{^1\text{H}\}$ -NMR (120 MHz, CDCl_3 , δ); -22.0 (s). Anal. Calc. for $\text{C}_{26}\text{H}_{56}\text{SI}_2\text{P}_4\text{Pd}_2$: C, 30.64; H, 5.54; N, 2.75; S, 3.15. Found: C, 30.87; H, 5.89; N, 2.59; S, 3.26. Reactions of *t*-butyl, cyclohexyl isocyanides with **5** in CH_2Cl_2 were carried out analogously to give *trans,trans*-(Me_3P) $_2$ IPd-C(=N-*t*-Bu) $\text{C}_4\text{H}_2\text{SC}(\text{N-}t\text{-Bu})\text{-PdI}(\text{PMe}_3)_2$ (**13**) as a pale yellow solid (49%). IR (KBr, $\nu(\text{C}=\text{N})$ cm^{-1}): 1579. ^1H -NMR (300 MHz, CDCl_3 , δ); 1.44 (t, $J = 3.4$ Hz, 18H, PMe_3), 1.49 (s, 18H, $-\text{CH}_3$), 7.64 (s, 2H, thienylene). $^{13}\text{C}\{^1\text{H}\}$ -NMR (75 MHz, CDCl_3 , δ); 16.4 (t, $J(\text{CP}) = 14.5$ Hz, PMe_3), 31.0 (s, $-\text{CH}_3$), 57.7 (t, $J(\text{CP}) = 1.5$ Hz, $\text{C}(\text{CH}_3)_3$), 128.0 (s, thienylene), 153.8 (t, $J(\text{CP}) = 12$ Hz, thienylene), 171.4 (t, $J(\text{CP}) = 5.0$ Hz, C=N). $^{31}\text{P}\{^1\text{H}\}$ -NMR (120 MHz, CDCl_3 , δ); -20.1 (s). Anal. Calc. for $\text{C}_{26}\text{H}_{56}\text{N}_2\text{SI}_2\text{P}_4\text{Pd}_2$: C, 30.64; H, 5.54; N, 2.75; S, 3.15. Found: C, 30.87; H, 5.48; N, 2.48; S, 3.20.

trans,trans-(Me_3P) $_2$ IPd-C(=N-cyclohexyl) $\text{C}_4\text{H}_2\text{SC}(\text{N-cyclohexyl})\text{-PdI}(\text{PMe}_3)_2$ (**14**) was obtained as a pale yellow solid (60%). IR (KBr, $\nu(\text{C}=\text{N})$ cm^{-1}) 1574. ^1H -NMR (300 MHz, CDCl_3 , δ); 1.46 (t, $J = 3.5$ Hz, 18H, PMe_3), 1.2–1.7 (m, 20H, $-\text{C}_6\text{H}_{11}$), 3.89 (m, 2H, $-\text{C}_6\text{H}_{11}$), 7.53 (s, 2H, thienylene). $^{13}\text{C}\{^1\text{H}\}$ -NMR (75 MHz, CDCl_3 , δ); 16.7 (t, $J(\text{CP}) = 15.1$ Hz, PMe_3), 24.5 (s, $-\text{C}_6\text{H}_{11}$), 25.6 (s, C_6H_{11}), 33.8 (s, C_6H_{11}), 67.9 (s, C_6H_{11}), 127.9 (s, thienylene), 151.9 (t, $J(\text{CP}) = 8.7$ Hz, thienylene), 175.9 (t, $J(\text{CP}) = 4.7$ Hz, C=N). $^{31}\text{P}\{^1\text{H}\}$ -NMR (120 MHz, CDCl_3 , δ); -18.9 (s). Anal. Calc. for $\text{C}_{30}\text{H}_{60}\text{N}_2\text{SI}_2\text{P}_4\text{Pd}_2$: C, 33.63; H, 5.64; N, 2.62; S, 2.99. Found: C, 33.87; H, 5.62; N, 2.21; S, 3.37.

3.7. X-ray structure determination

Crystals of **1**, **7**, and **9** suitable for X-ray crystallography were obtained by recrystallization from tetrahydrofuran–hexane, diethyl ether, and benzene–hexane (or toluene–hexane) mixtures, respectively. X-ray data for **1** were collected with use of a Mac Science MXC diffractometer equipped with an Mo X-ray tube and a graphite crystal monochromator. X-ray data for **7** and

9 were collected with use of a Siemens P4 diffractometer. Details on crystal and intensity data for **1**, **7** and **9** are given in Table 3. For all the three crystals, three check reflections were measured every 100 reflections throughout data collection and showed no significant variations in intensity. Intensity data were corrected for Lorentz and polarization effects. Decay corrections were also made. The intensity data were empirically corrected with psi-scan data.

The orientation matrix and unit cell parameters of **1** were determined from 25 machine-centered reflections with $20^\circ < 2\theta < 30^\circ$. All calculations for **1** were carried out with use of the SHELX-97 [25] programs. The orientation matrix and unit cell parameters of **7** and **9** were determined from 50 reflections with $15.0^\circ < 2\theta < 25.0^\circ$. All calculations for **7** and **9** were carried out with use of the Siemens SHELXTL programs [26].

The unit cell parameters and systematic absences of **1**, $h0l$ ($l = 2n + 1$) and $0k0$ ($k = 2n + 1$), unambiguously indicated $P2_1/c$ as a space group. The structure was solved by the heavy-atom method. All non-hydrogen atoms were refined anisotropically. All hydrogen atoms were generated in idealized positions and refined in a riding model.

The unit cell parameters of **7** suggested a triclinic space group. A statistical analysis of intensities sug-

gested a centrosymmetric space group and the structure analysis converged only in $P\bar{1}$. The structure was solved by the direct method. All non-hydrogen atoms were refined anisotropically, except for the carbon atoms in the triethylphosphine (PET_3) ligands. The triethylphosphine carbon atoms exhibited an extremely high struc-

Table 4

Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{Å}^3 \times 10^3$) for **1**

| | <i>x</i> | <i>y</i> | <i>z</i> | U_{eq}^a |
|-------|----------|----------|----------|-------------------|
| Pd | 2467(1) | 3135(1) | 2618(1) | 39(1) |
| I | 2361(1) | 707(1) | 2731(1) | 70(1) |
| S | 3165(2) | 5796(2) | 3722(3) | 98(1) |
| P(1) | 3925(1) | 3008(1) | 2139(1) | 50(1) |
| P(2) | 1010(1) | 3416(2) | 3090(1) | 49(1) |
| C(1) | 2554(4) | 4970(5) | 2534(5) | 51(1) |
| C(2) | 2008(3) | 5740(3) | 1323(3) | 69(1) |
| C(3) | 2325(6) | 7051(5) | 1885(9) | 85(2) |
| C(4) | 2908(6) | 7082(7) | 3064(11) | 94(3) |
| C(5) | 4304(6) | 4348(7) | 1492(9) | 86(2) |
| C(6) | 5006(5) | 2681(9) | 3521(6) | 88(2) |
| C(7) | 3960(5) | 1835(6) | 1059(6) | 68(2) |
| C(8) | −101(5) | 3340(8) | 1705(6) | 75(2) |
| C(9) | 866(6) | 4845(8) | 3795(7) | 83(2) |
| C(10) | 736(6) | 2288(8) | 4079(7) | 81(2) |

^a U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensor.

Table 3
Crystallographic data and details of refinement of **1**, **7**, and **9**

| | 1 | 7 | 9 |
|---|---|---|---|
| Chemical formula | $\text{C}_{10}\text{H}_{21}\text{IP}_2\text{SPd}$ | $\text{C}_{28}\text{H}_{62}\text{Br}_2\text{P}_4\text{S}-\text{Pd}_2$ | $\text{C}_{16}\text{H}_{38}\text{Br}_2\text{P}_4\text{SPd}_2 \cdot 0.5\text{C}_6\text{H}_6$ |
| Formula weight | 468.57 | 927.34 | 798.14 |
| Crystal system | Monoclinic | Triclinic | Monoclinic |
| Space group | $P2_1/c$ | $P\bar{1}$ | $P2_1/n$ |
| <i>a</i> (Å) | 14.066(4) | 14.621(2) | 14.179(2) |
| <i>b</i> (Å) | 10.941(3) | 15.839(2) | 15.019(2) |
| <i>c</i> (Å) | 11.685(3) | 18.494(3) | 16.418(3) |
| α (°) | | 74.14(1) | |
| β (°) | 110.92(2) | 83.58(1) | 115.17(1) |
| γ (°) | | 80.92(1) | |
| <i>V</i> (Å ³) | 1679.7(8) | 4058(1) | 3164(1) |
| <i>Z</i> | 4 | 4 | 4 |
| μ (mm ^{−1}) | 3.231 | 3.081 | 3.936 |
| <i>F</i> (000) | 904 | 1872 | 1592 |
| <i>D</i> _{calc.} (g cm ^{−3}) | 1.853 | 1.518 | 1.686 |
| Crystal size (mm × mm × mm) | 0.2 × 0.3 × 0.4 | 0.62 × 0.50 × 0.34 | 0.4 × 0.3 × 0.3 |
| Scan range | $5^\circ < 2\theta < 48^\circ$ | $3.5^\circ < 2\theta < 50^\circ$ | $3.5^\circ < 2\theta < 45^\circ$ |
| Unique reflections | 3782 | 13042 | 4244 |
| Used reflections ($I \geq 2\sigma(I)$) | 2477 | 12592 | 4054 |
| No. of parameters | 177 | 428 | 240 |
| Scan type | $\omega-2\theta$ | ω | ω |
| Goodness-of-fit on F^2 | 1.013 | 1.004 | 1.007 |
| Max/min in $\Delta\rho$ (e Å ^{−3}) | 0.726, −0.667 | 1.074, −0.802 | 0.459, −0.713 |
| <i>T</i> _{min} | 0.377 | 0.1910 | 0.3430 |
| <i>T</i> _{max} | 0.532 | 0.3170 | 0.5085 |
| <i>R</i> | 0.0353 | 0.0629 | 0.0486 |
| <i>wR</i> ₂ ^a | 0.0925 | 0.1545 | 0.1032 |

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

Table 5

Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{\AA}^3 \times 10^3$) for **7**

| | <i>x</i> | <i>y</i> | <i>z</i> | U_{eq}^a |
|-------|-----------|-----------|-----------|-------------------|
| Pd(1) | 7005(1) | 1386(1) | 1408(1) | 50(1) |
| Pd(2) | 3975(1) | 3090(1) | −1006(1) | 54(1) |
| Pd(3) | 8692(1) | −3583(1) | 6403(1) | 54(1) |
| Pd(4) | 11923(1) | −1825(1) | 4088(1) | 56(1) |
| Br(1) | 8089(1) | 1154(1) | 2414(1) | 90(1) |
| Br(2) | 2684(1) | 4094(1) | −1701(1) | 93(1) |
| Br(3) | 7358(1) | −3905(1) | 7355(1) | 100(1) |
| Br(4) | 13132(1) | −931(1) | 3325(1) | 108(1) |
| S(1) | 5417(1) | 2565(1) | 306(1) | 53(1) |
| S(2) | 10166(1) | −2321(1) | 5340(1) | 54(1) |
| P(1) | 5865(2) | 667(2) | 2204(1) | 66(1) |
| P(2) | 8055(2) | 2192(2) | 586(1) | 65(1) |
| P(3) | 2962(2) | 2524(2) | 10(1) | 68(1) |
| P(4) | 5053(2) | 3720(2) | −1926(1) | 69(1) |
| P(5) | 9788(2) | −4104(2) | 7286(1) | 64(1) |
| P(6) | 7682(2) | −2945(2) | 5466(2) | 74(1) |
| P(7) | 10819(2) | −1230(2) | 3214(1) | 69(1) |
| P(8) | 12871(2) | −2298(2) | 5089(1) | 70(1) |
| C(1) | 6179(7) | 184(7) | 3176(6) | 80(3) |
| C(2) | 5421(9) | −250(9) | 3735(8) | 117(4) |
| C(3) | 5495(8) | −218(7) | 1902(6) | 85(3) |
| C(4) | 6257(11) | −938(10) | 1824(9) | 140(5) |
| C(5) | 4817(8) | 1424(7) | 2297(7) | 88(3) |
| C(6) | 4985(11) | 2204(10) | 2531(9) | 141(6) |
| C(7) | 7842(8) | 2562(7) | −399(6) | 85(3) |
| C(8) | 8531(10) | 3113(9) | −934(8) | 121(4) |
| C(9) | 8163(10) | 3201(9) | 874(8) | 120(4) |
| C(10) | 7304(12) | 3727(11) | 1010(10) | 155(6) |
| C(11) | 9243(10) | 1680(10) | 605(9) | 123(5) |
| C(12) | 9340(13) | 825(12) | 468(10) | 168(7) |
| C(13) | 6175(6) | 1589(5) | 562(5) | 55(2) |
| C(14) | 6110(6) | 1102(6) | 86(5) | 63(2) |
| C(15) | 5447(6) | 1490(6) | −474(5) | 62(2) |
| C(16) | 5024(6) | 2290(6) | −441(5) | 56(2) |
| C(17) | 3324(9) | 1372(8) | 546(7) | 103(4) |
| C(18) | 2702(11) | 1085(10) | 1308(8) | 133(5) |
| C(19) | 2899(9) | 3157(8) | 712(7) | 103(4) |
| C(20) | 2731(10) | 4128(9) | 414(8) | 125(5) |
| C(21) | 1769(9) | 2536(8) | −181(7) | 102(4) |
| C(22) | 1689(11) | 1958(10) | −700(8) | 134(5) |
| C(23) | 6168(9) | 3113(9) | −2045(7) | 108(4) |
| C(24) | 6865(10) | 3509(9) | −2661(8) | 124(5) |
| C(25) | 5094(14) | 4899(13) | −1901(11) | 182(8) |
| C(26) | 5312(13) | 4955(12) | −1189(10) | 163(7) |
| C(27) | 4660(12) | 4042(11) | −2930(9) | 138(5) |
| C(28) | 4449(17) | 3150(15) | −3093(13) | 230(11) |
| C(29) | 10742(9) | −4885(8) | 7046(7) | 100(4) |
| C(30) | 10417(12) | −5716(11) | 7010(9) | 148(6) |
| C(31) | 9356(7) | −4641(7) | 8233(6) | 80(3) |
| C(32) | 10041(9) | −4947(8) | 8835(7) | 105(4) |
| C(33) | 10321(8) | −3185(7) | 7411(6) | 85(3) |
| C(34) | 9654(10) | −2527(10) | 7725(9) | 135(5) |
| C(35) | 8113(12) | −2834(11) | 4526(9) | 143(6) |
| C(36) | 7471(14) | −2377(13) | 3905(11) | 181(8) |
| C(37) | 6611(13) | −3308(13) | 5580(11) | 170(7) |
| C(38) | 6817(19) | −4235(18) | 5489(15) | 270(13) |
| C(39) | 7330(2) | −1775(18) | 5469(16) | 261(13) |
| C(40) | 7261(14) | −1441(13) | 6051(11) | 175(7) |
| C(41) | 9757(6) | −3331(6) | 5627(5) | 58(2) |
| C(42) | 10252(6) | −3878(6) | 5211(5) | 63(2) |
| C(43) | 10946(6) | −3456(6) | 4691(5) | 64(2) |

Table 5 (Continued)

| | <i>x</i> | <i>y</i> | <i>z</i> | U_{eq}^a |
|-------|-----------|-----------|----------|-------------------|
| C(44) | 11007(6) | −2610(6) | 4685(4) | 53(2) |
| C(45) | 9945(9) | −477(8) | 3600(7) | 103(4) |
| C(46) | 10331(11) | 227(10) | 3806(9) | 134(5) |
| C(47) | 10139(9) | −1998(8) | 3010(7) | 100(4) |
| C(48) | 9405(11) | −1593(10) | 2453(9) | 140(5) |
| C(49) | 11156(9) | −576(8) | 2304(7) | 101(4) |
| C(50) | 11744(11) | −1091(10) | 1827(9) | 138(5) |
| C(51) | 13212(12) | −1352(11) | 5339(10) | 155(6) |
| C(52) | 12336(10) | −696(10) | 5458(9) | 137(5) |
| C(53) | 12471(9) | −3003(8) | 5938(7) | 104(4) |
| C(54) | 13089(10) | −3333(9) | 6622(8) | 122(5) |
| C(55) | 14044(12) | −2779(11) | 4883(10) | 151(6) |
| C(56) | 14014(14) | −3782(12) | 4846(11) | 179(8) |

^a Equivalent isotropic U defined as one third of the trace of the orthogonalized U_{ij} tensor.

Table 6

Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{\AA}^3 \times 10^3$) for **9**

| | <i>x</i> | <i>y</i> | <i>z</i> | U_{eq}^a |
|-------|----------|----------|----------|-------------------|
| Pd(1) | 7604(1) | 5909(1) | 2543(1) | 43(1) |
| Pd(2) | 3085(1) | 4116(1) | 1889(1) | 48(1) |
| Br(1) | 9332(1) | 5174(1) | 2971(1) | 65(1) |
| Br(2) | 6437(1) | 7818(1) | 2075(1) | 75(1) |
| S(1) | 2893(2) | 5640(2) | 1663(2) | 61(1) |
| P(1) | 7169(2) | 5632(2) | 1050(2) | 51(1) |
| P(2) | 7961(2) | 6088(2) | 4041(2) | 59(1) |
| P(3) | 4044(2) | 2844(2) | 2149(2) | 64(1) |
| P(4) | 1493(2) | 3595(2) | 1803(2) | 61(1) |
| C(1) | 4057(8) | 5138(6) | 1916(6) | 47(3) |
| C(2) | 5006(8) | 5367(6) | 2057(6) | 50(3) |
| C(3) | 5314(9) | 6290(6) | 2020(6) | 52(3) |
| C(4) | 6275(7) | 6557(6) | 2197(6) | 44(2) |
| C(11) | 5929(8) | 6027(7) | 220(6) | 63(3) |
| C(12) | 7159(9) | 4444(7) | 818(7) | 76(3) |
| C(13) | 8090(9) | 6076(8) | 657(7) | 82(4) |
| C(21) | 7036(10) | 6686(9) | 4321(8) | 95(4) |
| C(22) | 9161(9) | 6663(10) | 4682(8) | 103(5) |
| C(23) | 8117(12) | 5033(8) | 4600(8) | 103(5) |
| C(31) | 5389(8) | 2945(7) | 2331(8) | 78(4) |
| C(32) | 4148(11) | 2194(9) | 3116(10) | 109(5) |
| C(33) | 3514(11) | 2033(8) | 1239(9) | 107(5) |
| C(41) | 400(9) | 4320(9) | 1154(10) | 107(5) |
| C(42) | 1446(11) | 3557(11) | 2876(9) | 115(5) |
| C(43) | 955(11) | 2511(9) | 1349(10) | 112(5) |
| C(6) | 140(4) | −560(3) | 570(3) | 262(15) |
| C(5) | 780(3) | 20(3) | 610(3) | 265(15) |
| C(7) | 810(4) | 520(3) | 20(4) | 320(2) |

^a Equivalent isotropic U defined as one third of the trace of the orthogonalized U_{ij} tensor.

tural disorder and the anisotropic refinements including these atoms were unstable, and therefore they were refined isotropically. All hydrogen atoms were generated in idealized positions and refined in a riding model.

The unit cell parameters and systematic absences of $9, h0l$ ($h + l = 2n + 1$) and $0k0$ ($k = 2n + 1$), unambiguously indicated $P2_1/n$ as the space group. The structure was solved by the heavy-atom method. All non-hydrogen atoms were refined anisotropically, except for the carbon atoms in the co-crystallized benzene. The benzene molecule exhibited an extremely high structural disorder and lied on the crystallographic inversion point. Therefore, the benzene carbon atoms (C(5)–C(7)) were refined isotropically. All hydrogen atoms were generated in idealized positions and refined in a riding model. Final atomic positional parameters for non-hydrogen atoms are given in Tables 4–6. Atomic coordinates of hydrogen atoms and all bond distances and angles are available from the author (Y.J. Kim).

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