

Preparation and reactions of methylpalladium(II) and -platinum(II) azido complexes

The crystal structure of *trans*-PdMe(N₃)(PMe₃)₂ and *trans*-PdMe[CN₄(C₆H₁₁)](PMe₃)₂

Yong-Joo Kim^{a,*}, Dae-Hun Kim^a, Jae-Young Lee^a, Soon-W. Lee^b

^a Department of Chemistry, Kangnung National University, Kangnung 210-702, South Korea

^b Department of Chemistry, Sung Kyun Kwan University, Natural Science Campus, Suwon 440-746, South Korea

Received 16 October 1996; revised 6 November 1996

Abstract

PdMe(OCOCF₃)(tmeda) (tmeda = *N,N,N',N'*-tetramethylethylenediamine) reacts with NaN₃ to give PdMe(N₃)(tmeda) (**1**). The tmeda ligand in complex **1** is easily replaced by addition of phosphine or amine ligands such as PMe₃, bis(diphenylphosphino)methane (dppm), 1,2-bis(diphenylphosphino)ethane (dppe), 1,3-bis(diphenylphosphino)propane (dppp) and 2,2'-bipyridine (bpy) to give the corresponding palladium(II) azido complexes with the phosphine or amine ligand, PdMe(N₃)L₂ (**2**: L = PMe₃; **3**: L₂ = dppm; **4**: L₂ = dppe; **5**: L = dppp; **6**: L₂ = bpy). The platinum(II) azido complex, *trans*-PtMe(N₃)(PMe₃)₂ (**8**), is obtained from ligand exchange of PtMe(N₃)(COD) (**7**) by PMe₃. The methylpalladium(II) and -platinum(II) azido complexes are isolated in high yields and are thermally stable in the solid state as well as in solution. X-ray diffraction analysis of **2** shows the structure which has a distorted square planar coordination around the Pd center with a Pd–N(azido group) bond distance of 2.132(9) Å. Reactions of **2** and of **8** with an equal amount of *tert*-butyl, cyclohexyl, and 2,6-dimethylphenyl isocyanides cause 1,3-dipolar addition of the isocyanides to the azido ligand to give the complexes, *trans*-MMe[CN₄(R)](PMe₃)₂ (M = Pd, R = C(CH₃)₃ (**9**), C₆H₁₁ (**10**), C₆H₃-Me₂ (**11**); M = Pt, R = C(CH₃)₃ (**12**)) with a five-membered heterocyclic ring (C-coordinated tetrazolato group). The molecular structure of **10** determined by X-ray diffraction study displays a slightly distorted square planar coordination around the Pd center with a five-membered heterocyclic ring. Bond parameters indicate localization of π-electron density in the C–N bond and a delocalization of the negative charge over the other three nitrogen atoms. Reactions of complex **2** with protonating agents such as benzenthioi and phenylacetylene are also described.

Keywords: Palladium; Azido complexes; Platinum; Crystal structure

1. Introduction

Transition metal azido complexes have been extensively investigated because of their analogy with organic azides which undergo various reactions such as organic nitrogen (or imido) formation through the cleavage of the N–N bond by photolysis or heterocycles formation by 1,3-dipolar addition (for reviews see Refs. [1,2]). Earlier work by Beck and coworkers demonstrated 1,3-dipolar addition and some carbonylation of Ni(II), Pd(II), and Pt(II) azido complexes with chelating or tertiary phosphine ligand [3,4]. Recently, several Ni(II), Pd(II), and Pt(II) azido complexes with chelating or tertiary phosphine ligand have been prepared and

proved to be effective precursors for the metal nitrido (or imido) species or cluster compounds [5–9]. On the other hand, various mono-, di-, and tetranuclear nickel complexes with chelating amine ligands including an azido group as a bridging or terminal ligand have been widely studied from the structural and magnetic viewpoints [10]. However, the chemical reactivities about the late transition metal mono azido complexes having alkyl, aryl or halogeno ligand are relatively rare. Further, combination of the alkyl (or aryl) ligand and azido ligand coordinated to the late transition metal might possess a considerable potential as a precursor of metal amide complex or organic amines by the use of a suitable reducing agent or thermal condition on the coordinated azido group. This study is also closely related to the late-transition-metal-catalyzed organic

* Corresponding author.

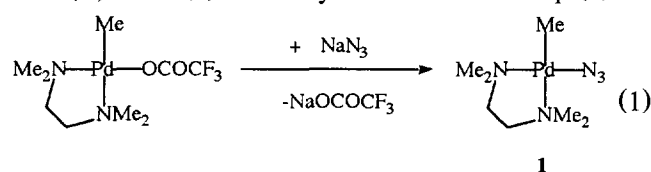
synthesis such as the transformation of organic azides to amines.

In this work, as the initial step for the utility of the metal azido complexes, we have investigated preparation, characterization, and chemical reactions of a series of new methylpalladium(II) and -platinum(II) azido complexes with chelating phosphine, tertiary phosphine, and amine ligands.

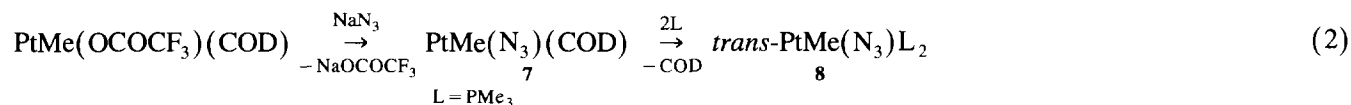
2. Results and discussion

2.1. Preparation and reactions of methylpalladium(II) and -platinum azido complexes

The azido group has been usually introduced into transition metal complexes by metathesis reactions of halogeno metal complexes with sodium azide. Previously we have reported that alkylpalladium(II) trifluoroacetate complexes having phosphine ligand are easily prepared by protonolysis of dialkylpalladium(II) complexes with trifluoroacetic acid and that their trifluoroacetato groups are readily replaced by sodium azide to give alkylpalladium(II) azido complexes [11]. Thus, we initially prepared methylpalladium(II) trifluoroacetate complex containing the *N,N,N',N'*-tetramethylethylenediamine (tmeda) ligand and then examined further treatment of it with sodium azide to form methylpalladium(II) azide (**1**) in 94% yield as shown in Eq. (1).



The reaction occurs in aqueous THF solution similarly to common substitution reactions of the metal



Those ligand exchange reactions of the complexes containing tmeda or COD ligand provide a convenient method for transition metal azido complexes similar to the preparation of the transition metal alkyl complexes by use of alkylmetal complexes with tmeda or COD ligand as the starting material.

Pale yellow crystals of **2** were obtained from a diethyl ether solution at -20°C and X-ray analysis was undertaken. The molecular structure of **2** with the atomic numbering scheme is shown in Fig. 1, in which N1A (site occupation factor 0.25), the disordered counterpart of N1, is omitted for clarity. Complex **2** shows a distorted square plane, which consists of a methyl, two

halide by sodium azide. It is proved that the trifluoroacetate group is playing a role as a good leaving group. The isolated complex **1** is stable at room temperature in the solid state as well as in solution but shows slight light sensitivity. Complex **1** is characterized by IR, NMR, and elemental analysis. The IR spectrum shows a strong absorption band at 2032 cm^{-1} which can be assigned to the asymmetric stretching vibration. Other spectroscopic data are consistent with the proposed structure.

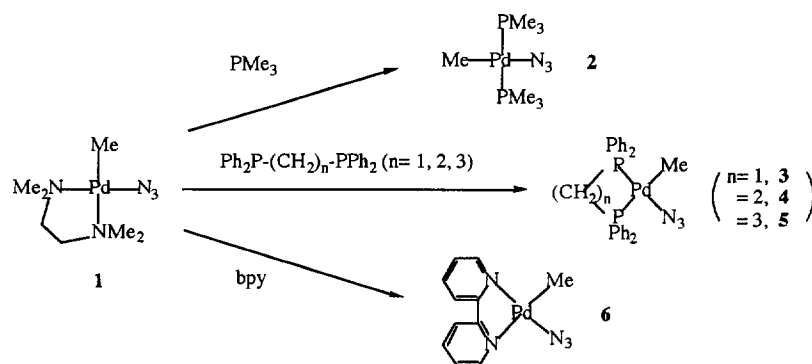
It is well known that tmeda or 1,5-cyclooctadiene (COD) ligand coordinated to a late transition metal is labile and easily replaced by other N- or P-donor ligands [12–14]. The same exchange reaction using complex **1** is applied here to afford the corresponding alkylpalladium(II) azido complexes by interaction of PdMe(N₃)(tmeda) (**1**) with an equivalent amount of trimethylphosphine, chelating phosphines, and bipyridyl as shown in Scheme 1.

These reactions easily occur to give new alkylpalladium(II) azido complexes **2–6** which are obtained in high yields as white or yellow crystalline solids. They are stable at room temperature in the solid state as well as in solution. Complex **2** is independently obtained also from metathetical reactions of *trans*-PdMe(X)(PMe₃)₂ (X = Cl, OCOCF₃) with excess NaN₃. The complexes are characterized by IR, NMR (¹H, ¹³C{¹H}, and ³¹P{¹H}), and elemental analyses. IR spectra show the characteristic band of $\nu_{\text{as}}(\text{N}_3)$ at ca. $2030\text{--}2040\text{ cm}^{-1}$. Other spectral data well support the proposed structure.

On the other hand, for methylplatinum(II) azido complexes we used PtMe₂(COD) as a starting material due to poor yield of PtMe₂(tmeda). First, the ligand substitution reaction of PtMe(OCOCF₃)(COD) by NaN₃ similar to Eq. (1) affords complex **7** in quantitative yield and then the replacement reaction by PMe₃ gives complex **8** in 92% yield as shown in Eq. (2).

PMe₃ at mutually trans positions, and one azido ligand. The plane, defined by Pd, P1, P2 and C1 is essentially planar with the average atomic displacement of 0.032 Å from this plane. The nitrogen atom (N1), directly bonded to Pd, lies off out of this plane by 0.55(2) Å. In addition, the dihedral angle between this plane and the plane of the azido group is 81(2)°.

The Pd–N1 bond length (2.132(9) Å) is slightly larger than those found in [(C₆H₅CH₂)₃P]₂Pd(N₃)₂ (2.045(6) Å) [15] or Pd₂(N₃)²⁻ (2.004(5) Å) [16], implying a greater trans influence for CH₃ than the azido group. The bond angle of Pd–N1–N2 is 128.7(8)° which is almost similar to those of previous coordinated



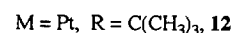
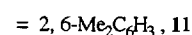
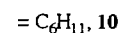
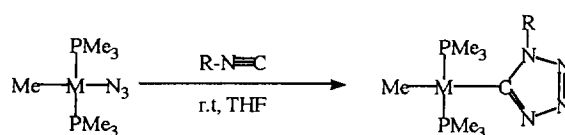
Scheme 1.

azides [2]. However, the bond angle ($164.8(10)^\circ$) of the N_3 group is significantly bent in comparison with other linear N_3 ($173\text{--}180^\circ$) group in the known coordinated azide [2]. The $N1\text{--}N2$ ($1.206(12)\text{ \AA}$) distance is relatively longer than the $N2\text{--}N3$ ($1.144(9)\text{ \AA}$) distance, as was the case in the above coordinated azide, indicating significant π -bonding of the latter than that before.

2.2. Reaction of 2 and of 8 with isocyanides

In order to gain insight into the chemical reactivities about the above methylpalladium(II) and -platinum azido complexes we first initiated a small molecule insertion into the coordination bond using isocyanides which are isoelectronic with CO. Reactions of 2 and of 8 with an equal amount of *tert*-butyl, cyclohexyl, and 2,6-dimethylphenyl isocyanides gave the complexes with a five-membered heterocyclic ring (*C*-coordinated tetrazolato group) by 1,3-dipolar addition of isocyanides to the azido moiety of methylpalladium and -platinum(II) azido complexes as shown in Eq. (3). The isolated complexes are obtained as white crystals which are stable at room temperature in the solid state as well as in solution and characterized by IR, NMR (^1H , $^{13}\text{C}\{^1\text{H}\}$ and $^{31}\text{P}\{^1\text{H}\}$) spectroscopy, and elemental analyses. Complex 10 has

been characterized by a single-crystal X-ray diffraction study.



These reactions smoothly proceed to give the corresponding methylpalladium(II) and -platinum(II) complexes having a five-membered ring and their completion can be monitored easily by the disappearance of the asymmetric stretching band of the N_3 group in the IR spectra of the reaction mixture and by appearance of a new band in the $1200\text{--}1500\text{ cm}^{-1}$ region of the product. Under an excess amount of isocyanides the formation reactions of complexes 10 and 11 afford the adducts $\text{PdMe}(\text{CN}_4\text{R})(\text{PMe}_3)_2 \cdot (\text{CNR})$ ($R = \text{cyclohexyl}, 2,6\text{-dimethylphenyl}$) having a weakly coordinated isocyanide whose $\nu(\text{C}\equiv\text{N})$ band is observed at ca. 2200 cm^{-1} . The coordinated isocyanides are easily removed by recrystallization of the product. Also, the other insertion product such as the imino-bonded complex [17] by isocyanide insertion to the metal–methyl bond was not observed. The ^1H and ^{13}C NMR spectra of the complexes 9–12 show signals due to $\text{Pd}\text{--}\text{CH}_3$ hydrogen atoms as a triplet coupled with two phosphorus of PMe_3 . The carbon signal of the *C*-coordinated tetrazolato ring in the $^{13}\text{C}\{^1\text{H}\}$ NMR spectra of the above complexes also shows a triplet coupled with two phosphorus of PMe_3 . The PMe_3 signals in the ^1H and ^{13}C NMR spectra appear as apparent triplets due to virtual coupling.

The cyclo addition reactions of Pd(II) and Pt(II)

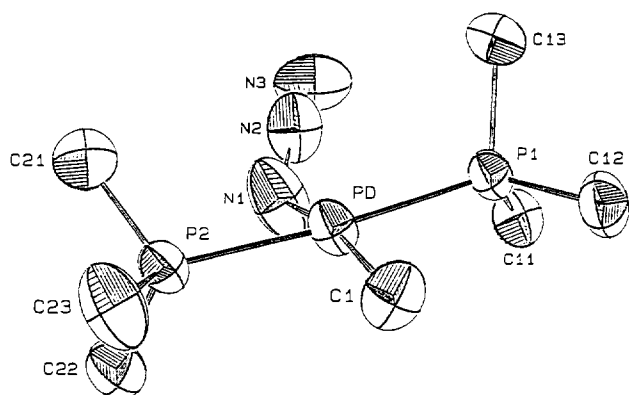


Fig. 1. ORTEP drawing of 2 showing the atomic labeling scheme and 50% probability thermal ellipsoids.

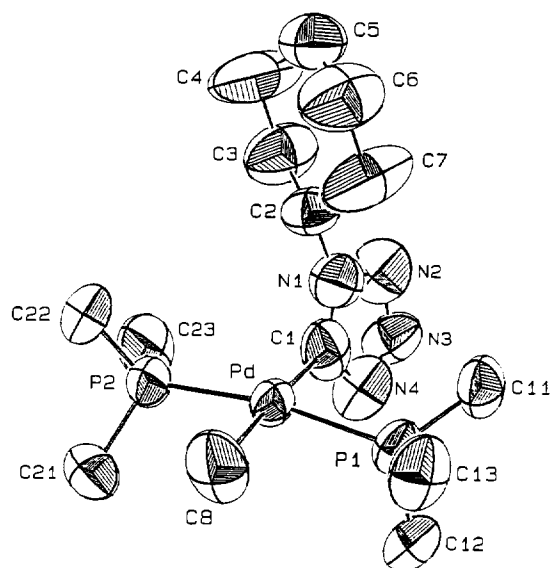


Fig. 2. ORTEP drawing of **10** showing the atomic labeling scheme and 50% probability thermal ellipsoids.

diazido complexes with isocyanides results in formation of the complexes with *C*-coordinated tetrazolato ring which were originally studied by Beck and coworkers [3,4], while similar reactions of azido complexes of Pd(II) [18], Cu(I), Ag(I), and Au(I) [19] having terminal or bridging azido ligands with CS₂ and CF₃CN give the complexes with an *N*-coordinated tetrazolato ring.

The formation of the CN₄(R) group probably proceeds through the coordination of isocyanide on the square planar complex to give the five-coordinated intermediate which then undergoes intramolecular rearrangement. Previously Treichel et al. [20] showed that reaction of [L₂Pt(CNCH₃)₂][BF₄]₂ (L = PPh₃) with N₃ anion gave [L₂Pt(CNCH₃)(CN₄CH₃)][BF₄] and with iodine also gave [L₂Pt(CNCH₃)₂I][BF₄] as a five-coordinated complex.

Crystals of **10** for X-ray study were obtained from a THF–hexane solution. The molecular structure with the atomic numbering scheme in Fig. 2 shows an expected structure having a *C*-coordinated tetrazolato ligand. The structure displays a slightly distorted square planar coordination around the Pd center including the tetrazolato

ligand. The coordination plane, defined by Pd, P1, P2, C1, and C8, is nearly planar with the average atomic displacement of 0.073 Å from the plane. The five-membered ring, defined by C1, N1, N2, N3, and N4, is essentially planar with the average atomic displacement of 0.005 Å. The Pd–C1 and Pd–C8 bond lengths (2.054(8), 2.095(7) Å) are typical values of for Pd–C(sp³) σ-bonds [21], which are generally within 2.01 to 2.12 Å, reflecting a similar trans influence between the complexes. The C1–N1 bond length (1.223 Å) which is the normal value in free ketimines [22] and C1–N4 (1.397 Å) is also significantly shorter than the C–N single bond length (1.472 Å) [23] due to a partial double bond character. The N2–N3 and N3–N4 bond lengths (1.279(8) and 1.291(8) Å) are slightly longer than typical N=N double bonds, such as *trans*-azobenzene (1.247(2) Å) [24], but their bond lengths when compared with the N–N single bonds (1.45 Å) [25] are close to the N=N double bond, suggesting a considerable localization of π-electron density in the bond. The Pd–C1–N1 angle (128.7(8)°) is almost the same as that of Pd–C1–N4 (126.0(7)°). All these data therefore indicate localization of π-electron density in the C1–N1 bond and a delocalization of the negative charge over the N2–N3–N4 part of the ring, which is different from the proposed structure. In order to confirm the electron delocalization in the above tetrazolato ring, we have compared the corresponding bond distances and angles of the previous known X-ray data of the transition metal complex with a *C*-coordinated tetrazolato ring, [As(C₆H₅)₄][Au(CN₄R)₄] (R = *i*-C₃H₇) [26] and other related complexes with *N*-coordinated tetrazolato ring, Pd(N₄CR)₂(PPh₃)₂ (R = Ph) [4] in Fig. 3. The C1–N1 bond which is originated from free isocyanide and N2–N3–N4 bond distances in the complex **10** are relatively shorter than those of other tetrazolato complexes, but other N1–N2 bond and C1–N4 bond distances are longer than those of the other two complexes. However, the bond angles of the tetrazolato ring in the *C*-coordinated complex in both **10** and Au(CN₄R)₄[−] are almost similar. In contrast, each bond distance in the tetrazolato ring of the other two complexes shows almost similar

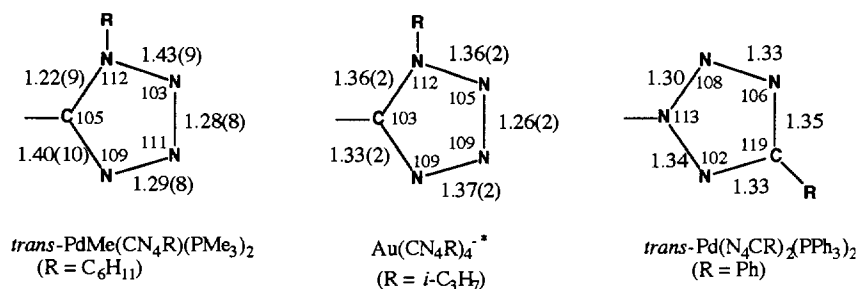
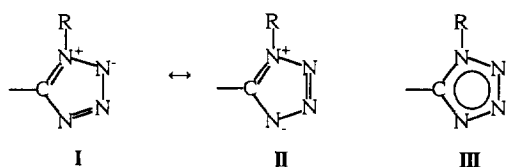


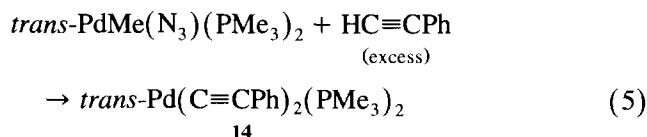
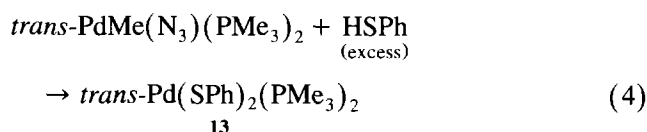
Fig. 3. Comparison of bond distances (Å) and angles (deg) in the tetrazolato ring of the complexes. The asterisk sign indicates the average value of bond lengths and angles of the four tetrazolato ligands.

bond distances, supporting the electronic delocalization of the five-membered ring. Therefore, the following five-membered structures such as **I** and **II** in the tetrazolato ring of complex **10**, suggesting a localization of π -electron density in the C1–N1 bond and a delocalization of the negative charge over the N2–N3–N4 part of the ring, are presumed as the main contribution to the electronic structure rather than structure **III**.



2.3. Reaction of **2** with various reagents

When excess benzenethiol was added to a THF solution of $trans\text{-PdMe}(\text{N}_3)(\text{PMe}_3)_2$ at room temperature, bisthiolato complex $trans\text{-Pd}(\text{SPh})_2(\text{PMe}_3)_2$ (**13**) was obtained in 84% yield as a yellow precipitate, as shown in Eq. (4). A similar reaction with excess phenylacetylene also gives the bisacetylide complex $trans\text{-Pd}(\text{C}\equiv\text{CPh})_2(\text{PMe}_3)_2$ (**14**) in 26% yield.



In Eq. (4), the reaction rapidly proceeds to give sole bisthiolato complex with evolution of methane but under an equimolar amount of benzenethiol the reaction gives a mixture of bisthiolato complex and starting material. The expected $trans\text{-Pd}(\text{SPh})(\text{N}_3)(\text{PMe}_3)_2$ or $trans\text{-PdMe}(\text{SPh})(\text{PMe}_3)_2$ by a stepwise deprotonation of palladium–methyl or azido bond was not observed. In Eq. (5), under excess amount of phenylacetylene (over 4 equiv.) the reaction produces the bisacetylide complex **14** and starting material. The pure bisacetylide complex can be separated from recrystallization. Recently, we have found that the reaction of $trans\text{-PdMe}(\text{OR})(\text{PMe}_3)_2 \cdot (\text{HOR})$ ($\text{R} = \text{CH}(\text{CF}_3)\text{Ph}$) with phenylacetylene (1.5 equiv.) gives $trans\text{-PdMe}(\text{C}\equiv\text{CPh})(\text{PMe}_3)_2$ which further reacts with excess phenylacetylene to give $trans\text{-Pd}(\text{C}\equiv\text{CPh})_2(\text{PMe}_3)_2$ [27,28]. Very recently Field et al. [29] have shown that the azido ligands in $\text{Fe}(\text{N}_3)_2(\text{dmpe})_2$ are readily re-

placed by acetylide in the presence of sodium methoxide to give $\text{Fe}(\text{C}\equiv\text{CR})_2(\text{dmpe})_2$ ($\text{R} = \text{Ph}, t\text{-Bu}$). On the other hand, the reaction of $trans\text{-PdMe}(\text{Cl})(\text{PMe}_3)_2$ with excess phenylacetylene even at 60°C does not produce acetylide complex. Thus, the observed bond strength order effecting the trans influence between the ligands throughout the above ligand replacement reaction is $\text{Pd-Cl} > \text{Pd-C}(\text{acetylide})$ or $\text{Pd-SPh} > \text{Pd-N}(\text{azido})$ or $\text{Pd-C}(\text{methyl})$. Further, the above resulting protonation into the palladium–azido bond shows very intriguing properties in relation to Pd–N bond activation.

In summary we have prepared several new alkylpalladium(II) and -platinum(II) azido complexes in the present study. These complexes undergo 1,3-dipolar addition of isocyanides and protonation into the metal–azido bond. Further investigation of properties of the complexes including reduction into the metal–azido bond is under way.

3. Experimental

All manipulations of air-sensitive compounds were performed under N_2 or argon atmosphere with use of standard Schlenk techniques. Solvents were distilled from *n*-benzophenone. Bis(diphenylphosphino)methane (dppm), 1,2-bis(diphenylphosphino)ethane (dppe), 1,3-bis(diphenylphosphino)propane (dppp), PMe_3 and isocyanides (*tert*-butyl, cyclohexyl, and 2,6-dimethylphenyl) were commercial-grade reagents and used without further purification. $\text{PdMe}_2(\text{tmeda})$ [14], $trans\text{-PdMe}_2(\text{PMe}_3)_2$ [30], and $\text{PtMe}_2(\text{COD})$ [13] were prepared by the literature method.

Elemental analyses were carried out by the analytical laboratory at the Tokyo Institute of Technology in Japan and the Basic Science Institute in South Korea. NMR spectra were recorded on JEOL-FX 100 and Bruker-500 spectrometers. IR spectra were recorded on a Hitachi 270-30 spectrophotometer.

3.1. Preparation of $\text{PdMe}(\text{N}_3)(\text{tmeda})$, (**1**)

To an ethereal solution (35 ml) containing $\text{PdMe}_2(\text{tmeda})$ (0.757 g, 2.99 mmol) was slowly added $\text{CF}_3\text{CO}_2\text{H}$ (0.340 g, 2.99 mmol). The initially colorless solution turned to a pale green suspension with gas evolution on stirring at room temperature. After stirring for 1 h the precipitated solids were filtered, washed with *n*-hexane (1.00 g, 95%). Recrystallization from THF–*n*-hexane gave pale yellow crystals of $\text{PdMe}(\text{OCOCF}_3)(\text{tmeda})$. ^1H NMR (CDCl_3 , 500 MHz, δ): 0.37 (s, 3H, Pd–Me), 2.45, 2.61 (s, 12H, N– Me_2), 2.47, 2.65 (m, 4H, N– CH_2). $^{13}\text{C}\{^1\text{H}\}$ NMR (125 MHz, CDCl_3 , δ): –2.96 (s, Pd–Me), 47.43, 51.30 (s, N– Me_2), 57.07, 63.63 (s, N– CH_2), 115.7 (q, CF_3 , $J(\text{CF})$

= 290 Hz), 161.5 (q, CCF_3 , $J(\text{CF}) = 35$ Hz). Anal. Calcd. for $\text{C}_9\text{H}_{19}\text{F}_3\text{O}_2\text{N}_2\text{Pd}$: C, 30.83; H, 5.46; N, 7.99. Found: C, 30.56; H, 5.20; N, 7.87.

To a THF solution (5 ml) of $\text{PdMe}(\text{OCOCF}_3)(\text{tmeda})$ (0.717 g, 2.04 mmol) was added aqueous THF solution of NaN_3 (0.198 g, 3.06 mmol) by a canula. After stirring for 4 h at room temperature the reaction mixture was evaporated to give pale yellowish residues in vacuo and then extracted with CH_2Cl_2 . The collected yellow solution was reduced to 2 ml and *n*-hexane (5 ml) was added. The resulting pale yellow solids were filtered, dried in vacuo. The yield of **1** was 0.543 g (94%). IR (KBr): 2032 cm^{-1} (N_3). $^1\text{H NMR}$ (CDCl_3 , 500 MHz, δ): 0.32 (s, 3H, Pd–Me), 2.41, 2.56 (s, 12H, N–Me₂), 2.43, 2.62 (m, 4H, N–CH₂). $^{13}\text{C}\{^1\text{H}\}$ NMR (125 MHz, CDCl_3 , δ): 1.13 (s, Pd–Me), 47.39, 50.64 (s, N–Me₂), 57.34, 63.08 (s, N–CH₂). Anal. Calcd. for $\text{C}_7\text{H}_{19}\text{N}_5\text{Pd}$: C, 30.06; H, 6.85; N, 25.05. Found: C, 29.98; H, 6.76; N, 24.94.

3.2. Ligand exchange reaction of **1** with PMe_3 , *dppm*, *dppe*, *dppp*, and *bpy*

To a THF solution (8 ml) of **1** (0.543 g, 1.91 mmol) was added PMe_3 (4.20 mmol, 1 M THF solution). After stirring for 1 h at room temperature the solution was fully evaporated and washed with *n*-hexane. Recrystallization from THF–*n*-hexane gave white crystals of **2** (0.478 g, 79%). IR (KBr): 2040 cm^{-1} (N_3). $^1\text{H NMR}$ (CDCl_3 , 500 MHz, δ): 0.05 (t, 3H, $J = 6.2$ Hz, Pd–Me), 1.37 (bs, 18H, PMe_3). $^{13}\text{C}\{^1\text{H}\}$ NMR (125 MHz, CDCl_3 , δ): –9.85 (s, Pd–Me), 13.21 (t, $J = 13.7$ Hz, PMe_3). $^{31}\text{P}\{^1\text{H}\}$ NMR (200 MHz, CDCl_3 , δ): –13.0 (s). Anal. Calcd. for $\text{C}_7\text{H}_{21}\text{N}_3\text{P}_2\text{Pd}$: C, 26.64; H, 6.71; N, 13.32. Found: C, 26.96; H, 6.72; N, 13.02.

Complex **2** was independently prepared from reactions of *trans*- $\text{PdMe}(\text{X})(\text{PMe}_3)_2$ (X = Cl, OCOCF_3) with excess NaN_3 .

Similar ligand exchange reactions of **1** with an equimolar amount of *dppm*, *dppe*, *dppp*, and *bpy* were carried out. $\text{PdMe}(\text{N}_3)(\text{dppm})$, **3**: 92%. IR (KBr): 2044 cm^{-1} (N_3). $^1\text{H NMR}$ (CDCl_3 , 500 MHz, δ): 0.43 (s, 3H, $J = 2.7$ Hz, Pd–Me), 3.89 (bt, 2H, P–CH₂), 7.39–7.57 (m, 20H, aromatic). $^{13}\text{C}\{^1\text{H}\}$ NMR (125 MHz, CDCl_3 , δ): 3.61 (bt, Pd–Me), 29.4 (bs, P–CH₂), 128.3, 129.3, 131.5, 133.4 (s, aromatic). $^{31}\text{P}\{^1\text{H}\}$ NMR (200 MHz, CDCl_3 , δ): 17.7 (s). Anal. Calcd. for $\text{C}_{26}\text{H}_{25}\text{N}_3\text{P}_2\text{Pd}$: C, 56.99; H, 4.59; N, 7.67. Found: C, 56.78; H, 4.88; N, 7.37. $\text{PdMe}(\text{N}_3)(\text{dppe})$, **4**: 96%. IR (KBr): 2028 cm^{-1} (N_3). Spectroscopic data are consistent with the previous literature data [11]. $\text{PdMe}(\text{N}_3)(\text{dppp})$, **5**: 97%. IR (KBr): 2028 cm^{-1} (N_3). $^1\text{H NMR}$ (CDCl_3 , 500 MHz, δ): 0.58 (dd, 3H, $J = 3.1$, 7.4 Hz, Pd–Me), 1.86 (m, 2H, –CH₂), 2.33, 2.43 (m, 4H, P–CH₂), 7.38, 7.41, 7.61, 7.68 (m, 20H, aromatic). $^{13}\text{C}\{^1\text{H}\}$ NMR (125 MHz, CDCl_3 , δ): 16.3 (d, $J =$

93 Hz, Pd–Me), 19.1 (d, $J = 5.2$ Hz, –CH₂), 27.1 (broad dd, $J = 19.8$ Hz, P–CH₂), 29.0 (dd, $J = 8.7$, 29.6 Hz, P–CH₂), 128.3, 128.6, 130.1, 130.7, 130.8, 131.1, 132.4, 132.7, 133.2, 133.3 (s, aromatic). $^{31}\text{P}\{^1\text{H}\}$ NMR (200 MHz, CDCl_3 , δ): –6.6, 27.3 (dd, $J = 50.9$ Hz). Anal. Calcd. for $\text{C}_{28}\text{H}_{29}\text{N}_3\text{P}_2\text{Pd}$: C, 58.39; H, 5.08; N, 7.29. Found: C, 58.48; H, 5.31; N, 6.73. $\text{PdMe}(\text{N}_3)(\text{bpy})$, **6**: 30%. IR (KBr): 2040 cm^{-1} (N_3). $^1\text{H NMR}$ (CDCl_3 , 500 MHz, δ): 0.96 (s, 3H, Pd–Me), 7.54 (m, 2H, aromatic), 8.04 (m, 4H, aromatic), 8.71 (m, 2H, aromatic). $^{13}\text{C}\{^1\text{H}\}$ NMR was not observed due to low solubility. Anal. Calcd. for $\text{C}_{11}\text{H}_{11}\text{N}_5\text{Pd}$: C, 41.33; H, 3.47; N, 21.91. Found: C, 41.30; H, 3.24; N, 22.40.

The platinum azide complex was analogously prepared using the procedure described for **1** and using $\text{PtMe}_2(\text{COD})$ as a starting material. $\text{PtMe}(\text{OCOCF}_3)(\text{COD})$ (96%): $^1\text{H NMR}$ (100 MHz, CDCl_3 , δ): 0.37 (s, 3H, Pt–Me), 2.12 (m, 8H, –CH₂), 4.20, 4.93 (bs, 4H, –CH). Anal. Calcd. for $\text{C}_{11}\text{H}_{15}\text{F}_3\text{Pt}$: C, 30.63; H, 3.51. Found: C, 30.80; H, 3.43. $\text{PtMe}(\text{N}_3)(\text{COD})$, **7** (98%): IR (KBr): 2056 cm^{-1} (N_3). $^1\text{H NMR}$ (CDCl_3 , 500 MHz, δ): 0.69 (s, 3H, $J(\text{Pt–H}) = 72$ Hz, Pt–Me), 2.35 (m, 8H, –CH₂), 4.47, 5.19 (s, 4H, –CH). $^{13}\text{C}\{^1\text{H}\}$ NMR (125 MHz, CDCl_3 , δ): 6.40 (s, $J(\text{PtC}) = 677$ Hz, Pt–Me), 27.98 (s, $J(\text{PtC}) = 18$ Hz, –CH₂), 31.68 (s, $J(\text{PtC}) = 20$ Hz, –CH₂), 82.63 (s, $J(\text{PtC}) = 197$ Hz, –CH), 111 (s, $J(\text{PtC}) = 20$ Hz, –CH). Anal. Calcd. for $\text{C}_9\text{H}_{15}\text{N}_3\text{Pt}$: C, 30.00; H, 4.20; N, 11.66. Found: C, 30.07; H, 4.10; N, 11.38. *trans*- $\text{PtMe}(\text{N}_3)(\text{PMe}_3)_2$, **8** (92%): IR (KBr): 2040 cm^{-1} (N_3). $^1\text{H NMR}$ (CDCl_3 , 500 MHz, δ): 0.26 (t, 3H, $J(\text{PtH}) = 80$ Hz, Pt–Me), 1.44 (t, 18H, $J(\text{PtH}) = 29$ Hz, PMe_3). $^{13}\text{C}\{^1\text{H}\}$ NMR (125 MHz, CDCl_3 , δ): –25.0 (bs, $J(\text{PtC}) = 638$ Hz, Pt–Me), 12.83 (t, $J(\text{PtC}) = 37$ Hz, PMe_3). $^{31}\text{P}\{^1\text{H}\}$ NMR (200 MHz, CDCl_3 , δ): –10.8 (s, $J(\text{PtP}) = 2781$ Hz). Anal. Calcd. for $\text{C}_7\text{H}_{21}\text{N}_3\text{P}_2\text{Pt}$: C, 20.79; H, 5.24; N, 10.40. Found: C, 20.91; H, 5.25; N, 10.42.

3.3. Reaction of **2** and of **8** with isocyanides (*tert*-butyl, cyclohexyl, 2,6-dimethylphenyl)

To a THF (5 ml) solution containing **2** (0.233 g, 0.74 mmol) was added *tert*-butyl isocyanide (0.068 g, 0.74 mmol) at room temperature. After stirring for 3 h the reaction mixture was fully evaporated and then washed with *n*-hexane (2 ml \times 3), with ether (1 ml \times 3). Recrystallization from THF–*n*-hexane gave white crystals of *trans*- $\text{PdMe}[\text{CN}_4(\text{R})](\text{PMe}_3)_2$ (R = C(CH₃)₃), **9** (0.117 g, 43%). $^1\text{H NMR}$ (CDCl_3 , 500 MHz, δ): 0.30 (t, 3H, $J = 6.8$ Hz, Pd–Me), 1.15 (t, 18H, $J = 3.3$ Hz, Pd– PMe_3), 1.30 (m, 3H), 1.70 (m, 1H), 1.86 (m, 4H), 2.02 (m, 2H), 4.38 (m, 1H, C₆H₁₁). $^{13}\text{C}\{^1\text{H}\}$ NMR (125 MHz, CDCl_3 , δ): –6.83 (t, $J = 7.7$ Hz, Pd–Me), 14.51 (t, $J = 15$ Hz, Pd– PMe_3), 25.2, 25.6, 33.9, 58.3 (s, C₆H₁₁), 173.0 (t, $J(\text{CP}) = 17$ Hz, a carbon of tetra-

zolato ring). $^{31}\text{P}\{^1\text{H}\}$ NMR (200 MHz, CDCl_3 , δ): –14.0 (s). Anal. Calcd. for $\text{C}_{12}\text{H}_{30}\text{N}_4\text{P}_2\text{Pd}$: C, 36.14; H, 7.58; N, 14.05. Found: C, 36.26; H, 7.85; N, 14.27.

Similar complexes *trans*-PdMe[CN₄(R)](PMe₃)₂ (R = C₆H₁₁ (**10**), C₆H₃-Me₂ (**11**)) were obtained as white crystals using the procedure described for **9**, employing an equimolar amount of cyclohexyl and 2,6-dimethylphenyl isocyanide respectively. **10** (56%). ^1H NMR (CDCl_3 , 500 MHz, δ): –0.29 (t, 3H, $J = 7.0$ Hz, Pd–Me), 1.11 (t, 18H, $J = 3.2$ Hz, PdPMe₃), 1.70 (s, 9H, C(CH₃)₃). $^{13}\text{C}\{^1\text{H}\}$ NMR (125 MHz, CDCl_3 , δ): –8.25 (t, $J = 8.0$ Hz, Pd–Me), 14.5 (t, $J = 15$ Hz, Pd–PMe₃), 31.2, 57.1 (s, C(CH₃)₃), 170.8 (t, $J(\text{CP}) = 17$ Hz, a carbon of tetrazolato ring). $^{31}\text{P}\{^1\text{H}\}$ NMR (200 MHz, CDCl_3 , δ): –14.1 (s). Anal. Calcd. for $\text{C}_{14}\text{H}_{32}\text{N}_4\text{P}_2\text{Pd}$: C, 39.58; H, 7.59; N, 13.19. Found: C, 39.57; H, 7.67; N, 13.03. **11** (66%). ^1H NMR (CDCl_3 , 500 MHz, δ): 0.03 (t, 3H, $J = 6.9$ Hz, Pd–Me), 1.39 (t, 18H, $J = 3.0$ Hz, Pd–PMe₃), 2.36 (s, 6H, Me), 6.65 (t, 1H, aromatic), 6.90 (d, 2H, aromatic). $^{13}\text{C}\{^1\text{H}\}$ NMR (125 MHz, CDCl_3 , δ): –10.7 (bs, Pd–Me), 13.6 (t, $J = 14$ Hz, Pd–PMe₃), 19.5 (s, Me), 118.9, 127.7, 130.9, 145.6 (s, aromatic), 183.2 (broad singlet, a carbon of tetrazolato ring). $^{31}\text{P}\{^1\text{H}\}$ NMR (200 MHz, CDCl_3 , δ): –13.5 (s). Anal. Calcd. for $\text{C}_{16}\text{H}_{30}\text{N}_4\text{P}_2\text{Pd}$: C, 43.01; H, 6.77; N, 12.54. Found: C, 43.37; H, 6.93; N, 12.26.

To a THF (10 ml) solution of **8** (0.275 g, 0.68 mmol) was added *tert*-butyl isocyanide (57 mg, 0.68 mmol) at room temperature. The initial colorless solution instantly turned to a suspension and then changed into a

Table 1
Crystallographic data for **2** and **10**

Complex	2	10
Formula	$\text{C}_7\text{H}_{21}\text{N}_3\text{P}_2\text{Pd}$	$\text{C}_{14}\text{H}_{32}\text{N}_4\text{P}_2\text{Pd}$
Fw	316.62	424.78
Crystal system	monoclinic	monoclinic
Space group	$P2_1/c$	$P2_1/n$
<i>a</i> (Å)	11.422(4)	17.421(5)
<i>b</i> (Å)	9.923(3)	17.573(5)
<i>c</i> (Å)	12.578(4)	6.693(3)
β (deg)	107.84(3)	91.92(3)
<i>V</i> (Å ³)	1357.0(8)	2047(1)
d_{calc} (g cm ^{–3})	1.550	1.378
μ (mm ^{–1})	1.572	1.062
<i>F</i> (000)	644	880
No. of reflections	2251	2733
Used reflections ($I > 2\sigma(I)$)	1676	2499
No. of parameters	131	191
<i>Z</i>	4	4
Scan range	$4 < 2\theta < 45^\circ$	$3 < 2\theta < 45^\circ$
Scan type	$\omega - 2\theta$	$\omega - 2\theta$
GOF on F^2	1.045	1.034
Max. in $\Delta\rho$ (e [–] Å ^{–3})	0.816	0.537
wR_2 ^a	0.1094	0.1044
<i>R</i>	0.0411	0.0419

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

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

Pd(1)–C(1)	2.044(7)	Pd(1)–P(2)	2.319(2)
Pd(1)–N(1)	2.132(9)	N(1)–N(2)	1.206(12)
Pd(1)–P(1)	2.310(2)	N(2)–N(3)	1.144(9)
C(1)–Pd(1)–N(1)	168.0(4)	C(13)–P(1)–Pd(1)	111.1(2)
C(1)–Pd(1)–P(1)	90.1(2)	C(21)–P(2)–Pd(1)	110.5(3)
C(1)–Pd(1)–P(2)	92.7(2)	N(1)–Pd(1)–P(1)	92.2(3)
N(1)–Pd(1)–P(2)	85.9(3)	N(2)–N(1)–Pd(1)	128.7(8)
P(1)–Pd(1)–P(2)	175.09(6)	N(3)–N(2)–N(1)	164.8(10)
C(11)–P(1)–C(12)	103.1(3)		
C(21)–P(2)–C(23)	102.0(4)		

homogeneous solution. On stirring for 3 h the reaction mixture was fully evaporated to give white solids which were washed with *n*-hexane (2 ml × 2), ether (1 ml × 3). Recrystallization from THF–*n*-hexane gave white crystals of *trans*-PtMe[CN₄(R)](PMe₃)₂ (R = C(CH₃)₃), **12** (0.180 g, 54%). ^1H NMR (CDCl_3 , 500 MHz, δ): –0.01 (t, 3H, $J = 7.4$, $J(\text{PtH}) = 55.3$ Hz, Pt–Me), 1.22 (t, 18H, $J = 3.4$, $J(\text{PtH}) = 32$ Hz, Pt–PMe₃), 1.73 (s, 9H, C(CH₃)₃). $^{13}\text{C}\{^1\text{H}\}$ NMR (125 MHz, CDCl_3 , δ): –14.7 (t, $J(\text{CP}) = 8.3$, $J(\text{PtC}) = 451$ Hz, Pt–Me), 13.8 (t, $J(\text{CP}) = 38$, $J(\text{PtC}) = 38$ Hz, Pt–PMe₃), 31.1, 57.5 (s, C(CH₃)₃), 168.0 (t, $J(\text{CP}) = 11.7$ Hz, a carbon of tetrazolato ring). $^{31}\text{P}\{^1\text{H}\}$ NMR (200 MHz, CDCl_3 , δ): –18.4 (s, $J(\text{PtP}) = 2714$ Hz). Anal. Calcd. for $\text{C}_{12}\text{H}_{30}\text{N}_4\text{P}_2\text{Pt}$: C, 29.57; H, 6.20; N, 11.50. Found: C, 29.57; H, 6.27; N, 11.39.

3.4. Reactions of **2** with benzenethiol and phenylacetylene

To a THF (4 ml) solution of **2** (0.235 g, 0.74 mmol) was benzenethiol (0.205 g, 1.86 mmol) at room temperature. The initial colorless solution instantly turned to a yellow suspension with gas evolution. After stirring for 3 h the yellow solids were filtered, washed with *n*-hexane (2 ml × 2). Recrystallization from THF–*n*-hexane gave crystals of *trans*-Pd(SPh)₂(PMe₃)₂, **13** (0.295 g, 84%). ^1H NMR (CDCl_3 , 500 MHz, δ): 1.31 (t, 18H, $J(\text{PH}) = 3.4$ Hz, PMe₃), 6.80 (t, 1H, aromatic), 7.19 (t, 2H, aromatic), 7.68 (d, 2H, aromatic). $^{31}\text{P}\{^1\text{H}\}$ NMR (200 MHz, CDCl_3 , δ): –13.1 (s). Anal. Calcd. for $\text{C}_{18}\text{H}_{28}\text{P}_2\text{PdS}_2$: C, 45.33; H, 5.92; S, 13.45. Found: C, 45.66; H, 6.15; S, 13.03.

Similar reaction of **2** with an equimolar amount of benzenethiol gave complex **13** and unreacted starting material (5:1 ratio by ^{31}P NMR integration).

Complex **13** was also obtained from the reaction of *trans*-PdMe₂(PMe₃)₂ with excess benzenethiol and identified with the spectroscopic data of the complex.

To a THF (4 ml) solution of **2** (0.260 g, 0.82 mmol) was added phenylacetylene (0.420 g, 4.11 mmol) at room temperature. On stirring for 9 h the white solids were precipitated; stirring was continued for 48 h. The final

Table 3
Selected bond lengths (Å) and angles (deg) for **10**

Pd(1)–C(1)	2.054(8)	N(1)–C(1)	1.223(9)
Pd(1)–C(8)	2.095(7)	N(1)–N(2)	1.431(9)
Pd(1)–P(2)	2.285(2)	N(1)–C(2)	1.472(8)
Pd(1)–P(1)	2.297(2)	N(2)–N(3)	1.279(8)
P(1)–C(11)	1.806(7)	N(3)–N(4)	1.291(8)
P(2)–C(22)	1.813(8)	N(4)–C(1)	1.397(10)
C(2)–C(7)	1.423(10)	C(2)–C(3)	1.484(9)
C(1)–Pd(1)–C(8)	176.7(4)	C(1)–N(1)–N(2)	112.1(7)
C(1)–Pd(1)–P(2)	94.6(2)	C(1)–N(1)–C(2)	128.6(8)
C(1)–Pd(1)–P(1)	88.9(2)	N(2)–N(1)–C(2)	119.3(7)
C(8)–Pd(1)–P(2)	87.3(2)	N(3)–N(2)–N(1)	103.0(6)
C(8)–Pd(1)–P(1)	88.8(2)	N(2)–N(3)–N(4)	111.4(6)
P(2)–Pd(1)–P(1)	170.47(7)	N(3)–N(4)–C(1)	108.5(7)
N(1)–C(1)–N(4)	105.0(7)	N(1)–C(2)–C(3)	110.2(6)
N(1)–C(1)–Pd(1)	128.7(8)	C(7)–C(2)–C(3)	113.4(7)
N(4)–C(1)–Pd(1)	126.0(7)		

solids were filtered, washed with *n*-hexane (2ml × 2). Recrystallization from THF–*n*-hexane gave white crystals of *trans*-Pd(C≡CPh)₂(PMe₃)₂, (**14**) (0.105 g, 28%). The filtrate showed partially dissolved complex **14** and starting materials. IR (KBr): 2100 cm⁻¹ (C≡C) ¹H NMR (CDCl₃, 500 MHz, δ): 1.68 (t, 18H, *J*(PH) = 3.6 Hz, PMe₃), 7.15 (t, 1H, aromatic), 7.22 (t, 2H, aromatic), 7.34 (d, 2H, aromatic). ³¹P{¹H} NMR (200 MHz, CDCl₃, δ): –13.4(s). Anal. Calcd. for C₂₂H₂₈P₂Pd: C, 57.34; H, 6.12. Found: C, 57.61; H, 6.36.

3.5. X-ray structure determination

All X-ray data were collected with use of a Mac Science 4-circle diffractometer equipped with an Mo X-ray tube and a graphite crystal monochromator. Details on crystal and intensity data are given in Table 1. The orientation matrix and unit cell parameters were

Table 4
Atomic coordinates (×10⁴) and isotropic thermal parameters (Å² × 10³) for **2**

Atom	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> _{eq} ^a
Pd(1)	2609(1)	392(1)	1712(1)	47(1)
P(1)	3992(1)	–1352(2)	2327(1)	44(1)
P(2)	1093(2)	2022(2)	1120(1)	48(1)
N(1)	2376(12)	633(11)	3319(8)	96(4)
N(1A)	1692(20)	–119(26)	2951(21)	49(6)
N(2)	2263(6)	–224(7)	3961(5)	71(2)
N(3)	2351(7)	–869(8)	4735(6)	87(2)
C(1)	3069(7)	502(8)	266(6)	65(2)
C(11)	5102(6)	–1031(8)	3678(5)	64(2)
C(12)	4938(6)	–1934(7)	1496(6)	66(2)
C(13)	3216(7)	–2877(7)	2552(6)	68(2)
C(21)	–265(8)	1529(9)	1448(8)	88(3)
C(22)	1496(7)	3639(7)	1826(7)	72(2)
C(23)	475(8)	2509(8)	–334(6)	82(2)

^a *U*_{eq} is defined as one-third of the trace of the orthogonalized *U*_{*ij*} tensor.

Table 5
Atomic coordinates (×10⁴) and isotropic thermal parameters (Å² × 10³) for **10**

Atom	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> _{eq} ^a
Pd(1)	1275(1)	2165(1)	785(1)	69(1)
P(1)	369(1)	1411(2)	2223(2)	77(1)
P(2)	2007(1)	3006(1)	–926(3)	89(1)
N(1)	2258(4)	864(4)	–379(9)	105(2)
N(2)	2283(5)	187(4)	–1563(12)	126(2)
N(3)	1652(4)	215(4)	–2592(10)	102(2)
N(4)	1259(4)	813(5)	–2166(11)	119(2)
C(1)	1666(5)	1224(4)	–691(12)	100(2)
C(2)	2900(4)	1035(4)	1035(10)	88(2)
C(3)	3644(4)	913(7)	67(13)	141(3)
C(4)	4323(5)	1057(10)	1551(18)	213(7)
C(5)	4269(5)	662(6)	3385(16)	139(3)
C(6)	3552(6)	795(8)	4307(13)	168(4)
C(7)	2849(5)	655(9)	2904(13)	195(6)
C(8)	811(5)	3106(4)	2243(15)	132(3)
C(11)	578(4)	414(4)	2601(11)	96(2)
C(12)	–474(4)	1410(5)	516(12)	109(2)
C(13)	–32(5)	1679(5)	4577(11)	117(3)
C(21)	1459(5)	3766(5)	–2153(15)	137(3)
C(22)	2741(4)	3495(5)	566(14)	130(3)
C(23)	2510(5)	2631(5)	–3049(14)	134(3)

^a *U*_{eq} is defined as one-third of the trace of the orthogonalized *U*_{*ij*} tensor.

determined from 25 machine-centered reflections with 20 < 2θ < 30°. Intensities of three check reflections were monitored after every 1 h during data collection. Data were corrected for Lorentz and polarization effects. Decay corrections were made. The intensity data were empirically corrected with ψ-scan data. All calculations were carried out on a personal computer with use of the SHELXS-86 [31] and SHELXL-93 programs [32].

A pale yellow crystal of **2** and white crystal **10**, shaped as a block, of approximate dimensions 0.2 × 0.3 × 0.5 mm³ and 0.2 × 0.3 × 0.4 mm³, were used for crystal and intensity data collection respectively. The unit cell parameters and systematic absences, *h*00 (*h* = 2*n* + 1), 0*k*0 (*k* = 2*n* + 1), *h*01 (*h* = 2*n* + 1), unambiguously indicated *P*2₁/*c* and *P*2₁/*n* as a space group. The structure was solved by the heavy atom methods. All non-hydrogen atoms were refined anisotropically. All hydrogen atoms were positioned geometrically and refined using a riding model. The selected bond distances and bond angles are shown in Tables 2 and 3. Final atomic positional parameters for non-hydrogen atoms are shown in Tables 4 and 5 respectively. Anisotropic thermal parameters, full bond distances and angles, and tables of observed and calculated structure factors are available from the authors.

Acknowledgements

This work was supported by the Korea Science and Engineering Foundation (951-0303-035-2). We are also

grateful to Professor Kohtaro Osakada at the Tokyo Institute of Technology for helpful discussions.

References

- [1] (a) J. Strahle, *Comments Inorg. Chem.*, **4** (1985) 295. (b) S. Cenini and G. La Monica, *Inorg. Chim. Acta*, **18** (1976) 279.
- [2] Z. Dori and R.F. Ziolo, *Chem. Rev.*, **73** (1973) 247.
- [3] (a) P. Kreutzer, Ch. Weis, H. Bock, J. Erbe and W. Beck, *Chem. Ber.*, **116** (1983) 2691. (b) K. Werner and W. Beck, *Chem. Ber.*, **105** (1972) 3209. (c) W. Beck, K. Burger and W.P. Fehlhammer, *Chem. Ber.*, **104** (1971) 1816. (d) W. Beck, W.P. Fehlhammer, H. Bock and M. Bauder, *Chem. Ber.*, **102** (1969) 3637. (e) W. Beck, W.P. Fehlhammer, P. Pollmann and H. Schachl, *Chem. Ber.*, **102** (1969) 1976. (f) W. Beck and W.P. Fehlhammer, *Angew. Chem. Int. Ed. Engl.*, **6** (1967) 169.
- [4] P. Kreutzer, Ch. Weis, H. Boehme, T. Kemmerich, W. Beck, C. Spencer and R. Mason, *Z. Naturforsch. Teil B*, **27** (1972) 745.
- [5] A. Becalska, R.J. Batchelor, F.W.B. Einstein, R.H. Hill and B.J. Palmer, *Inorg. Chem.*, **31** (1992) 3118.
- [6] H. Klein, S. Haller, H. König, M. Dartiguenave, Y. Dartiguenave and M. Menu, *J. Am. Chem. Soc.*, **113** (1991) 4673.
- [7] G. Alibrandi, L. Monsu Scolaro, D. Minniti and R. Romeo, *Inorg. Chem.*, **29** (1990) 3467.
- [8] Y.-J. Kim, J.-C. Choi and K.-H. Park, *Bull. Korean Chem. Soc.*, **15** (1994) 690.
- [9] (a) J. Strahle, *J. Organomet. Chem.*, **488** (1995) 15. (b) M. Breuer and J. Strahle, *Z. Anorg. Allg. Chem.*, **619** (1993) 1564. (c) M. Laupp and J. Strahle, *Angew. Chem. Int. Ed. Engl.*, **33** (1994) 207.
- [10] (a) A. Escuer, R. Vicente, M.S. El Fallah, X. Solans and M. Font-Bardia, *Inorg. Chim. Acta*, **247** (1996) 85. (b) J. Ribas, M. Monfort, B.K. Ghosh, R. Cortes, X. Solans and M. Font-Bardia, *Inorg. Chem.*, **35** (1996) 864 and references cited therein.
- [11] Y.-J. Kim and J.-Y. Lee, *Bull. Korean Chem. Soc.*, **16** (1995) 558.
- [12] P.M. Maitlis, P. Espinet and M.J.H. Russel, in G. Wilkinson, F.G.A. Stone and E.W. Abel (Eds.), *Comprehensive Organometallic Chemistry*, Vol. 6, Pergamon, Oxford, 1982.
- [13] H.C. Clark and L.E. Manzer, *J. Organomet. Chem.*, **59** (1973) 411.
- [14] W. de Graaf, J. Boersma, W.J.J. Smeets, A.L. Spek and G. van Koten, *Organometallics*, **8** (1989) 2907.
- [15] B. Bendiksen, W.C. Riley, M.W. Babich, J.H. Nelson and R.A. Jacobson, *Inorg. Chim. Acta*, **57** (1982) 29.
- [16] W.P. Fehlhammer and L.F. Dahl, *J. Am. Chem. Soc.*, **94** (1972) 3377.
- [17] (a) G.P. Delis, P.G. Aubel, P.W. van Leeuwen, K. Vrieze, N. Veldman and A.L. Spek, *J. Chem. Soc. Chem. Commun.*, (1995) 2233. (b) P. Veya, C. Floriani, A. Chiesi-villa and C. Rizzoli, *Organometallics*, **13** (1994) 441. (c) Y. Yamamoto, T. Tanase, T. Yanai, T. Asano and K. Kobayashi, *J. Organomet. Chem.*, **456** (1993) 287. (d) K. Onitsuka, K. Yanai, F. Takei, T. Joh and S. Takahashi, *Organometallics*, **13** (1994) 3862. (e) B. Crociani, M. Sala, A. Polo and G. Bombieri, *Organometallics*, **5** (1986) 1369.
- [18] L. Busetto and A. Palazzi, *Inorg. Chim. Acta*, **13** (1975) 233.
- [19] (a) R.F. Ziolo and Z. Dori, *J. Am. Chem. Soc.*, **90** (1968) 6560. (b) R.F. Ziolo, J.A. Phich and Z. Dori, *Inorg. Chem.*, **11** (1972) 626. (c) A.P. Gaughan, K.S. Bowman and Z. Dori, *Inorg. Chem.*, **11** (1972) 601.
- [20] P.M. Treichel, W.J. Knebel and R.W. Hess, *J. Am. Chem. Soc.*, **93** (1971) 5424.
- [21] B. Crociani, G. Bandoli and D.A. Clemente, *J. Organomet. Chem.*, **184** (1980) 269.
- [22] G. Wilkison, R.D. Gillard and J.A. McCleverty, *Comprehensive Coordination Chemistry*, Vol. 2, Pergamon, Oxford, 1987, p. 127.
- [23] *Handbook of Chemistry and Physics*, Chemical Rubber Co., Cleveland, OH, 67th edn., 1986–1987, p. F-216.
- [24] J.A. Bouwstra, A. Schouten and J. Kroon, *Acta Crystallogr. Sect. C*, **39** (1983) 1121.
- [25] L. Pauling, *The Nature of the Chemical Bond*, Cornell University Press, Ithaca, NY, 1960, p. 239.
- [26] W.P. Fehlhammer and L.F. Dahl, *J. Am. Chem. Soc.*, **94** (1972) 3370.
- [27] Y.-J. Kim, K. Osakada and A. Yamamoto, *J. Organomet. Chem.*, **452** (1993) 247.
- [28] Y.-J. Kim, K. Osakada and A. Yamamoto, unpublished results.
- [29] L.D. Field, A.V. George, S.R. Pike, I.E. Buys and T.W. Hambley, *Polyhedron*, **14** (1995) 3133.
- [30] Y.-J. Kim, K. Osakada, A. Takenaka and A. Yamamoto, *J. Am. Chem. Soc.*, **112** (1990) 1096.
- [31] G.M. Sheldrick, *Acta Crystallogr. Sect. A*, **46** (1990) 467.
- [32] G.M. Sheldrick, *SHELXL-93*, University of Göttingen, 1993.