Cyclopalladated azido complexes containing C,N-donor (HC~N = 2-(2'-thienyl)pyridine, azobenzene, 3,3'-dimethyl azobenzene, N,N'-dimethylbenzylamine, 2-phenylpyridine) ligands: reactivity towards organic unsaturated compounds and catalytic properties[†]

Kyung-Eun Lee,^{a,b} Hyeong-Tak Jeon,^a Sam-Yong Han,^a Jungyeob Ham,^c Yong-Joo Kim^{*a} and Soon W. Lee^b

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Cyclopalladated azido dimers having various *C*,*N*-donor ligands, $[Pd(\mu-N_3)(C,N-L^n)]_2$ (L¹H = 2-(2'-thienyl)pyridine; L²H = azobenzene; L³H = 3,3'-dimethylazobenzene; L⁴H = *N*,*N*'-dimethylbenzylamine; L⁵H = 2-phenylpyridine), underwent cleavage with tertiary (or chelating) phosphines to form the cyclopalladated $[Pd(N_3)(PR_3)(C,N-L)]$, the σ -bonded $[Pd(N_3)(PR_3)_2(C-L)]$, or the dinuclear-cyclopalladated $[PdN_3(PR_3)(C,N-L)]_2(\mu-P-P)$ complexes. In particular, treating $[Pd(\mu-N_3)(C,N-L)]_2$ with the basic chelating phosphine (depe or dmpe) produced the homoleptic bis(chelating) complex $[Pd(C,N-L^n)_2]$ (n = 1-3). Complex $[Pd(N_3)(PR_3)(C,N-L^4)]$ or $[Pd(N_3)(PR_3)_2(C-L^4)]$ reacted with aryl isocyanides to selectively give the imidoyl $[Pd(N_3)(-C=N-Ar)(PR_3)(N-L^4)]$ or the imidoyl carbodiimido complex $[Pd(N=C=N-Ar)(-C=N-Ar)(PR_3)(N-L^4)]$, which was formed by the CN-Ar insertion into the orthometallated Pd-C bond on the phenyl moiety or the interaction into the Pd-N₃ bond of the supporting ligand. In addition, reactions of $[Pd(N_3)(PR_3)_2(C-L^n)]$ (n = 1, 2, 4) with R-NCS {R = *i*-Pr, C₆H₄-NCS, (CH₃)₃Si} gave the *S*-coordinated tetrazole-thiolato Pd(II) complexes. Finally, the catalytic activity of the cyclopalladated azido complexes was evaluated.

Introduction

Cyclometallated Pd(II) complexes possessing the C~N chelating ligands have gained much attention because they catalyze various organic reactions and act as key intermediates in organic and organometallic syntheses.¹⁻⁷ However, only a few cases of these type of Pd(II) complexes containing pseudo-halogen ligands such as an azido group have been studied for their biological activity or thermal behavior.^{8,9} The azido ligand in transitionmetal complexes is known to react with organic unsaturated compounds to give heterocycles by dipolar cycloaddition or nitrene compounds by thermal or photoirradation.¹⁰ In particular, the C,N-ligand in cyclopalladated complexes is shown to be labile towards tertiary (or chelating) phosphines.¹¹⁻¹⁵ In this context, the azido group introduction into the cyclometallated system, that is, the combination of both ligands (the azido ligand and C,N-ligand), may induce a novel reactivity. Moreover, the catalytic properties of these azido complexes have not yet been explored.

Recently, we observed that reactions of the cyclometallated $Pd(\Pi)$ -azido complexes containing phenyl (or thienyl) pyridyl derivatives as the *C*,*N*-donor ligands with organic isocyanides

or isothiocyanates gave novel organometallic compounds.¹⁶ As an extension of this work, we prepared and investigated the monoand dinuclear cyclopalladated azido complexes containing a series of *C*,*N*-donor ligands $[Pd(N_3)(PR_3)(C,N-L^n)]$, $[Pd(N_3)(PR_3)_2(C-L^n)]$, and $[Pd(N_3)(C,N-L^n)]_2(\mu-P\sim P)$ (n = 1-5 in Chart 1). Here, we describe the preparation of the novel cyclopalladated Pd–azido complexes and their reactivity towards phosphines (Scheme 1). We also report the selective insertion of small molecules such as organic isocyanides into the Pd–C bond in these complexes, along with their catalytic activity for C–C coupling reactions.



Results and discussion

Preparation of the cyclometallated Pd(II)–azido complexes possessing *C*,*N*-donors

The cyclopalladated azido dimer $[Pd(\mu-N_3)(C,N-L^n)]_2$ in Scheme 2 could be prepared from $[Pd(\mu-Cl)(C,N-L^n)]_2$ and NaN₃ in DMSO/excess H₂O. The subsequent addition of the corresponding phosphine readily converted these complexes into

^aDepartment of Chemistry, Kangnung National University, Gangneung 210-702, Korea. E-mail: yjkim@kangnung.ac.kr; Fax: +82-33-647-1183; Tel: +82-33-640-2308

^bDepartment of Chemistry, Sungkyunkwan University, Natural Science Campus, Suwon 440-746, Korea

^cKorea Institute of Science and Technology, 290 Daejeon-dong, Gangneung 210-340, Korea

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the desired azido or novel complexes (Schemes 3–7). Consistent with the expectation based on stoichiometry, the cyclopalladated $[Pd(N_3)(PR_3)(C,N-L)]$ (Path A), the *C*-coordinated $[Pd(N_3)(PR_3)_2(C-L)]$ (Path B), and the dinuclear $[Pd(N_3)(C,N-L)]_2(\mu-P-P)$ (Path C) azides were formed when the dimer was treated with the stoichiometric amount of monodentate or chelating phosphines (Scheme 3). Formation of the products was monitored by examining the characteristic N₃ stretching band at 2028–2060 cm⁻¹.





Although several cleavage reactions of the Cl-bridged cyclopalladated complexes by phosphines to give neutral or ionic complexes are known,¹¹⁻¹⁵ only one example associated with the N₃-bridged cyclopalladated complexes is known to date.⁸

The products were characterized by spectroscopic and analytical data, and their colors, yields, and analytical data are listed in Table 1. Complexes 1, 3, 7, 12, 21, and 24 were structurally



Scheme 4



15, X = CI; R = Me 16, X = CI; R = Et





characterized by X-ray diffraction (for compounds 1, 3, 7, and 12 see Fig. 1–4). Schemes 4–7 illustrate specific examples of the cleavage of the cyclopalladated azido dimers by chelating phosphines (Path C in Scheme 3).

Table 1 Color, yields, and analytical data for the isolated complexes

			Analyses ^b		
Complex ^{<i>a</i>}	Color	Yield (%)	C (%)	H (%)	N (%)
$\frac{1}{1 \left[Pd(N_3)(PMe_3)(C,N-L^1) \right]}$	Yellow	49	37.28	3.85	14.43
	XX71 · · ·	00	(37.46)	(3.93)	(14.56)
$2 [Pd(N_3)(PMe_3)(C,N-L^4)]$	White	80	39.89	6.01	15.63
3 $[Pd(N_2)(PEt_2)(C N-L^4)]$	White	45	50 21	2.85	18 31
	,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,		(50.61)	(2.92)	(18.44)
$4 [Pd(N_3)(PMe_2Ph)(C,N-L^4)]$	White	74	48.43	5.84	13.21
	N7 11	0.6	(48.52)	(5.51)	(13.31)
$5 [Pd(N_3)(PCy_3)(C,N-L^*)]$	Yellow	96	57.52	8.44	9.71
6 $[Pd(N_2)(PMe_2)_2(C-L^1)]$	White	63	38.91	(8.00)	(9.93)
	() life	05	(39.10)	(5.25)	(12.16)
$7 [Pd(N_3)(PMe_3)_2(C-L^2)]$	Purple	82	44.96	6.02	14.17
			(44.87)	(5.85)	(14.54)
8 [Pd(N ₃)(PEt ₃) ₂ (C-L ²)]	Purple	89	51.16	7.48	12.67
$(\mathbf{D}_{\mathbf{J}}(\mathbf{N}_{\mathbf{J}}))(\mathbf{D}_{\mathbf{J}}(\mathbf{r},\mathbf{D}_{\mathbf{r}})))(\mathbf{C}_{\mathbf{J}},\mathbf{L}^{2})$	Orongo	96	(50.93)	(6.95)	(12.37)
9 $[Pd(N_3)(P(n-PT)_3)_2(C-L^-)]$	Orange	80	55.90 (55.42)	8.27 (7.91)	(10.77)
10 $[Pd(N_2)(PMe_2)_2(C-L^4)]$	White	94	41.26	7.24	13.52
1 (3)(3)2(-)]			(41.44)	(6.95)	(12.89)
11 $[Pd(N_3)(C,N-L^1)]_2(\mu-dppf)$	Brown	94	52.86	3.78	9.11
	X7.11	5.4	(53.30)	(3.44)	(9.56)
$12 \left[\mathrm{Pd}(\mathrm{N}_3)(C, N-\mathrm{L}^2) \right]_2(\mu-\mathrm{dppp})$	Yellow	/4	51.87	3.69	10.60
13 $[Pd(N_{*})(C, N_{*}I^{1})]_{*}(u_{*}dnnh)$	Vellow	96	(32.49)	(3.72)	(10.88)
$15 [1 d(13)(0,11 \pm)]_2(\mu \text{ upp} b)$	Tenow	<i>y</i> 0	(52.93)	(3.86)	(10.74)
14 $[Pd(N_3)(C,N-L^1)]_2(\mu$ -depe)	Yellow	60	40.86	4.43	13.26
			(40.83)	(4.41)	(13.61)
15 $[Pd(Cl)L^1]_2(\mu$ -dmpe)	Yellow	37	38.64	3.78	3.63
20 $\left[\mathbf{D}_{\mathbf{A}}(C, \mathbf{N}, \mathbf{L}_{\mathbf{A}}) \right]$	Dumla	75	(38.21)	(3.74)	(3.71)
20 $[Pd(C, N-L^2)_2]$	Pulple	75	(64.06)	4.00	(10.52)
21 $[Pd(N_3)(C,N-L^2)]_2(\mu-dppb)$	Orange	93	57.17	4.43	12.72
			(57.52)	(4.27)	(12.90)
22 $[Pd(N_3)(C,N-L^4)]_2(\mu-depe)$	Yellow	86	43.87	6.28	14.35
			(43.59)	(6.27)	(14.52)
23 $[Pd(N_3)(C,N-L^4)]_2(\mu-dppp)$	Yellow	51	55.12	5.03	11.17
24 $[Pd(N_{1})(C, N_{2}L^{5})]$, (u-dene)	Vellow	56	(55.28)	(3.13)	(11.40)
$24 [1 u(1v_3)(0, 1v-1)]_2(\mu-ucpc)$	Tenow	50	(47.36)	(4.97)	(13.81)
25 $[Pd(N_3)(-C(=N-R))(N-L^4)(PMe_3)]$	Yellow	68	55.30	7.63	12.79
$(\mathbf{R} = \mathbf{C}_{6}\mathbf{H}_{3}-2, 6-i-\mathbf{P}\mathbf{r}_{2})$			(54.99)	(7.02)	(12.83)
$26 [Pd(N=C=N-R)(-C(=N-R))(N-L^4)(PMe_3)]$	Yellow	46	64.74	8.33	8.05
$(\mathbf{R} = \mathbf{C}_{6}\mathbf{H}_{3}-2, 6-i-\mathbf{P}\mathbf{r}_{2})$ 27 [D4(N=C=N_{1}-\mathbf{P})/(C(-N_{1}-\mathbf{P}))/(N_{1}-4)/(\mathbf{P})/(C_{2}-\mathbf{P})]	V-11	72	(64.71)	(7.86)	(7.94)
$27 [Pd(N=C=N-R)(-C(=N-R))(N-L^{2})(PMe_{3})]$ (R = C.H2.6-Me.)	Yellow	/3	61.04	(6.63)	9.60
$28 \{ Pd(S[CN_4(R)])(C-L^1)(PMe_3)_2 \}$	White	53	40.58	5.82	12.33
$(\mathbf{R} = i \cdot \mathbf{Pr})$			(40.61)	(5.56)	(12.46)
29 $[Pd(NCS)(P(n-Pr)_3)_2(C-L^2)]$	Orange	87	56.17	8.08	6.16
		15	(55.89)	(7.72)	(6.31)
30 { $Pd(PMe_3)_2(S[CN_4]-)(C-L^4)$ } ₂ (μ -C ₆ H ₄)	White	47	43.43	6.45	12.86
			(42.98)	(0.08)	(13.19)

^{*a*} HL¹ = 2-(2'-thienyl)pyridine; HL² = azobenzene; HL³ = 3,3'-dimethylazobenzene; HL⁴ = N,N'-dimethylbenzylamine; HL⁵ = 2-phenylpyridine. ^{*b*} Calculated values are given in parentheses. Abbreviations: dppf = 1,2-bis(diphenyl)ferrocene; dppp = 1,3-bis(diphenylphosphino)propane; dppb = 1,4-bis(diphenylphosphino)butane; depe = 1,2-bis(diethylphosphino)ethane; dmpe = 1,2-bis(dimethylphosphino)methane.

As shown in Scheme 4, bulky bis(phosphine) reagents [dppf = 1,1'-bis(diphenylphosphino)ferrocene; dppp = 1,3-bis(diphenylphosphino)propane; dppb = 1,4-bis(diphenylphosphino)butane] stoichiometrically cleave the N₃-bridged cyclopalladated dimer having the 2-thienylpyridine group to give the (chelating phosphine)-bridged dinulear Pd azides $[Pd(N_3)(C,N-L^1)]_2(\mu-P\sim P)$ (11–13) in high yields.

Interestingly, reactions of $[Pd(\mu-X)(C,N-L^1)]_2$ (X = N₃ or Cl) with an equimolar amount of depe or dmpe, more basic bis(phosphine) reagents, produce a mixture of the dinuclear compound $[Pd(X)(C,N-L^1)]_2(\mu-P\sim P)$ (X = N₃, depe (14); Cl, dmpe (15); Cl, depe, (16)) as a major product, the homoleptic bis(chelated) compound $[Pd(C,N-L^1)_2]$ (17) as a minor product, and the bis(phosphine) dihalide compound $[(P\sim P)PdX_2]$



Scheme 7



Fig. 1 ORTEP drawing⁴² of **1**. Selected bond lengths (Å) and angles (°): Pd1–C7 2.002(2), Pd1–N2 2.094(2), Pd1–N1 2.116(1), Pd1–P1 2.2350(4), N2–N3 1.175(2), N3–N4 1.143(2); C7–Pd1–N2 170.55(7), C7–Pd1–N1 81.22(6), N2–Pd1–N1 89.45(6), N1–Pd1–P1 172.92(4), N3–N2–Pd1 127.6(1), N4–N3–N2 175.8(2).

(Scheme 5). The molecular structure of compound 17 was determined by X-ray diffraction (Fig. 5). In contrast, similar treatments with two equivalents of phosphine give the ionic complex $[Pd(C,N-L^1)(P-P)](N_3)$ (18), in which the azido group acts as a counterion. In these reactions, compared with the Clbridged cyclopalladated complexes, the N₃-bridged analogs are cleaved to the bis(chelated) compounds in lower yields. It is worth noting that the bulkier chelating phosphines (that is, dppf, dppp, and dppb) cleave the dimer $[Pd(\mu-X)(C,N-L)]_2$ to give the (chelating phosphine)-bridged dinulear Pd compounds (Schemes 4 and 6), rather than the bis(chelated) mononuclear compounds.

Reactions of the N₃- or Cl-bridged dinuclear compounds containing azobenzene derivatives with one equivalent depe smoothly proceeds to quantitatively give a bis(chelated) compound $\{[Pd(C,N-L^2)_2]$ (19) or $[Pd(C,N-L^3)_2]$ (20) $\}$ and $[Pd(depe)X_2]$ (Scheme 6). In contrast, similar reactions with the less basic



Fig. 2 ORTEP drawing of 3. Selected bond lengths (Å) and angles (°): Pd1–C1 2.028(3), Pd1–N2 2.124(3), Pd1–N1 2.153(3), Pd1–P1 2.258(1), N2–N3 1.189(5), N3–N4 1.148(5); C1–Pd1–N2 170.5(1), C1–Pd1–N1 81.9(1), N2–Pd1–N1 91.7(1), C1–Pd1–P1 95.0(1), N2–Pd1–P1 91.4(1), N3–N2–Pd1 130.4(3), N4–N3–N2 176.4(5).



Fig. 3 ORTEP drawing of 7. Selected bond lengths (Å) and angles (°): Pd1–C1 2.009(3), Pd1–N3 2.142(3), Pd1–P1 2.321(1), Pd1–P2 2.329(1), N1–N2 1.220(4), N3–N4 1.158(5), N4–N5 1.175(5); C1–Pd1–N3 177.3(1), C1–Pd1–P1 88.00(9), N3–Pd1–P1 91.32(9), P1–Pd1–P2 176.35(3), N4–N3–Pd1 121.4(3), N3–N4–N5 176.5(4).

phosphine dppb produces the expected dinuclear Pd(II) azide $[Pd(N_3)(C,N-L^2)]_2(\mu$ -dppb) (21), whose structure was determined by X-ray diffraction (Fig. 6). In addition, reactions of the N₃bridged dimer having L⁴H or L⁵H with those chelating phosphines produce only the phosphine-bridged dinuclear compound, $[Pd(N_3)(C,N-L^4)]_2(\mu$ -P~P) (μ -P~P = depe (22), dppp (23)) or $[Pd(N_3)(C,N-L^5)]_2(\mu$ -depe) (24) (Scheme 7, Fig. 7). No other bis(chelated) compounds, such as $[Pd(C,N-L^4)_2]$ or $[Pd(C,N-L^5)_2]$, were observed. These results suggest that the ability of the C,N-ligands to form a homoleptic bis(chelated) compound is in



Fig. 4 ORTEP drawing of 12. Selected bond lengths (Å) and angles (°): Pd1–C1 2.009(3), Pd1–N1 2.113(2), Pd1–N2 2.082(4), Pd1–P1 2.2375(7), Pd2–C37 2.010(3), Pd2–N5 2.115(2), Pd2–N6 2.109(3), Pd2–P2 2.2442(7); C1–Pd1–N2 169.5(2), C1–Pd1–N1 80.9(1), N1–Pd1–N2 89.0(1), C1–Pd1–P1 93.50(8), C37–Pd2–N6 169.3(1), C37–Pd2–N5 81.2(1), N5–Pd2–N6 88.1(1), C37–Pd2–P2 91.82(8), N2–N3–N4 155.5(7), N8–N7–N6 176.5(3).

decreasing order of azobenzene derivatives (L^2 or L^3) > thienylpyridine (L^1) > 2-phenylpyridine (L^5) $\approx N,N'$ -dimethylbenzylamine (L^4) and that the C-donor atom is bound to the Pd metal more strongly than the N-donor atom.

The homoleptic bis(chelated) compounds $[Pd(C,N-L^1)_2]$ (17)¹⁷ and $[Pd(C,N-L^2)_2]$ (19)^{18,19} were previously prepared by treating the dichloro- or Cl-bridged Pd compounds with the transmetallating reagent (mercurated or lithiated) possessing those *C*,*N*-donor ligands.¹⁷⁻²⁷ In particular, these type of compounds possessing azobenezene or phenylpyridine derivatives have gained considerable attention due to their applications in photoactive or liquid–crystalline materials.²⁰ Therefore, their facile preparation is currently an important research topic. As shown in Schemes 5 and 6, our synthetic route to the bis(chelated) compounds by the use of basic chelating phosphines appears to be unique in that those bis(chelated) products can be readily isolated from the other products containing phosphine ligands.

Reactivity toward organic isocyanides and isothiocyanates

Insertion of unsaturated organic molecules such as organic isocyanides (CN–R) into the M–C bond in the orthometallated compounds containing an aryl moiety of the *C*,*N*-donor ligand is an important step in preparing a variety of organic heterocycles.²⁸⁻³⁰ We previously reported the reactions of organic isocyanides with group 10 metal azides having the *C*,*N*-donor ligands, pyridyl or pyridyl–thiophene derivatives (Chart 2). These reactions produced complexes containing an imidoyl group or a *C*-coordinated tetrazolato ring, depending on the nature of the incoming isocyanides or the *C*,*N*-donor ligands.¹⁶ With





Fig. 5 (a) ORTEP drawing of 17. Selected bond lengths (Å) and angles (°): Pd1–C7 1.990(2), Pd1–C16 1.996(2), Pd1–N2 2.179(2), Pd1–N1 2.181(2); C7–Pd1–C16 95.67(8), C7–Pd1–N2 176.18(7), C16–Pd1–N2 80.51(7), C7–Pd1–N1 80.62(7), C16–Pd1–N1 175.27(6), N2–Pd1–N1 103.19(6). (b) Packing diagram of complex 17. (c) A space-filling model for a dimeric unit for complex 17: red, Pd; yellow, S; purple: N; grey: C; white, H.

these results in mind, we initiated insertion studies of organic isocyanides towards the cyclopalladated azides.

The cyclopalladated azide complex $[Pd(N_3)(PMe_3)(C,N-L^4)]$ (2) readily inserts one equivalent of isocyanide into the Pd–C (phenyl) bond to give the corresponding imidoyl compound $[Pd(N_3)$ $(-C(=N-Ar)(N-L^4)(PMe_3)]$ (Ar = C₆H₃-2,6-*i*-Pr₂; **25**) (Scheme 8). The molecular structure of **25** in Fig. 8 clearly demonstrates the formation of the proposed imidoyl Pd(II) azide. The following addition of another equivalent of isocyanide to complex **25** produces the novel carbodiimido Pd(II) complex $[Pd(N=C=N-Ar)(-C(=N-Ar)(N-L^4)(PMe_3)]$ (**26**). These type of complexes can also be prepared in a single step; that is, complexes **26** and **27** can be prepared by treating $[Pd(N_3)(PMe_3)(C,N-L^4)]$ (**2**) and $[Pd(N_3)(PMe_3)_2(C-L^4)]$ (**10**) with two equivalents of the



Fig. 6 ORTEP drawing of **21**. Selected bond lengths (Å) and angles (°): Pd1–C1 2.006(3), Pd1–N4 2.102(2), Pd1–N1 2.109(3), Pd1–P1 2.2571(7), N1–N2 1.180(4), N2–N3 1.159(4); N4–N5 1.266(4); C1–Pd1–N4 79.0(1), C1–Pd1–N1 166.9(1), N4–Pd1–N1 94.3(1), C1–Pd1–P1 95.01(9), N4–Pd1–P1 173.79(8), N1–Pd1–P1 91.32(9), N3–N2–N1 175.9(4). Two halves of this compound are related by the crystallographic center of symmetry.



Fig. 7 ORTEP drawing of 24. Selected bond lengths (Å) and angles (°): Pd1–N1 2.000(3), Pd1–C1 2.091(3), Pd1–N2 2.119(3), Pd1–P1 2.2473(9), P1–C12 1.826(4); N1–Pd1–C1 80.7(1), N1–Pd1–N2 170.1(1), C1–Pd1–N2 91.3(1), C12–P1–Pd1 112.7(1), N4–N3–N2 176.5(4).

corresponding CN–Ar (Ar = C_6H_3 -2,6-*i*-Pr₂, C_6H_3 -2,6-Me₂), respectively. The formation of products (**25–27**) can be readily followed by monitoring the characteristic IR bands of the imidoyl group (C=N), carbodiimido group, and azido groups. The IR bands of the carbodiimido group (for **26** and **27**) agree well with those found in our previous work.¹⁶ In particular, complexes **26** and **27** were further characterized by HMQC (or HMBC) techniques to accurately assign aromatic substituents in the imidoyl (–C=N–Ar) and carbodiimidoyl (N=C=N–Ar) fragments.

On the other hand, reactions of the bis(phosphine) Pd(II) azides (6, 9, 10), which have a σ -bonded *C*-L¹, *C*-L², or *C*-L⁴ ligand, with several organic isothiocyanates (R = 2,6-Me₂C₆H₃, C₆H₄– NCS, (CH₃)₃Si) produced the *S*-coordinated tetrazole–thiolato Pd complex *trans*-[Pd(SCN₄–2,6-Me₂C₆H₃)(PMe₃)₂(*C*-L¹)] (28) by the dipolar cycloaddition of R–NCS to the Pd–azido bond, the



Fig. 8 ORTEP drawing of 25. Selected bond lengths (Å) and angles (°): Pd1–C10 2.005(4), Pd1–N3 2.147(4), Pd1–N1 2.215(3), Pd1–P1 2.257(1), N1–C3 1.502(5), N2–C10 1.274(4), N2–C11 1.417(4); C10–Pd1–N3 174.2(2), C10–Pd1–N1 89.6(1), N3–Pd1–N1 84.9(2), C10–Pd1–P1 94.3(1), N3–Pd1–P1 91.4(1), N1–Pd1–P1 172.4(1).



Scheme 8

Pd(II) isothiocyanate complex *trans*-[Pd(NCS)(P(*n*-Pr₃)₂(*C*-L²)] (29) by the replacement of N₃ with NCS, or the dinuclear Pd tetrazole–thiolato complex {Pd(PMe₃)₂(S[CN₄])(*C*-L⁴)}₂(μ -C₆H₄) (30) by the dipolar cycloaddition of R–NCS to the Pd–azido bond (Scheme 9). Molecular structures of 28 (Fig. 9) and 29 (Fig. 10) were confirmed by X-ray diffraction. However, we could not observe cyclometallation products formed by phosphine dissociation. One of the reasons may be the relatively weak nucle-ophilicity of the isothiocyanates, compared to the corresponding isocyanides, toward a metal center.

Structures of compounds

Details on crystal data, intensity collection, and refinement details of 1, 3, 7, 12, 17, 21, 24, 25, 28 and 29 are given in Table 2. In all structures, the coordination of the Pd metal is essentially square-planar.





In complex 12, two $[Pd(C,N-L^1)(N_3)(PPh_2)]_2$ moieties are linked by a propylene fragment, and each Pd is planar four-coordinate (Fig. 4). Interestingly, one azido group (N6–N7–N8) is essentially linear with the bond angle of 176.5(3)°, whereas the other (N2–N3–N4) is severely bent with the bond angle of 155.5(7)°. Unfortunately, we cannot provide a reasonable explanation for this phenomenon.

In complex 17, the molecule has a pseudo- C_2 axis passing through the Pd metal (Fig. 5(a)). The carbon donors are *trans* to the nitrogen donors, which leads to the cisoid orientation of two sulfur atoms. The Pd-C bond distances are shorter than the Pd-N bond distances, indicating that the carbon atoms have stronger trans-influence power than the nitrogen atoms. A packing diagram of complex 17 is presented in Fig. 5(b), which shows an intriguing structural feature, a pseudo-dimeric unit. This unit is formed by the π - π stacking between the thiophene ring in one molecule and the pyridine ring in another. There are two distinct separations between centroids of the two rings (3.75 and 3.92 Å), and the Pd \cdots Pd separation is 3.75 Å. This type of π - π interaction is known to be important for the formation of coordination polymers. In particular, for face-to-face interactions, the centroid-centroid separations are typically found to be in the range of 3.4–3.8 Å.³¹ A space-filling model of the dimer unit clearly demonstrates its π - π interaction (Fig. 5(c)).

In complex **25**, an imidoyl moiety, formed by the selective insertion of the isocyanide ($C \equiv N-Ar$) into the Pd–C bond in C,N-donor ligand, is observed (Fig. 8). In complex **28** (Fig. 9(a)), interestingly, the square-planar Pd metal is further bound to the S atom in the neighboring molecule by van der Waals contacts (Pd \cdots S = 3.4471(**8**) Å). These contacts connect the molecules approximately along the *b*-axis to give a 1-dimensional helical network (Fig. 9(b)). A space filling model (Fig. 9(c)) clearly demonstrates the helical structure. For comparison, the van der Waals radii of Pd and S atoms are 1.63 and 1.80 Å, respectively.

Catalytic application for cross-coupling reactions

Suzuki–Miyaura coupling of aryl halides with aryl boronic acid is an efficient tool for the preparation of various biaryl compounds.³² The coupling reactions catalyzed by cyclopalladated complexes containing C~N donor ligands have been studied.^{1,32-38} However, the coupling reactions using cyclometallated complexes containing pseudo-halide ligands are relatively rare. In this context, we evaluated the catalytic activity of our cyclopalladated azido complexes for the Suzuki–Miyaura coupling (Scheme 10). In a typical catalytic reaction, a catalyst (1 mol%) in toluene was added to a mixture of aryl bromide, phenylboronic acid, and K₂CO₃ in the molar ratio of 1:1.3:2. Reaction conditions and product yields are listed in Table 3.



Scheme 10

Chart 3 presents the Pd catalysts used in the experiments. Table 3 shows that all the Pd catalysts exhibit high activity especially for para-acetyl-substituted bromobenzene and 4-cyanobromobenzene (entries 1-10), in some cases even with 0.1 mol%Pd catalyst (entry 9). Also, the coupling reactions involving paraacetyl-substituted bromobenzenes generally give higher yields than those involving 4-bromoanisole or ortho-bromoanisole (entries 11 and 12), and this reactivity was also observed for other known Pd-catalyzed coupling reactions.³²⁻³⁷ In particular, the reactions with the dinuclear cyclopalladated azides (entries 6-8) in ethanol in place of toluene gave relatively higher yields than those with mono or σ -bonded Pd(II) azides, probably due to the higher solubility of the dinuclear species. Unfortunately, the reactions involving the chloro-substituted aryl compounds exhibited poor reactivity for our compounds (entries 13-15). The results of the catalytic experiments indicate that our cyclopalladated azido compounds are rather efficient catalysts for the cross-coupling of aryl bromides and phenylboronic acid. However, we believe that further studies are necessary to tune our compounds that can undergo the catalytic reactions under milder conditions.

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	-	3	7	12	17	21 .(CH ₂ Cl ₂) ₂	24·(CH ₂ Cl ₂) ₂	25	28	29
Formula	$C_{12}H_{15}N_4PPdS$	$C_{15}H_{27}N_4PPd$	$\mathrm{C}_{18}\mathrm{H}_{27}\mathrm{N}_{5}\mathrm{P}_{2}\mathrm{Pd}$	C ₄₅ H ₃₈ N ₈ P ₂ - Pd ₂ S ₂	$C_{18}H_{12}N_2PdS_2$	C ₅₄ H ₅₀ Cl ₄ N ₁₀ - P ₂ Pd ₂	$C_{34}H_{44}Cl_4N_8$ - P_2Pd_2	$\mathrm{C}_{25}\mathrm{H}_{38}\mathrm{N}_{5}\mathrm{PPd}$	$C_{19}H_{31}N_5P_2-PdS_2$	C ₃₁ H ₅₁ N ₃ P ₂ PdS
FW	384.71	400.78	481.79	1029.69	426.82	1255.58	981.31	545.97	561.95	666.15
Temperature/K	296(2)	293(2)	293(2)	296(2)	296(2)	296(2)	296(2)	293(2)	296(2)	293(2)
Crystal size/mm ³	$0.60 \times 0.30 \times 0.20$	$0.32 \times 0.30 \times 0.12$	$0.38 \times 0.26 \times 0.22$	$0.20 \times 0.12 \times 0.08$	$0.30 \times 0.16 \times 0.08$	$0.48 \times 0.24 \times 0.16$	$0.30 \times 0.24 \times 0.20$	$0.74 \times 0.42 \times 0.38$	$0.24 \times 0.20 \times 0.16$	$0.28 \times 0.22 \times 0.20$
Crystal system	Monoclinic	Monoclinic	Monoclinic	Triclinic	Monoclinic	Monoclinic	Monoclinic	Monoclinic	Monoclinic	Triclinic
Space group	$P2_1/c$	$P2_1/n$	$P2_1/c$	$P\bar{1}$	$P2_1/c$	$P2_1/c$	$P2_1/c$	$P2_1/n$	$P2_1/n$	P1
a'Å	10.4930(3)	11.220(2)	13.473(47)	9.7470(1)	9.3366(3)	19.0312(9)	11.592(1)	12.075(2)	14.0772(2)	9.354(2)
b/Å	11.9648(3)	10.274(2)	9.376(3)	15.0138(2)	9.9803(3)	9.1873(4)	16.830(2)	10.950(3)	11.9202(2)	9.495(2)
c/Å	12.7272(3)	16.122(2)	17.467(5)	15.8289(2)	17.2315(6)	16.2466(8)	10.558(1)	20.463(5)	15.9738(3)	11.390(2)
$\alpha/^{\circ}$				110.141(1)			69.85(2)			
β/° ~/°	112.487(1)	98.05(1)	91.60(2)	100.559(1) 96.776(1)	104.864(2)	102.573(2)	101.61(5) 76 59(2)	100.34(1)	107.590(1)	68.53(2)
// 17 / Å 3	(1176 2011	1040 7/5)		(1)07/.00	1551 04/0)		(7)200	(1)6996	10/11 2220	(6)6 220
2/2	(1)/C.0/+I	(c)7.0701 A	(1)cn77	2070./0(+)	(6)+6.1001 A	(7)(-7117	(+)0.1102	2002(1) A	(1)71.UUL2 A	(c)c.110
Z - 2 - 2 - 3	1 731	1 4/7	1 151	2 1 631	1 607	1 504	2 1 615	1 367	1 461	1 761
u cal, g cm	16/11	1.005	0.008	1.078	1.02/ 1.463	1.204	C10.1	202.1 0 778	1.401	107.1
	0/1-1	C/0.1	00.00	10.02	010	0701	000	1136	1150	250
<i>T</i> (000)	0 4660	024 0.3571	904 0 2005	00122	040 0.6670	0.6500	900 0 7016	0 7573	2011	000 066550
L min	0.4007	0,000	2022 0	2010.0	0.0019	20200	0.7051	C7C1.0	106/.0	
I max	0.72540	0.1/10	0.4/00	0.918/	0.8919 272 275	02020	108/.0	0.951	C2C8.U	0.8998 2670
No of refine interview	25.040	2,211	4001 3004	1 60 06	24 323	61715	50 424 4060	4920	142 004 6307	2670 2670
No of refine unique $N = 0$	2000 3360	7785	3004 3300	9012 6814	2005 23/15	5024 5071	4900	3501	2600 1660	2029 2536
R(int)	0.0231	0.0367	0.0576	0.0440	0.0759	0.0335	0.0761	0.0376	0.0520	0,000
No. of params refined	173	191	235	532	256	325	226	289	262	344
Max., in $\Delta \rho/e \text{ Å}^{-3}$	0.484	0.678	0.581	1.228	0.307	0.827	1.409	0.469	0.578	0.445
Min., in $\Delta \rho/e$ Å ⁻³	-0.516	-0.464	-0.704	-0.444	-0.321	-0.872	-1.107	-0.493	-0.378	-0.533
GOF on F^2	1.042	1.094	1.047	0.921	1.028	1.016	1.059	1.018	1.048	1.043
R_1^a	0.0186	0.0331	0.0339	0.0348	0.0205	0.0392	0.0408	0.0396	0.0347	0.0277
$\mathrm{w}R_2^{b}$	0.0462	0.0837	0.0821	0.0732	0.0499	0.0893	0.1093	0.0853	0.0752	0.0693
R (all data)	0.0206	0.0414	0.0437	0.0557	0.0268	0.0638	0.0548	0.0631	0.0606	0.0288
wR_2^b (all data)	0.0477	0.0921	0.0880	0.0810	0.0534	0.1004	0.1197	0.0957	0.0851	0.0703
" $R_1 = \sum \ F_{ m o} - F\ /\sum$	$ F_{\mathrm{o}} $. ^b w $R_2 = \sum [r$	$W(F_o^2 - F_c^2)^2]/\sum[$	$w(F_o^2)^2]^{1/2}$.							



Fig. 9 (a) ORTEP drawing of **28**. Selected bond lengths (Å) and angles (°): Pd1–C3 2.020(2), Pd1–P2 2.3042(9), Pd1–P1 2.3151(8), Pd1–S2 2.4005(7), S2–C16 1.715(3), N2–N3 1.350(4), N3–N4 1.285(4), N4–N5 1.341(3), N5–C16 1.348(3); P2–Pd1–P1, 174.75(3), P2–Pd1–S2 88.79(3), P1–Pd1–S2 96.34(3), C1–S1–C4 91.1(1), C16–S2–Pd1 103.56(9), C16–N2–N3. (b) Projection of complex **28** perpendicular to the (100) plane, showing a 1-dimensional helical network approximately along the *b*-axis. (c) A space filling model of the packing of compound **28** showing its helical structure: red, Pd; yellow, S; orange: P; purple: N; grey: C.

In summary, we prepared a series of cyclopalladated azides having *C*,*N*-donor ligands and found their lability toward chelating phosphines to give neutral dinuclear and bis(chelated) compounds. We observed the selective insertion of small molecules such as organic isocyanides into the Pd–C or Pd–azido bond in those azido complexes to give the imidoyl Pd(II) azides or the imidoyl Pd(II) carbodiimides. Interestingly, the crystal structure of complex **28**, *trans*-{PdS[CN₄(*i*-Pr)](PMe₃)₂(*C*-L¹)}, was found to have a 1-dimensional helical network formed by the intermolecular Pd \cdots S van der Waals contacts. Finally, our cyclopalladated azides appeared to be potential catalysts for Suzuki–Miyaura coupling of aryl bromides and phenylboronic acid.



Fig. 10 ORTEP drawing of 29. Selected bond lengths (Å) and angles (°): Pd1–C2 2.021(6), Pd1–N1 2.078(6), Pd1–P1 2.327(2), Pd1–P2 2.338(2), S1–C1 1.629(5), N1–C1 1.153(7), N2–N3 1.257(6); C2–Pd1–N1 177.0(3), C2–Pd1–P1 91.2(2), N1–Pd1–P1 87.5(2), C2–Pd1–P2 88.2(2), N1–Pd1–P2 93.2(2), P1–Pd1–P2 179.23(8), C1–N1–Pd1 172.9(5), N1–C1–S1 178.4(5).



Experimental

General, materials and measurements

All manipulations of air-sensitive compounds were performed under N₂ or Ar by standard Schlenk-line techniques. Solvents were distilled from Na–benzophenone. The analytical laboratories at Kangnung National University carried out elemental analyses with a CE instrument EA1110. IR spectra were recorded on a Perkin Elmer BX spectrophotometer. NMR (¹H, ¹³C{¹H}, and ³¹P{¹H}) spectra were obtained on a JEOL Lamda 300 MHz spectrometer. Chemical shifts were referenced to internal Me₄Si or to external 85% H₃PO₄. Mass (FAB) spectra were obtained at the Korea Basic Science Institute (Seoul). [Pd(μ -Cl)(C,N-L)]₂ were prepared by the literature or modified methods.^{38,39} 2,6-Diisopropylphenyl isocyanide was prepared as described in the literature.⁴⁰

Entry	Aryl bromide	Pd catalyst	Reaction time/h	Product	Isolated yield (%)
1	OBr	1	1		96
2	0 Br	2	1	\sim	96
3	O Br	5	1		95
4	OBr	10	1	\sim	93
5	OBr	11	1		94 (69) ^b
6	OBr	12	1		87 (99) ^c
7	OBr	13	1		88 (99) ^c
8	OBr	23	1		92 (99) ^c
9 ^d	O Br	2	1		93
10	NCBr	2	1		92
11	MeOBr	2	1	MeO	56 (70) ^e
12	OMe Br	2	1	OMe	63
13	°→−Ci	2	20	$\searrow - \bigtriangledown > - \bigtriangledown >$	14 (22) ^f (16) ^g
14		2	5		24
15	MeO-CI	2	5	MeO	NR

 Table 3
 Suzuki–Miyaura cross-coupling reaction of arylhalides and phenylboronic acid catalyzed by palladacycles⁴

^{*a*} All reactions were carried out with 0.2 mmol aryl halide and 0.26 mmol phenylboronic acid. ^{*b*} Reaction was performed at room temperature for 24 h. ^{*c*} Ethanol in place of toluene was used as a solvent. ^{*d*} Reaction was carried out with 1.0 mmol 4'-bromo acetophenone and 1.3 mmol phenylboronic acid in the presence of 0.1 mol% Pd catalyst **2** and 4.0 mmol K₂CO₃. ^{*c*} Pd catalyst **5** was used. ^{*f*} Ethanol was used as a solvent. ^{*g*} Pd catalyst **23** and ethanol as a solvent were used under the same reaction conditions.

Preparations

 $[Pd(\mu-N_3)(C,N-L^n)]_2$ (n = 1-5). $[Pd(\mu-N_3)(C,N-L^1)]_2$ was prepared by a modified literature method.⁸ To a homogeneous solution of $[Pd(\mu-Cl)L^1]_2$ (0.464 g, 0.768 mmol) in DMSO (100 cm³) was added a solution of NaN₃ (0.150 g, 2.30 mmol) in H₂O (2 cm³). After stirring for 18 h at room temperature, excess H₂O was added to the mixture to give yellow precipitate. The solids were filtered with a glass frit and washed with H₂O and *n*-hexane. The product was dried under vacuum to give yellow product (0.389 g, 82%). [Pd(μ -N₃)(*C*,*N*-L¹)]₂: (Found: C, 34.94; H, 1.83; N, 17.64. C₁₈H₁₂N₈Pd₂S₂ requires: C, 35.02; H, 1.95; N, 18.15).

 $[Pd(\mu-N_3)(C,N-L^2)]_2$, $[Pd(\mu-N_3)(C,N-L^3)]_2$, $[Pd(\mu-N_3)(C,N-L^4)]_2$,⁸ and $[Pd(\mu-N_3)(C,N-L^5)]_2$ were similarly prepared and used as starting materials in the subsequent reactions (Schemes 3–6) without recrystallization due to their poor solubility in common

organic solvents. $[Pd(\mu-N_3)(C,N-L^2)]_2$: (Found: C, 43.37; H, 2.66; N, 20.72. $C_{24}H_{18}N_{10}Pd_2$ requires: C, 43.72; H, 2.75; N, 21.24). $[Pd(\mu-N_3)(C,N-L^3)]_2$: (Found: C, 46.46; H, 3.98; N, 19.49. $C_{28}H_{26}N_{10}Pd_2$ requires: C, 47.01; H, 3.66; N, 19.58). $[Pd(\mu-N_3)(C,N-L^5)]_2$: (Found: C, 43.38; H, 2.61; N, 18.22. $C_{22}H_{16}N_8Pd_2$ requires: C, 43.65; H, 2.66; N, 18.51).

Cleavage of $[Pd(\mu-N_3)(C,N-L)]_2$ by tertiary (2 or 4 equivalents) or chelating phosphine (1 equivalents)

Path A. To a Schlenk flask containing $[Pd(\mu-N_3)(C,N-L^1)]_2$ (0.340 g, 0.55 mmol) were added CH₂Cl₂ (15 cm³) and PMe₃ (0.084 g, 1.10 mmol). An initial dark yellow suspension slowly turned to a homogeneous brown solution. After stirring for 2 h at room temperature, the solvent was removed, and the resulting residue was washed with *n*-hexane to give yellow solids. Recrystallization from CH₂Cl₂-n-hexane gave yellow crystals of $[Pd(N_3)(PMe_3)(C,N-L^1)]$ (1, 0.210 g, 49%). v_{max} (KBr, cm⁻¹) 2040 (N₃); $\delta_{\rm H}$ (CDCl₃) 1.76 (d, 9H, J = 11 Hz, P(CH₃)₃), 6.94 (dd, 1H, $J = 1.5, 4.9 \text{ Hz}, \text{H}^4$), 7.12 (ddt, 1H, $J = 1.3, 5.5, 7.5 \text{ Hz}, \text{H}^5$), 7.37 (dd, 1H, J = 1.1, 4.7 Hz, H⁵), 7.39 (m, 1H, H³), 7.75 (dt, 1H, J = 1.7, 7.7 Hz, H⁴), 8.74 (m, 1H, H⁶); $\delta_{\rm C}$ (CDCl₃) 15.7 (d, $J_{P-C} = 33$ Hz, P(CH₃)₃), 117.4 (d, $J_{P-C} = 1.9$ Hz, C³), 120.4 (d, $J_{P-C} = 3.7$ Hz, C⁵), 126.5 (d, $J_{P-C} = 4.4$ Hz, C^{5'}), 133.1 (d, $J_{P-C} =$ 8.1 Hz, C^{4'}), 139.6 (s, C⁴), 142.5 (d, $J_{P-C} = 2.5$ Hz, C^{2'}), 148.3 (s, C^{3'}), 153.5 (d, $J_{P-C} = 8.7$ Hz, C⁶), 159.0 (d, $J_{P-C} = 2.4$ Hz, C²); δ_P (CDCl₃)-3.83 (s).



Complexes **2–5** [Pd(N₃)(PR₃)(*C*,*N*-L⁴)] (PR₃ = PMe₃, PEt₃, PMe₂Ph, PCy₃) were analogously prepared. Data for **2**: v_{max} (KBr, cm⁻¹) 2056 (N₃); $\delta_{\rm H}$ (CDCl₃) 1.63 (d, 9H, *J* = 11 Hz, P(CH₃)₃), 2.69 (d, 6H, *J* = 2.7 Hz, NMe₂), 3.90 (d, 2H, *J* = 2.6 Hz, CH₂), 6.96–7.06 (m, 4H, Ph); $\delta_{\rm C}$ (CDCl₃) 14.5 (d, *J*_{P-C} = 32 Hz, P(CH₃)₃), 49.7 (d, *J*_{P-C} = 2.8 Hz, NMe₂), 72.0 (d, *J*_{P-C} = 3.5 Hz, CH₂), 123.1 (s, C³), 124.5 (s, C⁴), 125.8 (d, *J*_{P-C} = 5.0 Hz, C5), 135.7 (d, *J*_{P-C} = 10 Hz, C⁶), 149.2 (d, *J*_{P-C} = 1.8 Hz, C²), 150.0 (br, C¹); $\delta_{\rm P}$ (CDCl₃) –3.33 (s).

Data for **3**: v_{max} (KBr, cm⁻¹) 2041 (N₃); δ_{H} (CDCl₃) 1.20 (dt, 9H, J = 7.5, 9 Hz, P(CH₂CH₃)₃), 1.94 (dq, 6H, J = 7.7, 9.5 Hz, P(CH₂CH₃)₃), 2.68 (d, 6H, J = 2.6 Hz, NMe₂), 3.91 (d, 1H, J =2.1 Hz, CH₂), 6.92–7.04 (m, 4H, Ph); δ_{C} (CDCl₃) 8.66 (d, $J_{\text{P-C}} =$ 1.2 Hz, P(CH₂CH₃)₃), 15.6 (d, $J_{\text{P-C}} = 29$ Hz, P(CH₂CH₃)₃), 49.5 (d, $J_{\text{P-C}} = 2.8$ Hz, NMe₂), 72.1 (d, $J_{\text{P-C}} = 3.4$ Hz, CH₂), 123.9 (s, C³), 124.3 (s, C⁴), 125.7 (d, $J_{\text{P-C}} = 4.3$ Hz, C5), 135.4 (d, $J_{\text{P-C}} =$ 8.4 Hz, C⁶), 149.2 (d, $J_{\text{P-C}} = 2.2$ Hz, C²), 149.5 (d, $J_{\text{P-C}} = 5.2$ Hz, C¹); δ_{P} (CDCl₃) 32.5 (s).

Data for 4: v_{max} (KBr, cm⁻¹) 2060 (N₃); $\delta_{\rm H}$ (CDCl₃) 1.83 (d, 6H, J = 10 Hz, P(CH₃)₂Ph), 2.78 (d, 6H, J = 2.7 Hz, NMe₂), 3.95 (d, 2H, J = 2.5 Hz, CH₂), 6.52 (dt, 1H, J = 1.1, 5.9 Hz, Ar), 6.68 (dt, 1H, J = 1.3, 7.3 Hz, Ar), 6.88–7.01 (m, 2H, Ar), 7.45–7.50 (m, 3H, Ar), 7.87–7.94 (m, 2H, Ar); $\delta_{\rm C}$ (CDCl₃) 15.2 (d, $J_{\rm P-C} = 33$ Hz, P(CH₃)₂Ph), 49.8 (d, $J_{\rm P-C} = 2.8$ Hz, NMe₂), 72.1 (d, $J_{\rm P-C} = 3.5$ Hz, CH₂), 122.8 (s, C³), 124.3 (s, C⁴), 125.7 (d, $J_{\rm P-C} = 5.6$ Hz), 128.9 (d, $J_{\rm P-C} = 11$ Hz), 131.1 (d, $J_{\rm P-C} = 2.8$ Hz), 132.2 (d, $J_{\rm P-C} =$

12 Hz), 136.2 (d, $J_{P-C} = 11$ Hz), 149.0 (d, $J_{P-C} = 2.2$ Hz, C²), 149.3 (d, $J_{P-C} = 5.0$ Hz, C¹); δ_P (CDCl₃) 11.8 (s).

Data for **5**: v_{max} (KBr, cm⁻¹) 2028 (N₃); $\delta_{\rm H}$ (CDCl₃) 1.19 (m, 9H, P(C₆H₁₁)₃), 1.55–1.97 (m, 24H, P(C₆H₁₁)₃), 2.21–2.33 (m, 3H, P(C₆H₁₁)₃), 2.67 (d, 6H, J = 2.6 Hz, NMe₂), 3.94 (d, 2H, J =1.3 Hz, CH₂), 6.86–7.00 (m, 3H, Ph), 6.86–7.00 (m, 1H, Ph); $\delta_{\rm C}$ (CDCl₃) 26.4 (d, $J_{\rm P-C} = 1.2$ Hz, P(C₆H₁₁)₃), 27.7 (d, $J_{\rm P-C} = 11$ Hz, P(C₆H₁₁)₃), 30.0 (s, NMe₂), 33.6 (d, $J_{\rm P-C} = 22$ Hz, P(C₆H₁₁)₃), 49.6 (d, $J_{\rm P-C} = 2.5$ Hz, CH₂), 72.6 (d, $J_{\rm P-C} = 3.1$ Hz, CH₂), 122.9 (s, C³), 123.8 (s, C⁴), 125.3 (d, $J_{\rm P-C} = 3.7$ Hz, C5), 136.6 (d, $J_{\rm P-C} = 5.6$ Hz, C⁶), 148.6 (d, $J_{\rm P-C} = 1.9$ Hz, C²), 150.4 (d, $J_{\rm P-C} = 3.7$ Hz, C¹); $\delta_{\rm P}$ (CDCl₃) 43.1 (s).



Path B. CH₂Cl₂ (30 cm³) and PMe₃ (0.308 g, 4.04 mmol) were added to [Pd(μ-N₃)(*C*,*N*-L¹)]₂ (0.624 g, 1.01 mmol) in a Schlenk flask. After stirring for 18 h, the solvent was removed and washed with *n*-hexane to give white solids. Recrystallization from CH₂Cl₂-diethyl ether ($\nu/\nu = 2:1$) gave white crystals of [Pd(N₃)(PMe₃)₂(*C*-L¹)] (**6**, 0.591 g, 63%). ν_{max} (KBr, cm⁻¹) 2035 (N₃); $\delta_{\rm H}$ (CDCl₃) 1.16 (s, 18H, P(CH₃)₃), 6.97 (d, 1H, J = 4.9 Hz, H⁴), 7.10 (ddt, 1H, J = 1.1, 4.8, 9.8 Hz, H⁵), 7.37 (d, 1H, J = 4.9 Hz, H⁵), 7.70 (dt, 1H, J = 8.0 Hz, H³), 8.56 (dt, 1H, J = 1.0, 4.3 Hz, H⁴), 9.00 (d, 1H, J = 8.0 Hz, H⁶); $\delta_{\rm C}$ (CDCl₃) 13.5 (s, P(CH₃)₃), 118.3 (s, C³), 120.8 (s, C⁵), 126.8 (s, C⁵), 133.9 (s, C⁴), 136.2 (s, C⁴), 139.1 (s, C²), 143.0 (s, C³), 149.5 (s, C⁶), 154.9 (s, C²); $\delta_{\rm P}$ (CDCl₃) -14.2 (s).

Complexes 7–10 [Pd(N₃)(PR₃)₂(C-L²)] (PR₃ = PMe₃, PEt₃, P(*n*-Pr)₃) and [Pd(N₃)(PMe₃)₂(C-L⁴)] were similarly prepared.

Data for 7: v_{max} (KBr, cm⁻¹) 2032 (N₃); $\delta_{\rm H}$ (CDCl₃) 1.07 (t, 18H, J = 3.2 Hz, P(CH₃)₃), 7.07–7.17 (m, 2H, Ar), 7.44–7.53 (m, 4H, Ar), 7.79 (m, 1H, 8.07 (m, 2H, Ar); $\delta_{\rm C}$ (CDCl₃) 13.5 (t, J = 14 Hz, P(CH₃)₃), 122.7 (s, C⁸), 123.7 (s, C³), 127.1 (s, C⁹), 129.4, 129.6, 130.6, 137.4 (br, C⁶), 152.3 (s, C⁷), 152.3 (s, C¹), 156.3 (s, C²); $\delta_{\rm P}$ (CDCl₃)–17.3 (s).

Data for **8**; v_{max} (KBr, cm⁻¹) 2031 (N₃); $\delta_{\rm H}$ (CDCl₃) 1.01 (qnt, 18H, J = 8.0 Hz, P(CH₂CH₃)₃), 1.45 (m, 12H, P(CH₂CH₃)₃), 7.07 (dt, 2H, J = 3.5, 9.2 Hz, H^{5'}, H⁶), 7.42–7.66 (m, 5H), 8.03–8.06 (m, 2H, H^{2'}); $\delta_{\rm C}$ (CDCl₃) 7.76 (s, P(CH₂CH₃)₃), 14.5 (t, $J_{\rm P-C} =$ 12 Hz, P(CH₂CH₃)₃), 122.6 (s, C⁸), 122.9 (s, C³), 123.5 (s, C⁹), 129.1, 129.2, 130.5, 137.4 (t, $J_{\rm P-C} =$ 4.4 Hz, C⁶), 152.3 (s, C⁷), 153.8 (s, C¹), 156.8 (s, C²); $\delta_{\rm P}$ (CDCl₃) 12.0 (s).

Data for **9**: v_{max} (KBr, cm⁻¹) 2035 (N₃); $\delta_{\rm H}$ (CDCl₃) 0.85 (br, 18H, P(CH₂CH₂CH₃)₃), 1.39 (m, 24H, P(CH₂CH₂CH₃)₃), 7.04– 7.07 (br, H^{5'}, H⁶), 7.44–7.62 (m, 5H), 8.03–8.06 (m, 2H, H^{2'}); $\delta_{\rm C}$ (CDCl₃) 15.9 (t, $J_{\rm P-C}$ = 6.8 Hz, P(CH₂CH₂CH₃)₃), 17.5 (s, P(CH₂CH₂CH₃)₃), 24.9 (t, $J_{\rm P-C}$ = 12 Hz, P(CH₂CH₂CH₃)₃), 121.0 (s, C⁸), 122.9 (s, C³), 123.5 (s, C⁹), 129.0, 129.1, 130.4, 137.5, 152.4 (s, C⁷), 155.1 (s, C¹), 156.8 (s, C²); $\delta_{\rm P}$ (CDCl₃) 4.39 (s).

Data for **10**: v_{max} (KBr, cm⁻¹) 2033 (N₃); $\delta_{\rm H}$ (CDCl₃) 1.19 (s, 18H, P(CH₃)₃), 2.31 (s, 6H, NMe₂), 3.51 (s, 2H, CH₂), 6.88–6.91 (m, 2H, H⁴, H⁵), 7.06–7.09 (m, 1H, H⁶), 7.18–7.22 (m, 1H, H³); $\delta_{\rm C}$ (CDCl₃) 13.6 (br, 18H, P(CH₃)₃), 46.4 (s, 6H, NMe₂), 69.1 (s,

CH₂), 122.7 (s, C³), 126.0 (s, C⁴), 128.1 (s, C⁵), 135.2 (s, C⁶), 143.1 (s C²), 154.0 (s, C¹); δ_P (CDCl₃) –15.1 (s).

Path C. To a Schlenk flask containing $[Pd(\mu-N_3)(C,N-L^1)]_2$ (0.250 g, 0.40 mmol) were added CH₂Cl₂ (85 cm³) and dppf (0.224 g, 0.40 mmol). After stirring for 5 h, the solvent was removed, and the resulting residue was washed with diethyl ether to give dark yellow solids, which were recrystallized from CH₂Cl₂*n*-hexane gave dark yellow crystals of $[Pd(N_3)(C,N-L^1)]_2(\mu-dppf)$ (11, 0.445 g, 94%). v_{max} (KBr, cm⁻¹): 2034 (N₃); δ_{H} (CDCl₃) 4.44 $(q, 4H, Fe(C_5H_4)), 5.07$ (br, 4H, Fe (C_5H_4)), 5.76 (dd, 2H, J = 1.7, 5.0 Hz, $H^{4'}$), 6.89 (dd, 2H, J = 0.9, 5.0 Hz, $H^{5'}$), 7.15 (br, 2H, Ar), 7.31–7.49 (m, 16H, Ar), 7.57–7.64 (m, 6H, Ar), 7.77 (dt, 2H, J = 1.7, 7.9 Hz, H⁴), 8.69 (m, 2H, H⁶); $\delta_{\rm C}$ (CDCl₃) 75.7 (t, J = 3.7 Hz, Fe(C_5 H₄)), 75.8 (s, Fe(C_5 H₄)), 117.5 (s, C³), 120.4 (d, $J_{P-C} = 3.7 \text{ Hz}, \text{ C}^5$), 124.7 (d, $J_{P-C} = 4.4 \text{ Hz}, \text{ C}^5$), 128.3 (d, $J_{P-C} =$ 11 Hz, C^{4'}), 130.2, 130.9, 130.9 (d, $J_{P-C} = 3.1$ Hz, Ar), 133.7 (d, $J_{P-C} = 1.2$ Hz, Ar), 135.8 (d, $J_{P-C} = 8.1$ Hz, Ar), 139.6 (s, C⁴), 142.0 $(d, J_{P-C} = 2.5 \text{ Hz}, C^2), 148.6 (s, C^3), 154.2 (d, J_{P-C} = 7.4 \text{ Hz}, C^6),$ 159.6 (d, $J_{P-C} = 2.5$ Hz, C²); δ_P (CDCl₃) 28.8 (s).

Similar treatments of $[Pd(\mu-N_3)(C,N-L^1)]_2$, $[Pd(\mu-N_3)(C,N-L^3)]_2$, $[Pd(\mu-N_3)(C,N-L^3)]_2$, $[Pd(\mu-N_3)(C,N-L^4)]_2$, and $[Pd(\mu-N_3)(C,N-L^5)]_2$ with 1 equivalent dppp, dppb, and depe gave the corresponding azido complexes **12–14** and **21–24**. Analytical and spectroscopic data of **23** were in agreement with those reported by Caires and co-workers.⁸

Data for **12**: v_{max} (KBr, cm⁻¹) 2038 (N₃); $\delta_{\rm H}$ (CDCl₃) 2.15 (br, 2H, –*CH*₂), 2.83 (br, 4H, P–*CH*₂), 5.89 (dd, 2H, *J* = 1.7, 5.0 Hz, H⁴), 6.88 (dd, 2H, *J* = 0.7, 5.0 Hz, H⁵), 7.16 (br, 4H, Ar), 7.30–7.41 (m, 14H), 7.68–7.80 (m, 10H), 8.78 (br, 2H, H⁶); $\delta_{\rm C}$ (CDCl₃) 21.9 (s, *CH*₂), 27.8 (d, *J*_{P-C} = 13 Hz, P–*CH*₂), 29.2 (d, *J*_{P-C} = 16 Hz, P–*C*H₂), 117.4 (s, C³), 120.3 (d, *J*_{P-C} = 3.1 Hz, C⁵), 125.2 (d, *J*_{P-C} = 3.8 Hz, C⁵), 128.7 (d, *J*_{P-C} = 11 Hz), 129.6, 130.2, 131.0, 133.5 (d, *J*_{P-C} = 12 Hz), 135.0 (d, *J*_{P-C} = 8.1 Hz), 139.6 (s,), 141.9 (d, *J*_{P-C} = 2.5 Hz, C²), 148.5 (s, C³), 154.0 (d, *J*_{P-C} = 5.6 Hz, C⁶), 159.4 (br, C²); $\delta_{\rm P}$ (CDCl₃) 31.1 (s).

Data for **13**: ν_{max} (KBr, cm⁻¹) 2036 (N₃); $\delta_{\rm H}$ (CDCl₃) 1.86 (br, 4H, P–CH₂), 2.61 (br, 4H, P–CH₂), 5.94 (dd, 2H, J = 1.7, 5.0 Hz, H^{4'}), 6.90 (dd, 2H, J = 1.1, 5.0 Hz, H, H^{5'}), 7.12 (ddt, 2H, J = 1.3, 5.0, 7.4 Hz, H⁵), 7.34–7.48 (m, 14H, Ar), 7.71–7.83 (m, 10H, Ar), 8.80 (m, 2H, H⁶); $\delta_{\rm C}$ (CDCl₃) 26.2 (d, $J_{\rm P-C} = 1.7$ Hz, P–CH₂), 27.3 (d, $J_{\rm P-C} = 32$ Hz, P–CH₂), 117.4 (d, $J_{\rm P-C} = 1.2$ Hz, C³), 120.4 (d, $J_{\rm P-C} = 3.8$ Hz, C⁵), 125.2 (d, $J_{\rm P-C} = 4.3$ Hz, C^{5'}), 128.7 (d, $J_{\rm P-C} =$ 11 Hz, Ar), 129.7, 130.4, 131.1 (d, $J_{\rm P-C} = 3.1$ Hz, Ar, 133.6 (d, $J_{\rm P-C} = 12$ Hz, Ar), 135.1 (d, $J_{\rm P-C} = 8.7$ Hz, Ar), 139.6 (s, Ar), 141.9 (d, $J_{\rm P-C} = 2.5$ Hz, C^{2'}), 148.6 (s, C^{3'}), 154.1 (d, $J_{\rm P-C} = 5.6$ Hz, C⁶), 159.4 (d, $J_{\rm P-C} = 3.1$ Hz, C²); $\delta_{\rm P}$ (CDCl₃) 31.7 (s).

Data for **14**: v_{max} (KBr, cm⁻¹) 2039, 2052 (N₃); δ_{H} (CDCl₃) 1.17 (dd, 12H, J = 7.5, 12 Hz, P–(CH₂CH₃)₂), 2.11 (m, 8H, P–CH₂), 2.38 (br, 4H, P–CH₂), 6.92 (dd, 2H, J = 4.9 Hz, H⁴), 7.13 (m, 2H, H⁵), 7.20 (d, 2H, J = 7.9 Hz), 7.28 (d, 2H, J = 7.9 Hz), 7.74 (dt, 2H, J = 1.7, 7.7 Hz, H⁴), 8.69 (m, 2H, H⁶); δ_{C} (CDCl₃) 8.17 (s, CH₂), 15.8 (d, $J_{\text{P-C}} = 15$ Hz, P–CH₂), 18.9 (t, $J_{\text{P-C}} = 15$ Hz, P–CH₂), 117.3(s, C³), 120.4 (d, $J_{\text{P-C}} = 1.6$ Hz, C⁵), 126.6 (t, $J_{\text{P-C}} =$ 1.6 Hz, C⁵), 132.8 (t, $J_{\text{P-C}} = 3.1$ Hz, C⁴), 139.4 (s, C⁴), 142.4 (d, $J_{\text{P-C}} = 1.3$ Hz, C³), 152.7 (t, $J_{\text{P-C}} = 4.0$ Hz, C⁶), 159.1 (t, $J_{\text{P-C}} =$ 1.2 Hz, C²); δ_{P} (CDCl₃) 34.0 (s).

Data for **21**: v_{max} (KBr, cm⁻¹) 2041 (N₃); δ_{H} (CDCl₃) 1.71 (br, 4H, P–CH₂), 2.50 (br, 4H, P–CH₂), 6.47 (t, 1H, J = 6.75 Hz, Ar), 6.70 (dt, 1H, J = 1.3, 7.5 Hz, Ar), 7.09 (m, 1H, Ar), 7.36–7.52

(m, 9H, Ar), 7.73–7.79 (m, 4H, Ar), 7.87–7.97 (m, 3H, Ar); $\delta_{\rm C}$ (CDCl₃) 13.5 (t, J = 14 Hz, P(CH₃)₃), 122.7 (s, C⁸), 123.7 (s, C³), 127.1, 129.4, 129.6, 130.6, 137.4 (br, C⁶), 152.3 (s, C⁷), 152.3 (s, C¹), 156.3 (s, C²); $\delta_{\rm P}$ (CDCl₃) 34.1 (s).

Data for **22**: v_{max} (KBr, cm⁻¹) 2037 (N₃); $\delta_{\rm H}$ (CDCl₃) 1.10 (dt, 12H, J = 7.5, 17 Hz, P(CH₂CH₃)₂), 1.93 (m, 8H, P(CH₂CH₃)₂), 2.14 (d, 4H, J = 2.1 Hz, PCH₂), 2.67 (s, 12H, NMe₂), 3.91 (s, 4H, CH₂), 6.97 (m, 8H, Ar); $\delta_{\rm C}$ (CDCl₃) 8.43 (s, P(CH₂CH₃)₂), 15.5 (t, $J_{\rm P-C} = 13.7$ Hz, P(CH₂CH₃)₂), 17.8 (t, $J_{\rm P-C} = 13.7$ Hz, P(CH₂CH₃)₂), 49.5 (s, NMe₂), 72.1 (s, CH₂), 123.2 (s, C³), 124.6 (s, C⁴), 126.1 (d, $J_{\rm P-C} = 2.2$ Hz, C⁵), 135.1 (d, $J_{\rm P-C} = 4.3$ Hz, C⁶), 149.1 (d, $J_{\rm P-C} = 0.9$ Hz, C²), 159.2 (br, C¹); $\delta_{\rm P}$ (CDCl₃) 34.0 (s).

Data for **24**: v_{max} (KBr, cm⁻¹) 2036 (N₃); $\delta_{\rm H}$ (CDCl₃) 1.15 (dt, 12H, J = 7.5, 17 Hz, P(CH₂CH₃)₂), 1.97–2.23 (m, 8H, P(CH₂CH₃)₂), 2.38 (s, 4H, PCH₂), 6.90 (dt, 2H, J = 0.9, 7.5 Hz, H⁵). 7.01 (dt, 2H, J = 1.4, 7.3 Hz, H^{5'}), 7.15–7.19 (m, 2H, Ar), 7.27 (m, 2H, Ar), 7.33 (dd, 2H, J = 1.5, 7.7 Hz, H^{3'}), 7.64 (d, 2H, J = 8.0 Hz, H³), 7.83 (dt, 2H, J = 1.7, 8.0 Hz, H⁴), 8.88 (m, 2H, H⁶); $\delta_{\rm C}$ (CDCl₃) 8.41 (s, P(CH₂CH₃)₂), 15.3 (dd, $J_{\rm P-C} = 14$ Hz, P(CH₂CH₃)₂), 18.2 (t, $J_{\rm P-C} = 14$ Hz, P(CH₂CH₃)₂), 118.2 (s, C³), 122.4 (s, C⁵), 124.2 (s, C^{5'}), 124.8 (s, C^{4'}), 129.8 (t, $J_{\rm P-C} = 2.5$ Hz, C⁶), 135.9 (t, $J_{\rm P-C} = 4.9$ Hz, C^{3'}), 147.4 (s, C⁴), 148.9 (s, C^{1'}), 154.0 (s, C⁶), 163.9 (s, C^{2'}), 165.3 (s, C²); $\delta_{\rm P}$ (CDCl₃) 32.9 (s).

Reactions of $[Pd(\mu-X)(C,N-L^1)]_2$ (X = N₃, Cl) with 1 or 2 equivalents chelating phosphine. CH₂Cl₂ (75 cm³) and depe (0.102 g, 0.49 mmol) were added to $[Pd(\mu-N_3)(C,N-L^1)]_2$ (0.305 g, 0.49 mmol) in a Schlenk flask. After stirring for 18 h, the slightly insoluble materials remained. The filtrate was evaporated and then extracted with benzene (10 cm³ × 3). The collected solution was evaporated to give yellow solids, which were recrystallized from CH₂Cl₂–*n*-hexane to give orange solids of complex 17 (0.030 g, 14%). The residues were recrystallized form CH₂Cl₂–*n*-hexane to give pale yellow solids of $[Pd(N_3)(C,N-L^1)]_2(\mu$ -depe) (14, 0.243 g, 60%).

Data for **17**: $\delta_{\rm H}$ (CDCl₃) 7.07 (dt, 1H, J = 1.3, 7.4 Hz, H⁵), 7.45 (d, 2H, J = 4.8 Hz, H⁵), 7.47 (overlap, 2H, H^{3+4'}), 7.65 (d, J = 4.7 Hz, H^{5'}), 7.71 (m, 2H, H⁴), 8.48 (m, 1H, H⁶); $\delta_{\rm C}$ (CDCl₃) 118.2 (s, C³), 119.7 (s, C⁵), 126.3 (s, C^{5'}), 135.8 (d, C^{4'}), 138.6 (s, C⁴), 141.5 (s, C^{2'}), 147.9 (s, C^{3'}), 158.1 (s, C⁶), 160.5 (s, C²). Complex **17** was could also be prepared from Pd(Et₂S)₂Cl₂ and 2 equivalents of lithiated 2-(2'-thienyl)pyridine.¹⁷

The similar reaction of $[Pd(\mu-N_3)(C,N-L^1)]_2$ (0.305 g, 0.49 mmol) with 2 equivalents depe (0.204 g, 0.98 mmol) gave white solids of $[Pd(C, N-L^1)(depe)](N_3)$ (18, 0.297 g, 58%). The solids were slightly hygroscopic and characterized by spectroscopic (IR, ¹H, ¹³C and ³¹P NMR) analyses. v_{max} (KBr, cm⁻¹) 2035 (N₃); $\delta_{\rm H}$ (CDCl₃) 1.26 (two dt, 12H, J = 7.5, 16 Hz, P(CH₂CH₃)₂), 2.09– 2.51 (m, 12 H, P-CH₂), 7.06-7.09 (m, 1H, H⁴), 7.35-7.47 (m, 2H, $H^{5} + H^{3}$), 7.65 (dd, $J = 1.0, 8.0 Hz, 1H, H^{5'}$), 7.89 (dt, 1H, J = 1.5, 7.7 Hz, H⁴), 8.74 (m, 1H, H⁶); $\delta_{\rm C}$ (CDCl₃) 9.51 (dd, $J_{\rm P-C} = 14$ Hz, $P(CH_2CH_3)_2$, 18.2 (d, $J_{P-C} = 21$ Hz, $P(CH_2CH_3)_2$), 20.1 (d, J_{P-C} = 21 Hz, $P(CH_2CH_3)_2$), 20.1 32 Hz, P(CH_2CH_3)₂), 22.0 (dd, $J_{P-C} = 8.1$, 29 Hz, P– CH_2 –), 25.9 $(dd, J_{P-C} = 17, 32 Hz, P-CH_2-), 119.1 (d, J_{P-C} = 3.7 Hz, C^3), 122.5$ $(d, J_{P-C} = 4.4 \text{ Hz}, \text{C}^5), 127.7 (dd, J_{P-C} = 3.1, 11 \text{ Hz}, \text{C}^4), 133.3 (t, t)$ $J_{P-C} = 7.2$ Hz, C⁴), 140.2, 151.1 (d, $J_{P-C} = 5.0$ Hz), 160.8 (t, $J_{P-C} =$ 1.2 Hz), 160.7 (dd, $J_{P-C} = 2.5$, 3.7 Hz), 162.8 (d, $J_{P-C} = 6.2$ Hz), 164.3 (d, $J_{P-C} = 6.3$ Hz); δ_P (CDCl₃) 56.1 (d, J = 31 Hz), 69.5 (d, J = 18 Hz).

CH₂Cl₂ (60 cm³) and depe (0.119 g, 0.58 mmol) were added to $[Pd(\mu-Cl)(C,N-L^1)]_2$ (0.350 g, 0.58 mmol), and the mixture was stirred for 18 h. The resulting solution was filtered and evaporated to give yellow residues, which were solidified with diethyl ether to give yellow solids. Recrystallization from CH₂Cl₂–*n*-hexane gave orange crystals of $[Pd(C,N-L^1)_2]$ (**17**, 0.060 g, 24%). The filtrate was evaporated under vacuum to give pale yellow solids, which were recrystallized from CH₂Cl₂–diethyl ether to give a mixture of $[PdCl(C,N-L^1)]_2(\mu$ -depe) (**16**) and (depe)PdCl₂. δ_H (CDCl₃) 1.76 (br t, 12H, J = 5.1 Hz, P(CH₂CH₃)₂), 1.93 (m, 8H, P(CH₂CH₃)₂), 2.48 (s, 4H, P–CH₂), 6.96 (d, 2H, J = 5.0 Hz, H⁴), 7.08 (m, 2H, H⁵), 7.22 (d, 2H, J = 5.0 Hz, H⁵), 7.33 (d, 2H, J = 7.5 Hz, H³), 7.71 (dt, 2H, J = 1.5, 7.7 Hz, H⁴), 9.20 (m, 2H, H⁶). The ¹³C NMR data could not be obtained due to its poor solubility. δ_P (CDCl₃) 9.70 (s).

The similar reaction of $[Pd(\mu-Cl)(C,N-L^1)]_2$ with 1 equivalent dmpe gave a mixture of **17** and $[PdCl(C,N-L^1)]_2(\mu-dmpe)$ (**15**). Data for **15**: $\delta_{\rm H}$ (CDCl₃) 1.76 (dd, 12H, J = 5.3 Hz, P(CH₃)₂), 2.48 (m, 4H, P–CH₂), 6.96 (m, 2H, H⁴), 7.08 (br, 2H, H⁵), 7.22 (d, 2H, J = 4.9 Hz, H⁵), 7.33 (d, 2H, J = 5.0, 8.0 Hz, H³), 7.77 (dt, 2H, J = 1.7, 7.7 Hz, H⁴), 9.15 (m, 2H, H⁶); $\delta_{\rm C}$ (CDCl₃) 15.0 (dd, $J_{\rm P-C} = 16$ Hz, P(CH₃)₂), 26.2 (dd, $J_{\rm P-C} = 17$ Hz, P-CH₂), 117.2(s, C³), 120.1(s, C⁵), 126.2 (s, C⁵), 133.2(s, C⁴), 139.4 (s, C⁴), 142.3 (d, $J_{\rm P-C} = 1.3$ Hz, C²), 149.0 (s, C³), 153.2 (t, $J_{\rm P-C} = 3.1$ Hz, C⁶), 159.1 (t, $J_{\rm P-C} = 1.2$ Hz, C²); $\delta_{\rm P}$ (CDCl₃) 9.69 (s).

Reactions of $[Pd(\mu-X)(C,N-L^3)]_2$ or $[Pd(\mu-X)(C,N-L^2)]_2$ (X = N₃, Cl) with 1 equivalent chelating phosphine

CH₂Cl₂ (90 cm³) and depe (0.075 g, 0.37 mmol) were added to [Pd(μ -N₃)(*C*,*N*-L³)]₂ (0.262 g, 0.37 mmol). An initial red suspension slowly turned to an orange solution. After stirring for 4 h, the solvent was removed completely, and the resulting residue was extracted several times with diethyl ether to give dark red solids of [Pd(*C*,*N*-L³)₂] (**20**, 0.159 g, 83%). The remaining white solids were identified by IR and ¹H NMR to be [Pd(N₃)₂(depe]]. $\delta_{\rm H}$ (CDCl₃) 2.07 (s, 6H, Me), 2.45 (s, 6H, Me), 6.93–7.02 (m, 2H, Ar), 7.22–7.30 (m, 3H, Ar), 7.92–7.97 (m, 2H, Ar); $\delta_{\rm C}$ (CDCl₃) 20.7 (s, Me), 21.0 (s, Me), 118.2 (s, C⁸), 123.0 (s, C³), 128.2 (s, C⁹), 130.3, 131.3, 133.3, 135.5, 136.8, 138.2, 151.6 (s, C⁷), 153.2 (s, C¹), 165.7 (s, C²).

Reactions of $[Pd(\mu-X)(C,N-L^2)]_2$ (X = N₃, Cl) with 1 equivalent depe were analogously carried out to give $[Pd(C,N-L^2)_2]$ (19, 79%) and $[Pd(depe)Cl_2]$. The complex 19 could also be prepared from Hg[C-L²]₂ and $[Pd(\mu-Cl)(C,N-L^2)]_2$ with Pd₂(dba)₃ or 2-lithio-N,N-dimethylbenzylamine. Analytical and spectroscopic data of 19 coincided with those in the literature.¹⁸

Reactions of $[Pd(N_3)(PMe_3)(C,N-L^4)]$ with CN-R $(R = 2,6-i-Pr_2C_6H_3)$

To a Schlenk flask containing $[Pd(N_3)(PMe_3)(C,N-L^4)]$ (2, 0.295 g, 0.82 mmol) were added CH₂Cl₂ (5 cm³) and 2,6-diisopropylphenyl isocyanide (0.169 g, 0.90 mmol). After stirring for 18 h, the solvent was removed, and then the resulting residue was solidified with diethyl ether. The solids were filtered off and washed with hexanes to give crude solids, which were recrystallized from CH₂Cl₂-diethyl ether to give yellow crystals of $[Pd(N_3)(-C=N-C_6H_3-2,6-i-Pr_2)(PMe_3)(N-L^4)]$ (25, 0.305 g, 68%). v_{max} (KBr, cm⁻¹) 2032 (N₃);

 $δ_{\rm H} ({\rm CDCl}_3, -40 °{\rm C}) 0.99 (d, 9{\rm H}, J_{\rm P-H} = 11 {\rm Hz}, {\rm P}({\rm CH}_3)_3), 1.12 (d, 3{\rm H}, J = 6.7 {\rm Hz}, {\rm C}({\rm CH}_3)_2), 1.19 (d, 3{\rm H}, J = 6.6 {\rm Hz}, {\rm C}({\rm CH}_3)_2), 1.31 (d, 3{\rm H}, J = 6.9 {\rm Hz}, {\rm C}({\rm CH}_3)_2), 1.78 (d, 3{\rm H}, J = 6.8 {\rm Hz}, {\rm C}({\rm CH}_3)_2), 2.53 (s, 3{\rm H}, {\rm NMe}_2), 2.80 (s, 3{\rm H}, {\rm NMe}_2), 3.07 (dd, 1{\rm H}, J = 5.4, 12 {\rm Hz}, {\rm CH}_2), 3.46 ({\rm sep}, 1{\rm H}, J = 7.4 {\rm Hz}, {\rm CH}({\rm CH}_3)_2), 7.02-7.04 (m, 1{\rm H}, {\rm Ar}), 7.12-7.21 (m, 2{\rm H}, {\rm Ar}), 7.29-7.38 (m, 2{\rm H}, {\rm Ar}), 7.44-7.50 (m, 2{\rm H}, {\rm Ar}); δ_{\rm C} ({\rm CDCl}_3, {\rm r.t.}) 15.6 (d, J_{\rm P-C} = 31 {\rm Hz}, {\rm P}({\rm CH}_3)_3), 25.0 (s, {\rm CH}({\rm CH}_3)_2), 29.2 (s, {\rm CH}({\rm CH}_3)_2), 48.0 (br, {\rm NMe}_2), 65.0 (d, J_{\rm P-C} = 1.9 {\rm Hz}, {\rm CH}_2), 122.7 ({\rm s}, {\rm C}^3), 123.7 ({\rm s}, {\rm C}^4), 124.6, 127.1, 129.7, 130.0, 131.9, 145.1 (d, J_{\rm P-C} = 5.3 {\rm Hz}, {\rm Ar}), 145.2 (d, J_{\rm P-C} = 6.8 {\rm Hz}, {\rm Ar}), 190.5 (d, J_{\rm P-C} = 3.5 {\rm Hz}, {\rm C=N}); δ_{\rm F} ({\rm CDCl}_3, {\rm r.t.}) -9.08 ({\rm s}).$

Reactions of $[Pd(N_3)(PMe_3)_2(C-L^4)]$ (15) with CN-R (R = 2,6-*i*-Pr₂C₆H₃) or 2,6-Me₂C₆H₃)

CH₂Cl₂ (3 cm³) and 2,6-diisopropylphenyl isocyanide (0.246 g, 13.1 mmol) were added to a Schlenk flask containing $[Pd(N_3)(PMe_3)_2(C-L^4)]$ (10, 0.272 g, 0.63 mmol) in that order. After stirring for 18 h, the solvent was removed, and then the resulting residue was solidified with *n*-hexane : diethyl ether (v/v = 1: 1). The resulting solids were filtered off and washed with hexane to give crude solids. Recrystallization from CH₂Cl₂-n-hexane gave yellow crystals of $[Pd(N=C=N-R)(-C(=N-R)(PMe_3)(N-L^4)]$ (R = 2,6*i*-Pr₂C₆H₃) (**26**, 0.132 g, 30%). v_{max} (KBr, cm⁻¹) 2130 (N=C=N); $\delta_{\rm H}$ (CDCl₃, -40 °C) 0.94 (d, 9H, $J_{\rm P-H}$ = 11 Hz, P(CH₃)₃), 1.09 $(d, 3H, J = 6.7 \text{ Hz}, CH(CH_3)_{2b}), 1.18 (dd, 15H, J = 3.3, 6.9 \text{ Hz},$ $CH(CH_{3})_{2a+c}$, 1.30 (d, 3H, J = 6.9 Hz, $C(CH_{3})_{2c}$), 1.73 (d, 3H, J = 6.7 Hz, C(CH₃)_{2b}), 2.63 (s, 3H, NMe₂), 2.81 (s, 3H, NMe₂), $3.06 (dd, 1H, J = 5.6, 12 Hz, CH_2), 3.44 (sep, 1H, J = 6.8 Hz,$ $CH_{c}(CH_{3})_{2}$), 3.63 (sep, 2H, J = 6.8 Hz, $CH_{a}(CH_{3})_{2}$), 3.80 (d, 1H, J = 12 Hz, CH_2), 4.40 (sep, 1H, J = 6.8 Hz, $CH_b(CH_3)_2$), 6.87– 6.92 (m, 1H, Ar), 7.02 (d, 2H, J = 7.4 Hz, Ar), 7.12–7.21 (m, 4H, Ar), 7.29–7.34 (m, 2H, Ar), 7.45–7.49 (m, 1H, Ar); $\delta_{\rm C}$ (CDCl₃, r.t.) 16.3 (d, $J_{P-C} = 32$ Hz, $P(CH_3)_3$), 23.5 (s, $CH(CH_3)_2$), 25.0 (s, CH(CH₃)₂), 25.0 (s, CH(CH₃)₂), 29.2 (s, CH(CH₃)₂), 48.0 (br, NMe₂), 65.8 (br, CH₂), 120.0 (s, C³), 122.4 (s, C⁴), 123.7, 124.1, 127.0, 129.7, 130.0, 132.1, 141.7, 142,1, 145.5 (d, $J_{P-C} = 5.3$ Hz), 145.6 (d, $J_{P-C} = 6.8$ Hz), 165.0 (br); δ_P (CDCl₃, r.t.) -8.37 (s).

The reaction of **25** with 1 equivalent CN–R (R = 2,6-*i*- $Pr_2C_6H_3$) also gave the same product (78%). The obtained product was identified by spectroscopic (IR and ¹H, ¹³C and ³¹P-NMR) analyses.

Reaction of **10** with CN–R (R = 2,6-Me₂C₆H₃) was analogously carried out to give [Pd(N=C=N–R)($-C(=N-R)(PMe_3)(N-L^4)$] (**27**, 73%). v_{max} (KBr, cm⁻¹) 2117 (N=C=N); $\delta_{\rm H}$ (CDCl₃, r.t.) 1.01 (d, 9H, $J_{\rm P-H}$ = 11 Hz, P(CH₃)₃), 2.33 (s, 6H, NMe₂), 2.37 (s, 3H, Me), 2.63 (s, 3H, Me), 2.79 (s, 3H, Me), 3.03 (s, 4H, Me + CH₂), 3.86 (br, 1H, CH₂), 6.65 (t, 1H, J = 7.4 Hz, Ar), 6.88–6.92 (m, 4H, Ar), 7.09–7.18 (m, 3H, Ar), 7.28 (dt, 1H, J = 1.4, 7.4 Hz, Ar), 7.42 (dt, 1H, J = 1.3, 7.4 Hz, Ar); $\delta_{\rm C}$ (CDCl₃, r.t.) 16.2 (d, $J_{\rm P-C}$ = 32 Hz, P(CH₃)₃), 19.5 (s, Me), 21.5 (s, Me), 48.4 (br, NMe₂), 64.7 (d, J = 16 Hz, –CH₂), 119.2 (s, C³), 123.5, 124.0, 127.2, 127.8, 129.8, 130.8, 132.1, 144.8, 145.4, 148.3, 188.0 (C=N) $\delta_{\rm P}$ (CDCl₃, r.t.) –7.98 (s).

Reactions of $[Pd(N_3)(PMe_3)_2(C-L^1)]$ (6), $[Pd(N_3)(P(n-Pr)_3)_2(C-L^2)]$ (9), and $[Pd(N_3)(PMe_3)_2(C-L^4)]$ (10) with R-NCS (R = *i*-Pr, (CH₃)₃Si, C₆H₄-NCS). To a Schlenk flask containing $[Pd(N_3)(PMe_3)_2(C-L^1)]$ (6, 0.262 g, 0.57 mmol) were added CH₂Cl₂

(4 cm³) and isopropyl isothiocyanate (0.086 g, 0.85 mmol). After stirring for 18 h, the reaction mixture was evaporated completely under vacuum, and then the resulting residue was solidified with *n*-hexane. The solids were filtered and washed with hexane (2 × 5 cm³). Recrystallization from CH₂Cl₂–*n*-hexane gave the white crystals of *trans*-{PdS[CN₄(R)](*C*-L¹)(PMe₃)₂} (**28**, 0.170 g, 53%). $\delta_{\rm H}$ (CDCl₃) 1.04 (br s, 18H, P(CH₃)₃), 1.56 (d, 6H, *J* = 6.8 Hz, CH(CH₃)₂), 5.02 (sep, 1H, 6.8 Hz, CH(CH₃)₂), 7.08 (d, 1H, *J* = 5.0 Hz, H⁴), 7.10 (ddt, 1H, *J* = 1.1, 4.8, 9.8 Hz, H⁵), 7.39 (d, 1H, *J* = 4.9 Hz, H⁵), 7.90 (dt, 1H, *J* = 8.0 Hz, H³), 8.54 (dt, 1H, *J* = 1.0, 4.3 Hz, H⁴), 9.72 (br d, 1H, *J* = 8.0 Hz, H⁶); $\delta_{\rm C}$ (CDCl₃) 14.0 (t, *J*_{P-C} = 16 Hz, P(CH₃)₃), 21.8 (s, CH(CH₃)₂), 49.6 (s, CH(CH₃)₂), 120.4 (s, C³), 121.0 (s, C⁵), 126.5 (s, C⁵), 134.3 (s, C⁴), 137.0 (s, C⁴), 139.1 (s, C^{2'}), 143.0 (s, C^{3'}), 149.1 (s, C⁶), 154.8 (s, C²); $\delta_{\rm P}$ (CDCl₃)

Complex **29**, [Pd(NCS)(P(*n*-Pr)₃)₂(*C*-L²)], was similarly prepared from [Pd(N₃)(P(*n*-Pr)₃)₂(*C*-L²)] (**9**, 0.293 g, 0.50 mmol) and trimethylsilyl isothiocyanate (0.079 g, 0.60 mmol). v_{max} (KBr, cm⁻¹) 2087 (NCS); $\delta_{\rm H}$ (CDCl₃) 0.86 (br, 18H, P(CH₂CH₂CH₃)₃), 1.36 (br, 24H, P(CH₂CH₂CH₃)₃), 7.06–7.10 (br, Ar), 7.43–7.64 (m, 5H, Ar), 8.00 (m, 2H, Ar); $\delta_{\rm C}$ (CDCl₃) 16.0 (t, *J* = 6.9 Hz, P(CH₂CH₂CH₃)₃), 17.5 (s, P(CH₂CH₂CH₃)₃), 25.2 (t, *J* = 12 Hz, P(CH₂CH₂CH₃)₃), 121.5 (s, C⁸), 122.8 (s, C³), 123.7 (s, C⁹), 129.1, 129.3, 130.6, 136.3(s, NCS), 137.3 (t, *J*_{P-C} = 4.0 Hz, C⁶), 152.4 (s, C⁷), 153.1 (s, C¹), 157.0 (s, C²); $\delta_{\rm P}$ (CDCl₃) 4.68 (s).

Reaction of **10** with R–NCS (R = C₆H₄–NCS) (2:1 molar ratio) was analogously carried out to give {Pd(PMe₃)₂(S[CN₄]–) (*C*-L⁴)}₂(μ-C₆H₄), (**30**, 47%). $\delta_{\rm H}$ (CDCl₃) 1.10 (br, 36H, P(CH₃)₃), 2.34 (s, 12H, NMe₂), 3.65 (s, 4H, CH₂), 6.93–6.97 (m, 4H, Ar), 7.08–7.11 (m, 2H, Ar), 7.37–7.39 (m, 2H, Ar), 8.25 (s, 4H, Ar); $\delta_{\rm C}$ (CDCl₃) 14.0 (t, 18H, J_{P-C} = 14 Hz, P(CH₃)₃), 46.1 (s, NMe₂), 68.5 (s, CH₂), 122.5 (s, C³), 123.8 (s, C⁴), 125.9, 129.1 (s, C⁵), 135.6 (s, C⁶), 142.9 (s, C²), 157.6 (s, C¹), 163.0. The carbon signal of S[CN₄] could not be identified owing to its weak intensity. $\delta_{\rm P}$ (CDCl₃) –16.1 (s).

General procedure for Suzuki–Miyaura cross-coupling reactions. To a 13 × 90 mm test tube was added the phenylboronic acid (31.7 mg, 0.26 mmol), K₂CO₃ (55.3 mg, 0.4 mmol), Pd catalyst (1 × 10^{-3} mmol, 1 mol%), and aryl halide (0.2 mmol) with a stirring bar. Toluene (1.0 cm³) was added, and the resulting mixture was heated in an oil bath at 80 °C. The reaction was monitored by TLC. After the aryl bromide was totally consumed, the reaction mixture was cooled to room temperature and quenched with brine (1.0 cm³) and then extracted with EtOAc (3 × 1.0 cm³). The resulting organic solution was dried over MgSO₄ and concentrated on a rotary evaporator. The crude product was purified by preparation TLC (0.5 mm).

X-Ray structure determination

X-Ray data of complexes 1, 3, 7, 25, 28 and 29 were collected with a Siemens P4 diffractometer equipped with a Mo X-ray tube, except those of complexes 12, 17, 21, and 24 that were collected with a Bruker Smart APEX2 diffractometer. All calculations were carried out with the SHELX-97 programs.⁴¹ All structures were solved by direct methods. All non-hydrogen atoms were refined anisotropically, and all hydrogen atoms were generated in ideal positions and refined in a riding model.

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