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(π-Allyl)Pd Complexes Containing N-Heterocyclic Carbene and Pseudohalogen Ligands – Synthesis, Reactivity toward Organic Isothiocyanates and Isocyanides, and Their Catalytic Activity in Suzuki–Miyaura Cross-Couplings

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Keywords: Allyl ligands / Carbenes / Cross-coupling / Palladium / Pseudohalogens

Dinuclear (π-allyl)palladium chlorides, $[(\pi\text{-allyl})Pd(\mu\text{-Cl})]_2$, were cleaved by N-heterocyclic carbenes (NHCs) to give mononuclear (π-allyl)palladium–NHC chlorides, [(π-allyl)Pd(Cl)(NHC)] (**1**–**6**) [NHC = 1,3-bis(2,6-diisopropylphenyl)imidazol-2-ylidene (IPR), 1,3-bis(2,6-diisopropylphenyl)-4,5-dihydroimidazol-2-ylidine (SIPR), 1,3-bis(2,4,6-trimethylphenyl)imidazol-2-ylidene (IMes)]. Complexes **1**–**6** were subsequently treated with aqueous NaN_3, KSCN, KOCN, and CF_3COOAg to produce the corresponding mononuclear (π-allyl)palladium–NHC pseudohalogen complexes, [(π-allyl)Pd(X)(NHC)] (X = N_3, NCS, SCN, NCO, CF_3COO) (**7**–**30**). These products could also be obtained by treating dinuclear pseudohalogen-bridged Pd complexes, $[(\pi\text{-allyl})Pd(\mu\text{-X})]_2$, which were prepared by replacing the μ-Cl ligand in $[(\pi\text{-allyl})Pd(\mu\text{-Cl})]_2$, with aqueous NaN_3, KSCN, KOCN, or CF_3COOAg, followed by cleavage with the NHCs. Reactions of $[(\pi\text{-allyl})Pd(N_3)(NHC)]$ with organic isothiocyanates (R–NCS) or $CH_3O(CO)C{\equiv}CO(CO)CH_3$ resulted in selective 1,3-dipolar cycloaddition into the Pd–azido bond to give heterocyclic compounds. By contrast, analogous reactions of $[(\eta^3\text{-allyl})Pd(N_3)(IPr)]$ with an organic isocyanide (R–NC: R = *tert*-butyl, benzyl) gave the adduct $[(\eta^3\text{-allyl})Pd(N_3)(IPr)]\cdot(R\text{–}NC)$ as the only product or a mixture of the adduct and a dipolar cycloaddition product, $[(\eta^3\text{-allyl})Pd\{CN_4(R)\}(IPr)]$, depending on the isocyanides used. Finally, a series of (π-allyl)Pd–NHC pseudohalogen complexes, [(π-allyl)Pd(X)(NHC)], exhibited high catalytic activity in Suzuki–Miyaura cross-coupling reactions of aryl chlorides with arylboronic acids.

Introduction

In transition-metal-mediated organic syntheses, Pd-catalyzed C–C cross-coupling reactions are widely utilized.[1–4] In particular, palladium compounds containing labile ligands such as C,N-donor ligands have emerged as efficient precatalysts for Suzuki–Miyaura cross-coupling reactions.[5,6] Furthermore, to enhance catalytic efficiency in these catalytic reactions, several studies on cyclopalladated compounds containing N-heterocyclic carbenes (NHCs), one of the many sterically and/or electronically beneficial ligands, were reported.[7]

Recently, we reported that cyclopalladated azides containing C,N-donor ligands exhibit excellent catalytic activity in the Suzuki–Miyaura cross-coupling of haloaryl compounds, specifically aryl bromides and chlorides.[8] Their catalytic activity was dependent on the supporting ligand, a tertiary phosphane or an NHC ligand. For example, compounds with an NHC ligand showed higher catalytic activity for aryl chlorides than those with a combination of C,N-donor and tertiary phosphane ligands. On the basis of these results, we set out to find more effective Pd catalysts for the Suzuki–Miyaura coupling. For this purpose, we tried to combine ligands that were more flexible than the C,N-donor ligands with other supporting ligands such as pseudohalogens and NHC ligands.

In this context, an allyl ligand as a flexible group was first introduced to the Pd center, because the η^3-allyl ↔ η^1-allyl isomerization may facilitate C–C bond formation or reductive elimination during catalytic reactions. This isomerization is known for (allyl)Pd–NHC complexes, and it is regarded as important dynamic behavior that can be controlled by supporting ligands.[9–11] In addition, we introduced an NHC ligand and a pseudohalogen ligand as supporting ligands. Pseudohalogen ligands are known to be better leaving groups than halogen ligands in catalytic reactions. In summary, in this study, a set of the three aforementioned ligands (i.e., NHC, pseudohalogen, and allyl) were

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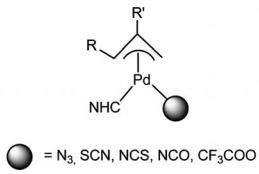
introduced to the Pd coordination sphere to induce unique reactivity and high catalytic activity.



Nolan and co-workers reported that several (π-allyl)Pd–NHC chloride complexes, [(π-allyl)Pd(Cl)(NHC)] [NHC = 1,3-bis(2,6-diisopropylphenyl)imidazol-2-ylidene (IPR), 1,3-bis(2,6-diisopropylphenyl)-4,5-dihydroimidazol-2-ylidine (SIPR), 1,3-bis(2,4,6-trimethylphenyl)imidazol-2-ylidene (IMes), etc.], exhibit highly efficient catalytic activity in the Suzuki–Miyaura coupling of aryl chlorides and aryl boronic acid.[12] The spectroscopic and dynamic behavior of (π-allyl)Pd complexes possessing halogen or pseudohalogen ligands, [(η^3-allyl)Pd(X)(IPr)] (X = Cl, Br, N_3, SCN, etc.), were previously reported.[9,10] Several ionic complexes, [(η^3-allyl)Pd(NHC)](X) (X = OTf, BF_4, PF_6, etc.), and neutral complexes, [(η^3-allyl)Pd(X)(NHC)] (X = I, Cl, Me), were also examined by spectroscopy.[13] However, the chemical reactivity (e.g., dipolar cycloaddition with organic unsaturated molecules) of the (π-allyl)palladium complexes containing various pseudohalogen ligands has not been reported. Furthermore, comparative catalytic evaluation of the pseudohalogen complexes and their halogen counterparts has yet to be explored. In this work, we prepared a series of neutral (π-allyl)Pd–NHC pseudohalogen complexes and examined their reactivity as well as their catalytic activity in Suzuki–Miyaura cross-coupling reactions.

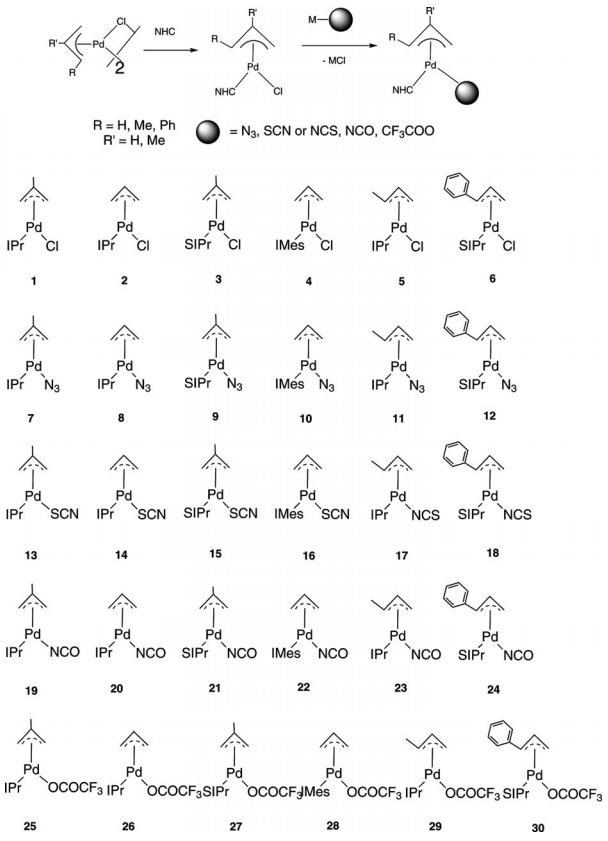
Results and Discussion

Preparation of (π-Allyl)Pd–NHC Pseudohalogen Complexes

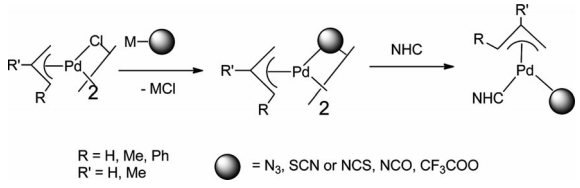
Dinuclear (π-allyl)palladium chlorides [(π-allyl)Pd(μ-Cl)]$_2$ were cleaved by the NHCs (2 equiv.) to give neutral mononuclear (π-allyl)palladium–NHC chlorides **1**–**6**, [(π-allyl)Pd(Cl)(NHC)] (NHC = IPr, SIPr, IMes). Subsequent transmetalation of complexes **1**–**6** by using an aqueous solution of NaN_3, KSCN, KOCN, or CF_3COOAg afforded the corresponding (π-allyl)palladium–NHC pseudohalogen complexes **7**–**30**, [(π-allyl)Pd(X)(NHC)] (X = N_3, NCS, SCN, NCO, CF_3COO) (Schemes 1).

Complexes **7**–**30** could also be obtained by treating dinuclear pseudohalogen-bridged Pd complexes, [(π-allyl)-Pd(μ-X)]$_2$, which were prepared from [(π-allyl)Pd(μ-Cl)]$_2$, with an aqueous solution of NaN_3, KSCN, KOCN, or CF_3COOAg followed by cleavage with the NHCs (2 equiv., see Scheme 2).

However, if [(η^3-crotyl)Pd(Cl)(IPr)] and [(η^3-cinnamyl)-Pd(Cl)(SIPr)] were treated with an equimolar amount of NaN_3 or KSCN to prepare complexes **12**, **17**, and **18** (pathway outlined in Scheme 1), impure products containing an unidentifiable contaminant were obtained. For this reason, the pathway outlined in Scheme 2 was used to synthesize



Scheme 1.



Scheme 2.

the dinuclear pseudohalogen-bridged Pd complexes [(π-allyl)Pd(μ-X)]$_2$ (X = N_3, NCS), which were then cleaved with the NHCs (2 equiv.) to yield the desired complexes. In addition, for the preparation of complexes **25**–**30**, [(π-allyl)-Pd(Cl)(NHC)] was treated with CF_3COOAg instead of CF_3COONa, which is commonly used to introduce the CF_3COO group to the transition-metal system. One possible explanation for the formation of the unidentifiable products by the nucleophilic attack of strong nucleophiles (NaN_3, KSCN, and CF_3COONa) at the π-allyl ligand may be the partial dissociation of the π-allyl ligand as well as the formation of the desired product.

In earlier work, Busetto,[14] Shaw,[15] and Wilke[16] reported that dinuclear N_3-, NCS-, CH_3COO-, and CF_3COO-bridged complexes, [(π-allyl)Pd(μ-X)]$_2$, are formed by the metathesis of a dinuclear (π-allyl)Pd chloride with nBu_4N_3, KSCN, CH_3COOAg, and CF_3COOAg, respectively. In addition, mononuclear and dinuclear complexes, [(π-allyl)Pd(solvent)(X)] (X = BF_4, SbF_6), [(π-allyl)-Pd(OTf)(NHC)] (Tf = trifluoromethanesulfonyl), and [(π-allyl)Pd(μ-X′)]$_2$ (X′ = BF_4, SbF_6, OTf) were also re-

ported.[13,17] Moreover, allyl trifluoroacetate was shown to oxidatively add to $[Pd(dba)_2]$ (dba = dibenzylideneacetone) to give a trifluoroacetate-bridged (π-allyl)Pd complex.[18]

The Pd–NHC pseudohalogen complexes were isolated in moderate-to-good yields. A few (π-allyl)Pd–NHC chlorides were previously prepared from NHC·HCl and dinuclear (π-allyl)Pd chloride dimers,[12c,19] and several (π-allyl)Pd–NHC chlorides are commercially available. Although many cleavage reactions of Cl-bridged (π-allyl)palladium complexes by NHCs are currently known,[10,12,13] examples involving dinuclear azido (or other pseudohalogen)-bridged (π-allyl)-palladium complexes have not been reported. The formation of (π-allyl)Pd–NHC azides **7**–**12** was followed by IR spectroscopy by monitoring the characteristic N_3 stretching band at 2022–2031 cm^{-1} (see Table 1). Interestingly, treatment of [(π-allyl)Pd(Cl)(NHC)] complexes **1**–**6** with KSCN afforded *S*- and *N*-coordinated (NCS) palladium complexes **13**–**19**, depending on the starting Pd compounds. The IR spectra of the complexes clearly display characteristic bands that can be attributed to *S*- and *N*-coordination of the NCS ligand to the Pd center. *S*-Coordinated complexes **13**–**16**, [(π-allyl)Pd(SCN)(NHC)], exhibit a sharp and strong stretching band above 2100 cm^{-1}, whereas *N*-coordinated complexes **17** and **18**, [(π-allyl)Pd(NCS)(NHC)], exhibit a strong but broad band below 2100 cm^{-1}. Similar IR spectroscopic assignments were made by Maitlis[20] and Norbury.[21] The bent Pd–SCN (in complexes **13**–**16**) and linear Pd–NCS (in complexes **17** and **18**) bonding modes can probably be explained in terms of steric congestion around the Pd metal. Complexes **17** and **18** contain the π-allyl ligand with a substituent (CH_3 or Ph) at the terminal carbon atom that would require a large space around the Pd metal, whereas complexes **13**–**16** do not. Consequently, the Pd metal in complexes **17** and **18** is exposed to greater steric congestion, and the linear Pd–NCS (*N*-coordination) fragment would be formed favorably. X-ray crystallographic analysis fully supports the formation of *S*- and *N*-coordinated NCS complexes (see Figure 3 for **14** and Figure 4 for **17**).

Table 1. Characteristic IR bands for complexes **7**–**30**.[a]

Complex	Pd–N_3 $\nu(N_3)$ [cm^{-1}]	Complex	Pd–SCN or Pd–NCS ν(SCN) or ν(NCS) [cm^{-1}]
7	2022	**13**	2104
8	2022	**14**	2104
9	2022	**15**	2101
10	2030	**16**	2101
11	2030	**17**	2088
12	2031	**18**	2098
Complex	Pd–NCO ν(NCO) [cm^{-1}]	Complex	Pd–$OC(O)CF_3$ $\nu_{sym}(CO_2)/\nu_{asym}(CO_2)$ [cm^{-1}]
19	2158	**25**	1681/1403
20	2194	**26**	1686/1406
21	2214	**27**	1685/1401
22	2214	**28**	1684/1409
23	2199	**29**	1683/1404
24	2186	**30**	1682/1409

[a] KBr.

(π-Allyl)Pd isocyanato [(π-allyl)Pd(NCO)(NHC)] complexes **19**–**24** (Table 1) display a characteristic strong band at 2158–2186 cm^{-1} that can be assigned to ν(NCO), and this is consistent with that found in other palladium isocyanato complexes.[22–24] Table 1 shows the strong IR bands characteristic of $\nu_{asym}(CO_2)$ and $\nu_{sym}(CO_2)$ at approximately 1680 and 1400 cm^{-1} for (π-allyl)palladium trifluoroacetates **25**–**30**, and this is indicative of an η^1-trifluoroacetato ligand. The difference in these stretching frequencies ($\Delta\nu \approx 280\ cm^{-1}$) is typical of metal–($\eta^1$-trifluoroacetato) complexes.[25,26] The ^1H NMR and ^{13}C NMR assignments for the (π-allyl)Pd–NHC pseudohalogen complexes were made on the basis of those reported in the literature.[9,10,12,13] Particularly, the ^{13}C NMR peaks at δ = 52.5–55.0 ppm, which are due to the terminal π-allyl carbon atom *trans* to the X ligand (*S*- or *N*-coordinated NCS), for complexes **13**–**18** are downfield shifted relative to the same peaks at δ = 40.3–47.4 ppm for complexes **7**–**12** and **19**–**30**, and this is a reflection of some electronic influence of the *trans* thiocyanato group in these complexes.

Structures of the Compounds

Single crystals suitable for X-ray crystallographic analysis were grown from solutions of THF/hexane at –35 °C. The crystal data, intensity collection, and refinement details are given in the Supporting information (Table S1). The molecular structures of complexes **7**, **8**, **14**, **17**, **19**, **22**, **25**, and **31** are given in Figures 1, 2, 3, 4, 5, 6, 7, and 8, respectively, in which each Pd metal is coordinated to one NHC ligand, one pseudohalogen ligand, and one η^3-allyl group. The coordination sphere of all the complexes can be best described as a distorted square plane if the coordination of the central allyl carbon atom to the Pd metal is ignored. In Table 2, selected bond lengths for all complexes are listed. The Pd–C1, Pd–$C2_{meso}$, and Pd–C3 bond lengths [2.075(5)–2.219(5) Å] in the π-allyl ligand are close to the values [2.082(9)–2.284(9) Å] for (π-allyl)Pd–NHC chlorides reported in the literature.[10,12b] Consistent with the relative strength of the *trans* effect, the Pd–C bond *trans* to the NHC is longer than that *trans* to the pseudohalogen.[9,10,12b]

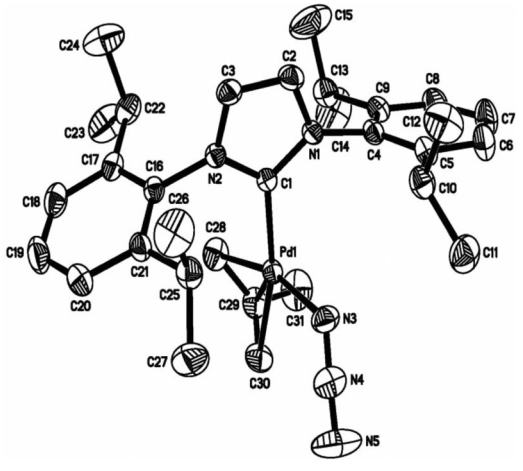


Figure 1. ORTEP drawing of [(η^3-2-methylallyl)Pd(N_3)(IPr)] (**7**).

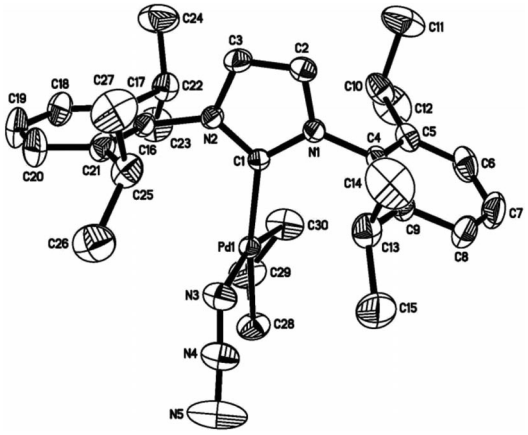


Figure 2. ORTEP drawing of [(η³-allyl)Pd(N$_3$)(IPr)] (**8**).

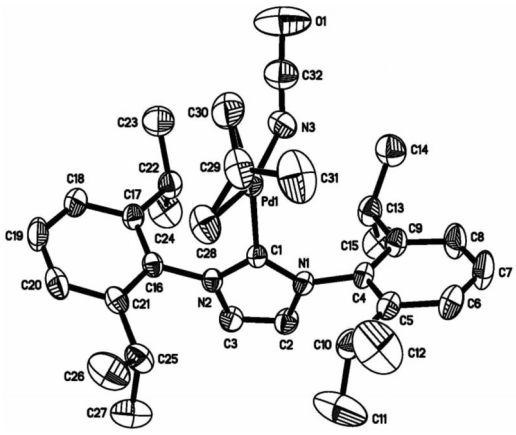


Figure 5. ORTEP drawing of [(η³-2-methylallyl)Pd(NCO)(IPr)] (**19**).

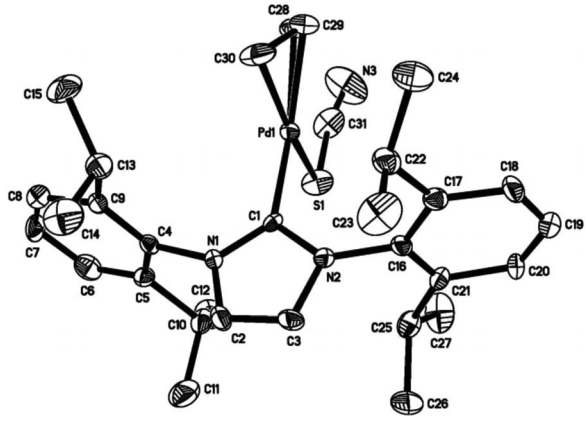


Figure 3. ORTEP drawing of [Pd(η³-allyl)(SCN)(NHC)] (**14**).

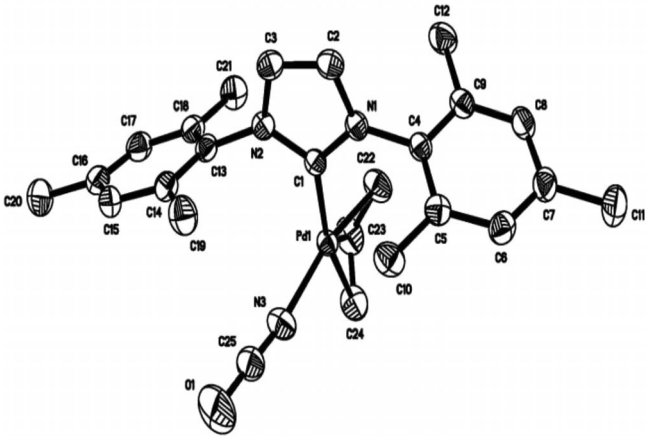


Figure 6. ORTEP drawing of [(η³-allyl)Pd(NCO)(IMes)] (**22**).

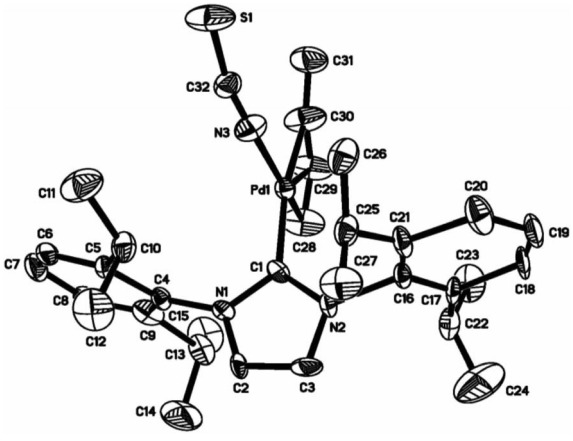


Figure 4. ORTEP drawing of [(η³-crotyl)Pd(NCS)(IPr)] (**17**).

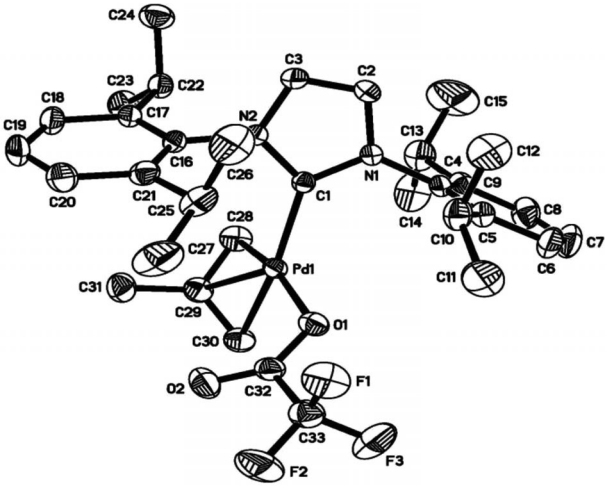


Figure 7. ORTEP drawing of [(η³-2-methylallyl)Pd(OCOCF$_3$)(IPr)] (**25**).

The NHC cyclic ring in all of the complexes is oriented essentially perpendicular to the molecular plane, and the Pd–C (NHC) bond lengths [2.034(3)–2.066(2) Å] fall in the range of the reported values [2.028(4)–2.062(2) Å] in [(π-allyl)Pd(Cl)(NHC)] complexes.[10,12b] The Pd–N$_3$ (azido) bond length [2.087(3) Å for **7** and 2.078(2) Å for **8**] is close to that in *trans*-[MePd(N$_3$)(PMe$_3$)$_2$] [2.132(9) Å][27a] and that in *trans*-[(*p*-MeC$_6$H$_4$)Pd(N$_3$)(PMe$_3$)$_2$] [2.114(3) Å][23] of the phosphane-containing Pd azido complexes, which indicates a relatively weak *trans* influence of the π-allyl ligand. The ORTEP drawings of **14** (Figure 3) and **17** (Figure 4) clearly demonstrate the *S*- and *N*-coordination of the NCS

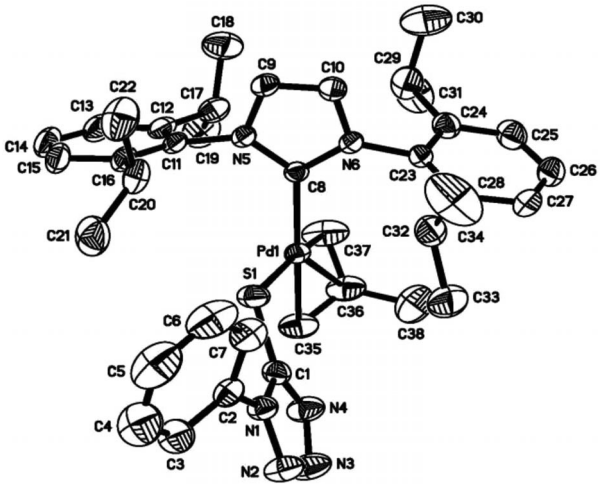


Figure 8. ORTEP drawing of [(η^3-2-methylallyl)Pd{CN_4(Ph)}(IPr)] (**31**).

tion-metal azides to afford complexes containing heterocycles is well known. In particular, organic isocyanides and isothiocyanates are known to react with transition-metal azides to give complexes containing *C*-coordinated[23,27,30–35] and *S*-coordinated[14,36–41] heterocyclic ligands. We previously reported that unsaturated organic compounds react with group 10 metal azides containing C,N-donor or phosphane ligands to give the corresponding carbodiimide or *S*-coordinated tetrazole compounds.[8a] With these results in mind, we first attempted the reactions of [(π-allyl)Pd(N_3)(NHC)] with various organic isothiocyanates (R–NCS: R = Ph, CH_2Ph, C_6H_4NCS; see Scheme 3). Consistent with our expectation, the *S*-coordinated heterocycles were isolated, which were formed by the dipolar cycloaddition of the isothiocyanate to the Pd–azido bond. By this reaction, mono- and dinuclear tetrazole–thiolato (π-allyl)Pd–NHC complexes were readily formed in moderate-to-good yields at room temperature.

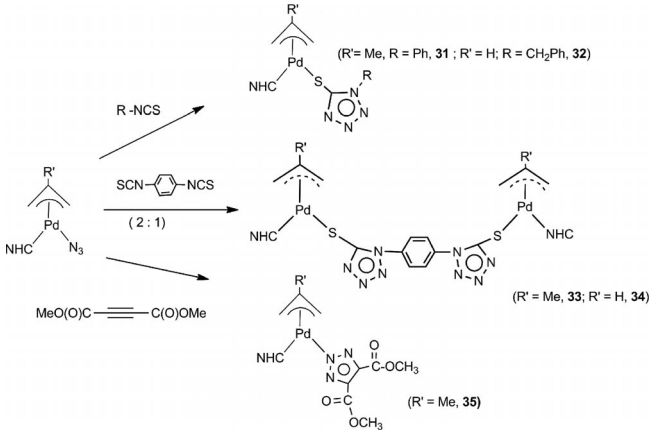
Table 2. Selected bond lengths for complexes **7**, **8**, **14**, **17**, **19**, **22**, **25**, and **31**.

Complex	Pd–C1 [Å]	Pd–C2 [Å]	Pd–C3 [Å]	Pd–C (NHC) [Å]	Pd–S [Å]	Pd–N [Å]	Pd–O [Å]
7	2.097(4)	2.151(4)	2.143(4)	2.046(3)	–	2.087(3)	–
8	2.103(3)	2.110(3)	2.168(3)	2.041(2)	–	2.078(2)	–
14	2.136(2)	2.144(3)	2.170(2)	2.066(2)	2.364(6)	–	–
17	2.075(5)	2.116(4)	2.219(5)	2.034(3)	–	2.073(3)	–
19	2.091(3)	2.150(3)	2.153(3)	2.039(2)	–	2.071(3)	–
22	2.091(2)	2.118(2)	2.202(2)	2.038(2)	–	2.067(2)	–
25	2.080(2)	2.132(2)	2.215(2)	2.041(2)	–	–	2.142(1)
31	2.114(3)	2.161(3)	2.164(3)	2.047(2)	2.335(7)	–	–

ligand, respectively. The Pd1–S1 bond length [2.364(6) Å] in complex **14** is almost the same as that in [Pd($SCN)_2$(dppm)] [2.364(2) Å, dppm = 1,1-bis(diphenylphosphanyl)methane] and that in [Pd(NCS)(SCN)(dppe)] [2.364(4) Å, dppe = 1,2-bis(diphenylphosphanyl)ethane]. The Pd1–N_3 (NCS) bond length [2.073(3) Å] in complex **17** is consistent with that found in [Pd(NCS)(SCN)(dppe)] [2.062(10) Å] and that in [Pd($Ph_2P(CH_2)_3N(CH_3)_2$)(SCN)(NCS)] [2.063(7) Å].[28] The Pd–N [2.067(2) and 2.071(3) Å] bond length in (π-allyl)Pd isocyanates [(η^3-2-methylallyl)Pd(NCO)(IPr)] (**19**) and [(η^3-allyl)Pd(NCO)(IMes)] (**22**) is close to that in **17**, but shorter than that [2.119(5) Å] in *trans*-[Pd(CH_3CO)(NCO)-($PMe_3)_2$].[23] The N–C bond length [1.128(4) for **19** and 1.114(3) Å for **22**] in the Pd–NCO fragment is shorter than the C–O bond length [1.204(4) Å for **19** and 1.198(3) Å for **22**], and this phenomenon is common in other metal isocyanato complexes.[29] The molecular structure of complex **25** is given in Figure 5, which shows a distorted square plane with an NHC, an η^3-2-methylallyl group, and an η^1-$OCOCF_3$ ligand.

Reactivity toward Organic Isothiocyanates (R–NCS), Isocyanides (R–NC), and Alkynes

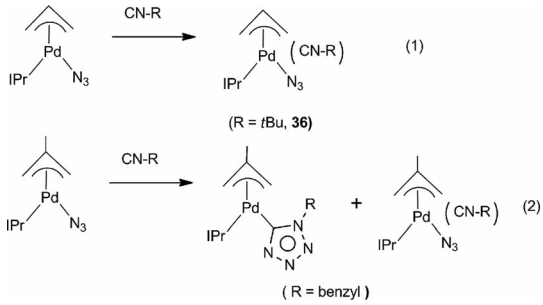
Dipolar cycloaddition of unsaturated organic molecules such as organic isothiocyanates (R–NCS), isocyanides (R–NC), organonitriles (R–CN), and alkynes with late-transi-



Scheme 3.

In contrast, the room-temperature reaction of complex **7** with dimethyl acetylenedicarboxylate (DMAD, 1 equiv.) proceeded to produce quantitatively the *N*-coordinated triazolato Pd [(η^3-2-methylallyl)Pd{(N_3C_2)($COOMe)_2$}] complex (see Scheme 3). The formation of the N1-bound isomer could not be confirmed by spectroscopy. The IR spectra of complexes **31**–**35** do not display the ν(N_3) band of the starting compounds, which supports the dipolar cycloaddition of the organic substrates to the Pd–N_3 bond. Moreover, the molecular structure of **31** in Figure 8, determined by X-ray diffraction, further confirms this reactivity.

Reactions of [(π-allyl)Pd(N_3)(NHC)] with equimolar amounts of organic isocyanides (*tert*-butyl or benzyl isocyanide) gave products that were quite different from those obtained from reactions with isothiocyanates. Upon reaction with *tert*-butyl isocyanide, the [(η^3-allyl)Pd(N_3)(IPr)]·(CN–*t*Bu) (**36**) adduct was obtained as the sole product (Scheme 4). A similar reaction of [(η^3-2-methylallyl)-Pd(N_3)(IPr)] with benzyl isocyanide gave a 1:1 mixture of [(η^3-2-methylallyl)Pd(N_3)(IPr)]·(CN–CH_2Ph) and [(η^3-2-methylallyl)Pd{CN_4(CH_2Ph)}(IPr)].



Scheme 4.

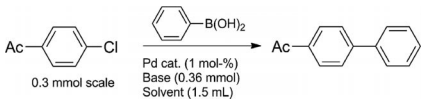
The IR spectrum of **36** displays strong absorption bands at 2081 and 2042 cm^{-1} that are assignable to ν(C≡N) and ν(N_3), respectively, whereas the IR spectrum of the starting isocyanide complex shows the ν(C≡N) band at 2136 cm^{-1}. The shift of the ν(C≡N) band to lower frequency may arise from the formation of the adduct (i.e., complex **36**). The ^{1}H NMR and ^{13}C NMR spectra of complex **36** do not indicate that isocyanide insertion to the Pd–C or Pd–N bond took place. If less-hindered benzyl isocyanide was employed, the IR spectrum of the product displays absorption bands at 2215 [ν(C≡N)] and 2024 [ν(N_3)] cm^{-1} [Scheme 4, Equation (2)]. In this case, the ν(C≡N) band is shifted to a high frequency [ν(C≡N) at 2152 cm^{-1} for free benzyl isocyanide]. The reason for the opposite shifts of the ν(C≡N) band for the *t*Bu–NC and $PhCH_2$–NC cases is not clear because of the limited data. In addition, the ^{1}H NMR spectrum of the first isolated product shows two distinct CH_3 signals with a 1:1 integration ratio, which is probably the result of a mixture of [(η^3-2-methylallyl)Pd(N_3)(IPr)]·(CN–R) and [(η^3-2-methylallyl)Pd{CN_4(R)(IPr)}] (R = benzyl). The signal at δ = 168.7 ppm in the ^{13}C NMR spectrum is assigned to the carbon atom of the tetrazolato ring (CN_4) formed by cycloaddition of the isocyanide to the Pd–N_3 bond, which is characteristic of Pd compounds having a *C*-coordinated tetrazolato ring.[30–35] The rather distinct reactivity between the two isocyanides in Scheme 4 may be explained on the basis of steric factors. The bulkier *tert*-butyl isocyanide seems to be reluctant to undergo cycloaddition to the Pd–N_3 bond. On the contrary, the steric problem is somewhat relieved for less-bulky benzyl isocyanide, and so a mixture of an adduct and a cycloaddition product is formed. In addition, related adducts were previously prepared from organic isocyanides and Ni^{II} or Pd^{II} isothiocyanato complexes.[40a,42]

Catalytic Application to Suzuki–Miyaura Cross-Coupling Reactions

The Suzuki–Miyaura cross-coupling of aryl halides with arylboronic acids is a well-known tool to form various C–C coupled compounds.[43] Many palladacycles containing a supporting NHC ligand are widely utilized for Suzuki–Miyaura C–C coupling reactions.[43c,43d] Recently, we also reported that palladacycles containing C,N-donor, NHC, and azido ligands act as highly efficient catalysts in C–C cross-coupling reactions.[8b] Our study also showed that the combination of a functional moiety and suitable supporting ligands around the metal center enhances the catalytic activity. In addition, studies on the effects of the pseudohalogen supporting ligands of the Pd–NHC complexes on the cross-coupling catalytic reactions are relatively rare.

In this context, we evaluated the catalytic activity of [(π-allyl)Pd(X)(NHC)] (X = halide, pseudohalide). To find the optimum conditions for the Suzuki–Miyaura cross-coupling reactions, we examined the catalytic activity of [(η^3-2-methylallyl)Pd(N_3)(IPr)] (**7**, 1 mol-%) for the reaction of *p*-chloroacetophenone, phenylboronic acid, and a base in a molar ratio of 1:1.2:2 in several solvents. Reaction conditions and product yields are listed in Table 3, which shows that the conditions outlined in entry 5 resulted in high activity for the coupling of *p*-chloroacetophenone with phenylboronic acid.

Table 3. Optimization of the Suzuki–Miyaura cross-coupling of 4-chloroacetophenone with phenylboronic acid catalyzed by [(η^3-2-methylallyl)Pd(N_3)(IPr)] (**7**).



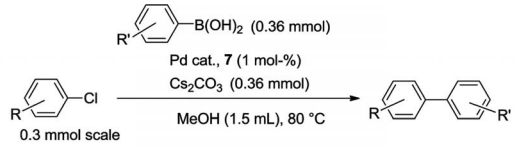
Entry	Solvent	Base	*T* [°C]	*t* [h]	Isolated yield [%]
1	EtOH	K_2CO_3	80	14	trace
2	toluene	K_2CO_3	80	3	83
3	MeOH	K_2CO_3	80	2	99
4	EtOH	Cs_2CO_3	80	0.5	84
5	MeOH	Cs_2CO_3	80	0.5	99
6	MeOH	Cs_2CO_3	60	1	80
7	MeOH	Cs_2CO_3	r.t.	14	trace
8[a]	MeOH	Cs_2CO_3	80	0.5	50
9	dioxane	Cs_2CO_3	80	0.5	49
10	*i*PrOH	Cs_2CO_3	80	0.5	76
11[b]	*i*PrOH	KO*t*Bu	80	0.5	93
12[b]	*i*PrOH	Cs_2CO_3	80	0.5	91
13[b]	*i*PrOH	KO*t*Bu	r.t.	15	51

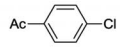
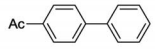
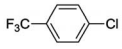
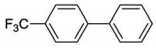
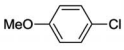
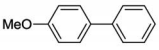
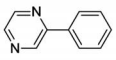
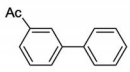
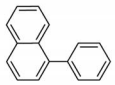
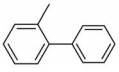
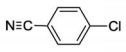
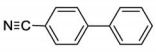
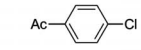
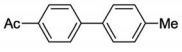
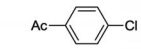
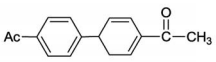
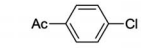
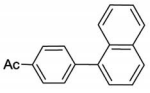
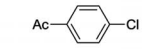
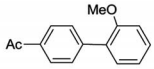
[a] Under an atmosphere of O_2. [b] Technical-grade *i*PrOH.

The optimized conditions were applied to other C–C cross-coupling reactions of various activated and unactivated aryl chlorides with arylboronic acids in the presence of Pd catalyst **7** (1 mol-%) at 80 °C in MeOH with Cs_2CO_3 as the base (Table 4). As expected, the coupling reactions involving various organoboronic acids (Table 4, entries 9–12) gave moderate-to-good yields. However, the relatively low yield for entry 7 is probably due to the steric hindrance or deactivation of the substituent of the organic halide dur-

ing oxidative addition within the catalytic cycle. Biphenyl was also observed as a major byproduct for the reaction of entry 7.

Table 4. Suzuki–Miyaura cross-coupling reactions of aryl chlorides with arylboronic acids catalyzed by complex **7**.[a]

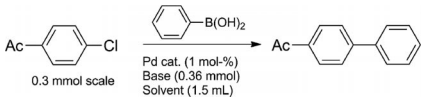


Entry	Aryl chloride	Product	Reaction time [min]	Isolated yield [%]
1			30	99
2			30	61
3			120	61
4			60	78
5			120	99
6			30	99
7			60	53
8			90	99
9[a]			60	98
10[b]			60	99
11[c]			60	98
12[d]			60	99

[a] *p*-Tolylboronic acid was used. [b] 4-Acetylphenylboronic acid was used. [c] Naphthalene-1-boronic acid was used. [d] 2-Methoxyphenylboronic acid was used.

To compare the catalytic activity of the (π-allyl)palladium–NHC halogen and pseudohalogen complexes, [(π-allyl)Pd(X)(NHC)] (X = N_3, Cl, NCS, SCN, NCO, CF_3COO), the cross-coupling reactions of *p*-chloroacetophenone with arylboronic acids were investigated. Most complexes gave high yields (see Table 5 and Figure 9), except thiocyanato (SCN) and isothiocyanato (NCS) complexes **13**–**18**. For this unusually low catalytic efficiency, we speculate that the dissociated SCN^- or NCS^- ion coordinates to the Pd center to prevent the formation of a zerovalent Pd^0–(NHC) intermediate, which is necessary for the subsequent oxidative addition of the organic halide to yield the final coupling products. Whereas the catalytic activity of Pd–NHC halogen complexes has been widely explored, the activity of the pseudohalogen analogues has not been investigated to date. The catalytic results in Figure 9 clearly demonstrate that the (π-allyl)Pd–NHC pseudohalogen (N_3, NCO, CF_3COO) and halogen (Cl) complexes exhibit high catalytic efficiency in Suzuki–Miyaura cross-coupling reactions.

Table 5. Suzuki–Miyaura cross-coupling yields in the reaction of 4-chloroacetophenone with phenylboronic acid catalyzed by complexes **1**–**30**.[a]



Pd cat.	Isolated yield [%]	Pd cat.	Isolated yield [%]
1	98	**16**	1
2	99	**17**	3
3	99	**18**	13
4	96	**19**	99
5	93	**20**	98
6	96	**21**	99
7	99	**22**	98
8	94	**23**	97
9	90	**24**	99
10	99	**25**	98
11	97	**26**	99
12	82	**27**	88
13	7	**28**	90
14	10	**29**	98
15	6	**30**	77

[a] All reactions were performed at 80 °C in MeOH with Cs_2CO_3 for 30 min.

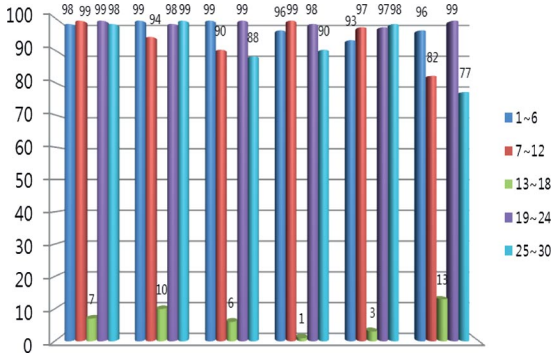


Figure 9. Comparison of [(π-allyl)PdX(NHC)]-catalyzed cross-coupling yields for the reaction of 4-chloroacetophenone with phenylboronic acid (vertical axis: % yield).

Conclusions

In summary, we prepared a series of (π-allyl)Pd–NHC pseudohalogen (N_3, SCN, NCS, NCO, CF_3COO) com-

plexes. In particular, treatment of [(η^3-crotyl)Pd(Cl)(IPr)] and [(η^3-cinnamyl)Pd(Cl)(SIPr)] with an aqueous solution of NaN_3 or KSCN led to incomplete substitution. Also, reactions of (π-allyl)Pd chlorides with CF_3COONa resulted in partial replacement of Cl by CF_3CO_2. These results strongly indicate the liability of the π-allyl moiety toward such nucleophiles, which is closely related to the potential catalytic activity of these complexes in Suzuki–Miyaura cross-coupling reactions. However, we observed selective dipolar cycloaddition of organic isothiocyanates (R–NCS) into the Pd–azido bond of (π-allyl)Pd–NHC azide complexes to give heterocyclic tetrazole–thiolato compounds. In contrast, reactions of (π-allyl)Pd–NHC azides with organic isocyanides (R–NC) did not give cycloaddition products but a [(π-allyl)Pd(N_3)(IPr)]·(R–NC) adduct or a mixture of the adduct and a dipolar cycloaddition compound, depending on the nature of the isocyanide. These results show the different behavior of electrophiles and nucleophiles toward our (π-allyl)Pd–NHC pseudohalogen complexes. Finally, for the Suzuki–Miyaura coupling of aryl chlorides with arylboronic acids, the (π-allyl)Pd–NHC pseudohalogen (N_3, NCO, CF_3CO_2) complexes exhibited higher catalytic efficiency relative to that exhibited by the thiocyanato (*S*- or *N*-coordinated) analogues.

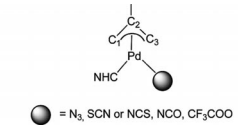
Experimental Section

General Methods, Materials, and Measurements: All manipulations of air-sensitive compounds were performed under an atmosphere of N_2 or Ar by standard Schlenk-line techniques. Solvents were distilled from Na–benzophenone. The analytical laboratories at Kangnung-Wonju National University performed the elemental analyses with a CE instruments EA1110. IR spectra were recorded with a Perkin–Elmer BX spectrophotometer. NMR (^1H, $^{13}C\{^1H\}$, and $^{31}P\{^1H\}$) spectra were obtained with JEOL Lamda 300 MHz and ECA 600 MHz spectrometers. Chemical shifts were referenced to internal Me_4Si. Mass (FAB) spectra were obtained at the Korea Basic Science Institute (Seoul). The [(η^3-2-methylallyl)Pd(μ-Cl)]$_2$, [(η^3-allyl)Pd(μ-Cl)]$_2$, [(η^3-crotyl)Pd(μ-Cl)]$_2$, and [(η^3-cinnamyl)-Pd(μ-Cl)]$_2$ derivatives were prepared by literature methods[44] or modified methods or purchased from Aldrich Co. or Strem Co.

Cleavage Reactions of [(η^3-2-Methylallyl)Pd(μ-Cl)]$_2$, [(η^3-Allyl)-Pd(μ-Cl)]$_2$, [(η^3-Crotyl)Pd(μ-Cl)]$_2$, and [(η^3-Cinnamyl)Pd(μ-Cl)]$_2$ with NHCs (2 equiv.)

A solution of IPr (0.648 g, 1.67 mmol) in THF (4 mL) was added to a Schlenk flask containing [(η^3-2-methylallyl)Pd(μ-Cl)]$_2$ (0.323 g, 0.83 mmol) by cannula, and then THF (2 mL) was added. The initial pale yellow suspension turned into a homogeneous pale yellow solution. After stirring for 2 h at room temperature, the solvent was removed under vacuum. The resulting residue was washed with *n*-hexane (3 times) to yield a white solid. Recrystallization from THF/*n*-hexane gave white crystals of [(η^3-2-methylallyl)Pd(Cl)(IPr)] (1, 0.960 g, 98%).

Similar reactions of [(η^3-allyl)Pd(μ-Cl)]$_2$, [(η^3-crotyl)Pd(μ-Cl)]$_2$, and [(η^3-cinnamyl)Pd(μ-Cl)]$_2$ with the NHCs (IPr, SIPr, IMes, 2 equiv.) gave corresponding mononuclear (π-allyl)palladium–NHC chlorides **2**–**6**. Complexes **2**, **4**, and **6** are commercially available. The spectroscopic data for the (π-allyl)Pd–NHC halogen and pseudohalogen complexes are available in the Supporting Information.



Preparation of [(η^3-2-Methylallyl)Pd(μ-N_3)]$_2$, [(η^3-Allyl)Pd(μ-N_3)]$_2$, [(η^3-Crotyl)Pd(μ-N_3)]$_2$, and [(η^3-Cinnamyl)Pd(μ-N_3)]$_2$

[(η^3-2-Methylallyl)Pd(μ-N_3)]$_2$ was prepared by a modified literature method.[8] To a yellowish suspension of [(η^3-2-methylallyl)Pd(μ-Cl)]$_2$ (1.07 g, 2.73 mmol) in CH_2Cl_2 (10 mL) was added a solution of NaN_3 (0.532 g, 8.19 mmol) dissolved in N_2-bubbled H_2O (1 mL) by cannula. After stirring for 3 h at room temperature, the reaction mixture was completely evaporated to yield a crude solid, which was extracted with CH_2Cl_2 (20 mL). The collected solution was evaporated to give a pale yellow solid, which was washed with *n*-hexane. The product was dried under vacuum to give [(η^3-2-methylallyl)Pd(μ-N_3)]$_2$ as a pale yellow product (1.10 g, 98%).

[(η^3-Allyl)Pd(μ-N_3)]$_2$ (98%), [(η^3-crotyl)Pd(μ-N_3)]$_2$ (97%), and [(η^3-cinnamyl)Pd(μ-N_3)]$_2$ (98%) were prepared similarly and were used as starting materials in subsequent reactions (Scheme 2) without further crystallization because of their poor solubility in common organic solvents.

Cleavage Reactions of [(η^3-2-Methylallyl)Pd(μ-N_3)]$_2$, [(η^3-Allyl)-Pd(μ-N_3)]$_2$, [(η^3-Crotyl)Pd(μ-N_3)]$_2$, and [(η^3-Cinnamyl)Pd(μ-N_3)]$_2$ with NHCs (2 equiv.)

According to Scheme 2: A solution of IPr (0.631 g, 1.62 mmol) in THF (4 mL) was added to a Schlenk flask containing [(η^3-2-methylallyl)Pd(μ-N_3)]$_2$ (0.332 g, 0.81 mmol) by cannula, and THF (2 mL) was added. The initial pale yellow suspension turned into a homogeneous pale orange solution. After stirring for 2 h at room temperature, the solvent was removed under vacuum. The resulting residue was washed with *n*-hexane (3×) to yield a white solid. Recrystallization from THF/*n*-hexane gave white crystals of [(η^3-2-methylallyl)Pd(N_3)(IPr)] (**7**, 0.769 g, 80%). $C_{31}H_{43}N_5Pd$ (592.13): calcd. C 62.88, H 7.31, N 11.83; found C 62.95, H 7.58, N, 11.87.

Cleavage reactions of [(η^3-allyl)Pd(μ-N_3)]$_2$, [(η^3-crotyl)]Pd(μ-N_3)]$_2$, and [(η^3-cinnamyl)Pd(μ-N_3)]$_2$ with the NHCs (IPr, SIPr, IMes; 2 equiv.) were analogously performed to give corresponding mononuclear (π–allyl)palladium–NHC azides **8**–**12**.

According to Scheme 1: To a solution of [(η^3-allyl)Pd(Cl)(IMes)] (**4**, 0.984 g, 2.02 mmol) in THF (6 mL) was added a solution of NaN_3 (0.144 g, 2.22 mmol) in N_2-bubbled H_2O (1 mL) by cannula. The initial yellow suspension turned into an orange solution. After stirring for 4 h at room temperature, the solvent was completely removed under vacuum, and the remaining solid was extracted with CH_2Cl_2 and washed with diethyl ether (2 mL × 3). Recrystallization from THF/hexane gave pale yellow crystals of [(η^3-allyl)-Pd(N_3)(IMes)] (**10**, 0.928 g, 93%).

The [(η^3-2-methylallyl)Pd(Cl)(IPr)], [(η^3-2-methylallyl)Pd(Cl)-(SIPr)], [(η^3-allyl)Pd(Cl)(IPr)], [(η^3-crotyl)Pd(Cl)(IPr)], and [(η^3-cinnamyl)Pd(Cl)(SIPr)] complexes were treated further with NaN_3 to prepare corresponding azido complexes **7**–**9**, **11**, and **12**. Spectroscopic data of the azido complexes were in agreement with those obtained by following the path outlined in Scheme 2.

[(η^3-Allyl)Pd(N_3)(IPr)] (8): Yield: 97%. $C_{30}H_{41}N_2Pd$ (536.08): calcd. C 62.33, H 7.15, N 12.11; found C 62.22, H 7.68, N 11.94.

Complexes **8**, **14**, and **20** were also reported by Pregosin and Albinati co-workers.[9]

[(η³-2-Methylallyl)Pd(N₃)(SIPr)] (9): Yield: 96%. $C_{31}H_{45}N_5Pd$ (594.14): calcd. C 62.67, H 7.63, N 11.79; found C 63.08, H 7.99, N 11.67.

[(η³-Allyl)Pd(N₃)(IMes)] (10): Yield: 93%. $C_{24}H_{29}N_5Pd$ (493.94): calcd. C 58.36, H 5.92, N 14.18; found C 58.72, H 6.37, N 13.93.

[(η³-Crotyl)Pd(N₃)(IPr)] (11): Yield: 83%. $C_{31}H_{43}N_5Pd$ (592.13): calcd. C 62.88, H 7.32, N 11.83; found C 63.07, H 7.75, N 11.70.

[(η³-Cinnamyl)Pd(N₃)(SIPr)] (12): Yield: 64%. $C_{36}H_{47}N_5Pd$ (656.21): calcd. C 65.89, H 7.22, N 10.67; found C 65.80, H 7.59, N 10.22.

Preparation of [(η³-2-Methylallyl)Pd(X)(NHC)] (NHC = IPr, SIPr)], [(η³-Allyl)Pd(X)(IPr)], [(η³-Allyl){Pd(X)(IMes)}], [(η³-Crotyl)Pd(X)(IPr)], and [(η³-Cinnamyl)Pd(X)(SIPr)] (X = SCN, NCS) (13–18)

According to Scheme 1: To a solution of [(η³-2-methylallyl)-Pd(Cl)(IPr)] (**1**, 0.102 g, 0.17 mmol) in THF (2 mL) was added a solution of KSCN (0.019 g, 0.19 mmol) dissolved in N_2-bubbled H_2O (1 mL) by cannula. After stirring for 3 h at room temperature, the solvent was completely removed under vacuum, and the remaining solid was extracted with CH_2Cl_2 and washed with a *n*-hexane (2 mL × 3). Recrystallization from THF/hexane gave white crystals of [(η³-2-methylallyl)Pd(SCN)(IPr)] (**13**, 0.102 g, 97%). $C_{32}H_{43}N_3SPd$ (608.19): calcd. C 63.19, H 7.13, N 6.91; found C 63.17, H 7.24, N, 6.75.

Analogous reactions of [(η³-2-methylallyl)Pd(Cl)(SIPr)], [(η³-allyl){Pd(Cl)(IPr)}], [(η³-allyl)Pd(Cl)(IMes)], [(η³-crotyl)Pd(Cl)-(IPr)], and [(η³-cinnamyl)Pd(Cl)(SIPr)] by using KSCN (1.1 equiv.) gave corresponding thiocyanato (SCN) or isothiocyanato (NCS) palladium–NHC complexes **14**–**18**.

According to Scheme 2: To a solution of [(η³-2-methylallyl)Pd(μ-Cl)]₂ (0.301 g, 0.76 mmol) in CH_2Cl_2 (3 mL) was added a solution of KSCN (0.156 g, 1.60 mmol) in N_2-bubbled H_2O (1 mL) by cannula. After stirring for 3 h at room temperature, the reaction mixture was completely evaporated to yield a crude solid, which was extracted with CH_2Cl_2 (17 mL). The collected solution was evaporated to give a crude solid, which was washed with *n*-hexane. Recrystallization from THF/hexane (1:4) gave pale yellow crystals of [(η³-2-methylallyl)Pd(μ-SCN)]₂ (0.280 g, 84%). A solution of IPr (0.268 g, 0.69 mmol) in CH_2Cl_2 (2 mL) was added to a solution of [(η³-2-methylallyl)Pd(μ-SCN)]₂ (0.151 g, 0.34 mmol) in CH_2Cl_2 (3 mL) by cannula. The initial pale yellow suspension turned into a yellow solution. After stirring for 3 h at room temperature, the solvent was removed under vacuum. The resulting residue was washed with *n*-hexane (3×) to yield a gray solid. Recrystallization from THF/*n*-hexane (1:6) gave white crystals of [(η³-2-methylallyl)-Pd(SCN)(IPr)] (**13**, 0.372 g, 89%).

[(η³-Allyl)Pd(SCN)(IPr)] (14): Yield: 95%. $C_{31}H_{41}N_3PdS$ (594.16): calcd. C 62.66, H 6.95, N 7.07; found C 62.59, H 7.03, N 6.82.

[(η³-2-Methylallyl)Pd(SCN)(SIPr)] (15): Yield: 98%. $C_{32}H_{45}N_3PdS$ (610.21): calcd. C 62.98, H 7.43, N 6.88; found C 62.96, H 7.60, N 6.49.

[(η³-Allyl)Pd(SCN)(IMes)] (16): Yield: 98%. $C_{25}H_{29}N_3PdS$ (510.00): calcd. C 58.88, H 5.73, N 8.24; found C 58.99, H 5.81, N 7.88.

[(η³-Crotyl)Pd(NCS)(IPr)] (17): Yield: 95%. $C_{32}H_{43}N_3PdS$ (608.19): calcd. C 63.19, H 7.13, N 6.91; found C 63.23, H 7.32, N 6.35.

[(η³-Cinnamyl)Pd(NCS)(SIPr)] (18): Yield: 63%. $C_{36}H_{47}N_5Pd$ (656.21): calcd. C 65.89, H 7.22, N 10.67; found C 65.80, H 7.59, N 10.22.

Preparation of [(η³-2-Methylallyl)Pd(NCO)(NHC)] (NHC = IPr, SIPr), [(η³-Allyl)Pd(NCO)(IPr)], [(η³-Allyl)Pd(NCO)(IMes)], [(η³-Crotyl)Pd(NCO)(IPr)], and [(η³-Cinnamyl)Pd(NCO)(SIPr)] (19–24)

According to Scheme 1: To a solution of [(η³-2-methylallyl)Pd(Cl)(IPr)] (**1**, 0.156 g, 0.26 mmol) in CH_2Cl_2 (4 mL) was added a solution of KOCN (0.026 g, 0.32 mmol) in N_2-bubbled H_2O (1 mL) by cannula. After stirring for 3 h at room temperature, the reaction mixture was completely evaporated to yield a crude solid, which was extracted with CH_2Cl_2 (20 mL). The collected solution was evaporated to give a crude solid, which was washed with *n*-hexane. Recrystallization from THF/hexane gave white crystals of [(η³-2-methylallyl)Pd(NCO)(IPr)] (**19**, 0.152 g, 96%). $C_{32}H_{43}N_3OPd$ (592.12): calcd. C 64.90, H 7.32, N 7.09; found C 64.55, H 7.33, N 7.25.

Analogous reactions of [(η³-2-methylallyl)Pd(Cl)(SIPr)], [(η³-allyl)-Pd(Cl)(IPr)], [(η³-allyl)Pd(Cl)(IMes)], [(η³-crotyl)Pd(Cl)(IPr)], and [(η³-cinnamyl)Pd(Cl)(SIPr)] by using KOCN (1.1 equiv.) gave corresponding isocyanato palladium–NHC complexes **20**–**24**.

According to Scheme 2: To a solution of [(η³-2-methylallyl)Pd(μ-Cl)]₂ (0.302 g, 0.77 mmol) in CH_2Cl_2 (3 mL) was added a solution of KOCN (0.131 g, 1.61 mmol) in N_2-bubbled H_2O (1 mL) by cannula. After stirring for 3 h at room temperature, the reaction mixture was completely evaporated to yield a crude solid, which was extracted with CH_2Cl_2 (6 mL). The collected solution was evaporated to give a crude solid, which was washed with *n*-hexane. Recrystallization from THF/hexane gave pale yellow crystals of [(η³-2-methylallyl)Pd(μ-NCO)]₂ (0.282 g, 97%). An solution of IPr (0.286 g, 0.74 mmol) in CH_2Cl_2 (4 mL) was added to a solution of [(η³-2-methylallyl)Pd(μ-NCO)]₂ (0.150 g, 0.37 mmol) in CH_2Cl_2 (2 mL) by cannula. The initial pale yellow suspension turned into a pale orange solution. After stirring for 3 h at room temperature, the solvent was removed under vacuum. The resulting residue was washed with *n*-hexane (3 times) to yield a white solid. Recrystallization from THF/*n*-hexane gave white crystals of [(η³-2-methylallyl)Pd(NCO)(IPr)] (**19**, 0.400 g, 92%).

[(η³-Allyl)Pd(NCO)(IPr)] (20): Yield: 82%. $C_{31}H_{41}N_3OPd$ (578.10): calcd. C 64.40, H 7.15, N 7.26; found C 64.28, H 7.25, N 7.25.

[(η³-2-Methylallyl)Pd(NCO)(SIPr)] (21): Yield: 97%. $C_{32}H_{45}N_3OPd$ (594.14): calcd. C 64.68, H 7.63, N 7.07; found C 64.47, H 7.75, N 7.10.

[(η³-Allyl)Pd(NCO)(IMes)] (22): Yield: 97%. $C_{25}H_{29}N_3OPd$ (493.94): calcd. C 60.79, H 5.92, N 8.51; found C 60.61, H 6.03, N 8.43.

[(η³-Crotyl)Pd(NCO)(IPr)] (23): Yield: 93%. $C_{32}H_{43}N_3OPd$ (592.12): calcd. C 64.91, H 7.32, N 7.09; found C 65.09, H 7.49, N 7.13.

[(η³-Cinnamyl)Pd(NCO)(SIPr)] (24): Yield: 89%. $C_{37}H_{47}N_3OPd$ (656.21): calcd. C 67.72, H 7.22, N 6.40; found C 67.40, H 7.33, N 6.43.

Preparation of [(η³-2-Methylallyl)Pd(OCOCF₃)(NHC)](NHC = IPr, SIPr), [(η³-Allyl)Pd(OCOCF₃)(IPr)], [(η³-Allyl)Pd(OCOCF₃)-(IMes)], [(η³-Crotyl Pd(OCOCF₃)(IPr)], and [(η³-Cinnamyl)Pd-(OCOCF₃)(SIPr)] (25–30)

According to Scheme 1: To a solution of [(η³-2-methylallyl)-Pd(Cl)(IPr)] (**19**, 0.154 g, 0.26 mmol) in CH_2Cl_2 (3 mL) was added a solution of $AgOCOCF_3$ (0.058 g, 0.26 mmol) in N_2-bubbled H_2O (2 mL) by cannula. After stirring for 1 h at room temperature, the reaction mixture was filtered to remove the precipitated salts, and

the filtrate was completely evaporated and then washed with *n*-hexane (2 mL × 3) to yield the crude product (0.169 g, 97%). Recrystallization from THF/hexane gave white crystals of [(η^3-2-methylallyl)Pd(OCOCF$_3$)(IPr)] (**25**). $C_{33}H_{43}N_2O_2F_3Pd$ (663.12): calcd. C 59.77, H 6.54, N 4.22; found C 60.14, H 4.07, N, 6.38.

Analogous reactions of [(η^3-2-methylallyl)Pd(Cl)(SIPr)], [(η^3-allyl)-Pd(Cl)(IPr)], [(η^3-allyl)Pd(Cl)(IMes)], [(η^3-crotyl)Pd(Cl)(IPr)], and [(η^3-cinnamyl)Pd(Cl)(SIPr)] with AgOCOCF$_3$ (1 equiv.) gave corresponding palladium–NHC trifluoroacetates **26**–**30**.

According to Scheme 2: To a solution of [(η^3-2-methylallyl)Pd(μ-Cl)]$_2$ (0.320 g, 0.81 mmol) in CH_2Cl_2 (3 mL) was added a solution of AgOCOCF$_3$ (0.376 g, 1.70 mmol) in N_2-bubbled H_2O (2 mL) by cannula. After stirring for 3 h at room temperature, the reaction mixture was completely evaporated to yield a crude solid, which was extracted with CH_2Cl_2 (20 mL). The collected solution was evaporated to give a crude solid, which was washed with *n*-hexane. Recrystallization from THF/hexane (3:30) gave pale yellow crystals of [(η^3-2-methylallyl)Pd(μ-OCOCF$_3$)]$_2$ (0.361 g, 81%). A solution of IPr (0.216 g, 0.55 mmol) in CH_2Cl_2 (2 mL) was added to a solution of [(η^3-2-methylallyl)Pd(μ-OCOCF$_3$)]$_2$ (0.152 g, 0.28 mmol) in CH_2Cl_2 (2 mL) by cannula. The initial yellow solution turned green. After stirring for 3 h at room temperature, the solvent was removed under vacuum. The resulting residue was washed with *n*-hexane (3 times) to yield a gray solid. Recrystallization from THF/*n*-hexane (7:40) gave white crystals of [(η^3-2-methylallyl)Pd(OCOCF$_3$)(IPr)] (**25**, 0.318 g, 86%).

[(η^3-Allyl)Pd(OCOCF$_3$)(IPr)] (26): Yield: 97%. $C_{32}H_{41}F_3N_2O_2Pd$ (649.10): calcd. C 59.21, H 6.37, N 4.32; found C 59.46, H 6.62, N 4.16.

[(η^3-2-Methylallyl)Pd(OCOCF$_3$)(SIPr)] (27): Yield: 96%. $C_{33}H_{45}F_3N_2O_2Pd$ (665.14): calcd. C 59.59, H 6.81, N 4.21; found C 59.89, H 7.18, N 4.60.

[(η^3-Allyl)Pd(OCOCF$_3$)(IMes)] (28): Yield: 96%. $C_{26}H_{29}F_3N_2O_2Pd$ (564.94): calcd. C 55.27, H 5.17, N 4.95; found C 55.57, H 5.52, N 5.06.

[(η^3-Crotyl)Pd(OCOCF$_3$)(IPr)] (29): Yield: 96%. $C_{33}H_{43}F_3N_2O_2Pd$ (663.12): calcd. C 59.77, H 6.53, N 4.22; found C 59.45, H 6.77, N 4.57.

[(η^3-Cinnamyl)Pd(OCOCF$_3$)(SIPr)] (30): Yield: 86%. $C_{38}H_{47}F_3N_2O_2Pd$ (727.21): calcd. C 62.76, H 6.51, N 3.85; found C 62.42, H 6.91, N 4.04.

Reactions of [(η^3-2-Methylallyl)Pd(N$_3$)(IPr)], [(η^3-2-Methylallyl)-Pd(N$_3$)(SIPr)], and [(η^3-Allyl)Pd(N$_3$)(IPr)] with Organic Isothiocyanates (R–NCS: R = Ph, CH$_2$Ph, SCN-*p*-C$_6$H$_4$) and DMAD: To a solution of [(η^3-2-methylallyl)Pd(N$_3$)(IPr)] (7, 0.244 g, 0.41 mmol) in THF (4 mL) was added phenyl isothiocyanate (0.086 mL, 0.45 mmol). After stirring for 3 h, the reaction mixture was evaporated completely under vacuum, and then the resulting residue was solidified with *n*-hexane. The solid was filtered and washed with hexane (5 mL × 2). Recrystallization from diethyl ether/*n*-hexane gave yellow crystals of [(η^3-2-methylallyl)Pd-{CN$_4$(Ph)}(IPr)] (**31**, 0.170 g, 53%). $C_{38}H_{48}N_6PdS$ (727.31): calcd. C 62.75, H 6.65, N 11.55; found C 62.98, H 6.85, N 11.61. ^{1}H NMR (300 MHz, CDCl$_3$, 23 °C): δ = 1.02 (d, J = 7.0 Hz, 6 H, *i*Pr CH_3), 1.05 (d, J = 7.0 Hz, 6 H, *i*Pr CH_3), 1.19 (s, 3 H, CH_3), 1.22 (d, J = 7.0 Hz, 6 H, *i*Pr CH_3), 1.29 (d, J = 7.0 Hz, 6 H, *i*Pr CH_3), 1.86 (s, 1 H, C*H*), 2.60 (s, 1 H, C*H*), 2.79 (sept., J = 6.6 Hz, 2 H, *i*Pr C*H*), 3.00 (d, J = 3.3 Hz, 1 H, C*H*), 3.05 (sept., J = 6.6 Hz, 2 H, *i*Pr C*H*), 3.75 (d, J = 2.9 Hz, 1 H, C*H*), 7.17 (s, 2 H, C*H*=), 7.22–7.26 (m, 4 H, Ar-*H*), 7.32–7.44 (m, 5 H, Ar-*H*), 7.72–7.75 (m, 2 H, Ar-*H*) ppm. ^{13}C{^{1}H} NMR (75 MHz, CDCl$_3$, 23 °C): δ = 22.2, 22.4, 22.8, 25.7, 26.5, 28.5 (s, *i*Pr *C*H), 28.6 (s, *i*Pr *C*H), 55.5 (C1), 69.6 (C3), 123.8 (C2$_{meso}$), 123.9, 124.3, 127.6, 128.4, 129.7, 130.4, 135.9, 136.3, 145.5, 145.9, 163.1 (*C*N$_4$), 186.2 (N*C*N) ppm.

Analogous reactions with benzyl isothiocyanate and *p*-phenylene diisothiocyanate were performed.

[(η^3-Allyl)Pd{CN$_4$(CH$_2$Ph)}(IPr)] (32): Yield: 91%. $C_{38}H_{48}N_6PdS$ (727.31): calcd. C 62.75, H 6.65, N 11.55; found C 62.59, H 6.80, N 11.18. ^{1}H NMR (300 MHz, CDCl$_3$, 23 °C): δ = 1.08 (d, J = 7.0 Hz, 6 H, *i*Pr CH_3), 1.17 (d, J = 6.6 Hz, 6 H, *i*Pr CH_3), 1.32 (d, J = 7.0 Hz, 6 H, *i*Pr CH_3), 1.38 (d, J = 7.0 Hz, 6 H, *i*Pr CH_3), 1.68 (d, J = 12 Hz, 1 H, C*H*), 2.46 (d, J = 13 Hz, 1 H, C*H*), 2.81 (sept., J = 7.0 Hz, 2 H, *i*Pr C*H*), 2.96 (d, J = 7.0 Hz, 1 H, C*H*), 3.03 (sept., J = 6.6 Hz, 2 H, *i*Pr C*H*), 3.23 (dd, J = 2.2, 7.3 Hz, 1 H, C*H*), 4.52 (m, 1 H, C*H*), 5.18 (s, 2 H, CH_2), 7.05–7.08 (m, 2 H, Ar-*H*), 7.18–7.19 (m, 4 H, Ar-*H*), 7.21 (s, 2 H, C*H*=), 7.26–7.29 (m, 4 H, Ar-*H*), 7.39–7.44 (m, 3 H, Ar-*H*) ppm. ^{13}C{^{1}H} NMR (75 MHz, CDCl$_3$, 23 °C): δ = 22.8, 22.9, 25.9, 26.6, 28.5 (s, *i*Pr *C*H), 28.6 (s, *i*Pr *C*H), 49.6 (C1), 55.8 (*C*H$_2$), 70.3 (C3), 115.2 (C2$_{meso}$), 123.8, 123.9, 127.5, 128.2, 128.3,130.0, 135.4, 135.7, 145.7, 146.0, 163.9 (*C*N$_4$), 185.3 (N*C*N) ppm.

[(η^3-2-Methylallyl)Pd{SCN$_4$-}(SIPr)]$_2$(μ-C$_6$H$_4$) (33): Yield: 97%. $C_{70}H_{94}N_{12}Pd_2S_2$ (1380.55): calcd. C 60.90, H 6.86, N 12.17; found C 60.55, H 6.93, N 12.08. ^{1}H NMR (300 MHz, CDCl$_3$, 23 °C): δ = 1.09 (s, 6 H, CH_3), 1.18 (d, J = 7.0 Hz, 12 H, *i*Pr CH_3), 1.25 (d, J = 6.6 Hz, 12 H, *i*Pr CH_3), 1.26 (d, J = 6.6 Hz, 12 H, *i*Pr CH_3), 1.38 (d, J = 7.0 Hz, 12 H, *i*Pr CH_3), 1.89 (s, 2 H, CH), 2.54 (d, J = 2.2 Hz, 2 H, C*H*), 2.94 (d, J = 2.9 Hz, 2 H, C*H*), 3.30 (sept., J = 7.0 Hz, 8 H, *i*Pr C*H*), 3.61 (m, 2 H, C*H*), 4.00 (m, 8 H, CH_2), 7.19–7.22 (m, 8 H, Ar-*H*), 7.33–7.38 (m, 4 H, Ar-*H*), 7.76 (s, 4 H, Ar-*H*) ppm. ^{13}C{^{1}H} NMR (75 MHz, CDCl$_3$, 23 °C): δ = 22.2 (*C*H$_3$), 23.5, 23.7, 26.7, 26.8, 28.5 (s, *i*Pr *C*H), 28.6 (s, *i*Pr *C*H), 53.9 (*C*H$_2$), 55.8 (C1), 70.0 (C3), 123.9 (C2$_{meso}$), 124.3, 124.6, 129.0, 130.9, 135.4, 136.2, 146.5, 147.2, 163.6 (*C*N$_4$), 213.1 (N*C*N) ppm.

[(η^3-Allyl)Pd{SCN$_4$-}(IPr)]$_2$(μ-C$_6$H$_4$) (34): Yield: 98%. $C_{68}H_{86}N_{12}Pd_2S_2$ (1348.46): calcd. C 60.57, H 6.43, N 12.46; found C 60.86, H 6.43, N 12.27. ^{1}H NMR (300 MHz, CDCl$_3$, 23 °C): δ = 1.07 (d, J = 7.0 Hz, 12 H, *i*Pr CH_3), 1.14 (d, J = 7.0 Hz, 12 H, *i*Pr CH_3), 1.26 (d, J = 6.6 Hz, 24 H, *i*Pr CH_3), 1.76 (d, J = 12 Hz, 2 H, C*H*), 2.77 (sept., J = 7.0 Hz, 4 H, *i*Pr C*H*), 2.79 (d, J = 14 Hz, 2 H, C*H*), 2.99 (sept., J = 7.0 Hz, 4 H, *i*Pr C*H*), 3.27 (dd, J = 2.2, 7.3 Hz, 2 H, C*H*), 3.74 (d, J = 7.3 Hz, 2 H, C*H*), 4.76 (m, 2 H, C*H*), 7.18 (s, 4 H, C*H*=), 7.22–7.26 (m, 8 H, Ar-*H*), 7.39–7.45 (m, 4 H, Ar-*H*), 7.72 (s, 4 H, Ar-*H*) ppm. ^{13}C{^{1}H} NMR (75 MHz, CDCl$_3$, 23 °C): δ = 22.6, 22.7, 25.8, 26.5, 28.6 (s, *i*Pr *C*H), 28.7 (s, *i*Pr *C*H), 55.9 (C1), 70.3 (C3), 115.5 (C2$_{meso}$), 123.9, 124.0, 124.2, 124.4, 130.0, 135.3, 135.5, 145.6, 145.9, 163.4 (*C*N$_4$), 184.9 (N*C*N) ppm.

[(η^3-2-Methylallyl)Pd{(N$_3$C$_2$)(COOMe)$_2$}] (35): To a Schlenk flask containing [(η^3-2-methylallyl)Pd(N$_3$)(IPr)] (**7**, 0.209 g, 0.35 mmol) was added THF (5 mL) and then DMAD (48 μL, 0.39 mmol). The orange solution immediately turned yellow. After stirring for 4 h at room temperature, the reaction mixture was fully evaporated under vacuum, and then the resulting solid was washed with hexane. Recrystallization from diethyl ether gave pale yellow crystals of **35** (0.235 g, 91%). IR (KBr): $\tilde{\nu}$ = 1731 (CO) cm^{-1}. $C_{37}H_{49}N_5O_4Pd$ (734.24): calcd. C 60.52, H 6.73, N 9.53; found C 60.42, H 6.96, N 9.38. ^{1}H NMR (300 MHz, CDCl$_3$, 23 °C): δ = 0.97 (d, J = 6.9 Hz, 6 H, *i*Pr CH_3), 1.05 (d, J = 6.9 Hz, 12 H, *i*Pr CH_3), 1.12 (d, J = 6.9 Hz, 6 H, *i*Pr CH_3), 1.24 (s, 3 H, CH_3), 1.80 (s, 2 H, C*H*), 2.72 (br., 1 H, C*H*), 2.89 (sept., J = 6.9 Hz, 2 H, *i*Pr C*H*), 3.32 (sept., J = 6.9 Hz, 2 H, *i*Pr C*H*), 3.82 (s, 6 H, CH_3), 3.81 (overlap, 1 H,

C*H*), 7.20–7.28 (m, 6 H, Ar-*H*), 7.36–7.42 (m, 2 H, Ar-*H*) ppm. $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$, 23 °C): δ = 22.3, 22.4 (*C*H_3), 22.6, 25.9, 26.5, 28.1 (s, *i*Pr *C*H), 51.5 (C1), 76.6 (C3), 123.9 (C2$_{meso}$), 124.0, 124.5, 129.8, 132.2, 136.1, 145.9, 146.4, 163.1 (*C*O), 186.9 (N*C*N) ppm.

Reaction of [(η^3-Allyl)Pd(N_3)(IPr)] or [(η^3-2-Methylallyl)Pd(N_3)-(IPr)] with Organic Isocyanides

To a solution of [(η^3-allyl)Pd(N_3)(IPr)] (**8**, 0.187 g, 0.32 mmol) in THF (4 mL) was added *tert*-butyl isocyanide (0.040 mL, 0.35 mmol). After stirring for 3 h, the reaction mixture was evaporated completely under vacuum, and then the resulting residue was solidified with *n*-hexane. The solid was filtered and washed with hexane (2 mL × 2). Recrystallization from diethyl ether at –70 °C gave pale yellow crystals of [(η^3-allyl)Pd(N_3)(IPr)]·(CN-*t*Bu) (**36**, 0.150 g, 70%). $C_{35}H_{50}N_6Pd$ (661.23): calcd. C 63.57, H 7.62, N 12.71; found C 63.32, H 8.04, N 12.36. ^1H NMR (300 MHz, $CDCl_3$, 23 °C): δ = 1.08 (s, 9 H, CH_3), 1.09 (d, *J* = 7.0 Hz, 6 H, *i*Pr CH_3), 1.16 (d, *J* = 7.0 Hz, 6 H, *i*Pr CH_3), 1.26 (d, *J* = 12 Hz, 1 H, C*H*), 1.35 (d, *J* = 7.0 Hz, 6 H, *i*Pr CH_3), 1.38 (d, *J* = 7.0 Hz, 6 H, *i*Pr CH_3), 2.64 (d, *J* = 13 Hz, 1 H, C*H*), 2.76 (sept., *J* = 7.0 Hz, 2 H, *i*Pr C*H*), 2.77 (overlap, 1 H, C*H*), 2.95 (sept., *J* = 6.6 Hz, 2 H, *i*Pr C*H*), 3.84 (dd, *J* = 2.2, 7.3 Hz, 1 H, C*H*), 4.71 (m, 1 H, C*H*), 7.11 (s, 2 H, C*H*=), 7.24–7.29 (m, 4 H, Ar-*H*), 7.40–7.45 (m, 2 H, Ar-*H*) ppm. $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$, 23 °C): δ = 22.7, 22.8, 25.7, 26.4, 28.6 (s, *i*Pr *C*H), 28.7 (s, *i*Pr *C*H), 31.8 (s, *C*H_3), 47.5 (C1), 51.1 [s, *C*(CH_3)$_3$], 68.9 (C3), 114.4 (C2$_{meso}$), 123.7, 123.9, 129.8, 135.8, 146.0, 146.3, 186.0 (N*C*N) ppm. The carbon signal for *C*≡N was not observed due to its weak intensity.

The analogous reaction of [(η^3-2-methylallyl)Pd(N_3)(IPr)] with benzyl isocyanide was carried out. ^1H NMR (300 MHz, $CDCl_3$, 23 °C): δ = 0.87 (s, 3 H, CH_3), 1.06 (d, *J* = 7.0 Hz, 6 H, *i*Pr CH_3), 1.11 (d, *J* = 7.0 Hz, 6 H, *i*Pr CH_3), 1.13 (s, 3 H, CH_3), 1.14 (d, *J* = 7.0 Hz, 6 H, *i*Pr CH_3), 1.18 (s, 2 H, CH_2), 1.19 (s, 2 H, CH_2), 1.26 (d, *J* = 7.0 Hz, 6 H, *i*Pr CH_3), 1.41 (br., 1 H, C*H*), 1.60 (s, 1 H, C*H*), 1.61 (s, 1 H, CH), 2.50 (br., 1 H, C*H*), 2.78 (sept., *J* = 7.0 Hz, 2 H, *i*Pr C*H*), 2.88 (d, 2 H, C*H*), 3.21 (sept., *J* = 6.6 Hz, 2 H, *i*Pr C*H*), 4.21 (d, *J* = 16 Hz, 1 H, C*H*), 4.43 (d, *J* = 16 Hz, 1 H, C*H*), 6.72 (s, 2 H, C*H*=), 7.10–7.17 (m, 8 H, Ar-*H*), 7.30–7.35 (m, 4 H, Ar-*H*), 7.46–7.51 (m, 4 H, Ar-*H*) ppm. $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$, 23 °C): δ = 22.6, 22.7, 23.0, 25.6, 26.3, 28.2, 28.3, 28.4, 28.5 (s, *i*Pr *C*H), 32.2, 33.5 (s, *C*H_3), 39.2, 44.7 (C1), 124.1, 124.2, 124.3, 126.4, 128.1, 129.8, 131.9, 136.7, 137.7, 146.0, 146.5, 168.7 (*C*N_4), 186.7 (N*C*N) ppm.

General Procedure for the Suzuki–Miyaura Cross-Coupling Reactions: To a long Schlenk tube (50 mL volume) was added the phenylboronic acid (31.7 mg, 0.26 mmol), K_2CO_3 (55.3 mg, 0.4 mmol), Pd catalyst (1×10^{-3} mmol, 1 mol-%), and the aryl halide (0.2 mmol) with a stirring bar. Methanol (1.0 mL) was added, and the resulting mixture was heated in an oil bath at 80 °C. The reaction was monitored by TLC. After the aryl chloride was totally consumed, the reaction mixture was cooled to room temperature and quenched with brine (1.0 mL) and then extracted with EtOAc (3 × 1.0 mL). The resulting organic solution was dried with $MgSO_4$ and concentrated under reduced pressure. The crude product was purified by preparative TLC (0.5 mm). The products were identified by IR and NMR (^1H and ^{13}C) spectroscopy and GC–MS data on the basis of literature data. Spectroscopic and GC–MS data for the organic compounds are available in the Supporting Information.

X-ray Structure Determination: All X-ray data were collected with a Bruker Smart APEX or APEX2 diffractometer equipped with a Mo X-ray tube. Collected data were corrected for absorption with SADABS based upon the Laue symmetry by using equivalent reflections.[45] All calculations were performed with the SHELXTL programs.[46] All structures were solved by direct methods. All non-hydrogen atoms were refined anisotropically, and all hydrogen atoms were generated in ideal positions and refined in a riding model.

CCDC-937998 (for **7**), -937999 (for **8**), -938000 (for **14**), -938001 (for **17**), -938002 (for **19**), -938003 (for **22**), -938004 (for **25**), and -938005 (for **31**) contain the supplementary crystallographic data for this paper. These data can be free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data-request/cif.

Supporting Information (see footnote on the first page of this article): Crystallographic and NMR spectroscopic data for (π-allyl)Pd–NHC pseudohalogen complexes and organic products.

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