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Synthesis and structures of η^1-allenyl and/or -propargyl Pd(II) complexes and their reactivity toward trimethylsilyl pseudohalides, organic thiols, and *N*-heterocyclic carbene ligands

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ABSTRACT

Facile oxidative additions of various propargyl halides to $[Pd(CH_2{=}CHPh)(PR_3)_2]$, which could be generated in situ from *trans*-$[PdEt_2(PR_3)_2]$ ($PR_3{=}PMe_3$, PEt_3, PMe_2Ph) and styrene, gave the bis(phosphine) η^1-allenyl and/or η^1-propargyl Pd(II) complexes. The chloro ligand in the η^1-allenyl Pd(II) complex could be replaced by pseudohalides to produce the new corresponding pseudohalo complexes, *trans*-$[XPd(CH{=}C{=}CH_2)(PMe_3)_2]$, when treated with trimethylsilyl pseudohalides (Me_3SiX: X = NCS, CN, N_3). The η^1-allenyl complex was also converted into the thiolato complexes when treated with various organic thiols. In addition, the phosphine ligand in the η^1-allenyl complex could be replaced by NHC (*N*-heterocyclic carbene) to produce η^1-allenyl or -propargyl Pd(II) complex possessing the NHC ligand, depending on the coordinated η^1-allenyl moiety. On the other hand, oxidative addition of phenyl propargyl sulfide to the $[Pd(CH_2{=}CHPh)(PMe_3)_2]$ gave a phenyl thiolato η^1-allenyl Pd(II) complex, *trans*-$[(C_6H_5S)Pd(CH{=}C{=}CH_2)(PMe_3)_2]$.

1. Introduction

η^1-Allenyl or -propargyl Pd(II) complexes are one of key intermediates in the Pd-catalyzed C–C coupling reactions or nucleophilic substitutions of allyllic or propargyl complexes with various nucleophiles including thiols [1–5]. Such complexes can be prepared by oxidative addition of organic allenyl or propargyl halides to zerovalent palladium complexes [6–9]. Studies on the isomeric conversion between the η^1-allenyl and η^1-propargyl Pd(II) and Pt(II) complexes were reported [6c,9,10]. In addition, reactions of the η^1-allenyl complexes with organozinc agents [7a], small molecules such as CO and organic isocyanides (CN–R) [11], alkali metal carbanions [8], and organic nucleophiles [12] were previously investigated. Further treatment of these complexes with another zerovalent complex to produce dinuclear Pd complexes, bridged by an allenyl or propargyl moiety, were also reported [7c,10c,d]. However, most η^1-allenyl Pd(II) or Pt(II) complexes in the above mentioned reactions contain less basic PPh_3 ligands as a supporting ligand. In this context, a systematic investigation of reactivity of the complexes containing various tertiary phosphine ligands is needed. In addition, it would be desirable to develop more efficient synthetic routes to (η^1-allenyl)–Pd(II) complexes.

In this work, we investigated oxidative additions of organic halides to $[Pd(CH_2{=}CHPh)(PR_3)_2]$ ($PR_3{=}PMe_3$, PEt_3, PMe_2Ph) to prepare new η^1-allenyl or η^1-propargyl Pd(II) complexes possessing basic phosphines. We also attempted to synthesize such complexes by the ligand substitution with trimethylsilyl pseudohalides. The reactivity of the products toward various organic thiols and NHC (*N*-heterocyclic carbene) was examined.

2. Experimental

2.1. General, materials, and measurements

All manipulations of air-sensitive complexes were performed under N_2 or Ar by standard Schlenk-line techniques. The analytical laboratories at Kangnung-Wonju National University carried out elemental analyses with a CE instruments EA1110. IR spectra were recorded on a Perkin Elmer BX spectrophotometer. NMR (^1H, $^{13}C\{^1H\}$, and $^{31}P\{^1H\}$) spectra were obtained on a JEOL Lamda 300 and ECA 600 MHz spectrometer. Chemical shifts were referenced to internal Me_4Si or to external 85% H_3PO_4. *Trans*-$[PdEt_2(PMe_3)_2]$ was prepared by the literature method [13b]. IPr (1,3-bis(2,6-diisopropylphenyl)imidazol-2-ylidene) was prepared by the literature method [14] or purchased from Strem or Sejin Chemical.

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*2.2. Preparation of trans-[XPd(CH═C═CH$_2$)(PR$_3$)$_2$] (A-type) (**1**–**4**) and trans-[BrPd(CH$_2$C≡CR)(PMe$_3$)$_2$] (R = SiMe$_3$, **5**; naphthyl, **6**)*

To a Schlenk flask containing *trans*-[PdEt$_2$(PMe$_3$)$_2$] (0.244 g, 0.77 mmol) at 0 °C were added sequentially styrene (0.241 ml, 1.54 mmol) and THF (2 ml). The mixture was heated at 55 °C for 1 h to give a yellow solution. At room temperature, propargyl chloride (0.061 ml, 0.85 mmol) was added to the mixture, and then the initial pale yellow solution turned to a yellow solution. After stirring the reaction mixture for 3 h, the solvent was removed completely under vacuum, and then the resulting oily residue was solidified with hexane. The solids were filtered and washed with hexane (1 ml × 3) to give pale yellow solids, which were recrystallized from excess diethyl ether to give pale yellow solids of *trans*-[ClPd(CH═C═CH$_2$)(PMe$_3$)$_2$] (**1**, 0.181 g, 71%). *Anal.* Calc. for $C_9H_{21}ClP_2Pd$: C, 32.45; H, 6.36. Found: C, 32.21; H, 6.36%. IR (KBr, cm^{-1}): *ν*(═C═) 1910. ^{1}H NMR ($CDCl_3$ in 300 MHz, *δ*): 1.41 (t, $^2J_{HP}$ = 3.5 Hz, 18H, PMe$_3$), 4.00 (dt, $^4J_{HH}$ = 6.6 Hz, $^5J_{HP}$ = 4.0 Hz, 2H, ═CH$_2$), 5.22 (tt, $^4J_{HH}$ = 6.6 Hz, $^3J_{HP}$ = 5.9 Hz, 1H, CH═). ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$, *δ*): 13.5 (t, $^1J_{PC}$ = 15 Hz, P(*C*H$_3$)$_3$), 65.8 (s,═CH$_2$), 79.1 (t, $^2J_{PC}$ = 8.6 Hz, Pd–*C*H═), 199.5 (t, $^3J_{PC}$ = 3.7 Hz, ═*C*═). ^{31}P{^{1}H} NMR (120 MHz in $CDCl_3$, *δ*): −15.9 (s).

η^1-Allenyl complexes *trans*-[XPd(CH═C═CH$_2$)(PR$_3$)$_2$] (**2**–**4**) were prepared analogously. *Trans*-[BrPd(CH═C═CH$_2$)(PMe$_3$)$_2$] (2, 79%): *Anal.* Calc. for $C_9H_{21}BrP_2Pd$: C, 28.63; H, 5.61. Found: C, 28.76; H, 5.77%. IR (KBr, cm^{-1}): *ν*(═C═) 1909. ^{1}H NMR ($CDCl_3$ in 300 MHz, *δ*): 1.45 (t, $^2J_{HP}$ = 3.7 Hz, 18H, PMe$_3$), 4.02 (dt, $^4J_{HH}$ = 6.6 - Hz, $^5J_{HP}$ = 4.0 Hz, 2H, ═CH$_2$), 5.29 (tt, $^4J_{HH}$ = 6.6 Hz, $^3J_{HP}$ = 5.9 Hz, 1H, CH═). ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$, *δ*): 14.3 (t, $^1J_{PC}$ = 15 Hz, P(*C*H$_3$)$_3$), 65.9 (s, ═*C*H$_2$), 81.5 (t, $^2J_{PC}$ = 7.8 Hz, Pd–*C*H), 198.9 (t, $^3J_{PC}$ = 3.4 Hz, ═*C*═). ^{31}P{^{1}H} NMR (120 MHz in $CDCl_3$, *δ*): −17.5 (s).

Trans-[ClPd(CH═C═CH$_2$)(PEt$_3$)$_2$] (**3**, 97%): *Anal.* Calc. for $C_{15}H_{33}ClP_2Pd$: C, 43.18; H, 7.97. Found: C, 43.48; H, 8.53%. IR (KBr, cm^{-1}): *ν*(═C═) 1909. ^{1}H NMR ($CDCl_3$ in 300 MHz, *δ*): 1.15 (qn, $^3J_{HP}$ = 7.9 - Hz, 18H, P(CH$_2$*C*H$_3$)$_3$), 1.82 (m, 12H, P(*C*H$_2$CH$_3$)$_3$), 3.95 (dt, $^4J_{HH}$ = 6.6 Hz, $^5J_{HP}$ = 3.7 Hz, 2H,═CH$_2$), 5.22 (tt, $^4J_{HH}$ = 6.6 Hz, $^3J_{HP}$ = 6.2 Hz, 1H, CH═). ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$, *δ*): 8.0 (s, P(CH$_2$*C*H$_3$)$_3$), 14.2 (t, $^1J_{PC}$ = 13 Hz, P(*C*H$_2$CH$_3$)$_3$), 65.3 (s, ═*C*H$_2$), 78.5 (t, $^2J_{PC}$ = 8.0 Hz, Pd–*C*H), 199.1 (t, $^3J_{PC}$ = 3.4 Hz, ═*C*═). ^{31}P{^{1}H} NMR (120 MHz in $CDCl_3$, *δ*): 14.5 (s).

Trans-[ClPd(CH═C═CH$_2$)(PMe$_2$Ph)$_2$] (**4**, 98%): *Anal.* Calc. for $C_{19}H_{25}ClP_2Pd$: C, 49.91; H, 5.51. Found: C, 50.32; H, 5.84%. IR (KBr, cm^{-1}): *ν*(═C═) 1912. ^{1}H NMR ($CDCl_3$ in 300 MHz, *δ*): 1.72 (t, $^2J_{HP}$ = 3.3 Hz, 12H, PMe$_2$Ph), 3.66 (dt, $^4J_{HH}$ = 6.6 Hz, $^5J_{HP}$ = 3.7 Hz, 2H,═CH$_2$), 4.91 (tt, $^4J_{HH}$ = 6.6 Hz, $^3J_{HP}$ = 5.9 Hz, 1H, CH═), 7.39 (m, 4H, Ph), 7.64 (m, 6H, Ph). ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$, *δ*): 12.6 (t, $^1J_{PC}$ = 15 Hz, P(*C*H$_3$)$_2$Ph), 66.1 (s, ═*C*H$_2$), 79.9 (t, $^2J_{PC}$ = 7.4 Hz, Pd–*C*H), 120.4 (t, $^2J_{PC}$ = 4.6 Hz, Ph), 129.7, 131.1 (t, $^1J_{PC}$ = 5.9 Hz, Ph), 134.6, 199.7 (t, $^3J_{PC}$ = 3.4 Hz, ═*C*═). ^{31}P{^{1}H} NMR (120 MHz in $CDCl_3$, *δ*): −6.7 (s).

To a Schlenk flask containing *trans*-[PdEt$_2$(PMe$_3$)$_2$] (0.236 g, 0.75 mmol) at 0 °C were added sequentially styrene (0.233 ml, 2.24 mmol) and THF (2 ml). The mixture was heated at 55 °C for 1 h to give a yellow solution. At room temperature, when 3-bromo-1-(trimethylsilyl)-1-propyne (0.134 ml, 0.82 mmol) was added to the mixture, the initial pale yellow solution turned to a yellow solution. After stirring the reaction mixture for 3 h, the solvent was removed, and the resulting oily residue was solidified with hexane. The solids were filtered and washed with hexane (1 ml × 3) to give pale yellow solids, which were recrystallized from excess diethyl ether to give pale yellow solids of *trans*-[BrPd(CH$_2$C≡C–SiMe$_3$)(PMe$_3$)$_2$] (**5**, 0.231 g, 69%). *Anal.* Calc. for $C_{12}H_{29}BrP_2SiPd$: C, 32.05; H, 6.50. Found: C, 32.34; H, 6.97. IR (KBr, cm^{-1}): *ν*(C≡C) 2142. ^{1}H NMR ($CDCl_3$ in 300 MHz, *δ*): 0.11 (s, 9H, Si(*C*H$_3$)$_3$), 1.52 (t, $^2J_{HP}$ = 3.3 Hz, 18H, PMe$_3$), 1.80 (t, $^3J_{HP}$ = 7.7 Hz, 2H, *C*H$_2$). ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$, *δ*): −3.6 (t, $^2J_{PC}$ = 2.2 Hz, *C*H$_2$), 0.1 (s, Si(*C*H$_3$)$_3$), 13.6 (t, $^1J_{PC}$ = 14 Hz, P(*C*H$_3$)$_3$), 84.5 (t, $^3J_{PC}$ = 1.8 Hz, *C*≡C–SiMe$_3$), 111.5 (s, C≡*C*–SiMe$_3$). ^{31}P{^{1}H} NMR (120 MHz in $CDCl_3$, *δ*): −15.9 (s).

Trans-[BrPd(CH$_2$C≡CR)(PMe$_3$)$_2$] (R = naphthyl, **6**, 86%) was prepared analogously. The pure complex **6** could be obtained by repeated recrystallizations in excess diethyl ether. *Anal.* Calc. for $C_{19}H_{27}BrP_2Pd$: C, 45.31; H, 5.40. Found: C, 45.42; H, 5.85%. IR (KBr, cm^{-1}): *ν*(C≡C) 2174. ^{1}H NMR ($CDCl_3$ in 300 MHz, *δ*): 1.58 (t, $^2J_{HP}$ = 3.3 Hz, 18H, PMe$_3$), 2.17 (t, $^3J_{HP}$ = 7.7 Hz, 2H, *C*H$_2$), 7.34–7.53 (m, 4H, Ar), 7.72–7.84 (m, 2H, Ar), 8.29–8.32 (m, 1H, Ar). ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$, *δ*): −3.0 (t, $^2J_{PC}$ = 2.2 Hz, *C*H$_2$), 14.2 (t, $^1J_{PC}$ = 15 Hz, P(*C*H$_3$)$_3$), 84.5 (s, *C*≡C–C$_{10}$H$_7$), 100.1 (s, C≡*C*–C$_{10}$H$_7$), 125.4, 126.1, 126.2, 126.3, 127.0, 128.2, 128.6, 128.7, 133.3. ^{31}P{^{1}H} NMR (120 MHz in $CDCl_3$, *δ*): −15.6 (s).

*2.3. Preparation of trans-[ClPd(C(Ph)═C═CH$_2$)(PR$_3$)$_2$] (**7**, PMe$_3$ and **8**, PMe$_2$Ph), trans-[ClPd(CH$_2$C≡CPh)(PEt$_3$)$_2$] (**9**) and trans-[BrPd(C(Me)–C═C═CH$_2$)(PMe$_3$)$_2$] (**10A**) and trans-[BrPd(CH$_2$C≡C–Me)(PMe$_3$)$_2$] (**10P**)*

To a Schlenk flask containing *trans*-[PdEt$_2$(PMe$_3$)$_2$] (0.203 g, 0.64 mmol) at 0 °C were added sequentially styrene (0.200 ml, 1.92 mmol) and THF (2 ml). The mixture was heated at 55 °C for 1 h to give a yellow solution. At room temperature, 3-chloro-1-phenyl-1-propyne (0.097 ml, 0.71 mmol) was added to the mixture. After stirring the reaction mixture for 3 h, the solvent was removed, and then the resulting oily residue was solidified with hexane. The solids were filtered and washed with hexane (1 ml × 3) to give pale yellow solids, which were recrystallized from excess diethyl ether to give white crystals of *trans*-[ClPd(C(Ph)═C═CH$_2$)(PMe$_3$)$_2$] (**7**, 0.164 g, 63%). *Anal.* Calc. for $C_{15}H_{25}ClP_2Pd$: C, 44.03; H, 6.16. Found: C, 44.15; H, 6.47%. IR (KBr, cm^{-1}): *ν*(═C═) 1898. ^{1}H NMR ($CDCl_3$ in 300 MHz, *δ*): 1.31 (t, $^2J_{HP}$ = 3.7 Hz, 18H, PMe$_3$), 4.37 (t, $^5J_{HP}$ = 3.5 Hz, 2H, ═CH$_2$), 7.11 (m, 1H, Ph), 7.22 (m, 2H, Ph), 7.67 (m, 2H, Ph). ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$, *δ*): 13.7 (t, $^1J_{PC}$ = 15 Hz, P(*C*H$_3$)$_3$), 68.6 (s,═*C*H$_2$), 98.2 (t, $^2J_{PC}$ = 8.6 Hz, Pd–*C*), 126.1, 127.9, 129.0, 140.2 (t, $^3J_{PC}$ = 2.5 Hz, Ph), 197.4 (s, ═*C*═). ^{31}P{^{1}H} NMR (120 MHz in $CDCl_3$, *δ*): −15.3 (s).

Complexes **8** and **9** were prepared analogously. *Trans*-[ClPd(C(Ph)═C═CH$_2$)(PMe$_2$Ph)$_2$] (**8**, 91%): *Anal.* Calc. for $C_{25}H_{29}ClP_2Pd$: C, 56.30; H, 5.48. Found: C, 56.52; H, 5.96%. IR (KBr, cm^{-1}): *ν*(═C═) 1903. ^{1}H NMR ($CDCl_3$ in 300 MHz, *δ*): 1.60 (dt, $^2J_{HP}$ = 3.3, 47 Hz, 12H, PMe$_2$Ph), 3.87 (t, $^5J_{HP}$ = 3.1 Hz, 2H, ═CH$_2$), 7.00–7.02 (m, 3H, Ph), 7.26–7.39 (m, 8H, Ph), 7.46–7.53 (m, 4H, Ph). ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$, *δ*): 12.6 (dt, $^1J_{PC}$ = 5.6, 15 Hz, P(*C*H$_3$)$_2$Ph), 68.5 (s, ═*C*H$_2$), 98.3 (t, $^2J_{PC}$ = 5.6 Hz, Pd–*C*), 125.7, 127.5, 128.1 (t, $^3J_{PC}$ = 4.6 Hz, Ph), 129.0, 129.4, 130.7 (t, $^3J_{PC}$ = 5.6 Hz, Ph), 134.6 (t, $^2J_{PC}$ = 22 Hz, Ph), 139.6 (t, $^4J_{PC}$ = 2.5 Hz, Ph), 197.8 (t, $^3J_{PC}$ = 4.6 Hz, ═*C*═). ^{31}P{^{1}H} NMR (120 MHz in $CDCl_3$, *δ*): −6.9 (s).

Trans-[ClPd(CH$_2$C≡CPh)(PEt$_3$)$_2$] (**9**, 97%): *Anal.* Calc. for $C_{21}H_{37}ClP_2Pd$: C, 51.13; H, 7.56. Found: C, 51.13; H, 7.70%. IR (KBr, cm^{-1}): *ν*(═C═) 2186. ^{1}H NMR ($CDCl_3$ in 300 MHz, *δ*): 1.14 (qn, $^3J_{HP}$ = 7.8 Hz, 18H, P(CH$_2$*C*H$_3$)$_3$), 1.86 (m, 12H, P(*C*H$_2$CH$_3$)$_3$), 1.93 (t, $^3J_{HP}$ = 3.3 Hz, 2H, CH$_2$), 7.21–7.25 (m, 5H, Ph). ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$, *δ*): −8.3 (t, $^2J_{PC}$ = 3.1 Hz, *C*H$_2$), 8.2 (s, P(CH$_2$CH$_3$)$_3$), 13.8 (t, $^1J_{PC}$ = 11 Hz, P(*C*H$_2$CH$_3$)$_3$), 80.7 (s, *C*≡C–Ph), 95.9 (s, C≡*C*–Ph). ^{31}P{^{1}H} NMR (120 MHz in $CDCl_3$, *δ*): 15.3 (s).

To a Schlenk flask containing *trans*-[PdEt$_2$(PMe$_3$)$_2$] (0.259 g, 0.81 mmol) at 0 °C were added sequentially styrene (0.255 ml, 2.43 mmol) and THF (2 ml). The mixture was heated at 55 °C for 1 h to give a yellow solution. On addition of 3-bromo-1-methyl-1-propyne (0.081 ml, 0.89 mmol) to the mixture, and then the initial pale yellow solution turned to a yellow solution. After stirring the reaction mixture for 3 h, the solvent was removed, and then the resulting oily residue was solidified with hexane. The solids were

filtered and washed with hexane (1 ml × 3) to give pale yellow solids, which were recrystallized from excess diethyl ether to give pale yellow solids of *trans*-[BrPd(C(Me)–C═C═CH_2)(PMe_3)$_2$] (**10A**) and *trans*-[BrPd(CH_2C≡C–Me)(PMe_3)$_2$] (**10P**) in the ratio of 60:40. *trans*-[BrPd(C(Me)–C═C═CH_2)(PMe_3)$_2$]: ^{1}H NMR ($CDCl_3$ in 300 MHz, δ): 1.51 (t, $^2J_{HP}$ = 3.3 Hz, 18H, PMe_3), 1.80 (t, $^4J_{HP}$ = 2.9 Hz, 3H, CH_3), 3.98 (dq, $^5J_{HH}$ = 3.3 Hz, $^5J_{HP}$ = 2.9 Hz, 2H, CH_2). ^{31}P{^{1}H} NMR (120 MHz in $CDCl_3$, δ): −16.0 (s). *Trans*-[BrPd(CH_2C≡C–Me)(PMe_3)$_2$]: ^{1}H NMR ($CDCl_3$ in 300 MHz, δ): 1.46 (t, $^2J_{HP}$ = 3.3 Hz, 18H, PMe_3), 1.51(overlap, 2H, CH_2), 1.72 (s, 3H, CH_3). ^{31}P{^{1}H} NMR (120 MHz in $CDCl_3$, δ): −17.0 (s).

2.4. Reactions of trans-[ClPd(CH═C═CH_2)(PR_3)$_2$] (**1**, PMe_3; **3**, PEt_3) with Me_3Si–X (X = NCS, CN, N_3)

To a Schlenk flask containing **1** (0.041 g, 0.12 mmol) were added THF (2 ml) and Me_3Si–NCS (0.052 ml, 0.37 mmol). After stirring for 3 h at room temperature, the resulting yellow solution was evaporated, and then the oily residue was solidified with *n*-hexane. The solids were filtered and washed with hexane (2 × 2 ml). Recrystallization from excess diethyl ether gave white crystals of *trans*-[(SCN)Pd(CH═C═CH_2)(PMe_3)$_2$] (**11**, 0.020 g, 46%). *Anal.* Calc. for $C_{10}H_{21}NP_2SPd$: C, 33.77; H, 5.95; N, 3.94. Found: C, 33.30; H, 6.30; N, 3.50%. IR (KBr, cm^{-1}): ν(═C═) 1913; ν(NCS) 2100. ^{1}H NMR ($CDCl_3$ in 300 MHz, δ): 1.41 (br, 18H, PMe_3), 4.03 (dt, $^4J_{HH}$ = 6.6 Hz, $^5J_{HP}$ = 4.0 Hz, 2H,═CH_2), 5.06 (br, 1H, CH═). ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$, δ): 13.5 (t, $^1J_{PC}$ = 15 Hz, P(CH_3)$_3$), 66.1 (s, ═CH_2), 76.1 (br, Pd–C*H*), 136.5 (s, N*C*S), 200.4 (br, ═*C*═). ^{31}P{^{1}H} NMR (120 MHz in $CDCl_3$, δ): −14.6 (s).

To a Schlenk flask containing **1** (0.200 g, 0.60 mmol) were added THF (3 ml) and Me_3Si–CN (0.240 ml, 1.80 mmol). After stirring for 3 h at room temperature, the resulting yellow solution was evaporated, and then the oily residue was solidified with *n*-hexane. The solids were filtered and washed with hexane (2 × 2 ml). Recrystallization from excess diethyl ether gave white crystals of *trans*-[(NC)Pd(CH═C═CH_2)(PMe_3)$_2$] (**12**, 0.190 g, 98%). *Anal.* Calc. for $C_{10}H_{21}NP_2Pd$: C, 37.11; H, 6.54; N, 4.33. Found: C, 37.12; H, 6.99; N, 4.42%. IR (KBr, cm^{-1}): ν(═C═) 1905; ν(CN) 2123. ^{1}H NMR ($CDCl_3$ in 300 MHz, δ): 1.43 (br, 18H, PMe_3), 3.75 (dt, $^4J_{HH}$ = 6.6 Hz, $^5J_{HP}$ = 4.0 Hz, 2H,═CH_2), 4.98 (m, 1H, CH═). ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$, δ): 15.0 (t, $^1J_{PC}$ = 16 Hz, P(CH_3)$_3$), 62.6 (s, ═CH_2), 82.6 (t, $^2J_{PC}$ = 8.1 Hz, Pd–C*H*), 138.9 (t, $^2J_{PC}$ = 18 Hz, C*N*), 200.5 (br, ═*C*═). ^{31}P{^{1}H} NMR (120 MHz in $CDCl_3$, δ): −15.2 (s).

To a Schlenk flask containing complex **1** (0.190 g, 0.57 mmol) were added THF (3 ml) and Me_3Si–N_3 (0.225 ml, 1.71 mmol). After stirring for 3 h at room temperature, the resulting yellow solution was completely evaporated, and then the oily residue was solidified with *n*-hexane. The solids were filtered and washed with hexane (2 × 2 ml). Recrystallization from excess diethyl ether gave white crystals of *trans*-[(N_3)Pd(CH═C═CH_2)(PMe_3)$_2$] (**13**, 0.150 g, 77%). IR (KBr, cm^{-1}): ν(═C═) 1910; ν(N_3) 2036. ^{1}H NMR ($CDCl_3$ in 300 MHz, δ): 1.14 (t, $^2J_{HP}$ = 3.5 Hz, 18H, PMe_3), 4.00 (dt, $^4J_{HH}$ = 6.6 Hz, $^5J_{HP}$ = 4.0 Hz, 2H, ═CH_2), 5.22 (tt, $^3J_{HP}$ = 5.9 Hz, 1H, CH═). ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$, δ): 13.5 (t, $^1J_{PC}$ = 15 Hz, P(CH_3)$_3$), 65.8 (s, ═CH_2), 79.1 (t, $^2J_{PC}$ = 8.6 Hz, Pd–C*H*), 199.5 (t, $^3J_{PC}$ = 3.7 Hz, ═*C*═). ^{31}P{^{1}H} NMR (120 MHz in $CDCl_3$, δ): −15.9 (s). In spite of several recrystallizations, the pure analytical data could not be obtained due to quite a similar solubility of this complex and [ClPd(N_3)(PMe_3)$_2$], and the observed peak integration ratio of ^{31}P{^{1}H} NMR spectrum was 90:10.

To a Schlenk flask containing complex **3** (0.633 g, 1.52 mmol) were added THF (6 ml) and Me_3Si–N_3 (0.598 ml, 4.54 mmol). After stirring for 3 h at room temperature, the resulting yellow solution was completely evaporated, and then the oily residue was solidified with diethyl ether at −34 °C. The solids were filtered and washed with hexane (2 × 2 ml). Recrystallization from excess diethyl ether gave white crystals of *trans*-[(N_3)Pd(CH═C═CH_2)(PEt_3)$_2$] (**14**, 0.551 g, 86%). *Anal.* Calcd. for $C_{15}H_{33}N_3P_2Pd$: C, 42.51; H, 7.85; N, 9.91. Found: C, 42.27; H, 7.91; 9.84%. IR (KBr, cm^{-1}): ν(═C═) 1909, ν(N_3) 2037. ^{1}H NMR ($CDCl_3$ in 300 MHz, δ): 1.14 (qn, ^4J = 7.9 Hz, 18H, P(CH_2CH_3)$_3$), 1.82 (m, 12H, P(CH_2CH$_3$)$_3$), 3.95 (dt, $^4J_{HH}$ = 6.6 Hz, $^5J_{HP}$ = 4.0 Hz, 2H, ═CH_2), 5.21 (tt, $^4J_{HH}$ = 6.6 Hz, $^3J_{HP}$ = 6.2 Hz, 1H, CH═). ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$, δ): 8.1 (s, P(CH_2CH_3)$_3$), 14.2 (t, $^1J_{PC}$ = 13 Hz, P(CH_2CH$_3$)$_3$), 65.3 (s,═CH_2), 78.5 (t, $^2J_{PC}$ = 8.0 Hz, Pd–C*H*), 199.1 (t, $^3J_{PC}$ = 3.4 Hz, ═*C*═). ^{31}P{^{1}H} NMR (120 MHz in $CDCl_3$, δ): 14.5 (s).

2.5. Reactions of trans-[ClPd(CH═C═CH_2)(PMe_3)$_2$] with RSH (R = C_6H_5, $C_6H_5CH_2$, C_6H_4–SH)

To a Schlenk flask containing complex **1** (0.128 g, 0.33 mmol) were added THF (3 ml) and C_6H_5SH (0.035 ml, 0.34 mmol). After stirring for 3 h at room temperature, the resulting orange solution was evaporated, and the oily residue was solidified with *n*-hexane. The solids were filtered and washed with hexane (3 × 2 ml). Recrystallization from a diethyl ether gave orange crystals of *trans*-[ClPd(SC_6H_5)(PMe_3)$_2$] (**15**, 0.240 g, 99%). *Anal.* Calc. for $C_{12}H_{23}ClP_2SPd$: C, 35.75; H, 5.75. Found: C, 35.74; H, 5.84%. ^{1}H NMR ($CDCl_3$ in 300 MHz, δ): 1.41 (t, $^2J_{HP}$ = 3.6 Hz, 18H, PMe_3), 6.93 (m, 1H, Ph), 7.04 (m, 2H, Ph), 7.56 (m, 2H, Ph). ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$, δ): 13.3 (t, $^1J_{PC}$ = 16 Hz, P(CH_3)$_3$), 122.3, 127.8, 130.5, 145.8 (s, Ph). ^{31}P{^{1}H} NMR (120 MHz in $CDCl_3$, δ): −12.3 (s).

Trans-[ClPd($SCH_2C_6H_5$)(PMe_3)$_2$] (**16**) was prepared analogously. *Trans*-[ClPd($SCH_2C_6H_5$)(PMe_3)$_2$] (**16**, 93%): *Anal.* Calc. for $C_{13}H_{25}ClP_2SPd$: C, 37.42; H, 6.04. Found: C, 37.42; H, 6.43%. ^{1}H NMR ($CDCl_3$ in 300 MHz, δ): 1.51 (t, $^2J_{HP}$ = 3.6 Hz, 18H, PMe_3), 3.46 (s, 2H, CH_2), 7.16 (m, 1H, Ph), 7.27 (m, 2H, Ph), 7.35 (m, 2H, Ph). ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$, δ): 13.4 (br, P(CH_3)$_3$), 36.2 (s, CH_2), 126.1, 128.4, 143.7 (s, Ph). ^{31}P{^{1}H} NMR (120 MHz in $CDCl_3$, δ): −13.6 (s).

To a Schlenk flask containing complex **1** (0.160 g, 0.48 mmol) were added THF (3 ml) and HS–C_6H_4–SH (0.034 g, 0.24 mmol). After stirring for 3 h at room temperature, the resulting orange solids were washed with *n*-hexane. Recrystallization from CH_2Cl_2/hexane gave orange crystals of *trans,trans*-[Pd(PMe_3)$_2$Cl]$_2$(μ-SC_6H_4-S) (**17**, 0.157 g, 90%): *Anal.* Calc. for $C_{18}H_{40}Cl_2P_4S_2Pd_2$: C, 29.69; H, 5.54. Found: C, 30.46; H, 5.79%. ^{1}H NMR ($CDCl_3$ in 300 MHz, δ): 1.33 (t, $^2J_{HP}$ = 3.3 Hz, 36H, PMe_3), 7.20 (s, 4H, Ph). ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$, δ): 13.3 (t, $^1J_{PC}$ = 16 Hz, P(CH_3)$_3$), 130.6, 139.0 (s, Ph). ^{31}P{^{1}H} NMR (120 MHz in $CDCl_3$, δ): −12.4 (s).

2.6. Reactions of trans-[ClPd(CH═C═CH_2)(PMe_3)$_2$] (**1**) and trans-[ClPd{(Ph)C═C═CH_2)(PMe_3)$_2$}] (**7**) with NHC (IPr)

To a Schlenk flask containing **1** (0.170 g, 0.51 mmol) was added IPr (0.198 g, 9.51 mmol) dissolved in THF (6 ml). After stirring the reaction mixture for 3 h at room temperature, the solvent was completely removed. To the resulting oily residue was added a diethyl ether/*n*-hexane (3:1) solution and then stored in the freezer to give crude solids. The solids were filtered, washed with hexane (2 ml × 2), and recrystallized from diethyl ether to give white crystals of [ClPd(IPr)(CH═C═CH_2)(PMe_3)], (**18**, 0.291 g, 88%). *Anal.* Calc for $C_{33}H_{48}ClN_2PPd$: C, 61.39; H, 7.49; N, 4.34. Found: C, 60.95; H, 7.94; N, 4.29%. IR (KBr, cm^{-1}): ν(═C═) 1916. ^{1}H NMR (300 MHz, $CDCl_3$, δ): 1.10 (d, $^2J_{HP}$ = 9.5 Hz, 9H, P(CH_3)$_3$), 1.11 (d, $^2J_{HH}$ = 6.6 Hz, 12H, CH(CH_3)$_2$), 1.42 (d, $^2J_{HH}$ = 6.6 Hz, 12 H, CH(CH_3)$_2$), 3.13 (sep, $^2J_{HH}$ = 6.6 Hz, 4 H, C*H*(CH$_3$)$_2$), 3.63 (dd, $^4J_{HH}$ = 6.6 Hz, $^5J_{HP}$ = 3.3 Hz, 2H, ═CH_2), 4.54 (dt, $^4J_{HH}$ = 6.6 Hz, $^3J_{HP}$ = 2.2 Hz, 1H, ═CH), 7.05 (d, $^3J_{HH}$ = 1.5 Hz, 2H, ═CH), 7.28 (m, 3H, Ar–*H*), 7.44 (m, 3 H, Ar–H). ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$, δ): 13.3 (d, $^1J_{PC}$ = 29 Hz, P(CH_3)$_3$), 23.2 (s, CH(CH_3)$_2$), 25.9 (s, CH(CH_3)$_2$), 28.6 (s, C*H*(CH$_3$)$_2$), 64.6 (s, ═CH_2), 77.9 (d, $^2J_{PC}$ = 9.9 Hz, Pd–C*H*),

123.5 123.6, 123.7, 129.4, 136.1, 145.9 (s, Ar), 181.7 (d, $^2J_{PC}$ = 168 - Hz, NCN), 200.1 (d, $^3J_{PC}$ = 5.6 Hz, =C=). $^{31}P\{^1H\}$ NMR (120 MHz in $CDCl_3$, δ): −15.0 (s).

To a Schlenk flask containing complex **7** (0.224 g, 0.55 mmol) was added IPr (0.213 g, 0.55 mmol) in THF (5 ml). After stirring the reaction mixture for 3 h at room temperature, the solvent was completely removed. To the resulting oily residue was added a diethyl ether/*n*-hexane (2:4) solution and then stored in the freezer to give crude solids. The solids were filtered, washed with hexane (2 ml × 2), and recrystallized from (diethyl ether)/hexane to give yellow crystals of [ClPd(IPr)(CH_2C≡CPh)(PMe_3)], (**19**, 0.328 g, 83%). *Anal.* Calc. for $C_{39}H_{52}ClN_2PPd$: C, 64.90; H, 7.27; N, 3.88. Found: C, 64.87; H, 7.68; N, 3.84%. IR (KBr, cm^{-1}): ν(C≡C) 2184. ^1H NMR (300 MHz, $CDCl_3$, δ): 1.12 (d, $^2J_{HH}$ = 6.6 Hz, 12H, CH(CH_3)$_2$), 1.20 (d, $^2J_{HP}$ = 9.5 Hz, 9H, P(CH_3)$_3$), 1.44 (d, $^2J_{HH}$ = 6.6 Hz, 12H, CH(CH_3)$_2$), 1.46 (d, $^3J_{HP}$ = 5.5 Hz, 2 H, CH_2), 2.88 (br, 4H, CH(CH$_3$)$_2$), 3.32 (br, 4H, CH(CH$_3$)$_2$), 7.03–7.38 (m, 11H, Ar–H). The ^1H signal of CH in the heterocyclic ring was overlapped to the aromatic signals. $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$, δ): −9.7 (d, $^2J_{PC}$ = 1.9 Hz, CH_2), 12.9 (d, $^1J_{PC}$ = 27 Hz, P(CH_3)$_3$), 23.2 (s, CH_2), 26.1 (s, CH(CH_3)$_2$), 28.7 (s, CH(CH_3)$_2$), 31.6 (s, CH(CH$_3$)$_2$), 78.7 (d, $^3J_{PC}$ = 3.7 Hz, C≡C–Ph), 98.5 (d, $^4J_{PC}$ = 2.7 Hz, C≡C–Ph), 123.6 123.7, 125.7, 126.5, 127.8, 129.6, 130.6, 130.7, 146.5 (s, Ar), 184.6 (d, $^2J_{PC}$ = 159 Hz, NCN). $^{31}P\{^1H\}$ NMR (120 MHz in $CDCl_3$, δ): −13.2 (s).

To a Schlenk flask containing the PMe_3–NHC–Pd(0) complex [(Me_3P)Pd(NHC)] (NHC = IPr) (0.340 g, 0.59 mmol) were added diethyl ether (5 ml) and propargyl chloride (47 μl, 0.65 mmol) at 0 °C. After stirring the reaction mixture for 1 h at room temperature, the solvent was completely removed. To the resulting oily residue was added *n*-hexane to give crude solids. The solids were filtered and recrystallized from *n*-hexane to give white crystals of [ClPd(IPr)(CH=C=CH_2)(PMe_3)], (**18**, 0.272 g, 71%). Its identity was confirmed by comparing its ^1H and ^{31}P NMR spectra with those of the ligand-substitution product.

The analogous reaction of [(Me_3P)Pd(NHC)] (NHC = IPr) with an equivalent of 3-chloro-1-phenyl-1-propyne gave the product [ClPd(IPr)(CH_2C≡CPh)(PMe_3)] (**19**, 0.118 g, 66%). The ^1H and ^{31}P NMR data of the product were compared with those of the ligand-substitution product.

2.7. Reaction of [Pd(styrene)(PMe_3)$_2$] with C_6H_5S–CH_2C≡CH

To a Schlenk flask containing *trans*-[$PdEt_2$(PMe_3)$_2$] (0.266 g, 0.84 mmol) at 0 °C were added sequentially styrene (0.289 ml, 2.52 mmol) and THF (3 ml). The mixture was heated at 55 °C for 1 h to give a yellow solution. At room temperature, on addition of phenyl propargyl sulfide (0.122 ml, 0.89 mmol) to the mixture, the initial pale yellow solution turned to a yellow solution. After stirring the reaction mixture for 3 h, the solvent was removed, and then the resulting oily residue was solidified with hexane. The solids were filtered and washed with hexane (1 ml × 3) to give pale yellow solids, which were recrystallized from diethyl ether to produce yellow crystals of *trans*-[(C_6H_5S)Pd(CH=C=CH_2)(PMe_3)$_2$] (**20**, 0.208 g, 59%). *Anal.* Calc. for $C_{15}H_{26}P_2SPd$: C, 44.29; H, 6.44. Found: C, 44.45; H, 6.75%. IR (KBr, cm^{-1}): ν(=C=) 1906. ^1H NMR ($CDCl_3$ in 300 MHz, δ): 1.34 (t, $^2J_{HP}$ = 3.3 Hz, 18H, PMe_3), 3.88 (dt, $^4J_{HH}$ = 6.6 Hz, $^5J_{HP}$ = 3.7 Hz, 2H,=CH_2), 5.29 (tt, $^4J_{HH}$ = 6.6 Hz, $^3J_{HP}$ = 5.1 Hz, 1H, CH=). $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$, *i*): 13.8 (t, $^1J_{PC}$ = 15 Hz, P(CH_3)$_3$), 63.2 (s,=CH_2), 83.7 (t, $^2J_{PC}$ = 9.9 Hz, Pd–CH), 121.2, 127.4, 132.1, 149.2 (t, $^3J_{PC}$ = 1.2 Hz, Ph), 199.2 (t, $^3J_{PC}$ = 3.4 Hz,=C=). $^{31}P\{^1H\}$ NMR (120 MHz in $CDCl_3$, δ): −15.6 (s).

2.8. X-ray structure determination

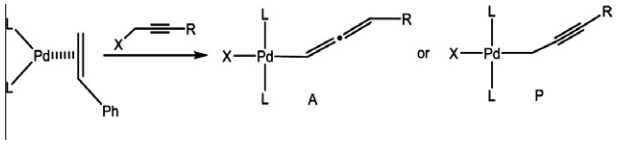
Single crystals of **8**, **9**, **11**, **15** and **19** for X-ray crystallography were grown from diethyl ether at −35 °C. All X-ray data were collected with a Bruker Smart APEX2 diffractometer equipped with a Mo X-ray tube. Collected data were corrected for absorption with SADABS based upon the Laue symmetry by using equivalent reflections [15]. All calculations were carried out with SHELXTL programs [16]. All structures were solved by direct methods. All non-hydrogen atoms were refined anisotropically, and all hydrogen atoms were positioned in ideal positions and refined in a riding model.

3. Results and discussion

3.1. Preparation of η^1-allenyl and/or -propargyl Pd(II) complexes

Oxidative addition of propargyl halides (XCH_2C≡CH) to the Pd–alkene complex, [Pd(CH_2=CHPh)(PR_3)$_2$] [13] gave the η^1-allenyl Pd(II) complexes, *trans*-[XPd(C=C=CH_2)(PR_3)$_2$] (A-type) (**1**–**4**), or the η^1-propargyl Pd(II) complexes, *trans*-[BrPd(CH_2C≡CR)(PMe_3)$_2$] (P-type) (R = $SiMe_3$, **5**; naphthyl, **6**), depending on the identity of organic halides and supporting ligands (Scheme 1). In a similar way, $ClCH_2$C≡C–Ph oxidatively adds to [Pd(CH_2=CHPh)(PR_3)$_2$] (PR_3=PMe_3, PMe_2Ph) to produce the η^1-allenyl complexes *trans*-[ClPd{C(Ph)=C=CH_2}(PR_3)$_2$] (**7** and **8**) (Scheme 2). In contrast, the same reaction involving the PEt_3 analog [Pd(CH_2=CHPh)(PEt_3)$_2$] exclusively gave the η^1-propargyl Pd(II) complex *trans*-[ClPd(CH_2C≡CPh)(PEt_3)$_2$] (**9**).

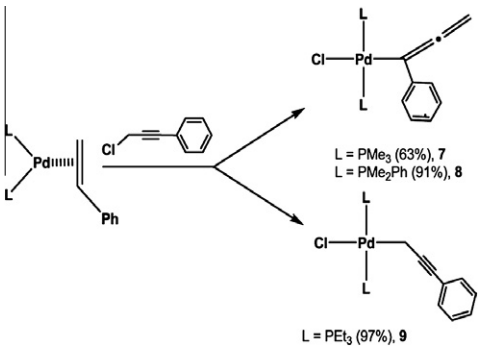
The IR spectra of the products clearly show characteristic bands at 1898–1912 cm^{-1} for ν(=·=) of the η^1-allenyl (**1**–**4** and **7**–**8**) or at 2142–2186 cm^{-1} for ν(C≡C) of the η^1-propargyl group (**5**–**6** and **9**). ^1H NMR peaks due to the CH and CH_2 in the η^1-CH=C=CH_2 (or η^1-CH_2C≡CR) ligands are consistent with those in the literature data [6–9]. The carbon signal (=·=) in the η^1-allenyl ligand of the above complexes appears at ca. 197–199 ppm in the $^{13}C\{^1H\}$ NMR spectra and also proves its existence. Interestingly, η^1-propargyl complexes **5**, **6**, and **9** show upfield shifts of the carbon atom (Pd–CH_2) at δ −3.6, −3.0 ppm ($^2J_{PC}$ = 2.2 Hz), and −8.3 ppm



A L = PMe_3 X = Cl R = H (88%), **1**
L = PMe_3 X = Br R = H (79%), **2**
L = PEt_3 X = Cl R = H (97%), **3**
L = PMe_2Ph X = Cl R = H (98%), **4**

P L = PMe_3 X = Br R = $SiMe_3$ (69%), **5**
L = PMe_3 X = Br R = Naphthyl (86%), **6**

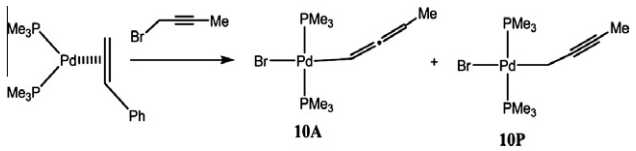
Scheme 1.



Scheme 2.

($^2J_{PC}$ = 3.1 Hz), respectively. Wojcicki and co-workers [17a] previously reported the closely related complex *trans*-[PtCl{CH_2-C≡CPh}(PPh_3)$_2$], whose ^{13}C NMR spectrum displays the Pt–CH_2 peak at δ −5.5 ppm (J_{PC} = 3.9 Hz), practically the same value as those found for complexes **5**, **6**, and **9**. At this point, we speculate that a combination of the electronegative *trans* Cl or Br group and the aryl alkynyl group nearly perpendicular to the molecular plane (see *ORTEP* drawing of **9** in Fig. 2), which is known as a better donor ligand than halide, might shield the Pd–CH_2 carbon to result in such an upfield shift. A singlet in the ^{31}P NMR data of the complexes strongly supports the *trans* conformation of complexes **1**–**9**.

NMR studies for complexes **1**–**9** except **6** indicates no equilibrium between η^1-allenyl and η^1-propargyl Pd(II) complexes. These data contrast with the previously reported NMR data that show an equilibrium product mixture of the η^1-allenyl and η^1-propargyl Pd(II) complexes in the ratio of 75:25, when [Pd(PPh_3)$_4$] reacted with $ClCH_2C$≡C–Ph [9a]. However, ^{1}H and ^{31}P{^{1}H} NMR data of initially isolated 6 show a mixture of η^1-allenyl and η^1-propargyl Pd(II) complexes in the ratio of 14:86, but the pure η^1-propargyl complex *trans*-[BrPd(CH_2C≡CR)(PMe_3)$_2$] (R = naphthyl, **6**) can be obtained by repeated recrystallizations. In contrast, it should be mentioned that reactions of [Pd(CH_2=CHPh)(PMe_3)$_2$] with 1 equiv of $BrCH_2$C≡C–Me in THF or *n*-hexane produced a mixture of the η^1-allenyl complex, *trans*-[BrPd{C(Me)=C=CH_2}(PMe_3)$_2$] (**10A**), and the η^1-propargyl Pd(II) complex, *trans*-[BrPd(CH_2-C≡CMe)(PMe_3)$_2$] (**10P**) in the ratio of 60:40, which was confirmed by NMR spectroscopy (Scheme 3). However, we could not separate it due to their similar solubility.



Scheme 3.

When a mixture of **10A** and **10P** is heated to 80 °C in toluene, the isomerization between η^1-allenyl and η^1-propargyl Pd(II) complex or other stereo isomerization (*trans* to *cis*) is not observed. This result may stem from the strong basicity of PMe_3 in complexes **10A** and **10P**. In other words, our PMe_3-coordinated η^1-allenyl and η^1-propargyl Pd(II) complexes compared to the PPh_3-coordinated Pd(II) complexes do not allow the interconversion between η^1-allenyl and η^1-propargyl Pd(II) complexes by phosphine dissociation to form an intermediate such as an η^3-allenyl complex to produce the isomer. This result is quite contrast to a couple of known isomerizations, including (1) an isomerization of *trans*-[XPt(CH_2C≡CPh)(PPh_3)$_2$] to *trans*-[XPt{C(Ph)=C=CH_2}(PPh_3)$_2$] (X = Cl, Br), an (η^1-propargyl) → allenyl platinum isomerization, under thermal conditions observed by Kurosawa and co-workers [10a], (2) a *cis* → *trans* isomerization of *cis*-[BrPt(CH_2-C≡CPh)(PPh_3)$_2$] under thermal conditions reported by Wojcicki and co-workers [17a], and (3) a *trans* → *cis* isomerization of *trans*-[PdBr(C=C=CRR′)(PPh_3)$_2$] (R = Me, *n*-C_5H_{11}, *t*-Bu; R′ = Me, H, Me, Et; R = R′ = $(CH_2)_5$) at room temperature observed by Elsevier co-workers [7c].

In case of propargyl halides (XCH_2C≡CH; X = Cl, Br), η^1-allenyl Pd(II) complexes (**1**–**4**) in Scheme 1 are selectively obtained. However, similar reactions of Pd(0) complexes with several propargyl halides containing substituents (XCH_2C≡C–R; R = Ph, $SiMe_3$, naphthyl, Me) produced various η^1-allenyl or/and η^1-propargyl complexes, depending on the substituents as well as supporting phosphine ligands. For example, Scheme 2 shows the formation of sole allenyl (**7** and **8**) or η^1-propargyl (**9**) Pd(II) complexes when $ClCH_2$C≡C–Ph is treated, depending on the phosphine ligands. In spite of limited information, these results suggest that the relative steric bulk (cone angle) of phosphine ligands (PMe_3 < PMe_2Ph < PEt_3) may play an important role in directing the selective formation of the η^1-allenyl or η^1-propargyl Pd(II) complex. By

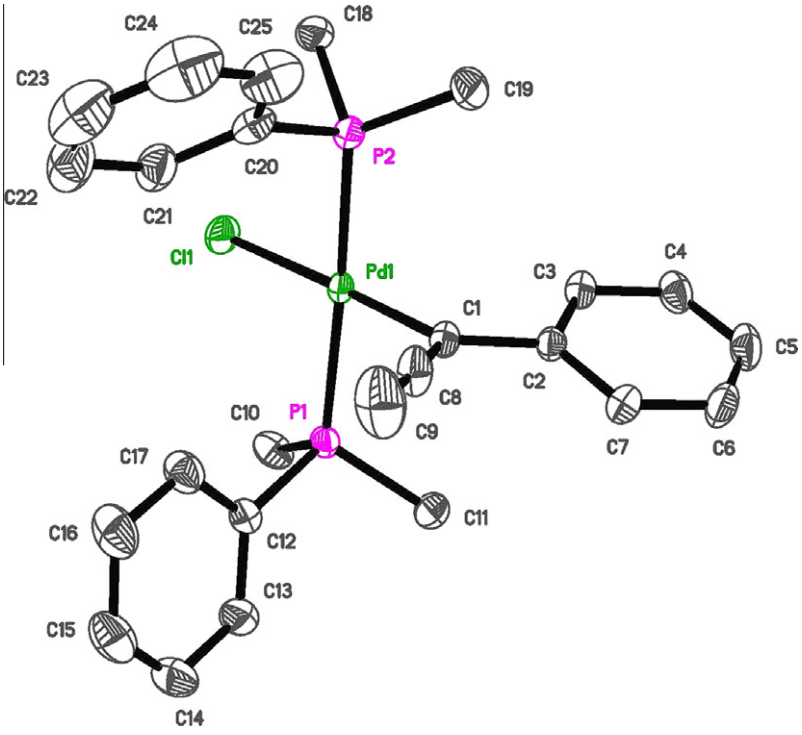


Fig. 1. *ORTEP* drawing of complex 8 showing the atom-labeling scheme and 50% probability thermal ellipsoids. Selected bond lengths (Å) and angles (°): Pd1–C1 2.027(2), Pd1–P2 2.3053(7), Pd1–P1 2.3079(7), Pd1–Cl1 2.3780(7), C1–C8 1.290(4), C1–C2 1.491(3), C8–C9 1.307(5); C1–Pd1–P2 88.84(8), C1–Pd1–P1 87.66(8), P2–Pd1–P1 172.11(2), C1–Pd1–Cl1 177.36(7), C8–C1–C2 121.3(2), C8–C1–Pd1 117.3(2), C2–C1–Pd1 121.5(2), C1–C8–C9 177.7(5).

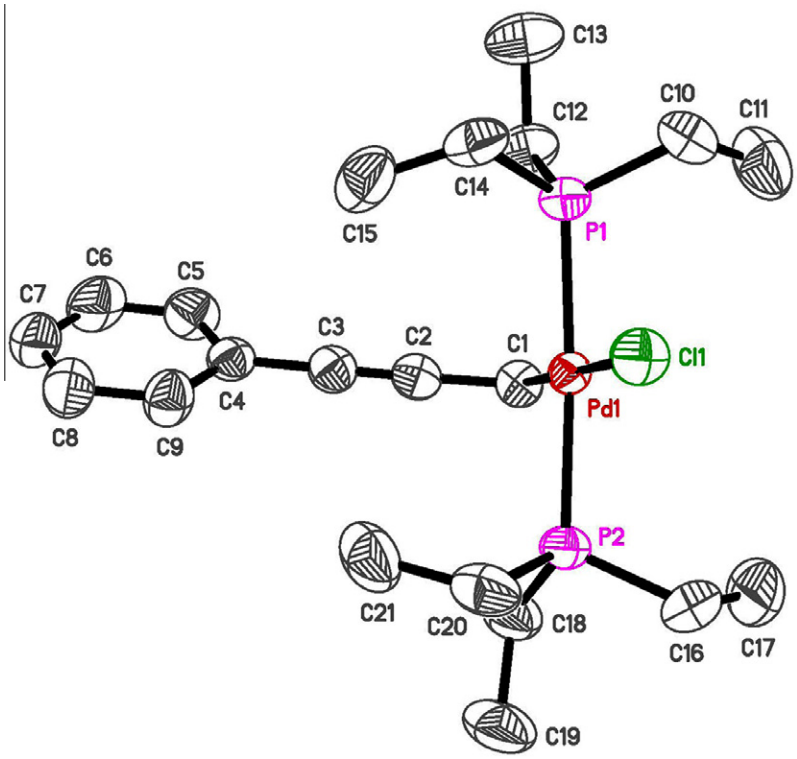


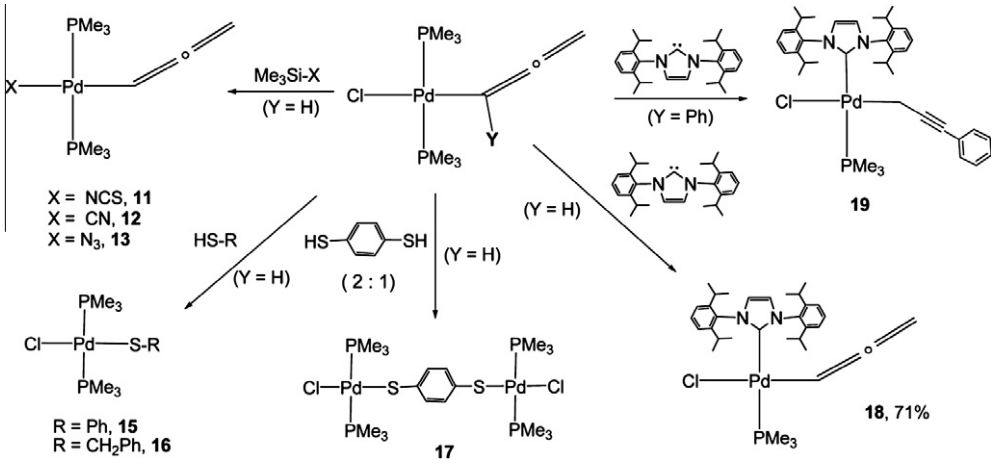
Fig. 2. *ORTEP* drawing of complex 9. Selected bond lengths (Å) and angles (°): Pd1–C1 2.071(2), Pd1–P2 2.3176(5), Pd1–P1 2.3207(5), Pd1–Cl1 2.3919(5), C1–C2 1.449(3), C2–C3 1.193(3); C1–Pd1–P2 91.83(6), C1–Pd1–P1 91.80(6), P2–Pd1–P1 174.19(2), C1–Pd1–Cl1 178.80(5), C2–C1–Pd1 108.3(1), C3–C2–C1 178.1(2).

contrast, Kurosawa and co-workers previously reported that $Pd(PPh_3)_4$ reacts with $ClCH_2C{\equiv}C–Ph$ to afford a mixture of η^1-allenyl and η^1-propargyl Pd(II) complexes in the ratio of 75:25 [9a]. Scheme 3 shows the formation of a similar mixture when $[Pd(CH_2{=}CHPh)(PMe_3)_2]$ is treated with $BrCH_2C{\equiv}C–Me$. It should be worth noting that a single product, η^1-propargyl Pd(II) complex (**5**), is only obtained when $BrCH_2C{\equiv}C–SiMe_3$ is used (Scheme 1). This is consistent with the case of *trans*-$[ClPd(CH_2C{\equiv}CSiMe_3)(PPh_3)_2]$ [9a]. Therefore, we believe that the basicity or steric bulk of phosphine ligands as well as electronic properties of propargyl halides based on the substituent may work together in the selective formation of the products.

Table 1
X-ray data collection and structure refinement for complexes **8**, **9**, **11**, **15** and **19**.

Complex	**8**	**9**	**11**	**15**	**19**
Empirical formula	$C_{25}H_{29}ClP_2Pd$	$C_{21}H_{37}ClP_2Pd$	$C_{10}H_{21}NP_2PdS$	$C_{12}H_{23}ClP_2PdS$	$C_{39}H_{52}ClN_2PPd$
Formula weight	533.27	493.30	355.68	403.16	721.65
T (K)	296(2)	296(2)	296(2)	296(2)	296(2)
Crystal system	triclinic	monoclinic	monoclinic	monoclinic	monoclinic
Space group	$P\bar{1}$	$P2_1/c$	$P2_1/c$	$P2_1/c$	$P2_1/n$
a (Å)	9.2242(3)	12.1748(5)	8.6682(1)	14.0682(6)	12.7346(3)
b (Å)	9.4337(3)	14.5911(6)	9.8587(2)	11.0519(4)	15.8979(3)
c (Å)	15.2031(4)	14.2045(6)	18.9137(3)	11.8852(5)	19.2990(4)
α (°)	89.970(1)	90	90	90	90
β (°)	81.774(1)	100.889(2)	95.411(1)	107.039(2)	98.601(1)
γ (°)	74.289(1)	90	90	90	90
V (Å^3)	1259.41(7)	2477.9(2)	1609.11(5)	1766.8(1)	3863.2(1)
Z	2	4	4	4	4
D_{cal} (g cm^{-3})	1.406	1.322	1.468	1.516	1.241
μ (mm^{-1})	0.979	0.988	1.457	1.481	0.618
$F(000)$	544	1024	720	816	1512
T_{max}	0.9085	0.8906	0.8446	0.8660	0.9185
T_{min}	0.8135	0.7427	0.6691	0.6649	0.8460
θ range (°)	1.35–28.35	1.70–28.29	2.16–28.31	1.51–28.37	1.67–28.39
No. of reflections collected	17602	42303	28739	29877	99016
No. of reflections independent	6031	6110	3992	4381	9593
No. of reflections with $I > 2\sigma(I)$	5301	4820	3275	3614	7070
Number of parameters	270	226	148	3614	397
Max., in $\Delta\rho$ (e Å^{-3})	0.787	0.364	0.541	0.503	0.515
Min., in $\Delta\rho$ (e Å^{-3})	−0.334	−0.253	−0.513	−0.422	−0.513
Goodness-of-fit *GOF* on F^2	1.059	1.027	1.039	1.033	1.029
R^a	0.0321	0.0250	0.0245	0.0284	0.0336
$wR_2{}^b$	0.0751	0.0530	0.0573	0.0654	0.0733

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



Scheme 4.

Molecular structures of complexes **8** and **9** are given in Figs. 1 and 2, respectively. Crystal refinement data are listed in Table 1. To our best knowledge, these structures represent the first molecular structures of η^1-allenyl or η^1-propargyl palladium(II) complexes. The *ORTEP* drawings for **8** and **9** clearly show a square-planar geometry containing η^1-allenyl group or η^1-propargyl group around the Pd center, respectively. The η^1-allenyl group for **8** is nearly perpendicular to the molecular plane with the dihedral angle of 89.59(7)°, which is similar to those reported for a number of η^1-allenyl Pt(II) complexes [7c,12,17b]. The allenyl group C1–C8–C9 is linear (177.7(5)°), and the bond distances of C1–C8 and C8–C9 (1.290(4) and 1.307(5) Å) are close to those in the η^1-allenyl Pt(II) complexes. The Pd–C bond length (2.027(2) Å) of **8** is close to those of *trans*-[PtBr(CH=C=CH_2)-(PPh_3)$_2$] [12] (2.040(5) Å), *trans*-[PtBr(CH=C=CMe_2)(PPh_3)$_2$] [7c] (2.10(3) Å), and [(PMe_3)$_3$Pt(C(Ph)=C=CH_2)][BPh_4] [17b] (2.084(9) and 2.090(9) Å). The bond angle, Pd–C1–C8 (117.3(2)°) is smaller than those of *trans*-[PtBr(CH=C=CH_2)(PPh_3)$_2$] (126.2(5)°), *trans*-[PtBr(CH=C=CMe_2)(PPh_3)$_2$] (131(4)°), and [(PMe_3)$_3$Pt(C(Ph)=C=CH_2)][BPh_4] (121.2(7)° and 118.4(7)°). The molecular structure of **9** in Fig. 2 also clearly indicates the formation of η^1-propargyl Pd(II) complex. The Pd1–C1 bond length (2.071(2) Å) is typical of the Pd–C(sp^3) σ-bond length [18]. The C2–C3 bond length (1.193(3) Å) in the propargyl fragment also falls in the range 1.181–1.195 Å, typically observed for the organic C≡C–C (sp^2, aromatic) fragments [19].

3.2. Reactivity toward trimethylsilyl pseudohalides, Me_3S–X (X = NCS, CN, N_3) and organic thiols R–SH (R = Ph, CH_2Ph, C_6H_4–SH)

Insertion of small molecules such as isocyanides or CO into the M–C bond is one of the fundamental steps in the late transition metal-catalyzed synthesis of organic unsaturated compounds [20–22]. Considering this reactivity, a similar reactivity may occur for the (σ-allenyl)–Pd or –Pt bonds. If this reactivity occurs, the σ-allenyl metal complexes can behave as important starting materials or precursors for the aforementioned reactions. In this context, the reactivity of the allenyl moiety of the η^1-allenyl Pd(II) complexes toward trimethylsilyl pseudohalides (Me_3SiX: X = NCS, CN, N_3) was investigated. First, the reaction of complex **1** with 3 equiv of trimethylsilyl isothiocyanate (Me_3Si–NCS) readily undergoes to give the iosthiocyanato allenyl complex *trans*-[(SCN)Pd(CH=C=CH_2)(PMe_3)$_2$] (**11**, 46%) by ligand replacement. Similarly, the chloride substitution with 3 equiv of Me_3Si–CN also produces the cyanato allenyl complex *trans*-[(NC)Pd(CH=C=CH_2)-(PMe_3)$_2$] (**12**, 98%), as shown in Scheme 4. In contrast, the reaction involving 3 equiv or excess Me_3Si–N_3 gave a mixture of *trans*-[(N_3-)Pd(CH=C=CH_2)(PMe_3)$_2$](**13**) and [PdCl(N_3)(PMe_3)$_2$] in the ratio of 90:10, which was determined by peak integration of $^{31}P\{^1H\}$ NMR spectra. However, the similar treatment with NaN_3 in the presence of water gave unidentified materials, probably due to the nucleophilic attack of the N_3^- at the allenyl moiety. In addition, the similar reaction of *trans*-[ClPd(CH=C=CH_2)(PEt_3)$_2$] (**3**) with Me_3SiN_3 selectively gives the ligand-substitution complex, *trans*-[(N_3)-Pd(CH=C=CH_2)(PEt_3)$_2$] (**14**), as a sole product.

The substitution of the chloro ligand by the pseudohalogen groups can be easily monitored by looking at the appearance of characteristic of pseudohalogen bands at 2036 for $\nu(N_3)$, at 2100 cm^{-1} for ν(NCS) or at 2119 cm^{-1} for ν(CN) in IR spectra, in addition to the change in the allenyl spectra at 1905–1912 cm^{-1}.

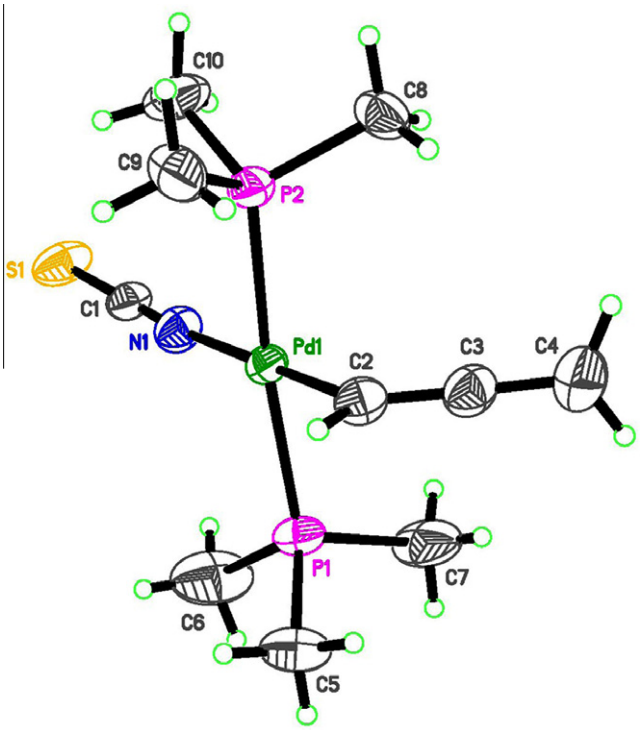


Fig. 3. *ORTEP* drawing of complex 11. Selected bond lengths (Å) and angles (°): Pd1–C2 2.010(2), Pd1–N1 2.058(2), Pd1–P1 2.3108(6), Pd1–P2 2.3116(6), S1–C1 1.632(3), N1–C1 1.149(3); C2–C3 1.284(4), C3–C4 1.295(4); C2–Pd1–N1 179.04(9),C2–Pd1–P1 86.77(7), N1–Pd1–P1 93.96(6), P1–Pd1–P2 172.69(2), N1–C1–S1 179.6(2), C2–C3–C4 178.6(3).

In $^{13}C\{^1H\}$ NMR spectra, the allenyl carbon appears as a triplet (J_{PC} = 3.7 Hz) at 195.5–200.5 ppm and this NMR pattern strongly supports the existence of the η^1-allenyl group in the products. The ORTEP drawing of *trans*-[(SCN)Pd(CH=C=CH$_2$)(PMe$_3$)$_2$] (**11**) in Fig. 3 clearly shows a square plane consisting of Pd, NCS, PMe$_3$, and an allenyl group. In particular, the isolated complex **12** is believed to be a key intermediate in the Pd-catalyzed cyanation of propargylic carbonates [23].

When complex **1** is treated with 1 equiv of organic thiol such as benzenethiol and benzylic thiol at room temperature, new thiolato complexes, *trans*-[ClPd(SR)(PMe$_3$)$_2$] (R = phenyl, **15**; benzyl, **16**), are readily obtained (Scheme 4). In addition, complex 1 reacts with 0.5 equiv of benzene-1,4-dithiol to produce a dinuclear dithiolato-bridged complex, *trans,trans*-[Pd(PMe$_3$)$_2$Cl]$_2$(μ-SC$_6$H$_4$S) (**17**, 90%). The IR stretching band (at 1910 cm^{-1}) of the allenyl group in the starting material disappeared, because of the elimination of the allenyl group. The molecular structure of **15** in Fig. 4 definitely demonstrates the substitution of the allenyl group by the nucleophilic attack of the organic thiols and shows a square-planar geometry.

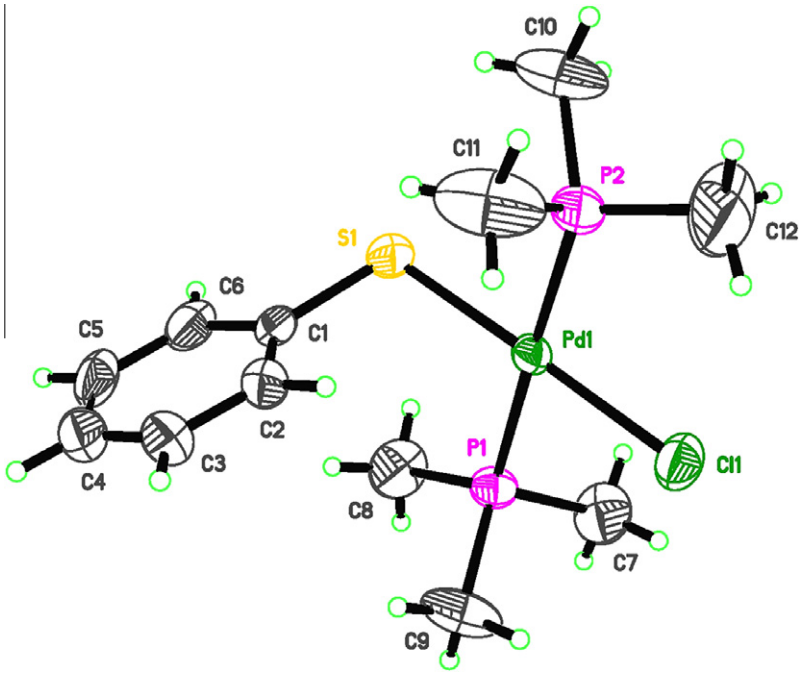


Fig. 4. *ORTEP* drawing of complex 15. Selected bond lengths (Å) and angles (°): Pd1–S1 2.2999(7), Pd1–P2 2.3096(7), Pd1–P1 2.3180(6), Pd1–Cl1 2.3449(7),S1–C1 1.763(3); S1–Pd1–P2 88.38(3), S1–Pd1–P1 92.77(3), P2–Pd1–P1 178.47(3), S1–Pd1–Cl1 177.72(3), C1–S1–Pd1 104.46(8).

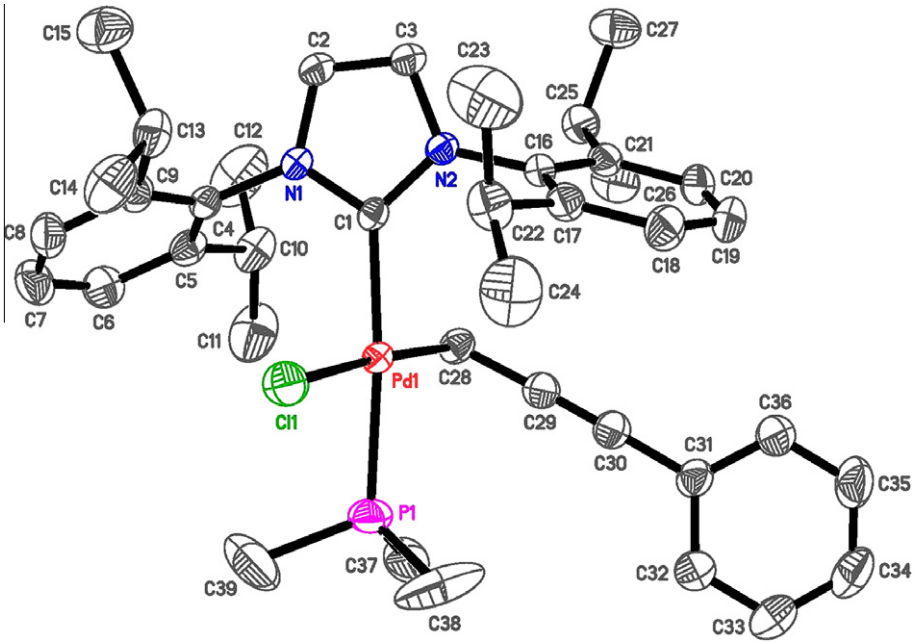


Fig. 5. *ORTEP* drawing of complex 19. The co-crystallized diethtyl ether molecule is omitted for clarity. Selected bond lengths (Å) and angles (°): Pd1–C1 2.052(2), Pd1–C28 2.072(2), Pd1–P1 2.2855(6), Pd1–Cl1 2.4110(6), C28–C29 1.429(3), C29–C30 1.204(3); C1–Pd1–C28 87.86(8), C1–Pd1–P1 173.12(6), C28–Pd1–P1 90.60(6), C28–Pd1–Cl1 174.91(6), C29–C28–Pd1 111.4(2), C30–C29–C28 177.3(3), C29–C30–C31 175.7(3).

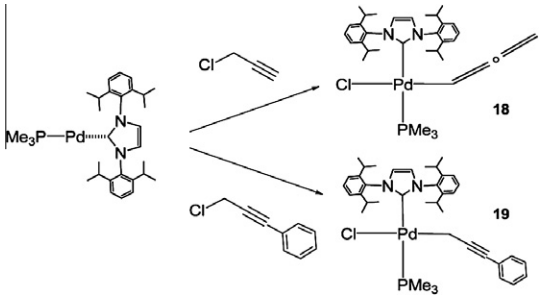
3.3. Reactivity toward NHC (N-heterocyclic carbene) ligand

NHC (*N*-heterocyclic carbene) ligands are well known as one of alternative complexes of tertiary phosphine ligands [24–27]. In this work, we also examined the ligand replacement by the NHC ligand. Complex **1** reacted with an equimolar amount of IPr (1,3-bis(2,6-diisopropylphenyl)imidazol-2-ylidene) to give the expected the IPr–Pd(II) complex [ClPd(IPr)(CH=C=CH_2)(PMe_3)] (**18**, 88%) by the substitution of the PMe_3 ligand. In contrast, the reaction of complex **7** with IPr as shown in Scheme 4 causes the selective formation of the η^1-propargyl Pd(II) complex [ClPd(IPr)(CH_2C≡CPh)(PMe_3)] (**19**, 83%). IR absorption bands of complexes **18** and **19** at 1916 (=·=) and 2184 (C≡C) cm^{-1} strongly support the existence of a characteristic η^1-allenyl or propargyl group coordinated to the Pd atom. The $^{13}C\{^1H\}$ NMR peak at 200.1 ppm also indicates the carbon atom (=·=) in the η^1-allenyl group of complex 18. The ORTEP drawing of complex 19 clearly reveals a square plane consisting of IPr, Cl, PMe_3, and a propargyl group (Fig. 5). The propargyl ligand is located slightly perpendicular to the molecular plane, which may relieve steric congestion between the bulky IPr ligand and the alkynyl group. The ^{13}C signal at −9.7 ppm with a doublet (d $^2J_{PC}$ = 1.9 Hz) of the Pd–C28 carbon also exhibits an upfield shift, indicating the effects of the strongly σ-donating IPr and electron-donating alkynyl ligands on the Pd to result in the shielding of that carbon atom.

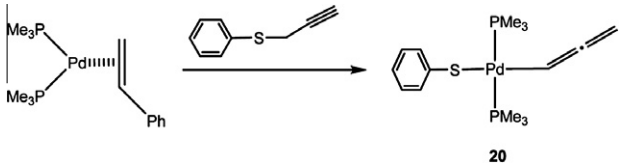
Earlier works by Kurosawa and co-workers [7c,9,10a,b] demonstrated the interconversion between η^1-allenyl Pd(II) and η^1-propargyl Pd(II) complexes via an η^3-allenyl/propargyl intermediate. Our reactions also seem to follow somewhat a similar mechanistic pathway. In a previous work, we reported the oxidative addition of small molecules such as dichloromethane or 1,2-dichloroethylene to the Pd(0) complex, [(Me_3P)Pd(NHC)] (NHC = IPr) [28]. In this work, we attempted to prepare complexes **18** and **19** by the similar oxidative additions with organic propargyl chlorides. As shown in Scheme 5, these reactions readily proceed to give corresponding oxidative-addition products, [ClPd(IPr)(CH=C=CH_2)(PMe_3)] (**18**, 71% yield) and [ClPd(IPr)(CH_2C≡CPh)(PMe_3)], (**19**, 66% yield), which have been characterized by spectroscopy. Bulkier 3-chloro-1-phenyl-1-propyne oxidatively adds to the Pd(0) complex to give the corresponding η^1-propargyl Pd(II) complex. These results suggest that the steric hindrance between the IPr group and the substituent on the propargyl halide for the selective formation of **18** and **19** plays a role in the reaction Pd(0) complex with propargyl halides as well as in the reaction of **7** with IPr.

3.4. Oxidative addition of propargyl phenyl sulfide to the Pd(0) complex

Propargyl phenyl sulfide readily undergoes oxidative addition to [Pd(CH_2=CHPh)(PMe_3)$_2$] to give the phenyl thiolato η^1-allenyl Pd(II) complex, *trans*-[(C_6H_5S)Pd(CH=C=CH_2)(PMe_3)$_2$] (**20**), in



Scheme 5.



Scheme 6.

71% yield (Scheme 6). The IR spectrum of this complex displays a characteristic band at 1905 cm^{-1} due to the ν(=·=). This result may provides an alternative method to prepare new η^1-allenyl Pd(II) complexes.

In summary, we prepared η^1-allenyl or η^1-propargyl Pd(II) complexes by the oxidative addition of organic propargyl halides to [Pd(CH_2=CHPh)(PR_3)$_2$] (PR_3=PMe_3, PEt_3, PMe_2Ph). In most cases, formation of these complexes depended on the nature of the supporting ligands and propargyl halides. Treatments of η^1-allenyl Pd(II) complex, *trans*-[(Cl)Pd(CH=C=CH_2)(PR_3)$_2$] (PR_3=PMe_3, PEt_3) with excess Me_3SiX (X = NCS, CN, N_3) caused the ligand substitution to give *trans*-[(X)Pd(CH=C=CH_2)(PR_3)$_2$]. Reactions of the η^1-allenyl Pd(II) complex with organic thiols gave new thiolato complexes, *trans*-[ClPd(SR)(PMe_3)$_2$] (R = phenyl, benzyl), and a new dinuclear dithiolato complex, *trans,trans*-[Pd(PMe_3)$_2$Cl]$_2$(μ-SC_6H_4S) in high yields. In particular, the reaction of *trans*-[ClPd(C(Ph)=C=CH_2)(PMe_3)$_2$] with 1 equiv of NHC (*N*-heterocyclic carbene, IPr) afforded an η^1-propargyl Pd(II) complex possessing the NHC ligand, [ClPd(IPr)(CH_2C≡CPh)(PMe_3)], via an η^3-allenyl/propargyl intermediate.

Acknowledgment

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Appendix A. Supplementary material

CCDC 875234–875238 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif. Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.ica.2012.12.011.

References

[1] (a) J. Tsuji, Palladium Reagents and Catalysts; Wiely: Chichester, 1995. (b) J. Tsuji, T. Mandai, Angew. Chem. Int. Ed. Engl. 34 (1995) 2589–2612.
[2] R. Zimmer, C.U. Dinesh, E. Nandanan, F.A. Khan, Chem. Rev. 100 (2000) 3067.
[3] S. Ma, Aldrich Chim. Acta 40 (2007) 91. and references therein.
[4] K. Tsutsumi, S. Ogoshi, K. Kakiuchi, S. Nishiguchi, H. Kurosawa, Inorg. Chim. Acta 296 (1999) 37.
[5] K. Tsutsumi, T. Yabukami, K. Fujimoto, T. Kawase, T. Morimoto, K. Kakiuchi, Organometallics 22 (2003) 2996.
[6] For reviews, see (a) J.-T. Chen, Coord. Chem. Rev. 190/192 (1999) 1143; (b) A. Wojcicki, Inorg. Chem. Commun. 5 (2002) 82; (c) H. Kurosawa, S. Ogoshi, Bull. Chem. Soc. Jpn. 71 (1998) 973.
[7] (a) C.J. Elsevier, H. Kleijn, K. Ruitenberg, P. Vermeer, J. Chem. Soc., Chem. Commun. (1983) 1529; (b) C.J. Elsevier, H. Kleijn, J. Boersma, P. Vermeer, Organometallics 5 (1986) 716; (c) J.M.A. Wouters, R.A. Klein, C.J. Elsevier, L. Haming, C.H. Stam, Organometallics 13 (1994) 4586.
[8] C.-C. Su, J.-T. Chen, G.-H. Lee, Y. Wang, J. Am. Chem. Soc. 116 (1994) 4999.
[9] (a) S. Ogoshi, K. Tsutsumi, H. Kurosawa, J. Organomet. Chem. 493 (1995) C19; (b) S. Ogoshi, T. Nishida, Y. Fukunishi, K. Tsutsumi, H. Kurosawa, J. Organomet. Chem. 620 (2001) 190.
[10] (a) S. Ogoshi, Y. Fukunishi, K. Tsutsumi, H. Kurosawa, Inorg. Chim. Acta 265 (1997) 9;

(b) K. Tsutsumi, S. Ogoshi, S. Nishiguchi, H. Kurosawa, J. Am. Chem. Soc. 120 (1998) 1938;
(c) S. Ogoshi, K. Tsutsumi, M. Ooi, H. Kurosawa, J. Am. Chem. Soc. 17 (1995) 10415;
(d) S. Ogoshi, T. Nishida, K. Tsutsumi, M. Ooi, T. Shinagawa, T. Akasaka, M. Yamane, H. Kurosawa, J. Am. Chem. Soc. 123 (2001) 3223.
[11] J.M.A. Wouters, R.A. Klein, C.J. Elsevier, K. Vrieze, M.C. Zoutberg, C.H. Stam, Organometallics 12 (1993) 3864.
[12] T.-M. Huang, R.-H. Hsu, C.-S. Yang, J.-T. Chen, G.-H. Lee, Y. Wang, Organometallics 13 (1994) 3657.
[13] (a) F. Ozawa, T. Ito, Y. Nakamura, A. Yamamoto, J. Organomet. Chem. 168 (1979) 375;
(b) Y.-J. Kim, K. Osakada, A. Takenaka, A. Yamamoto, J. Am. Chem. Soc. 112 (1990) 1096.
[14] L. Jafarpour, E.D. Stevens, S.P. Nolan, J. Organomet. Chem. 606 (2000) 49.
[15] G.M. Sheldrick, SADABS, Program for Absorption Correction, University of Göttingen, 1996.
[16] SHELXTL Bruker, Structure Determination Software Programs, Bruker, Analytical X-ray Instruments Inc., Madison, Wisconsin, USA, 1997.
[17] (a) M.W. Baize, P.W. Blosser, V. Plantevin, D.G. Schimpff, J.C. Galucci, A. Wojcicki, Organometallics 15 (1996) 164;
(b) P.W. Blosser, M. Calligaris, D.G. Schimpff, A. Wojcicki, Inorg. Chim. Acta 320 (2001) 110.
[18] B. Crociani, G. Bandoli, D.A. Clemente, J. Organomet. Chem. 184 (1980) 269.
[19] H.-J. Kim, S.W. Lee, Bull. Korean Chem. Soc. 20 (1999) 1089. and references therein.
[20] A. Yamamoto, Organotransition Metal Chemistry, Wiley-Interscience, New York, 1986.
[21] J.P. Collman, L.S. Hegedus, J.R. Norton, R.G. Finke, Principles and Applications of Organotransition Metal Chemistry, University Science Books, Mill Valley, CA, 1987.
[22] J. Tsuji, Palladium Reagents: Innovations in Organic Synthesis, Wiley, Chichester, UK, 1995.
[23] Y. Tsuji, M. Taniguchi, T. Yusada, T. Kawamura, Y. Obora, Org. Lett. 2 (2000) 2635.
[24] E.A.B. Kantchev, C.J. O'Brien, M.G. Organ, Angew. Chem., Int. Ed. 46 (2007) 2768.
[25] (a) N. Marion, S.P. Nolan, Acc. Chem. Res. 41 (2008) 1440;
(b)S.P. Nolan (Ed.), *N*-Heterocyclic Carbenes in Organic Synthesis, Wiley–VCH, New York, 2006;
(c) S. Diez-Gonzalez, S.P. Nolan, Top. Organomet. Chem. 21 (2007) 47.
[26] F.A. Glorious (Ed.), *N*-Heterocyclic Carbenes in Transition Metal Catalysis; Topics in Organometallic Chemistry, vol. 21, Springer-Verlag, Berin/ Heidelberg, Germany, 2007.
[27] C.M. Crudden, D.P. Allen, Coord. Chem. Rev. 248 (2004) 2247.
[28] J.-H. Lee, H.-T. Jeon, Y.-J. Kim, K.-E. Lee, Y.-O. Jang, S.W. Lee, Eur. J. Inorg. Chem. (2011) 1750.