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Synthesis and Characterization of Some Cationic η^3-Propargylpalladium Complexes

Ken Tsutsumi,* Tomohiro Kawase, Kiyomi Kakiuchi, Sensuke Ogoshi,*,† Yuji Okada,† and Hideo Kurosawa*,†

Graduate School of Materials Science, Nara Institute of Science and Technology, Takayama, Ikoma, Nara 630-0101

†Department of Applied Chemistry, Faculty of Engineering, Osaka University, Suita, Osaka 565-0871

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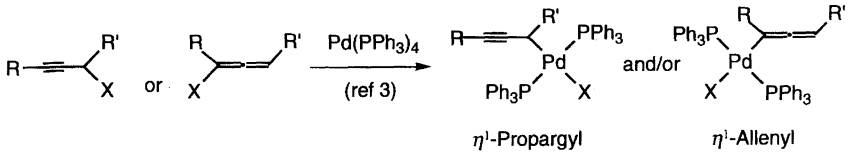
Some cationic η^3-propargylpalladium complexes were prepared upon treatment of the corresponding η^1-propargyl- or η^1-allenylbis(triphenylphosphine)palladium(II) chloride with Ag[BF_4] or Na[BPh_4]. The effectiveness of the latter reagent suggests that a η^1-propargyl- or η^1-allenyl(chloro)palladium complex equilibrates with a cationic η^3-propargylpalladium complex with the liberation of a Cl^- ligand. A qualitative comparison of trends in a series of analogous equilibrium systems suggests that the η^3-coordination mode is favored to a greater extent when (i) propargyl ligands have an alkyl substituent at the propargylic position, (ii) phosphine ligands are bidentate, such as dppe, (iii) polar solvents are used, and (iv) the liberating ligand is a Cl^- one. A possible implication of η^3-coordination of propargyl ligands in a catalytic cycle of Pd-catalyzed transformations of propargylic or allenylic substrates is presented.

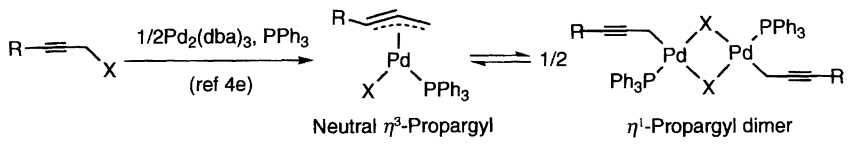
The chemistry of propargyl and allenyl transition-metal complexes continues to be extensively investigated.[1] Especially, much attention has been focused on palladium complexes because of their important role as key intermediates in many useful catalytic reactions of propargylic or allenylic substrates.[2] The first propargyl- and allenylpalladium complexes prepared by the conventional oxidative addition of propargyl or allenyl halides to $Pd(PPh_3)_4$ were of the η^1-bonding type (Scheme 1),[3] which has long been assumed to play a crucial role in the above mentioned catalytic cycles.

Recently, transition-metal complexes containing η^3-propargyl ligands have been attracting great attention because of their unique structures and reactivities.[4] With regard to η^3-propargylpalladium complexes, we reported on the first preparation of both neutral and cationic ones.[4e,4l] Neutral η^3-propargylpalladium complexes were obtained by the reaction of propargyl halides with $Pd_2(dba)_3$·$CHCl_3$ (dba = dibenzylideneacetone) and PPh_3 (Pd/PPh_3 = 1/1) (Scheme 2),[4e] where the η^3-type complex exists as an equilibrium mixture with halide-bridged η^1-propargyl dimer in solution. Cationic η^3-propargylpalladium complexes were prepared by the abstraction of halide ions with Ag salts from η^1-allenyl- and η^1-propargylpalladium halide complexes (Scheme 3),[4l,4m] according to a known method for platinum.[4i,4j] Moreover, another successful preparation using Na[BPh_4],[4l] instead of Ag salts, has led us to suggest that the equilibrium between cationic η^3-propargyl and η^1-propargyl/allenylpalladium complexes may also exist in solution (Scheme 4). This, together with an analogous suggestion involving the occurrence of a similar pre-equilibrium in the reaction of η^1-propargylpalladium complex with carbon nucleophiles,[5] has prompted us to investigate the η^3-η^1-propargyl/allenyl equilibrium in more detail.

In this paper we describe the synthesis and property of some cationic η^3-propargylpalladium complexes. We also examine the trends of η^1-η^3 equilibrium of propargyl ligand



Scheme 1.



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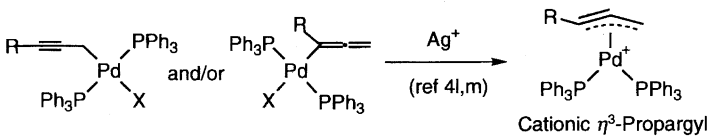
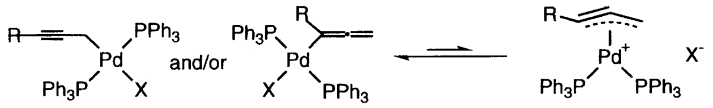


Scheme 3.



Scheme 4.

as a function of the nature of the propargyl group, liberating ligand (X), phosphine, and solvent. Part of this work has been described in a preliminary form.[4l]

Experimental

General. All reactions and manipulations of air- and moisture-sensitive compounds were carried out under an atmosphere of dry argon by the use of standard vacuum-line techniques. Melting points were determined on a Yanagimoto 1493 micro melting-point apparatus. NMR spectra were obtained on JEOL GSX-270, JEOL GSX-400, JEOL JNM-LA400, and Bruker AM 600 spectrometers. Chemical shifts are given in ppm using TMS or H_3PO_4 as a standard. High-resolution mass spectrum was taken with a JEOL JMS-700 mass spectrometer. Elemental analyses were obtained at the Analytical Center, Faculty of Engineering, Osaka University.

All of the solvents were distilled prior to use. Most commercially available reagents were used without further purification. *trans*-Pd(η^1-$CH_2C{\equiv}CSiMe_3$)(Cl)(PPh_3)$_2$ (**1a**),[3b] *cis*- and *trans*-Pt(η^1-$CH_2C{\equiv}CPh$)(Cl)(PPh_3)$_2$,[6a] ^{t}BuC≡CCH$_2$OH,[7] ^{t}BuC≡CCH(Me)OH,[7] Pd(PPh_3)$_4$,[8] and Pd$_2$(dba)$_3$·$CHCl_3$[9] were prepared according to the published methods. Chlorination and/or bromination of RC≡CCH(R′)OH (R = Ph, R′ = H; R = ^{t}Bu, R′ = Me; R = ^{t}Bu, R′ = H) was carried out according to a literature procedure.[10]

Preparation of a Mixture of *trans*-Pd(η^1-$CH_2C{\equiv}CPh$)(Cl)(PPh_3)$_2$ and *trans*-Pd(η^1-C(Ph)=C=CH_2)(Cl)(PPh_3)$_2$ (1b). In an adaptation of the literature procedure,[3b] to a suspension of 2.82 g (2.44 mmol) of Pd(PPh_3)$_4$ in 120 cm^3 of THF was added 523.8 mg (3.48 mmol) of PhC≡CCH_2Cl at 25 °C under an argon atmosphere. The color of the mixture changed to yellow within 10 min, and after 40 min, the volume of the solvent was reduced to half by a rotary evaporator. After the addition of 600 cm^3 of pentane, the yellow precipitate obtained was collected on a glass filter, and washed with 50 cm^3 of diethyl ether and 60 cm^3 of pentane. The yellow mixture of propargyl and allenyl complexes was dried under vacuum (1.17 g, 62%). Mp 136—140 °C (decomp); Propargyl type: ^{1}H NMR ($CDCl_3$) δ = 1.54 (s, 2H); ^{13}C{^{1}H} NMR ($CDCl_3$) δ = 6.76 (s, *C*H$_2$C), 86.13 (s, CH$_2$*C*), 94.38 (s, *C*CPh); ^{31}P{^{1}H} NMR ($CDCl_3$) δ = 27.33 (s); Allenyl type: ^{1}H NMR ($CDCl_3$) δ = 3.53 (s, 2H); ^{13}C{^{1}H} NMR ($CDCl_3$) δ = 68.08 (s, C*C*H$_2$), 103.20 (t, J_{PC} = 2.9 Hz, *C*CH$_2$), 199.60 (t, J_{PC} = 4.1 Hz, Ph*C*C); ^{31}P{^{1}H} NMR ($CDCl_3$) δ = 23.89 (s). Found: C, 69.05; H, 5.01%. Calcd for $C_{45}H_{37}ClP_2Pd$: C, 69.15; H, 4.77%.

Preparation of Cationic [Pd(η^3-$Me_3SiCCCH_2$)(PPh_3)$_2$][BF_4] (2a). To a solution of 50.7 mg (0.065 mmol) of **1a** in 2.5 cm^3 of CH_2Cl_2 was added 16.0 mg (0.082 mmol) of Ag[BF_4] at 25 °C under an argon atmosphere and the suspension was stirred for 15 min. The reaction mixture was filtered and the filtrate was concentrated under reduced pressure in a rotary evaporator. Then, the red solid was washed with four portions of 10 cm^3 of hexane, and reprecipitation from CH_2Cl_2/hexane gave white-yellow solids of **2a** (47.4 mg, 88%). Mp 108—109 °C (decomp); ^{1}H NMR ($CDCl_3$) δ = −0.29 (s, 9H), 3.07 (dd, J_{PH} = 7.8, 1.9 Hz, 2H); ^{13}C{^{1}H} NMR ($CDCl_3$) δ = 52.40 (dd, J_{PC} = 39.1, 6.2 Hz, C*C*H$_2$), 104.74 (d, J_{PC} = 40.4 Hz, Si*C*C), 113.84 (dd, J_{PC} = 8.1, 8.1 Hz, *C*CH$_2$); ^{31}P{^{1}H} NMR ($CDCl_3$) δ = 29.90 (d, J_{PP} = 46.4 Hz), 30.68 (d, J_{PP} = 46.4 Hz). Found: C, 60.82; H, 5.13%. Calcd for $C_{42}H_{41}P_2PdSiBF_4$: C, 60.84; H, 4.98%.

Preparation of Cationic [Pd(η^3-$PhCCCH_2$)(PPh_3)$_2$][BF_4] (2b). The procedure was similar to that for **2a**. Yield 94%; mp 99—100 °C (decomp); ^{1}H NMR ($CDCl_3$) δ = 3.26 (dd, J_{PH} = 7.6, 2.0 Hz, 2H), 6.75 (m, 5H); ^{13}C{^{1}H} NMR ($CDCl_3$) δ = 51.61 (dd, J_{PC} = 35.9, 5.9 Hz, C*C*H$_2$), 94.57 (dd, J_{PC} = 7.3, 7.3 Hz, *C*CH$_2$), 105.58 (dd, J_{PC} = 41.4, 4.9 Hz, Ph*C*C); ^{31}P{^{1}H} NMR ($CDCl_3$) δ = 30.16 (d, J_{PP} = 47.7 Hz), 30.85 (d, J_{PP} = 47.7 Hz). Found: C, 63.80; H, 4.54%. Calcd for $C_{45}H_{37}P_2PdBF_4$·(H_2O): C, 63.51; H, 4.62%.

Mesylation of ^{t}BuC≡CCH(Me)OH. In an adaptation of a literature procedure,[11] to a solution of 3.79 g (30.0 mmol) of ^{t}BuC≡CCH(Me)OH in 100 cm^3 of CH_2Cl_2 was added 6.27 cm^3 of NEt_3 at −60 °C under an argon atmosphere. After 50 min, to the solution was added 3.10 cm^3 (40.1 mmol) of CH_3SO_2Cl, and the mixture was stirred for 10 min. The reaction mixture was gradually warmed to 25 °C, and then poured into 200 cm^3 of H_2O. The resulting mixture was extracted with CH_2Cl_2 and the organic layer was dried over $MgSO_4$ and concentrated. The concentrate was distilled (77 °C/0.5 mmHg, 1 mmHg = 133.322 Pa) to give 5.51 g (90%) of ^{t}BuC≡CCH(Me)OSO_2Cl (**3**). ^{1}H NMR ($CDCl_3$) δ = 1.23 (s, 9H), 1.61 (d, J = 6.6 Hz, 3H), 3.12 (s, 3H), 5.28 (q, J = 6.6 Hz, 1H); ^{13}C{^{1}H} NMR ($CDCl_3$) δ = 22.94, 27.40, 30.53, 39.07, 69.16, 75.41, 97.28. HRMS Found: *m/z* 189.0591. Calcd for $C_8H_{13}O_3S$: [$M^+ - CH_3$], 189.0585.

Preparation of Cationic [Pd(η^3-^{t}BuCCCH(Me))(dppe)][OTf] (4). To a CH_2Cl_2 solution (5.0 cm^3) of 150.0 mg (0.14 mmol) of Pd$_2$(dba)$_3$·$CHCl_3$ and 115.5 mg (0.29 mmol) of dppe was added 65.1 mg (0.32 mmol) of **3** under an argon atmosphere. After 15 min, to the reaction mixture was added 149.6 mg (0.87 mmol) of Na[OTf] (OTf = trifluoromethanesulfonate), and the suspension was stirred for 20 min. The reaction mixture was concentrated in vacuo, and the orange residue was dissolved in CH_2Cl_2. After filtration, the filtrate was concentrated in vacuo again, and the residue was washed with seven portions of 10 cm^3 of ether. Recrystallization from CH_2Cl_2/ether/hexane gave yellow crystals of **4** (191.5 mg, 87%). Mp 80—82 °C (decomp); ^{1}H NMR ($CDCl_3$) δ = 0.97 (s, 9H), 1.07 (td, J_{PH} = 8.8 Hz, J_{HH} = 6.8 Hz, 3H), 4.30 (dq, J_{PH} = 7.1 Hz, J_{HH} = 6.8 Hz, 1H); ^{13}C{^{1}H} NMR ($CDCl_3$) δ = 17.08 (d, J_{PC} = 4.4 Hz, CH_3), 27.90 (dd, J_{PC} = 33.2, 13.5 Hz, P*C*H$_2$*C*H$_2$P), 30.15 (dd, J_{PC} = 33.9, 14.7 Hz, P*C*H$_2$*C*H$_2$P), 31.82 (s, C(*C*H$_3$)$_3$), 32.13 (s, *C*(CH$_3$)$_3$), 66.19 (dt, J_{PC} = 37.6, 6.5 Hz, C*C*H), 96.83 (d, J_{PC} = 6.3 Hz, *C*CH), 120.08 (d, J_{PC} = 34.6 Hz,

*C*CCH), 120.87 (q, J_{FC} = 321.3 Hz, *C*F_3); $^{31}P\{^1H\}$ NMR ($CDCl_3$) δ = 56.00 (d, J_{PP} = 42.8 Hz), 54.90 (d, J_{PP} = 42.8 Hz). Found: C, 51.25; H, 4.70%. Calcd for $C_{35}H_{37}F_3O_3P_2SPd\cdot(CH_2Cl_2)$: C, 50.99; H, 4.64%.

In Situ Reaction of Pd(η^1-$CH_2C{\equiv}CSiMe_3$)(Cl)(PPh_3)$_2$ (1a) with Na[BPh_4]. A mixture of 19.5 mg (0.025 mmol) of **1a** and 8.6 mg (0.025 mmol) of Na[BPh_4] was dissolved in 0.4 cm^3 of $CDCl_3$ and 0.2 cm^3 of $(CD_3)_2CO$ under an atmosphere of argon. The reaction was monitored by ^{1}H NMR. Cationic [Pd(η^3-$Me_3SiCCCH_2$)(PPh_3)$_2$][BPh_4] (**5a**) was obtained after 5 min (100%), which gradually decomposed to afford $Me_3SiC{\equiv}CCH_2Ph$ (30%) and $Me_3Si(Ph)C{=}C{=}CH_2$ (3%) in the solution after 4 h. ^{1}H NMR spectrum of **5a** ($CDCl_3$) δ = 2.99 (d, J_{PH} = 7.8 Hz, 2H). Registry No. $Me_3SiC{\equiv}CCH_2Ph$, 31683-47-3; $Me_3Si(Ph)C{=}C{=}CH_2$, 71321-00-1.

In Situ Reaction of a Mixture of *trans*-Pd(η^1-$CH_2C{\equiv}CPh$)(Cl)(PPh_3)$_2$ and *trans*-Pd(η^1-$C(Ph){=}C{=}CH_2$)(Cl)(PPh_3)$_2$ (1b) with Na[BPh_4]. The procedure was similar to that for **1a**. Cationic [Pd(η^3-$PhCCCH_2$)(PPh_3)$_2$][BPh_4] (**5b**) was obtained after 5 min (100%). ^{1}H NMR spectrum of **5b** ($CDCl_3$) δ = 3.15 (d, J_{PH} = 7.8 Hz, 2H).

In Situ Reaction of ^{t}BuC≡CCH(Me)Cl (6a) with 1/2Pd_2(dba)$_3$·$CHCl_3$ and dppe. To a $CDCl_3$ solution (0.6 cm^3) of **6a** (2.4 mg, 0.017 mmol) in an NMR tube were added 11.2 mg (0.011 mmol) of $Pd_2(dba)_3\cdot CHCl_3$ and 8.6 mg (0.022 mmol) of dppe under an atmosphere of argon. The reaction was monitored by ^{1}H NMR. Cationic [Pd(η^3-^{t}BuCCCH(Me))(dppe)][Cl] (**7a**) (45%) and *cis*-Pd(η^1-C(Bu^t)=C=CH(Me))(Cl)(dppe) (**8a**) (15%) were obtained after 30 min. ^{1}H NMR spectrum of **7a** ($CDCl_3$) δ = 0.96 (s, 9H), 1.07 (td, J_{PH} = 8.5 Hz, J_{HH} = 6.8 Hz, 3H), 4.25 (tq, J_{PH} = 4.4 Hz, J_{HH} = 6.8 Hz, 1H), ^{1}H NMR spectrum of **8a** ($CDCl_3$) δ = 0.57 (dd, J_{PH} = 8.9 Hz, J_{HH} = 6.8 Hz, 3H), 1.55 (s, 9H), 3.01 (q, J_{HH} = 6.8 Hz, 1H). The same reaction was carried out in DMF-d_7 (**7a**, 65%; **8a**, 8%) and C_6D_6 (**8a**, 7%).

In Situ Reaction of ^{t}BuC≡CCH(Me)Br (6b) with 1/2Pd_2(dba)$_3$·$CHCl_3$ and dppe. The procedure was similar to that of **6a**. Cationic [Pd(η^3-^{t}BuCCCH(Me))(dppe)][Br] (**7b**) (49%) and *cis*-Pd(η^1-C(^{t}Bu)=C=CH(Me))(Br)(dppe) (**8b**) (23%; major/minor = 9/5) were obtained after 30 min. ^{1}H NMR for **7b** ($CDCl_3$) δ = 0.94 (s, 9H), 1.05 (td, J_{PH} = 8.5 Hz, J_{HH} = 6.8 Hz, 3H), 4.24 (tq, J_{PH} = 4.3 Hz, J_{HH} = 6.8 Hz, 1H), ^{1}H NMR for **8b**-major ($CDCl_3$) δ = 0.59 (dd, J_{PH} = 9.3 Hz, J_{HH} = 6.6 Hz, 3H), 1.54 (s, 9H), 3.11 (q, J_{HH} = 6.6 Hz, 1H), ^{1}H NMR for **8b**-minor ($CDCl_3$) δ = 0.55 (dd, J_{PH} = 9.0 Hz, J_{HH} = 6.3 Hz, 3H), 1.52 (s, 9H), 2.99 (q, J_{HH} = 6.3 Hz, 1H).

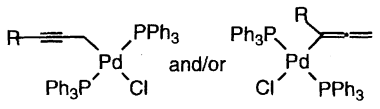
Reaction of ^{t}BuC≡CCH(Me)Cl (6a) with Pd(PPh_3)$_4$. To a $CDCl_3$ solution (0.6 cm^3) of **6a** (2.3 mg, 0.016 mmol) was added 16.6 mg (0.014 mmol) of Pd(PPh_3)$_4$ under an atmosphere of argon. The reaction was monitored by ^{1}H NMR. *trans*-Pd(η^1-C(^{t}Bu)=C=CH(Me))(Cl)(PPh_3)$_2$ (**9**) was obtained after 30 min (94%). ^{1}H NMR ($CDCl_3$) δ = 0.57 (d, J_{HH} = 6.6 Hz, 3H), 1.54 (s, 9H), 3.08 (q, J_{HH} = 6.6 Hz, 1H). The same reaction was carried out in DMF-d_7 (69%).

In Situ Reaction of ^{t}BuC≡CCH_2Cl (6c) with 1/2Pd_2(dba)$_3$·$CHCl_3$ and dppe. The procedure was similar to that of **6a**. *cis*-Pd(η^1-$CH_2C{\equiv}CBu^t$)(Cl)(dppe) (**10**) was obtained after 30 min (76%). ^{1}H NMR ($CDCl_3$) δ = 1.02 (s, 9H), 1.26 (s, 2H). The same reaction was carried out in DMF-d_7 (79%).

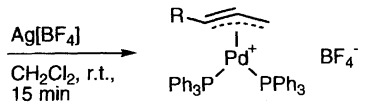
Results and Discussion

Synthesis and Property of Cationic η^3-Propargylpalladium(II) Complexes.

Cationic η^3-propargylpalladium complexes **2a**, **2b** were prepared by treating η^1-allenyl- and η^1-propargylbis(triphenylphosphine)palladium(II) chloride (**1a**, **1b**)[3b] with Ag[BF_4] (Eq. 1) in high yields. Since X-ray structural details of **2b** were reported[4m] after our preliminary publication,[4l] we avoid duplication of such data. The η^3-coordination mode in **2a** was established by NMR experiments. Thus, in the ^{13}C NMR spectrum of **2a** in $CDCl_3$, resonances of η^3-propargyl carbons at both terminal positions showed large carbon-phosphorus couplings (δ = 52.40, dd, J_{PC} = 39.1, 6.2 Hz, *C*CH_2; δ = 104.74, d, J_{PC} = 40.4 Hz, Si*C*C). Moreover, the resonance due to the central carbon of the propargyl group showed two small carbon-phosphorus couplings (δ = 113.84, dd, J_{PC} = 8.1, 8.1 Hz). Furthermore, the ^{31}P NMR resonances of two non-equivalent PPh_3 ligands showed phosphorus-phosphorus coupling (J_{PP} = 46.4 Hz). These features are all similar to those of **2b**, suggesting η^3-coordination of $Me_3SiCCCH_2$ ligand in **2a**.



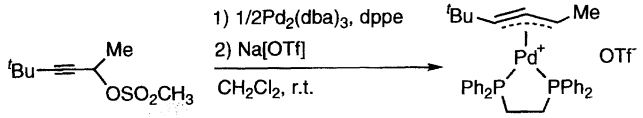
1a: R = $SiMe_3$ (propargyl)
1b: R = Ph (propargyl:allenyl = 25:75)



2a 88%
2b 94%

(1)

The preparation of another complex **4** was successful in good yield by the reaction of propargyl mesylate ^{t}BuC≡CCH(Me)OSO_2Me (**3**) with $Pd_2(dba)_3\cdot CHCl_3$, dppe (1,2-bis(diphenylphosphino)ethane), and Na[OTf] (Eq. 2).[12] In this reaction, the mesyl group (OSO_2Me) was a more efficient leaving one than halides, and was replaced by the OTf^- ion after oxidative addition. In the ^{13}C NMR spectrum of **4**, the resonances of propargyl terminal carbons showed large carbon-phosphorus coupling (J_{PC} = 37.6, 34.6 Hz) and the ^{31}P resonances of dppe ligands showed two signals at δ = 56.00 and 54.90 ppm with P-P coupling, which are similar to those of **2a** and **2b**. The ^{1}H NMR spectrum of **4** showed the methine proton resonance at δ = 4.30 ppm. The methine and methyl proton resonances have large proton-phosphorus coupling (J_{PH} = 7.1, 8.8 Hz respectively; established by homonuclear decoupling experiments).



3 **4** 87%

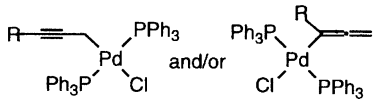
(2)

Surprisingly, the cationic η^3-propargylpalladium complexes prepared in this study did not react with methanol and ethanol at all,[13] in contrast to reactions of the corresponding platinum complexes with alcohol, which afforded

η^3-2-alkoxyallylplatinum complexes.[4i,4j,4m] The difference in the reactivity toward the alcohol, between Pd and Pt analogs might reflect a different stability of a possible intermediate, 3-alkoxy-1-metalla-2-cyclobutene (Pt intermediate being more stable than Pd analog) generated by a nucleophilic attack of an alkoxy group at the central carbon of the η^3-propargyl ligand, which subsequently undergoes protonation to give the η^3-2-alkoxyallyl complex. This explanation is consistent with a proposed origin of a unique metal effect in comparison of the bonding aspect of the metalla-3-cyclobutanone complex[14] between the Pd and Pt ones; the Pt atom stabilizes a metallacyclobutane framework more effectively by a resonance structure than the Pd atom does.

Complexes **1a** and **1b** also reacted with Na[BPh_4] to give the corresponding cationic η^3-propargylpalladium complexes (**5a**, **5b**), respectively (Eq. 3). Although these complexes gradually decomposed in solution, their quantitative formation in the early stage of the reaction was confirmed by ^{1}H NMR spectra (**5a**: δ CH_2 = 2.99 ppm, J_{PH} = 7.8 Hz, **5b**: δ CH_2 = 3.15 ppm, J_{PH} = 7.8 Hz). Complex **5a** afforded $Me_3SiC{\equiv}CCH_2Ph$ (30%) and $Me_3Si(Ph)C{=}C{=}CH_2$ (3%) in solution after 4 h at room temperature. On the other hand, the corresponding platinum complex, *cis*- and *trans*-Pt(η^1-$CH_2C{\equiv}CPh$)(Cl)(PPh_3)$_2$, did not react with Na[BPh_4] under the same conditions at all, which strongly suggests that the Pd atom favors the η^3-mode coordination of the allenyl or propargyl ligand more than the Pt atom does.

The occurrence of the reaction shown in Eq. 3 suggests pre-equilibrium between the η^1- and η^3-complexes involving dissociation of the chloride ion in solution (Scheme 4), similar to the known behavior of the η^3-allylpalladium complexes.[15] Although the spontaneous formation of the cationic species from **1a** and **1b** could not be detected spectroscopically, a suitable choice of both the propargyl and phosphine ligands enabled direct observations of the cationic η^3-propargylpalladium complexes with the liberation of a Cl^- ligand as an equilibrating species (see below).



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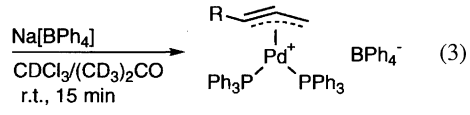
1b: R = Ph (propargyl:allenyl = 25:75)



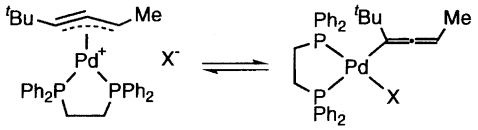
(3)

5a 100%
5b 100%

Cationic η^3-Propargylpalladium Formation in Solution. The reaction of ^{t}BuC≡CCH(Me)Cl (**6a**) with a half molar amount of $Pd_2(dba)_3{\cdot}CHCl_3$ and an equimolar amount of dppe gave an equilibrium mixture of cationic η^3-propargyl and neutral η^1-allenyl complexes **7a** and **8a** (Eq. 4). These complexes were generated only in NMR tubes due to gradual decomposition via β-hydrogen elimination (see later). The ^{1}H NMR data of **7a** are very similar to those of the triflate **4**. Upon forming the η^1-allenyl bond in **8a**, the signals of the methyl and methine protons at the allenyl terminus in **7a** (δ = 1.07, 4.25) moved to the higher magnetic field (δ = 0.57, 3.01); in particular, the signal of **8a** at δ = 3.01 is close to that of the authentic η^1-allenyl complex (**1b**; δ = 3.53), but far from that of the η^1-propargyl one (**1b**; δ = 1.54).

The equilibrium ratio of **7a** and **8a** was dependent on the nature of the solvent used. In $CDCl_3$, they exist a mixture of a ratio of 75/25 with the mutual interconversion being slower than the NMR time scale (25 °C). The ratios of **7a** and **8a** changed from 89/11 in DMF-d_7 (Run 2) to 0/100 in C_6D_6 (Run 3) depending on the solvent used, which indicates that cationic complex **7a** tends to be generated more easily in a polar solvent.

When ^{t}BuC≡CCH(Me)Br (**6b**) was used as a ligand instead of **6a**, the ratio of **7** and **8** changed from 75/25 (Run 1) to 68/32 (Run 4) in $CDCl_3$.[16] The equilibrium lies in favor of the cationic η^3-propargyl form by using **6a** instead of **6b**, which is consistent with the order of the leaving group ability from a metal center.[17a] Considering that soft metals, such as Pd(II), have strong affinity for soft ligands,[17b] **8b** containing the Pd–Br bond might be more stable than **8a** containing the Pd–Cl one.



(4)

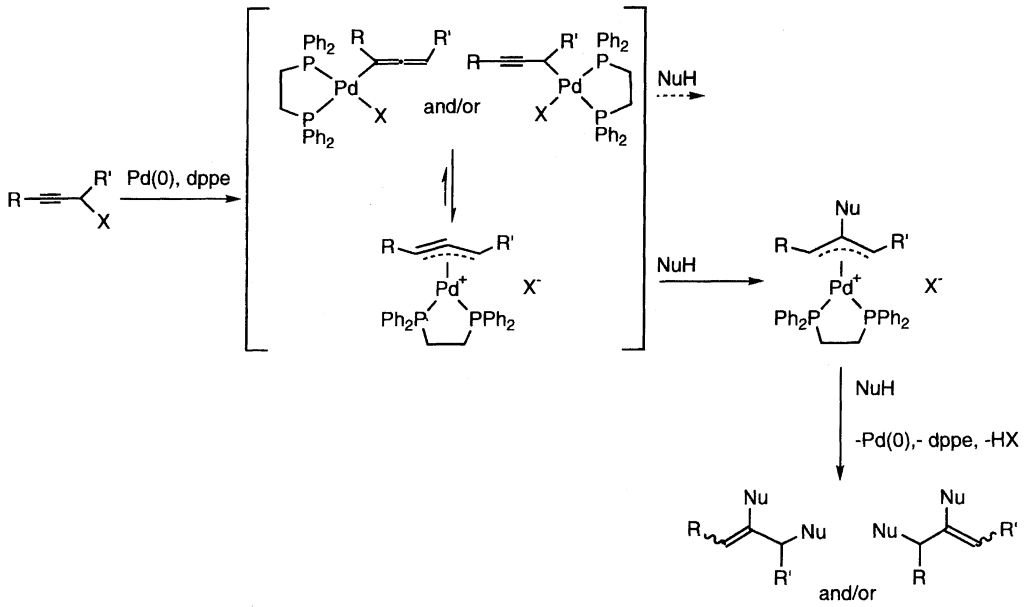
7a: X = Cl
7b: X = Br

8a
8b

Run	X	Solvent	**7**/**8**[a]
1	Cl	$CDCl_3$	75/25
2	Cl	DMF-d_7	89/11
3	Cl	C_6D_6	0/100
4	Br	$CDCl_3$	68/32

a) Ratios of **7** and **8** calculated by integrations of respective ^{1}H NMR signals at 25 °C.

In the reaction of $Pd(PPh_3)_4$ with **6a**, only η^1-allenyl complex, *trans*-Pd(η^1-C(Bu^t)=C=CH(Me))(Cl)(PPh_3)$_2$ (**9**), was obtained in either $CDCl_3$ or DMF-d_7. The chemical shift value of the methine proton in ^{1}H NMR spectrum of **9** at δ = 3.08 ppm is very close to that of **8a** at δ = 3.01 in $CDCl_3$. The reaction of ^{t}BuC≡CCH_2Cl (**6c**), instead of **6a**, with Pd(dppe) generated from a half molar amount of $Pd_2(dba)_3{\cdot}CHCl_3$ and an equimolar amount of dppe gave the η^1-propargyl complex Pd(η^1-$CH_2C{\equiv}CBu^t$)(Cl)(dppe) (**10**), as a sole product in either $CDCl_3$ or DMF-d_7. The chemical shift value of the methylene protons in the ^{1}H NMR spectrum of **10** at δ = 1.26 ppm, which is very similar to that of an analogous complex, *trans*-Pd(η^1-$CH_2C{\equiv}CBu^t$)(Cl)-(PPh_3)$_2$,[3b] reveals the η^1-propargyl coordination mode of **10**. These results suggest that the bidentate ligand (dppe) is more favorable for the η^3-coordination of the propargyl/allenyl ligand than triphenylphosphine. The introduction of the alkyl



Scheme 5.

substituent at the propargylic position causes the η^3-form to become more stable.

In solution **7**, **8**, and **9** gradually decomposed to give ^{t}BuC≡CCH=CH$_2$[18] through β-hydrogen elimination reaction. β-Elimination reaction requires formation of η^1-propargylpalladium intermediate which might equilibrate with η^1-allenyl and η^3-propargyl complexes **7** and **8**.[6]

Tsuji and co-workers reported on the reactions of propargyl carbonates with soft nucleophiles catalyzed by Pd(0), in which only the η^1-propargyl and η^1-allenyl species were proposed as catalytic intermediates.[2] In their mechanism, nucleophilic addition occurs first at the central carbon of η^1-allenyl moiety and then at the terminal carbon of the allyl group in the generated η^3-allylpalldium intermediate to afford doubly substituted products. However, it should be pointed out that the cationic η^3-propargylplatinum and palladium complexes tend to undergo a regioselective nucleophilic reaction at the central carbon atom[4i,4j,4m] and the η^1-allenyl and propargyl ligands are far less reactive toward nucleophiles than the η^3-propargyl ligand.[19] In fact, Chen indicated that the reaction of the η^1-allenylpalladium complex with Na[CH(CO$_2$Me)$_2$] proceeded via an equilibrium isomer cationic η^3-propargylpalladium complex.[5] Moreover, it was found that in the catalytic reactions bidentate ligands, such as dppe and dppp, were more effective than monodentate ligands.[2a] In view of these reactivity aspects and our present finding that dppe stabilizes cationic η^3-propargyl species more efficiently, we propose an alternative catalytic cycle involving cationic η^3-propargylpalladium complexes (Scheme 5).[20]

Conclusion

We described the synthesis and characterization of cationic η^3-propargylpalladium complexes, which might be the more reactive intermediate in the catalytic reactions. Palladium prefers the η^3-propargyl coordination fashion more than platinum. In addition, we observed the equilibrium mixture of cationic η^3-propargyl and neutral η^1-allenylpalladium complexes. The equilibrium lies increasingly in favor of the cationic η^3-propargyl complex as the alkyl substituent is introduced at the propargylic position, the liberating ligand is a Cl^- one, and the bidentate ligand (dppe) is used in a polar solvent.

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12 Synthesis of **4** might be possible from propargyl triflate ^{t}BuC≡CCH(Me)OTf. However propargyl triflate was not obtained by triflation of ^{t}BuC≡CCH(Me)OH according to the literature procedure,[11] which gave enyne compound ^{t}BuC≡CCH=CH$_2$ via β-elimination reaction.

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