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Preliminary communication

Synthesis and structure of cationic η^3-allenyl/propargylpalladium complexes

Sensuke Ogoshi *, Ken Tsutsumi, Hideo Kurosawa *

Department of Applied Chemistry, Faculty of Engineering, Osaka University, Suita, Osaka 565, Japan

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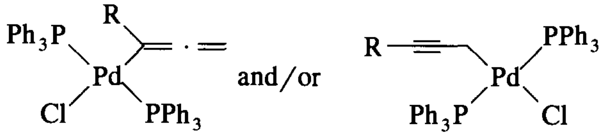
Abstract

Treatment of η^1-allenyl- or η^1-propargylpalladium bis(triphenylphosphine) chloride with $AgBF_4$ or $NaBPh_4$ afforded cationic η^3-allenyl/propargylpalladium complexes. The molecular structure and some properties of the η^3-allenyl/propargylpalladium were revealed.

Keywords: Palladium; Allenyl; Propargyl

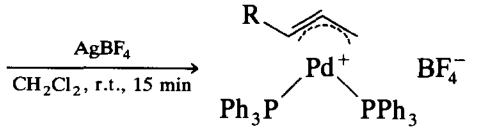
Recently, there has been much interest in allenyl and propargyl complexes of transition metals. Special attention has been paid to η^3-allenyl/propargyl complexes because of their unique structure and reactivity [1]. Previous works on the palladium analogues have centered on those containing the η^1-allenyl- and η^1-propargyl ligands [2] which may play a role in catalytic reactions [3], but no η^3-allenyl/propargylpalladium complex has been known. We report here the synthesis, structure and reactions of cationic η^3-allenyl/propargylpalladium complexes.

Cationic η^3-allenyl/propargylpalladium complexes (**2a**, **2b**) were prepared by treating η^1-allenyl- and η^1-propargylpalladium bis(triphenylphosphine) chloride (**1a**, **1b**) [2] with $AgBF_4$ (Eq. 1) [4]. In the ^{13}C NMR spectra, resonances of η^3-allenyl/propargyl carbons at positions 1 and 3 both showed large carbon–phosphorus coupling. Furthermore, the ^{31}P resonance of two nonequivalent PPh_3 ligands showed phosphorus–phosphorus coupling. These results indicate η^3 coordination of the allenyl/propargyl ligand to palladium with two PPh_3 coordination.



1a: R = $SiMe_3$(propargyl)

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



(1)

2a 88%

2b 94%

The molecular structure of **2b** is illustrated in Fig. 1 [5]. η^3-Allenyl/propargyl group is not linear (C1–C2–C3 = 154°), and palladium, phosphorus and η^3-allenyl/propargyl carbons are located almost on the same plane (dihedral angle between Pd–P1–P2 and C1–C2–C3 = 2.4°). The C1–C2 and C2–C3 bond lengths are 1.22(2) Å and 1.38(2) Å respectively, which indicates that there is considerable contribution of both allenyl and propargyl presentation to this structure. This structure is quite similar to that of the platinum analog

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* Corresponding authors.

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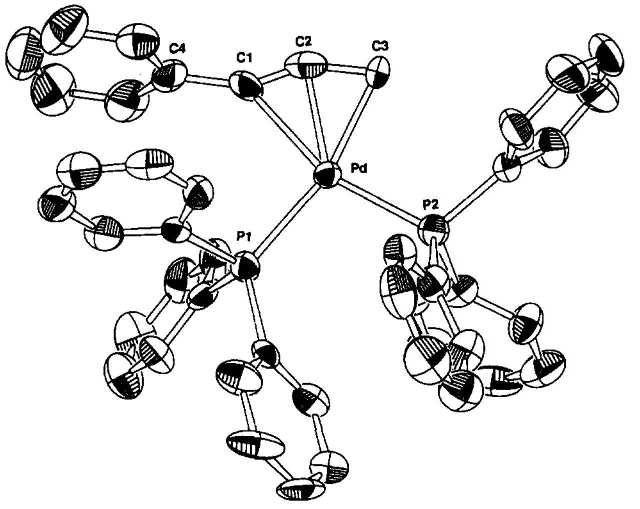
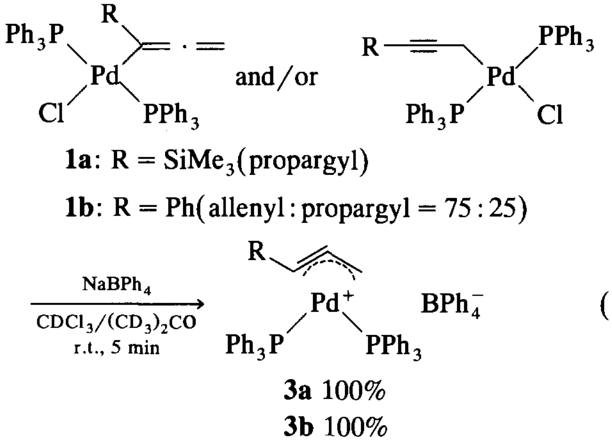


Fig. 1. Molecular Structure of **2b**. Selected bond distances (Å): Pd–P(1) = 2.337(4), Pd–P(2) = 2.292(4), Pd–C(1) = 2.33(2), Pd–C(2) = 2.15(2), Pd–C(3) = 2.16(2), C(1)–C(2) = 1.22(2), C(2)–C(3) = 1.38(2), C(1)–C(4) = 1.47(2). Selected angles (deg): C(1)–C(2)–C(3) = 154(1), C(2)–C(1)–C(4) = 153(1). Dihedral angles (deg): Pd–P(1)–P(2), C(1)–C(2)–C(3) = 4.82, Pd–P(1)–P(2), Pd–C(1)–C(3) = 2.38.

[1e] in that the degree of skeletal strain of the allenyl/propargyl ligand appears to be comparable in the two complexes. Surprisingly, however, the cationic η^3-allenyl/propargylpalladium complexes prepared in this study did not react with methanol and ethanol, in contrast to reactions of the corresponding platinum complexes with alcohol which afforded η^3-2-alkoxyallylplatinum complexes [1d,e]. The difference in reactivity with alcohol might reflect different stability of a possible intermediate, 2-alkoxymetallacyclobutene generated by nucleophilic attack of alkoxy group at the center carbon of the η^3-allenyl/propargyl ligand, which subsequently undergoes protonation to give the η^3-2-alkoxyallyl complexes. This explanation is consistent with a proposed origin of unique metal effect in the comparison of the bonding aspect of 2-oxodimethylenemethane complex [6] or the nucleophilic substitution of the 2-chloroallyl complex [7] between the Pd and Pt complexes; the Pt atom stabilizes a metallacyclobutane framework as a resonance structure or a reaction intermediate more effectively than the Pd atom does.

The complexes **1a** and **1b** also reacted with $NaBPh_4$ to give the corresponding cationic η^3-allenyl/propargylpalladium complexes (**3a**, **3b**), respectively (Eq. 2) [8]. Although these complexes decomposed gradually in solution and were not analyzed by elementary composition, they were confirmed to be formed almost quantitatively in the early stage by ^1H NMR spectra (**3a**: $\delta CH_2 = 2.99$, $J_{PH} = 7.8$ Hz, **3b**: $\delta CH_2 = 3.15$, $J_{PH} = 7.8$ Hz). The complex **3a** afforded $Me_3SiC{\equiv}CCH_2Ph$ (30%) and $Me_3Si(Ph)C{=}C{=}CH_2$ (3%) in the solution after 4 h at room temperature.

The occurrence of Eq. 2 points out pre-equilibrium between η^1- and η^3-complexes involving dissociation of the chloride ion in solution (Eq. 3) [9], although the cationic species in this equilibrium may be too small in amount to detect spectroscopically. Eq. 3 is similar to the known behavior of the η^3-allylpalladium complexes [10]. However, the corresponding platinum complex, *cis*- and *trans*-$(\eta^1\text{-PhC}{\equiv}CCH_2)Pt(PPh_3)_2Cl$, did not react with $NaBPh_4$ under the same conditions. This result suggests again that the Pd atom prefers η^3-mode coordination more than the Pt atom does even in the allenyl or propargyl complexes, as in the allylmetal complexes [6]. Further investigation is now progressing.



1a: R = $SiMe_3$(propargyl)

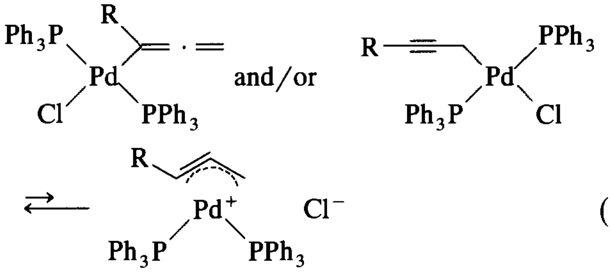
1b: R = Ph(allenyl : propargyl = 75 : 25)

$\xrightarrow[\text{CDCl}_3/(\text{CD}_3)_2\text{CO, r.t., 5 min}]{\text{NaBPh}_4}$

3a 100%

3b 100%

(2)



(3)

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[4] Selected data for **2a**: mp 108–109°C (dec); IR (KBr) 2178 cm^{-1}; ^1H NMR ($CDCl_3$) $\delta -0.29$ (s, 9H), 3.07 (dd, $J_{PH} = 1.9$, 7.8 Hz, 2H), 7.35 (m, 30H); ^{13}C NMR ($CDCl_3$) δ 52.40 (dd, $J_{CP} = 39.1$, 6.19 Hz, CCH_2), 104.74 (d, $J_{CP} = 40.4$ Hz, SiCC), 113.84 (dd, $J_{CP} = 8.1$, 8.1 Hz, $\mathit{C}CH_2$); ^{31}P NMR ($CDCl_3$, $P(OCH_3)_3$: δ 0.00) δ -113.98 (d, $J_{PP} = 46.4$Hz), -113.27 (d, $J_{PP} = 46.4$ Hz); Anal. Found: C, 60.82; H, 5.13. $C_{42}H_{41}PdSiP_2BF_4$ Calc.: C, 60.84; H, 4.98. **2b**: mp 99–100°C (dec); IR (KBr) 2190 cm^{-1}; ^1H NMR ($CDCl_3$) δ 3.26 (dd, $J_{PH} = 7.6$, 2.0 Hz, 2H), 6.75 (m, 5H), ^{13}C NMR ($CDCl_3$) δ 51.61 (d, $J_{CP} = 35.9$, 5.9 Hz, C*C*H2), 94.57 (dd, $J_{CP} = 7.3$, 7.3 Hz, CCH2), 105.58 (dd, $J_{CP} = 41.4$, 4.9 Hz, Ph*C*C); ^{31}P NMR ($CDCl_3$, $P(OCH_3)_3$: δ 0.00) δ -113.79 (d, $J_{PP} = 47.7$Hz), -113.10 (d, $J_{PP} = 47.7$ Hz); Anal. Found: C, 64.15; H, 4.66. $C_{45}H_{37}PdP_2BF_4$ Calc.: C, 64.89; H, 4.48.

[5] Crystal data for **2b**: $C_{45}H_{37}P_2PdBF_4$, triclinic, $P\bar{1}$(#2); $a = 12.034(1)$ Å, $b = 16.139(2)$ Å, $c = 10.555(2)$ Å, $\alpha = 105.49(1)°$, $\beta = 92.30(1)°$, $\gamma = 101.60(1)°$, $Z = 2$, $D_{calc} = 1.436$ g/cm^3. The data were collected at 23°C with Mo Kα radiation: $\mu = 6.16$ cm^{-1}, $2\theta_{max} = 55.0°$, 474 variables refined with 8849 unique reflections with $I > 3.00\sigma(I)$ to $R(F) = 0.080$ and $Rw(F) = 0.107$

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[8] In a typical reaction, 19.5 mg (0.025 mmol) of **1b** and 8.6 mg (0.025 mmol) of $NaBPh_4$ were dissolved under an atmosphere of argon in 0.4 ml of dry $CDCl_3$ and 0.2 ml of dry $(CD_3)_2CO$. The reaction was followed by ^1H NMR.

[9] Ref. 2c also suggested, without direct evidence, occurrence of a similar pre-equilibrium in the reaction of η^1-propargylpalladium complex with carbon nucleophiles.

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