

Preliminary communication

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

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Abstract

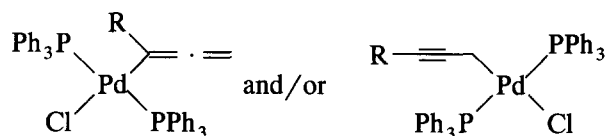
Treatment of η^1 -allenyl- or η^1 -propargylpalladium bis(triphenylphosphine) chloride with AgBF_4 or NaBPh_4 afforded cationic η^3 -allenyl/propargylpalladium complexes. The molecular structure and some properties of the η^3 -allenyl/propargylpalladium were revealed.

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.

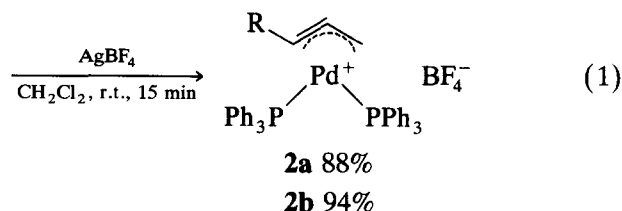
Cationic η^3 -allenyl/propargylpalladium complexes (**2a**, **2b**) were prepared by treating η^1 -allenyl- and η^1 -propargylpalladium bis(triphenylphosphine) chloride (**1a**, **1b**) [2] with AgBF_4 (Eq. 1) [4]. In the ^{13}C NMR spectra, resonances of η^3 -allenyl/propargyl carbons at positions 1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



2a 88%

2b 94%

The molecular structure of **2b** is illustrated in Fig. 1 [5]. η^3 -Allenyl/propargyl group is not linear ($\text{C1-C2-C3} = 154^\circ$), and palladium, phosphorus and η^3 -allenyl/propargyl carbons are located almost on the same plane (dihedral angle between Pd-P1-P2 and $\text{C1-C2-C3} = 2.4^\circ$). 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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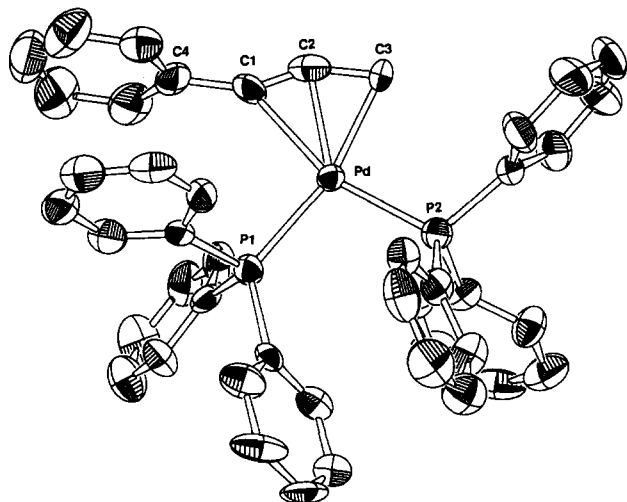
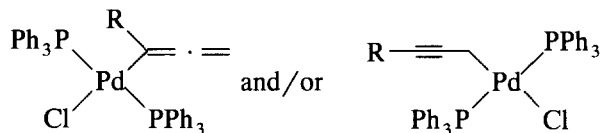


Fig. 1. Molecular Structure of **2b**. Selected bond distances (Å): Pd–P(1) = 2.337(4), Pd–P(2) = 2.292(4), Pd–C(1) = 2.33(2), Pd–C(2) = 2.15(2), Pd–C(3) = 2.16(2), C(1)–C(2) = 1.22(2), C(2)–C(3) = 1.38(2), C(1)–C(4) = 1.47(2). Selected angles (deg): C(1)–C(2)–C(3) = 154(1), C(2)–C(1)–C(4) = 153(1).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

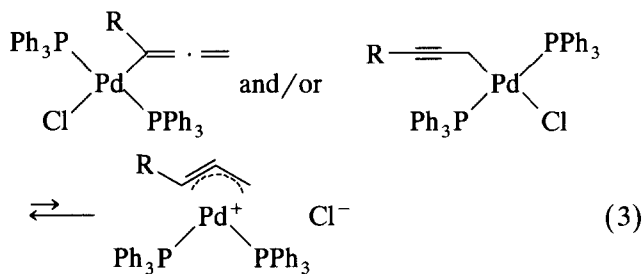
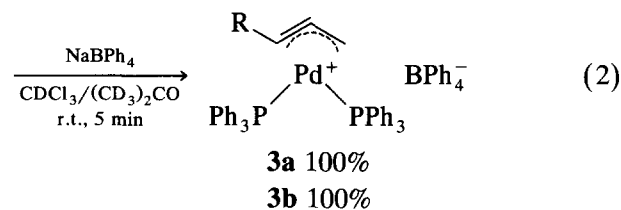
The complexes **1a** and **1b** also reacted with NaBPh₄ to give the corresponding cationic η^3 -allenyl/propargylpalladium complexes (**3a**, **3b**), respectively (Eq. 2) [8]. Although these complexes decomposed gradually in solution and were not analyzed by elementary composition, they were confirmed to be formed almost quantitatively in the early stage by ¹H NMR spectra (**3a**: δ_{CH_2} = 2.99, J_{PH} = 7.8 Hz, **3b**: δ_{CH_2} = 3.15, J_{PH} = 7.8 Hz). The complex **3a** afforded Me₃SiC≡CCH₂Ph (30%) and Me₃Si(Ph)C=C=CH₂ (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*-(η^1 -PhC≡CCH₂)Pt(PPh₃)₂Cl, did not react with NaBPh₄ 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 = SiMe₃ (propargyl)

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



Acknowledgment

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- [4] Selected data for **2a**: mp 108–109°C (dec); IR (KBr) 2178 cm^{-1} ; ^1H NMR (CDCl_3) δ -0.29 (s, 9H), 3.07 (dd, $J_{\text{PH}} = 1.9$, 7.8 Hz, 2H), 7.35 (m, 30H); ^{13}C NMR (CDCl_3) δ 52.40 (dd, $J_{\text{CP}} = 39.1$, 6.19 Hz, CCH_2), 104.74 (d, $J_{\text{CP}} = 40.4$ Hz, SiCC), 113.84 (dd, $J_{\text{CP}} = 8.1$, 8.1 Hz, CCH_2); ^{31}P NMR (CDCl_3 , $\text{P}(\text{OCH}_3)_3$: δ 0.00) δ -113.98 (d, $J_{\text{PP}} = 46.4\text{Hz}$), -113.27 (d, $J_{\text{PP}} = 46.4$ Hz); Anal. Found: C, 60.82; H, 5.13. $\text{C}_{42}\text{H}_{41}\text{PdSiP}_2\text{BF}_4$ 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, $J_{\text{PH}} = 7.6$, 2.0 Hz, 2H), 6.75 (m, 5H), ^{13}C NMR (CDCl_3) δ 51.61 (d, $J_{\text{CP}} = 35.9$, 5.9 Hz, CCH_2), 94.57 (dd, $J_{\text{CP}} = 7.3$, 7.3 Hz, CCH_2), 105.58 (dd, $J_{\text{CP}} = 41.4$, 4.9 Hz, PhCC); ^{31}P NMR (CDCl_3 , $\text{P}(\text{OCH}_3)_3$: δ 0.00) δ -113.79 (d, $J_{\text{PP}} = 47.7\text{Hz}$), -113.10 (d, $J_{\text{PP}} = 47.7$ Hz); Anal. Found: C, 64.15; H, 4.66. $\text{C}_{45}\text{H}_{37}\text{PdP}_2\text{BF}_4$ Calc.: C, 64.89; H, 4.48.
- [5] Crystal data for **2b**: $\text{C}_{45}\text{H}_{37}\text{P}_2\text{PdBF}_4$, triclinic, $P\bar{1}(\#2)$; $a = 12.034(1)$ Å, $b = 16.139(2)$ Å, $c = 10.555(2)$ Å, $\alpha = 105.49(1)^\circ$, $\beta = 92.30(1)^\circ$, $\gamma = 101.60(1)^\circ$, $Z = 2$, $D_{\text{calc}} = 1.436$ g/ cm^3 . The data were collected at 23°C with Mo K α radiation: $\mu = 6.16$ cm^{-1} , $2\theta_{\text{max}} = 55.0^\circ$, 474 variables refined with 8849 unique reflections with $I > 3.00\sigma(I)$ to $R(F) = 0.080$ and $R_w(F) = 0.107$.
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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 $(\text{CD}_3)_2\text{CO}$. The reaction was followed by ^1H NMR.
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