Synthesis, Structure, and Reactivity of Neutral η^3-Propargylpalladium Complexes

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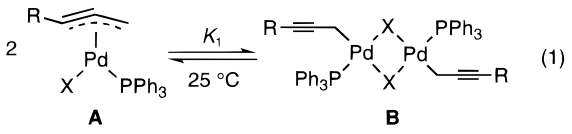
Compared to the considerable progress in the elucidation of polynuclear allenyl/propargyl complexes,[1,2] much less has been made on the elucidation of the bonding, structure, and reactivity of the η^3-propargyl ligand on a mononuclear metal center,[3] especially in neutral complexes.[3a,e,f,k] Exploration of new chemistry of η^3-propargylpalladium complexes appears of potentially synthetic and theoretical significance[4] in view of the major role played by η^3-allylpalladiums in organic synthesis.[5] We report here the first synthesis and stability and reactivity aspects of neutral η^3-propargylpalladium complexes.

The reaction of $RC{\equiv}CCH_2Cl$ with $Pd_2(dba)_3{\cdot}CHCl_3$ (dba = dibenzylideneacetone) and PPh_3 (Pd/PPh_3 = 1/1) in CH_2Cl_2 at 25 °C afforded new complexes $Pd(RCCCH_2)(Cl)(PPh_3)$ (**1a**, R = ^{t}Bu, 84%; **1b**, R = $(CH_3)_3Si$, 84%; **1c**, R = ^{t}Bu$(CH_3)_2Si$, 46%; **1d**, R = ^{i}Pr$_3$Si, 84%)[6] or $Pd(^i Pr_3SiCCCH_2)(X)(PPh_3)$ (**1e**, X = Br, 56%; **1f**, X = I, 61%) if the reaction carried out with added NaX. These complexes exist as a mixture of the η^3-propargyl monomer (**A**) and the halide-bridged η^1-propargyl dimer (**B**) in solution (eq 1, see below). The dimeric structure of **1d** in the



(1)

solid state was confirmed by X-ray crystallographic study (Supporting Information). The treatment of **1a** with C_6F_5Li gave $Pd(^tBuCCCH_2)(C_6F_5)(PPh_3)$ (**1g**, 52%), which exists in the monomeric η^3-propargyl structure both in the solid state (Figure 1)[7] and in a solution (VPO; found 638 at 1.08×10^{-2} M; calcd for monomer 631).

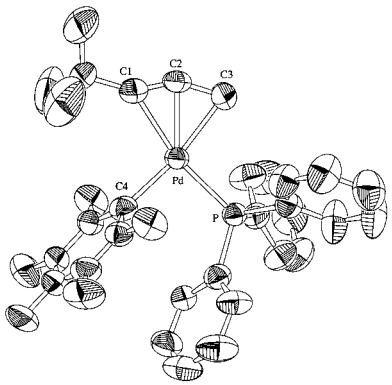


Figure 1. Molecular structure of **1g**. Selected bond distances (Å): Pd−C1 = 2.238(7), Pd−C2 = 2.116(6), Pd−C3 = 2.156(7), C1−C2 = 1.244(9), C2−C3 = 1.38(1). Selected angle (deg): C1−C2−C3 = 151.6(7).

The Pd−CH_2 bond in **1g** (2.156(7) Å) is considerably longer than that in **1d** (2.070(3) Å), possibly reflecting both intrinsic difference of bond strength between η^1- and η^3-coordination[8] and the stronger trans influence of C_6F_5 than that of Cl.[9] The geometry of η^3-propargyl ligand in **1g** is similar to that of $[Pd(\eta^3\text{-}PhCCCH_2)(PPh_3)_2]BF_4$;[3i,j] Pd, P, C4, and η^3-propargyl carbons are located almost on the same plane (dihedral angle between Pd−P−C4 and C1−C2−C3 = 3.93°).

The VPO molecular weights of **1d** at 35 °C (643 and 717 at concentrations 3.67×10^{-3} and 1.20×10^{-2} M in chloroform; calcd for monomer 600 and dimer 1199), and its ^{1}H and ^{13}C NMR spectra ($CDCl_3$) at room temperature showing two separate sets of resonances,[6] with the relative ratio dependent on the concentration, indicate that **1d** in chloroform exists as an equilibrium mixture of **A** and **B** (eq 1).[10] The equilibrium constants between η^3- and η^1-propargyl isomers for **1a**−**f** determined by NMR spectra in $CDCl_3$ and C_6D_6 at 25 °C show that the η^3-propargyl form is favored by the less bulky substituent R and more polar solvent (Table 1). Quite remarkably, the equilibrium lies increasingly in favor of the η^3-type monomer as chloride is replaced by bromide, and bromide by iodide. This is in contrast to the more general trend[11] that the ability of the halide ligand to act as a bridging ligand increases with increasing atomic number; this tendency was estimated by the degree of bridge splitting by a hard ligand such as amine. It may well be that the η^3-propargyl coordination may require the softer nature of the palladium center than the η^1-coordination, and this requirement would be better

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(6) Selected spectral data for **1d**. η^3-Type monomer: ^{1}H NMR ($CDCl_3$) δ 2.25 (s, 2H); ^{13}C NMR ($CDCl_3$) δ 35.64 (s, CCH_2), 104.19 (s, CCH_2), 105.17 (d, J_{CP} = 35.3 Hz, Si*C*C); ^{31}P NMR ($CDCl_3$) δ 30.72. η^1-Type dimer: ^{1}H NMR ($CDCl_3$) δ 1.95 (s, 2H); ^{13}C NMR ($CDCl_3$) δ 8.10 (s, CCH_2), 86.35 (s, *C*CH_2), 112.70 (s, Si*C*C); ^{31}P NMR ($CDCl_3$) δ 35.44; mp 196−200 °C (dec.). Anal. Calcd for $C_{30}H_{38}ClPPdSi$: C, 60.10; H, 6.39. Found: C, 60.33; H, 6.54.

(7) Crystal data for **1g**: $C_{31}H_{26}F_5PPd$, triclinic, $P\bar{1}$ (No. 2), a = 16.56(3) Å, b = 18.00(4) Å, c = 11.141(9) Å, α = 101.1(1)°, β = 107.5(1)°, γ = 63.5(2)°, Z = 4, D_{calcd} = 1.481 g/cm^3, T = 23 °C, $R(R_w)$ = 0.057(0.047). Crystal data for **2g**: $C_{67}H_{56}F_5P_3PdPt$, monoclinic, $P2_1/n$ (No. 14), a = 14.642(4) Å, b = 19.042(4) Å, c = 20.964(3) Å, β = 101.85(2)°, Z = 4, D_{calcd} = 1.568 g/cm^3, T = 23 °C, $R(R_w)$ = 0.048(0.028). Details of the crystallographic determinations are provided in the Supporting Information.

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(10) ^{13}C NMR spectral patterns of each component are similar to those of authentic samples of **1g** and *trans*-$Pd(\eta^1\text{-}^iPr_3SiCCCH_2)(Cl)(PPh_3)_2$, which was prepared similarly to the trimethylsilyl analogue reported: Elsevier, C. J.; Kleijn, H.; Boersma, J.; Vermeer, P. *Organometallics* **1986**, *5*, 716.

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Table 1. Equilibrium Constant K_1 (M^{-1}) of Eq 1

no.	R	X	In C_6D_6	In $CDCl_3$
1a	^{t}Bu	Cl	≪1	≪1
1b	Me_3Si	Cl	14	≪1
1c	^{t}Bu$(Me)_2$Si	Cl	30	2.4
1d	^{i}Pr$_3$Si	Cl	450	16
1e	^{i}Pr$_3$Si	Br	45	5.2
1f	^{i}Pr$_3$Si	I	21	≪1

fulfilled by the iodide. Another result of significance is the thermodynamic parameters for the equilibrium of **1a** in toluene-d_8 (25 to −80 °C), $\Delta H° = -9.0$ kJ mol^{-1} and $\Delta S° = -33$ J mol^{-1} K^{-1} which indicate that the η^3-type monomer is favored at 25 °C not by the enthalpy but by the entropy term.

We investigated reactivities of **1** with some nucleophiles. Although **1** did not react with MeOH and Et_2NH which added to the C≡C bond of cationic η^3-propargyl complexes of Pd and Pt,[3d,g,j] **1g** did react with a Pt(0) nucleophile in a formally analogous manner. Thus, addition of 1 equiv of $Pt(C_2H_4)(PPh_3)_2$ to **1g** in CH_2Cl_2 for 2 h at 25 °C afforded new complex **2g**[12] (75%), of which X-ray crystallographic analysis revealed a remarkable structure containing μ-η^2:η^3-^{t}BuCCCH$_2$ ligand (Figure 2).[7] The C1−C2 bond is longer and the C1−C2−C3 angle smaller than those of **1g**, and the η^3-ligand is no longer coplanar with the Pd−P−C4 plane (dihedral angle between Pd−P1−C4 and C1−C2−C3 = 49.16°). In contrast to other bimetal complexes containing μ-η^2:η^3-RCCCH$_2$ ligands,[2] **2g** does not possess a metal−metal bond (Pd−Pt = 3.33 Å). This fact, together with the great ease of its formation, makes the present complex quite a unique member of the complexes containing the similar type of ligands.

The addition of equimolar PPh_3 to **1a**−**f** in $CDCl_3$ generated η^1-propargylpalladium complexes almost quantitatively (eq 2, $K_2 > 100$ M^{-1}),[13] while both η^3- and η^1-propargyl complexes lie in equilibrium in the case of **1g** ($K_2 = 25$ M^{-1}), showing that the aryl is a better ligand than the halides to stabilize η^3-propargyl coordination. The corresponding η^3-allyl complex, Pd(η^3-^{t}BuCHCHCH$_2$)(C_6F_5)(PPh_3),[14] remained η^3-coordinated almost

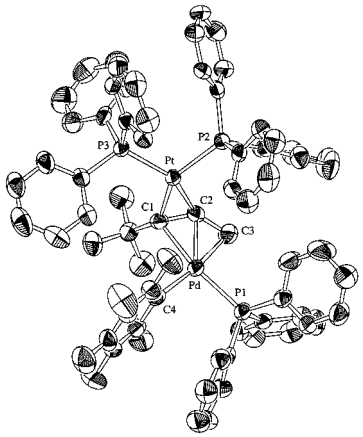
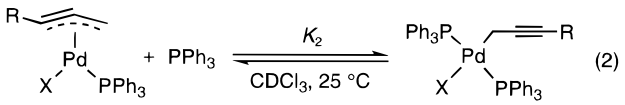


Figure 2. Molecular structure of **2g**. Selected bond distances (Å): Pd−C1 = 2.304(6), Pd−C2 = 2.153(6), Pd−C3 = 2.142(6), Pt−C1 = 2.063(6), Pt−C2 = 2.022(6), C1−C2 = 1.335(7), C2−C3 = 1.391(7). Selected angle (deg): C1−C2−C3 = 135.5(6).

exclusively ($K_2 < 10^{-2}$ M^{-1}),[13] even when treated with 10-fold excess PPh_3.



(2)

In summary, we showed the method of controlling η^3-propargyl coordination on mononuclear palladium center by appropriate choice of substituent R, ligand X, solvent, and amount of PPh_3 and their new reactivities. Further investigation including catalytic reactions is now in progress.[15]

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Supporting Information Available: Typical experimental procedures and spectral data of products, and tables of atomic coordinates and anisotropic thermal parameters of all atoms, bond distances, and angles for **1d**, **1g**, and **2g** (78 pages). See any current masthead page for ordering information and Web access instructions.

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(12) Spectral data for **2g**: ^{1}H NMR ($CDCl_3$) δ 2.87 (d, $J_{HP} = 7.8$, $J_{HPt} = 70.0$ Hz, 1H), 2.94 (d, $J_{HP} = 18.9$, $J_{HPt} = 79.3$ Hz, 1H); ^{13}C NMR ($CDCl_3$) δ 50.14 (s, *C*CH$_2$), 108.98 (d, $J_{CP} = 70.3$ Hz, $J_{CPt} = 338.4$ Hz, *C*CH$_2$), 112.62 (dd, $J_{CP} = 72.6$, 39.2 Hz, $J_{CPt} = 338.0$ Hz, ^{t}Bu*C*C); ^{31}P NMR ($CDCl_3$) δ 22.01 (d, $J_{PP} = 28.5$ Hz, $J_{PPt} = 3155.7$ Hz), 26.49 (d, $J_{PP} = 28.5$ Hz, $J_{PPt} = 3419.9$ Hz), 27.89 (s, $J_{PPt} = 41.9$ Hz); mp 155−158 °C (dec.). Anal. Calcd for $C_{67}H_{56}F_5P_3PdPt(CH_2Cl_2)_{0.5}$: C, 58.20; H, 4.12. Found: C, 58.57; H, 4.17.

(13) Estimated on the basis of the ^{1}H NMR detection limit (1/10) of the minor component relative to the major one.

(14) (a) This was prepared analogously to the η^3-C_3H_5 derivative[14b] and shown by ^{1}H NMR to contain PPh_3 located trans to ^{t}Bu substituent. (b) Numata, S.; Okawara, R.; Kurosawa, H. *Inorg. Chem.* **1977**, *16*, 1737.

(15) Complex **1** can be postulated as a new efficient intermediate in catalytic Stille-type coupling between RC≡CCH$_2$Cl and $PhSnBu_3$ to give RC≡CCH$_2$-Ph by the use of $Pd_2(dba)_3$·$CHCl_3$ and PPh_3 (Pd/PPh_3 = 1/1) which was more effective than $Pd(PPh_3)_4$ (see Supporting Information). When pyrolyzed in C_6D_6 at 70 °C, **1g** indeed gave ^{t}BuC≡CCH$_2$C$_6$F$_5$ (95%).