Mutual Isomerization of η1-Allenyl and η1-Propargyl Complexes of Platinum via a Five-coordinate η3-Allenyl/propargyl Intermediate

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The reversible spontaneous isomerization between η1-allenyl and η1-propargylplatinum complexes is reported, which is suggested to proceed via pseudorotation of a five-coordinate η3-allenyl/propargyl intermediate.

Increasing attention has been paid to structures and reactions of allenyl and propargyl complexes of transition metals.[1] It has generally been believed that in catalytic reactions η1-allenyl and η1-propargyl complexes can interconvert. Surprisingly, however, direct demonstration of the interconversion employing isolable complexes has so far been much more limited, in which only η1-propargyl complexes isomerized into η1-allenyl complexes irreversibly.[2] We wish to report here spontaneous reversible interconversion between η1-allenyl and η1-propargyl complexes of platinum(II) via a five-coordinate η3-allenyl/propargyl intermediate.

Oxidative addition of phenyl-substituted propargyl chloride to [Pt(PPh₃)₄] led to the formation of 1a. However, it is not certain whether this isomer was formed by thermodynamic or kinetic origin. Therefore, 1a was heated to 70 °C in C₆D₆ to see if any change resulted. Complex 1a underwent slow isomerization to give an equilibrium mixture of 1a and the propargyl derivative 2a (allenyl:propargyl = 95:5) (Scheme 1). No induction period was observed and the isomerization rate was first order in concentration of 1a for more than 2 half-lives. The rate constant (k_1) for isomerization of 1a into 2a in C₆D₆ at 70 °C was 3.7×10^{-6} s⁻¹. Isomerically pure 2a also could be isolated for the first time by recrystallization from a mixture of

1a and 2a.† We then confirmed that isomerization of 2a also occurred to give an equilibrium mixture of 1a and 2a. This is the first observation of isomerization from η1-allenyl to η1-propargyl complexes.

The spontaneous isomerization reaction is assumed to occur through an η3-allenyl/propargyl intermediate, such as the 18-electron complex (A) or 16-electron complexes, which may be ionic (B) or neutral (C) (Scheme 2). Addition of 40 mol% of PPh₃ did not affect the isomerization rate, which indicates that an intermediate such as C is unlikely. Significantly, bromide and iodide analogues 1b[1e] and 1c‡ underwent spontaneous isomerization in C₆D₆ at 70 °C faster than 1a (Br: k_1 = 2.2×10^{-5} s⁻¹, I: k_1 = 3.0×10^{-5} s⁻¹). The order of the rate constant k_1 (I > Br > Cl) is consistent with the order of π-bonding ability of the halide ligand[3a] in which a five-coordinate intermediate might be more stabilized, but not consistent with the order of the leaving group ability[3b] in which the formation of the ionic intermediate might be more facilitated. Moreover, the reaction of [Pt(η3-PhCCCH₂)(PPh₃)₂]·BF₄ 3[1e] with Bu₄NCl gave only 1a (cis:trans = 80:20).§

Even an organo(propargyl)platinum analogue (1d, X = C≡CPh),¶ which cannot form a cationic η3-allenyl/propargyl intermediate, underwent extremely rapid isomerization to give an equilibrium mixture of 1d and 2d in C₆D₆ at 70 °C in 1 h (k_1 = 8.0×10^{-4} s⁻¹) (Scheme 3). These results clearly indicate that the intermediate is a five-coordinate 18-electron η3-allenyl/propargyl species rather than the ionic η3 species.

The isomerization (propargyl → allenyl) must involve at least two steps; viz, initial coordination of C≡C above a square-plane (A1) and, as a final step, dissociation of the resulting allenyl C=C coordinated above a square-plane (A2) (Scheme 4). The transformation from A1 to A2 may proceed by two pathways. One is pseudo-rotation of the five-coordinate intermediate although the η3-allenyl/propargyl ligand is thought not to possess a sufficiently large bite angle to occupy two equatorial positions, and the other is rotation of the η3-allenyl/propargyl ligand about the Pt–allenyl/propargyl bond in pseudo-tetrahedral intermediates such as D similar to 18-electron [M(η3-allyl)L₃] complexes.[4]
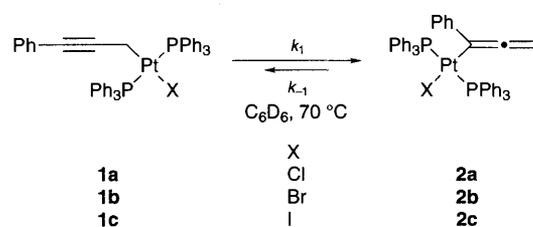
Scheme 1
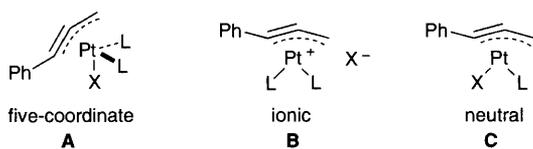
Scheme 2

Scheme 3 X = C≡CPh

Scheme 4

D
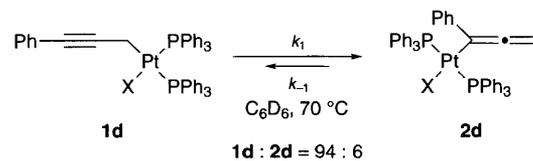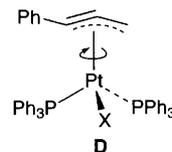
In summary, we have confirmed reversible interconversion between η1-allenyl and η1-propargyl complexes via five-coordinate η3-allenyl/propargyl intermediates. Further investigations are in progress.
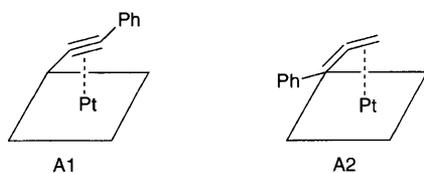
Footnotes

† *Selected spectral data* for 1a: mp 178–183 °C (decomp.); ¹H NMR (C₆D₆) δ 1.75 (t, J_{HP} = 7.8, J_{HPt} = 99.9 Hz, 2H), 6.95–7.14 (m, 18H), 7.20–7.29 (m, 5H), 7.98–8.15 (m, 12H); ³¹P NMR (C₆D₆) δ 22.79 (s, J_{PPt} = 3178 Hz);

Anal. Calc. for $C_{45}H_{37}ClP_2Pt$: C, 62.11; H, 4.29, Found: C, 61.79; H, 4.44%, **2a**: mp 180–185 °C (decomp.); ^1H NMR (C_6D_6) δ 3.51 (t, J_{HP} = 3.5, J_{HPt} = 52.7 Hz, 2H), 6.93–7.10 (m, 18H), 7.59–7.69 (m, 5H), 7.87–8.03 (m, 12H), ^{31}P NMR (C_6D_6) δ 19.63 (s, J_{PPt} = 3078 Hz); Anal. Found: C, 61.87; H, 4.56%.

‡ *Selected spectral data* for **1c**: mp 112–117 °C; ^1H NMR (C_6D_6) δ 1.99 (t, J_{HP} = 8.1, J_{HPt} = 98.0 Hz, 2H); Anal. Calc. for $C_{45}H_{37}IP_2Pt$: C, 56.2; H, 3.88, Found: C, 55.90; H, 4.09%.

§ Wojcicki and coworkers also reported a similar reaction of **3** with bromide anion to give the bromide analogue of only **1b** (*cis*:*trans* = 90:10).[1e]

¶ *Selected spectral data* for **1d**: mp 120–125 °C (decomp.); ^1H NMR (C_6D_6) δ 2.96 (dd, J_{HP} = 9.3, 10.4, J_{HPt} = 90.0 Hz, 2H), ^{31}P NMR (C_6D_6) δ 13.40 (d, J_{PP} = 17.8, J_{PPt} = 1569 Hz), 21.65 (d, J_{PP} = 17.8, J_{PPt} = 2434 Hz); Anal. Calc. for $C_{53}H_{42}P_2Pt$: C, 68.02; H, 4.52. Found: C, 68.04; H, 4.80%. For **2d**: ^1H NMR (C_6D_6) δ 3.47 (t, J_{HP} = 4.0, J_{HPt} = 32.8 Hz, 2H), ^{31}P NMR (C_6D_6) δ 17.66 (s, J_{PPt} = 2603 Hz).

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