Mutual Isomerization of η^1-Allenyl and η^1-Propargyl Complexes of Platinum *via* a Five-coordinate η^3-Allenyl/propargyl Intermediate

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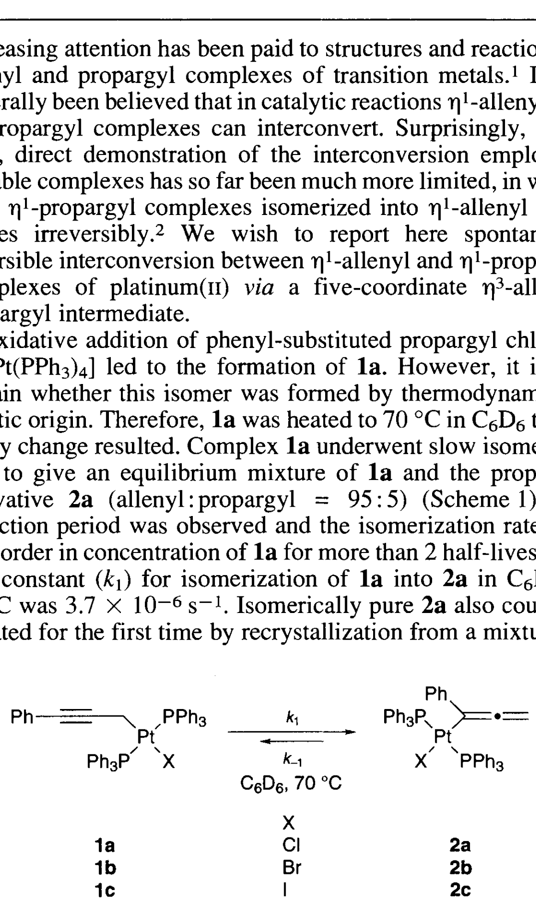
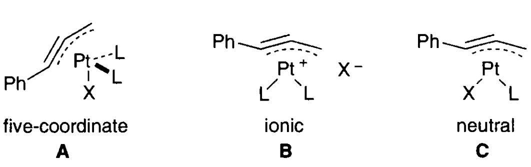
The reversible spontaneous isomerization between η^1-allenyl and η^1-propargylplatinum complexes is reported, which is suggested to proceed *via* pseudorotation of a five-coordinate η^3-allenyl/propargyl intermediate.

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 η^1-allenyl and η^1-propargyl complexes can interconvert. Surprisingly, however, direct demonstration of the interconversion employing isolable complexes has so far been much more limited, in which only η^1-propargyl complexes isomerized into η^1-allenyl complexes irreversibly.[2] We wish to report here spontaneous reversible interconversion between η^1-allenyl and η^1-propargyl complexes of platinum(II) *via* a five-coordinate η^3-allenyl/propargyl intermediate.

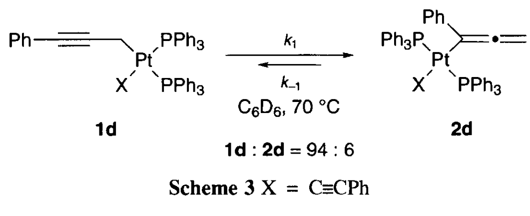
Oxidative addition of phenyl-substituted propargyl chloride to $[Pt(PPh_3)_4]$ led to the formation of **1a**. However, it is not certain whether this isomer was formed by thermodynamic or kinetic origin. Therefore, **1a** was heated to 70 °C in C_6D_6 to see if any change resulted. Complex **1a** underwent 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 C_6D_6 at 70 °C was $3.7 \times 10^{-6}\,s^{-1}$. 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 η^1-allenyl to η^1-propargyl complexes.



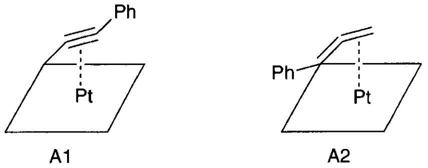
Scheme 1



Scheme 2



Scheme 3 X = C≡CPh

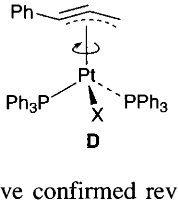


Scheme 4

The spontaneous isomerization reaction is assumed to occur through an η^3-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 PPh_3 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 C_6D_6 at 70 °C faster than **1a** (Br: $k_1 = 2.2 \times 10^{-5}\,s^{-1}$, I: $k_1 = 3.0 \times 10^{-5}\,s^{-1}$). 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 $[Pt(\eta^3\text{-}PhCCCH_2)(PPh_3)_2]\cdot BF_4$ **3**[1e] with Bu_4NCl gave only **1a** (*cis* : *trans* = 80 : 20).§

Even an organo(propargyl)platinum analogue (**1d**, X = C≡CPh),¶ which cannot form a cationic η^3-allenyl/propargyl intermediate, underwent extremely rapid isomerization to give an equilibrium mixture of **1d** and **2d** in C_6D_6 at 70 °C in 1 h ($k_1 = 8.0 \times 10^{-4}\,s^{-1}$) (Scheme 3). These results clearly indicate that the intermediate is a five-coordinate 18-electron η^3-allenyl/propargyl species rather than the ionic η^3 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 η^3-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 η^3-allenyl/propargyl ligand about the Pt–allenyl/propargyl bond in pseudo-tetrahedral intermediates such as **D** similar to 18-electron $[M(\eta^3\text{-allyl})L_3]$ complexes.[4]



D

In summary, we have confirmed reversible interconversion between η^1-allenyl and η^1-propargyl complexes *via* five-coordinate η^3-allenyl/propargyl intermediates. Further investigations are in progress.

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Footnotes

† *Selected spectral data* for **1a**: mp 178–183 °C (decomp.); ^1H NMR (C_6D_6) 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), ^{31}P NMR (C_6D_6) 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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