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Mechanistic studies on mutual isomerization of propargyl- and allenylplatinum(II) complexes

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Abstract

When heated in benzene, phenyl-substituted propargylplatinum(II) complexes, *trans*-Pt($CH_2C{\equiv}CPh$)(X)(PPh_3)$_2$ (**2**) (X = Cl, Br, I), isomerized gradually to the more stable allenyl isomers, *trans*-Pt($CPh{=}C{=}CH_2$)(X)(PPh_3)$_2$ (**3**), to give rise to an equilibrium mixture of **2**/**3** (5/95), from which **3** (X = Cl) was isolated as an isomerically pure sample. The allenyl complex **3** also gave rise to the same equilibrium mixture of **2**/**3** when heated under the same conditions. The rate of propargyl- to allenylplatinum(II) isomerization was examined as the function of the ligand X in **2**. The isomerization rate was first-order in the concentration of the propargyl complex, not affected by adding PPh_3, and increased in the order X = Cl < Br < I. The organo(propargyl)platinum(II) complex, *cis*-Pt($CH_2C{\equiv}CPh$)($C{\equiv}CPh$)(PPh_3)$_2$, isomerized even faster to the corresponding allenyl isomer than **2**. These kinetic aspects led us to suggest that the spontaneous propargyl- to allenylplatinum isomerization proceeds via intramolecular rearrangement of an 18-electron η^3-propargyl/allenyl intermediate, Pt(η^3-$CH_2C{\equiv}CPh$)(X)(PPh_3)$_2$. The isomerization from **2** to **3** was accelerated considerably by addition of Pt(PPh_3)$_2$L$_n$ (L = PPh_3, n = 2; L = C_2H_4, n = 1), but not at all by addition of $PtCl_2(PPh_3)_2$. © 1997 Elsevier Science S.A.

Keywords: Isomerization; Platinum complexes; Propargyl complexes; Allenyl complexes

1. Introduction

There is an increasing interest in the structure, bonding and reactivities of propargyl and allenyl complexes of transition metals [1]. This is a natural consequence of richness of the chemistry of complexes bearing allylic ligands with which the propargyl/allenyl ligands share a three-carbon, 1,3 alternate unsaturation. Earlier reports dealt with only η^1-bound propargyl and allenyl ligands, while recent works have laid emphasis on poly-hapto-bound propargyl/allenyl complexes with both mononuclear and multinuclear metallic centers [1,2]. In general, the tendency of propargyl/allenyl ligands to become η^3-bound is much weaker compared to that of allyl ligands. There are some reasons why the polyhapto-bound form of the propargyl/allenyl ligand attracts attention in the chemistry dealing with metal complexes of this ligand; one is attributed to the increased reactivity of the η^3-propargyl/allenyl ligand to nucleophiles as compared to the η^1-bound ligand [2c–n], or even electrophiles in the case of the bridging ligand over the Pd–Pd bond [2a].

Another interest lies in its role as the intermediate during interconversion between η^1-propargyl- and η^1-allenylmetal moieties (Scheme 1). Such interconversion is a practically important step, as is often postulated to take place in catalytic transformations with considerable ease, albeit without direct evidence [3]. On the isolable complex level, some precedents exist which described isomerization of η^1-propargyl complexes to η^1-allenyl complexes involving W, Re and Mn [4]. Mechanistic knowledge on the isomerization of propargyl/allenylpalladium complexes appears to be especially valuable because of the high synthetic applicability of these complexes. In Pd chemistry, efforts have continued which aimed at synthesizing η^1-propargyl/allenylpalladium complexes containing various substituents at both end carbons of the ligand [5] and cationic η^3-propargyl/allenylpalladium complexes [2b,c]. However, except for some stereochemical knowledge on the propargyl–allenyl interconversion [5a,b], limited information has been provided as to how such interconversion proceeded, and none has commented on the reversibility of this process. The lack of precise mechanistic support comes in part from failure of slowing down the inter-

Scheme 1.

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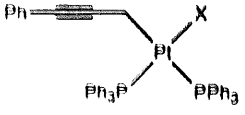
conversion rate in the palladium complexes to such an extent as to ensure accurate kinetic studies. We became interested in examining similar, but hopefully slower, propargyl–allenyl interconversion of platinum complexes in order to model the palladium system. Here we wish to describe the first reversible interconversion between η^1-propargyl- and η^1-allenylplatinum(II) complexes of which kinetic studies suggest involvement of intermediary 18-electron η^3-propargyl/allenylplatinum(II) species. Preliminary work has already been reported [6].

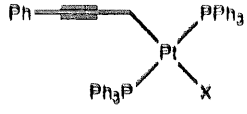
2. Results and discussion

Wojcicki and co-workers reported that reaction of $Pt(PPh_3)_2(C_2H_4)$ with $PhC{\equiv}CCH_2Br$ in hexane at 0°C initially afforded *cis*-$Pt(CH_2C{\equiv}CPh)(Br)(PPh_3)_2$ (**1b**) which subsequently isomerized to the *trans* isomer **2b** when heated in THF at 55°C [2c]. We found that the similar reaction of $Pt(PPh_3)_4$ with $PhC{\equiv}CCH_2Br$ in CH_2Cl_2 at room temperature led to isolation of only the *trans* isomer **2b** in 79% yield. The chloride complex **2a** was obtained from $PhC{\equiv}CCH_2Cl$ in a similar way. No allenylplatinum isomer contaminated **2a** or **2b**. On the other hand, the corresponding propargylpalladium analog is known to exist as a minor component of a rapidly equilibrating linkage isomer mixture [2c]; the major isomer has the Pd–allenyl bond. There is no reason to expect a different trend in linkage isomer stability between palladium and platinum complexes. Thus we examined if **2a** and **2b** undergo a linkage isomerization.



1a X= Cl

1b X= Br



2a X= Cl

2b X= Br

2c X= I

2d X= SPh

When heated in C_6D_6 at 70°C, the propargyl complex **2a** or **2b** isomerized gradually to the corresponding allenyl complex, *trans*-$Pt(CPh{=}C{=}CH_2)(X)(PPh_3)_2$ (**3a** or **3b**) (Eq. (1)), giving rise to an equilibrium mixture. The equilibrium lay in favor of **3** (**2**/**3** = 5/95). Repeated recrystallization of a benzene solution of an equilibrium mixture for **2a**/**3a** allowed us to isolate **3a**, which was stable at room temperature and fully characterized by elemental analysis and spectroscopically (see Section 3). We then confirmed that when heated in C_6D_6 at 70°C, **3a** also underwent smooth isomerization, giving rise to the same equilibrium mixture as that reached from **2a**. To our knowledge, this is the first observation of isomerization from η^1-allenyl- to η^1-propargylmetal complexes.

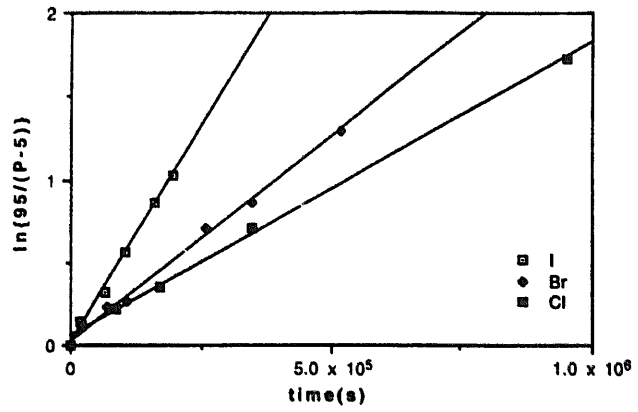
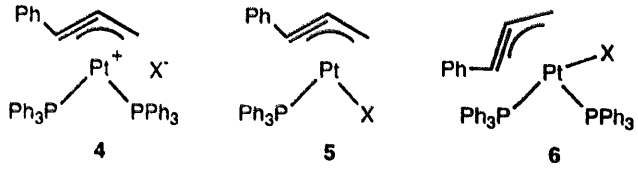
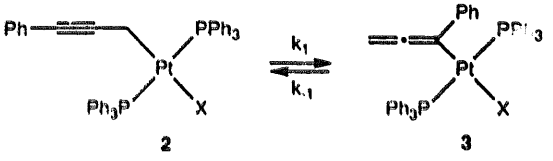


Fig. 1. First-order plot for isomerization of **2** to an equilibrium mixture of **2** and **3**. *P* denotes molar percentage of propargylplatinum complex.



4 **5** **6**

Scheme 2.

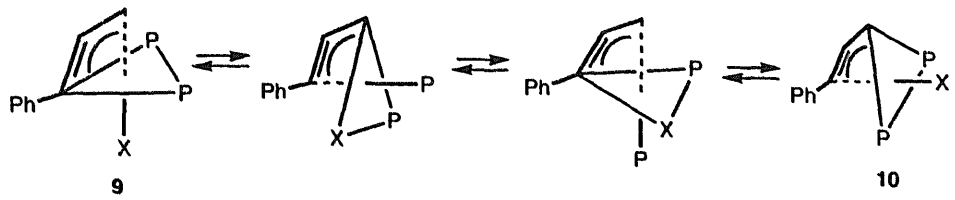


2 **3** (1)

The rate of isomerization of **2a** and **2b** was determined by following the decrease of the amount of **2** by ^{1}H NMR spectroscopy in C_6D_6 at 70°C. The iodide complex **2c** was prepared from **2a** and NaI, and subjected to a similar kinetic study of isomerization. The rate was first order in concentration of **2** for more than two half-lives, as shown in Fig. 1. From this was obtained $k_1 + k_{-1}$, and the ratio $k_1/k_{-1} = 19.0$ was determined by the relative amounts of the equilibrium composites. The rate constant k_1 increased in the order **2a** ($k_1 = 1.6 \times 10^{-6}$ s^{-1}) < **2b** ($k_1 = 2.4 \times 10^{-6}$ s^{-1}) < **2c** ($k_1 = 4.9 \times 10^{-6}$ s^{-1}) [1]. The reaction rate was not affected by adding free PPh_3 (40 mol%).

The interconversion shown in Eq. (1) may proceed via either of the following three η^3-propargyl/allenyl intermediates; cationic 16-electron complex **4** (X = Cl, Br, I), neutral 16-electron complex $Pt(\eta^3\text{-}CH_2C{\equiv}CPh)(X)(PPh_3)$ (**5**) formed by loss of PPh_3, and 18-electron complex $Pt(\eta^3\text{-}CH_2C{\equiv}CPh)(X)(PPh_3)_2$ (**6**) (Scheme 2). Among these, the intermediate **5** may not be likely in view of the insensitiveness of the reaction rate to free PPh_3 added. Moreover, ^{1}H and ^{31}P NMR data gave no evidence for dissociation of the PPh_3 ligand. The possibility of intermediate **4** seems also

[1] Rate constants increased somewhat in the presence of residual O_2; the rate data reported in Ref. [6] were obtained under such conditions.



Scheme 3.

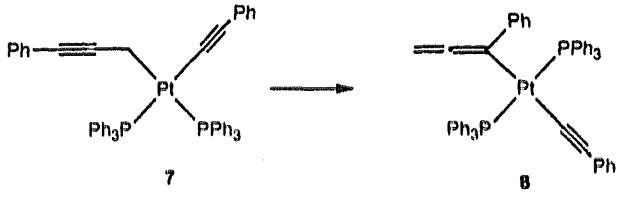
unlikely [2], since the reaction of **4** ($X=BF_4$) isolated separately with X^- ($X=Cl$, Br) never formed the η^1-allenyl–Pt framework; treatment of **4** ($X=BF_4$) with Bu_4NCl gave only **1a** at the initial stage, and a 4:1 mixture of **1a** and **2a** at the later stage (see Section 3). This is consistent with the previous report that treatment of **4** with Br^- gave a 9:1 mixture of **1b** and **2b** [2d]. Moreover, the order of the reaction rate (**2a** < **2b** < **2c**) is the reverse of the order of the ease with which X^- is liberated [7], and propargylplatinum analogs containing less ionizable ligands underwent even faster isomerization (see below).

We are led to propose that spontaneous isomerization of **2** to **3** proceeds through an intermediate of type **6** possessing an 18-electron configuration. The reactivity order (**2a** < **2b** < **2c**) may be explained by the higher electron density on the metal in **6** in this order which would cause increased π-backbonding to the η^3-bound propargyl/allenyl ligand. Alternatively, the reactivity trend is consistent with the order of the ability of X^- to stabilize the 18-electron intermediate via π-bonding [8]. In order to gain further insight into the factor which influences the stability of the 18-electron η^3-propargyl/allenyl intermediate, we then synthesized η^1-propargylplatinum(II) complexes having more donating, less dissociable ligands than the halides and examined their isomerization. These are the thiolate complex **2d** and the phenylacetylide complex *cis*-$Pt(CH_2C{\equiv}CPh)(C{\equiv}CPh)(PPh_3)_2$ (**7**).

2d was prepared from **2a** and sodium phenylthiolate in THF in moderate yield, and confirmed to have the indicated thiolate and propargyl ligands spectroscopically. However, heating a benzene solution of **2d** led to formation of an allenyl isomer to only a small extent (~ 10% in 5 h), with the major portion deactivated with respect to the isomerization. Though details remain to be established, the deactivation with regard to the isomerization is probably due to formation of the thiolate-bridging propargyl complex $[Pt(\mu\text{-SPh})(CH_2C{\equiv}CPh)(PPh_3)]_2$ and free PPh_3, as deduced from ^1H and ^{31}P NMR analysis (see Section 3). Similar dimerization via μ-SPh coordination has been found in organo(thiolate)platinum complexes [9]. At any rate, the degree of initial linkage isomerization of **2d** appears comparable to that of **2c**.

[2] Complex **2a** showed no tendency of Cl^- dissociation with concomitant η^1-propargyl coordination in marked contrast to the palladium analog, as suggested by the contrasting results obtained (no reaction for the former and η^1-propargyl complex formation for the latter) when these complexes were treated with $NaBPh_4$ [2b].

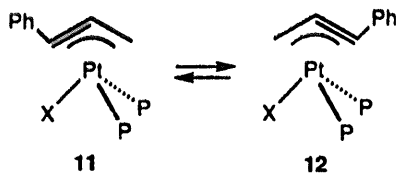
Preparation of **7** was accomplished by reaction of **2a** with PhC≡CLi which accompanied the rearrangement of *trans* to *cis* geometries of two PPh_3 ligands, as confirmed by ^{31}P NMR data. When heated at 70°C for 1 h in C_6D_6, **7** isomerized rapidly to give ~94% yield of the allenyl complex, *trans*-$Pt(CPh{=}C{=}CH_2)(C{\equiv}CPh)(PPh_3)_2$ (**8**) (Eq. (2)). Due to partial decomposition of **7** and **8** during the interconversion the accurate equilibrium composition of the reaction mixture could not be determined. However, it is remarkable that the first-order rate constant estimated from the proceeding of Eq. (2) up to ~75% conversion was 2.3×10^{-4} s^{-1} which can be compared with the much smaller values for Eq. (1) cited above. The ethynyl ligand in **7** may be even a better donor than the halide, enhancing the stability of the η^3-bound propargyl/allenyl intermediate in the linkage isomerization more efficiently. We have recently found a similar order of the ability of X (Ar > I > Cl) to stabilize η^3-coordination of the propargyl/allenyl ligand in complexes Pd(propargyl)(X)-(PPh_3) [10].



(2)

There must be several structural types of the 18-electron intermediates on the route from **2** to **3**. At the very beginning, the C≡C bond of **2** would approach the metal above the square plane, giving rise to a trigonal bipyramidal (TBP) structure **9** (Scheme 3) where two PPh_3 and CPh donors occupy the equatorial positions [3]. On similar grounds, the immediate precursor to **3** would be **10**. We assume two candidate pathways which are responsible for converting **9** to **10**. The first is pseudo-rotation of the five-coordinate complex in such a way (e.g. Scheme 3) as to avoid η^3-propargyl/allenyl coordination at the equatorial sites. The second is rotation of the η^3-propargyl/allenyl ligand about the Pt–propargyl/allenyl bond axis in **11** and **12** (Scheme 4) which would be obtained by slight deformation of **9** and **10** with respect to the intramolecular ligand–metal–ligand angles. It was predicted theoretically that a similar rotation of the η^3-allyl ligand in 18-electron $M(\eta^3\text{-allyl})L_3$ complexes does not

[3] In the ligand substitution of square-planar complexes both incoming and outgoing ligands are thought to occupy the equatorial site immediately after formation of or before cleavage of the metal–ligand bond.



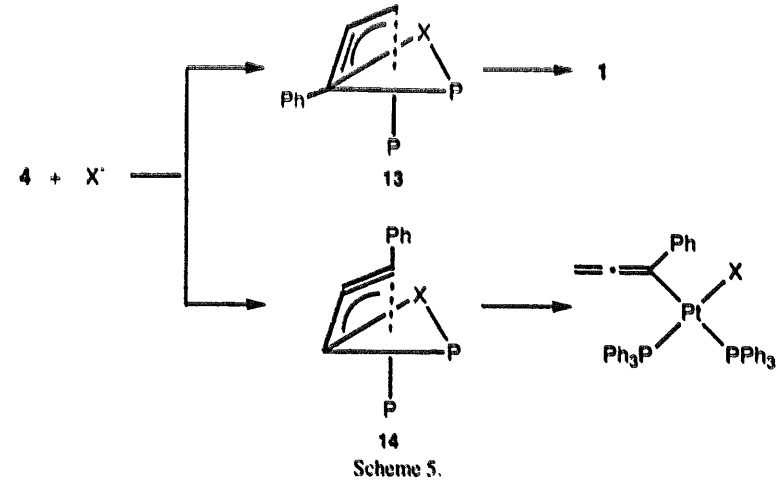
Scheme 4.

require a very high energy barrier [11]. At the moment we cannot determine which mechanism (Scheme 3 or 4) is more likely.

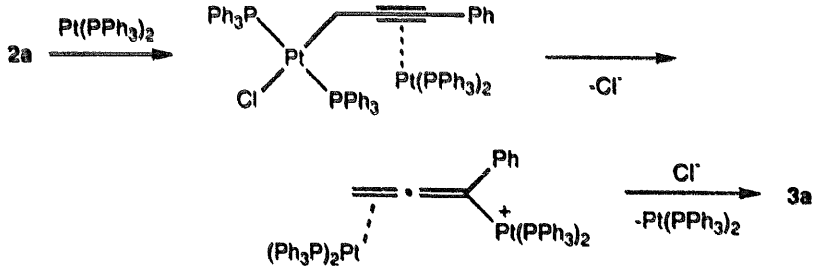
Comments should also be made as to why the attack of Cl^- or Br^- at the cationic η^3-propargyl/allenyl complex **4** gives only the propargyl isomer **1**, but not the allenyl isomer, whereas this reaction should also involve the 18-electron intermediate $Pt(\eta^3\text{-}CH_2C{\equiv}CPh)(X)(PPh_3)_2$. The incoming X^- may approach the metal above the square plane of **4**, thereby bringing either a CPh/PPh_3 set or a CH_2/PPh_3 set to the equatorial sites to give **13** or **14**, respectively (Scheme 5). The dissociation of the C≡C donor at the equatorial site in **13** would lead to the *cis*-propargyl complex **1**, while the dissociation of the $C{\equiv}CH_2$ donor in **14** would give *cis*-$Pt(CPh{\equiv}C{\equiv}CH_2)(X)(PPh_3)_2$. We assume that **14** is not formed to a significant extent upon attack of X^- at **4**, for **13** having the CPh end at the equatorial site would be sufficiently more stable than **14** having the axial CPh donor due to the less steric congestion about CPh in the former. Notice also that **13** and **14** are involved in Scheme 3 (the second complex is **14** and the third **13**). It must therefore be assumed that **13** does not undergo any pseudo-rotation step to give **14** or **10** under the conditions employed in the reaction of **4** with X^- (room temperature), which is much milder than that required for propargyl–allenyl interconversion (70°C). It should also be pointed out that the isomerization of **1** to its *trans* isomers **2**, a secondary process in the reaction of **4** with X^-, does not necessarily involve a similar type of 18-electron intermediate such as **6** or **13**. Such *cis* to *trans* isomerization can simply be catalyzed by free X^- ion via the five-coordinate η^1-propargyl intermediate $[Pt(\eta^1\text{-}CH_2C{\equiv}CPh)(X)_2(PPh_3)_2]^-$.

Finally, a possibility of propargyl to allenyl isomerization through intermolecular transfer of the organic ligand was examined. Addition of *cis*-$PtCl_2(PPh_3)_2$ to a benzene solution of **2a** did not affect the isomerization rate at all. On the other hand, the isomerization of **2a** to **3a** was accelerated by adding 0.1 equiv. of $Pt(PPh_3)_4$ or $Pt(PPh_3)_2(C_2H_4)$. Although the effect of these additives gradually faded with the prolonged heating of the reaction mixture, the increase of the rate of isomerization was clearly discernible at the initial stage of the reaction, e.g. compare the rate constant for the catalyzed reaction, $k_{initial} = 1.6\times10^{-5}\ s^{-1}$ at 70°C in C_6D_6 ($[\mathbf{2a}]_0 = 0.014$ M, $[Pt(PPh_3)_4] = 0.0014$ M up to 50% isomerization) with $k = 1.6\times10^{-6}\ s^{-1}$ for the spontaneous isomerization (see above).

The first step of the Pt(0)-catalyzed isomerization of **2** to **3** may involve approach of the $Pt(PPh_3)_2$ nucleophile at the C≡C part of **2**, followed by development of an allenyl–platinum(II) linkage. At the same time, there occurs liberation of the $Pt(PPh_3)_2$ fragment which had originally been a part of the propargyl–Pt(II) linkage of **2** (Scheme 6). This is a redox transmetallation between Pt(II) and Pt(0) fragments, analogous to the Co(III)–Co(I) transfer of the propargyl/



Scheme 5.



Scheme 6.

allenyl ligand accompanying linkage isomerization [12]. Analogous allyl group transfer between Pd(II) and Pd(0) fragments accompanying configurational inversion at the allylic sp^3 carbon has also been reported [13].

On the other hand, Pt(II)–Pt(II) transfer of the propargyl/allenyl ligand accompanying linkage isomerization appears to require a higher barrier than the Pt(II)–Pt(0) transfer discussed above. We have no explanation for this difference. A more precise mechanism for the intermolecularly catalyzed propargyl–allenyl isomerization is under intense investigation in this group.

2.1. Concluding remarks

We were able to demonstrate the first reversible interconversion between propargyl and allenyl complexes by employing the phenyl-substituted propargyl/allenylplatinum system. The corresponding palladium complexes exist also as a mixture of two isomeric forms, but the rate of interconversion is too rapid to be followed for mechanistic studies. Part of the reason for the faster isomerization of the palladium system than the platinum system is apparently the greater ease of the palladium atom to bind the propargyl/allenyl ligand in an η^3 fashion than the platinum atom, which we have demonstrated in previous work [2b]. Other than the spontaneous propargyl–allenyl interconversion, transition metal complexes with these ligands potentially undergo catalyzed interconversion, typical examples including the interconversion via redox transmetallation. We found this type of catalyzed interconversion between **2** and **3** in the presence of Pt(0) complexes.

3. Experimental

Most of the commercially available reagents were used without further purification. All manipulations were carried out under argon atmosphere by the use of standard vacuum line techniques. Solvents were dried by standard methods and distilled prior to use. ^1H and ^{31}P NMR spectra were obtained on JEOL GSX-400 and Bruker AM600 spectrometers. Internal tetramethylsilane and external $P(OMe)_3$ (143.15 ppm with respect to H_3PO_4) were used as references in ^1H and ^{31}P NMR, respectively.

3.1. Reaction of $Pt(PPh_3)_4$ with $PhC{\equiv}CCH_2X$ (X = Cl, Br)

To a CH_2Cl_2 solution (12 ml) of $Pt(PPh_3)_4$ (1.5 g, 1.21 mmol) was added 0.280 g (1.44 mmol) of $PhC{\equiv}CCH_2Br$ with stirring at room temperature. The solution changed its color gradually from yellow to pale brown. After 30 min, the solution was filtered, and the filtrate was evaporated under reduced pressure. Residues were recrystallized from CH_2Cl_2–n-hexane to give colorless solids, which were washed with n-hexane and dried; yield 79%. The product was confirmed to be *trans*-$Pt(CH_2C{\equiv}CPh)(Br)(PPh_3)_2$ by comparison of its ^1H NMR spectrum with that of an authentic sample [2c]. The analogous reaction of $PhC{\equiv}CCH_2Cl$ gave a similar result; yield of *trans*-$Pt(CH_2C{\equiv}CPh)(Cl)(PPh_3)_2$, 79%; m.p. 178–183°C (dec.). ^1H NMR (C_6D_6): 1.75 (t, J_{HP} = 7.8 Hz, J_{HPt} = 99.9 Hz, 2H). *Anal.* Calc. for $C_{45}H_{37}P_2ClPt$: C, 62.11; H, 4.29. Found: C, 61.79; H, 4.44%. The *cis* isomer *cis*-$Pt(CH_2C{\equiv}CPh)(Cl)(PPh_3)_2$ was obtained from $Pt(PPh_3)_2(C_2H_4)$ and $PhC{\equiv}CCH_2Cl$ in benzene. ^1H NMR (C_6D_6): 2.80 (dd, J_{HP} = 6.2, 9.2 Hz, J_{HPt} = 76.2 Hz, 2H). ^{31}P NMR (C_6D_6): −121.76 (d, J_{PP} = 16.1 Hz, J_{PPt} = 1834 Hz), −124.45 (d, J_{PP} = 16.1 Hz, J_{PPt} = 4440 Hz).

3.2. Preparation of trans-$Pt(CH_2C{\equiv}CPh)(I)(PPh_3)_2$

To a CH_2Cl_2 solution (3 ml) of **2a** (90 mg, 0.10 mmol) was added NaI (47 mg, 0.31 mmol) in 1 ml of acetone, and the mixture stirred for 3 min. The residues obtained by evaporation of the solvents were recrystallized from CH_2Cl_2–n-hexane to give pale yellow solids; yield 27 mg (27%); m.p. 112–117°C. ^1H NMR (C_6D_6): 1.99 (t, J_{HP} = 8.1, J_{HPt} = 98 Hz, 2H). *Anal.* Calc. for $C_{45}H_{37}P_2IPt$: C, 56.20; H, 3.88. Found: C, 55.90; H, 4.09%.

3.3. Preparation of trans-$Pt(CH_2C{\equiv}CPh)(SPh)(PPh_3)_2$

To a THF solution (8 ml) of **2a** (88 mg) was added NaSPh (27 mg) at room temperature. The mixture was stirred for 30 min, and the solvent evaporated under vacuum. The residue was extracted with CH_2Cl_2, and the CH_2Cl_2 solution washed with water and dried with $MgSO_4$. Crystallization from CH_2Cl_2–n-hexane gave 52 mg (54%) of yellow products; m.p. 154–158°C. ^1H NMR (C_6D_6): 2.00 (t, J_{HP} = 7.3 Hz, J_{HPt} = 79.9 Hz, 2H). ^{31}P NMR (C_6D_6): −117.5 (s, J_{PPt} = 3150 Hz). *Anal.* Calc. for $C_{51}H_{42}P_2SPt$: C, 64.89; H, 4.48. Found: C, 64.63; H, 4.56%.

3.4. Preparation of cis-$Pt(CH_2C{\equiv}CPh)(C{\equiv}CPh)(PPh_3)_2$

To a dry THF solution (6 ml) of *trans*-$Pt(CH_2C{\equiv}CPh)(Cl)(PPh_3)_2$ (201 mg; 0.231 mmol) at −78°C was added $PhC{\equiv}CLi$ (0.347 mmol), which had been prepared from $PhC{\equiv}CH$ and ^{n}BuLi in THF (1.1 ml). The reaction mixture was stirred for 5 min at this temperature, and then warmed to room temperature. To this mixture was added a few drops of methanol, and then 50 ml of CH_2Cl_2. The solution was washed with water (twice) and brine (once). The organic layer was dried over $MgSO_4$. The solvents were evaporated to dryness under reduced pressure. Residual solids were recrystallized from CH_2Cl_2–n-hexane to give yellow solids (108 mg, 50%); m.p. 120–125°C (dec.). ^1H NMR (C_6D_6): 2.96 (dd, J_{HP} = 9.3, 10.4 Hz, J_{HPt} = 90.0 Hz, 2H). ^{31}P NMR (C_6D_6): −126.6 (d, J_{PP} = 17.8 Hz, J_{PPt} = 1756 Hz), −118.4 (d, J_{PP} = 17.8 Hz, J_{PPt} = 2727 Hz). *Anal.* Calc. for $C_{53}H_{42}P_2Pt$: C, 68.02; H, 4.52. Found: C, 68.04; H, 4.80%.

3.5. Preparation of trans-Pt(CPh=C=CH$_2$)(C≡CPh)(PPh$_3$)$_2$

A dry benzene solution (10 ml) of *cis*-Pt(CH$_2$-C≡CPh)(C≡CPh)(PPh$_3$)$_2$ (111 mg) was stirred for 2 h at 70°C. The reaction mixture was filtered, and the filtrate was concentrated under reduced pressure. Residues were recrystallized from benzene–n-hexane to give brown solids (85 mg, 77%); m.p. 165–170°C (dec.). ^{1}H NMR (C_6D_6): 3.47 (t, J_{HP} = 4.0 Hz, J_{HPt} = 32.8 Hz, 2H). ^{31}P NMR (C_6D_6): −122.3 (s, J_{PPt} = 2918 Hz). *Anal.* Calc. for $C_{53}H_{42}P_2Pt$: C, 68.02; H, 4.52. Found: C, 68.14; H, 4.66%.

3.6. Kinetic measurements

To a C_6D_6 solution (0.7 ml) of complex **1** (0.01 mmol) in an NMR tube was added an appropriate amount of dioxane as internal standard. The NMR tube was sealed under vacuum, and heated at 70°C in an oil bath. The isomerization was monitored by ^{1}H NMR spectroscopy measured at 25°C. Plots of ln 95/(P − 5) versus time gave straight lines (P: molar percent of the propargyl isomer), as shown in Fig. 1, from whose slope $k_1 + k_{-1}$ can be obtained.

3.7. Preparation of trans-Pt(CPh=C=CH$_2$)(Cl)(PPh$_3$)$_2$

A benzene solution (70 ml) of an equilibrium mixture of **2a** and **3a** obtained from 0.28 g of **2a** (0.32 mmol) was passed through a short Florisil column. The solvent was evaporated completely. Recrystallization of the residue from CH_2Cl_2–n-hexane afforded 0.06 g (23%) of brownish solids; m.p. 180–185°C (dec.). ^{1}H NMR (C_6D_6): 3.51 (t, J_{HP} = 3.5 Hz, J_{HPt} = 52.7 Hz, 2H). *Anal.* Calc. for $C_{45}H_{37}P_2ClPt$: C, 62.11; H, 4.29. Found: C, 61.87; H, 4.56%.

3.8. Reaction of [Pt(η^3-CH$_2$C≡CPh)(PPh$_3$)$_2$]BF$_4$ with Bu$_4$N$^+$Cl$^-$

A mixture of [Pt(η^3-CH$_2$C≡CPh)(PPh$_3$)$_2$]BF$_4$ (0.01 mmol), obtained from **2b** and AgBF$_4$ [2c], and Bu$_4$N$^+$Cl$^-$ (0.015 mmol) was treated with C_6D_6 (0.6 ml) in an NMR tube. The tube was rigorously shaken, and sealed. ^{1}H NMR spectra immediately after the sealing showed almost quantitative formation of **1a**. **1a** isomerized to **2a** slowly in the reaction mixture (**1a**/**2a** = 80/20 after 2.5 h).

3.9. Thermolysis of 2d

In an NMR tube was placed 9.5 mg of **2d** and 0.9 ml of C_6D_6, and the tube sealed under Ar atmosphere. After being heated at 70°C for 1 h, the tube was examined by ^{1}H and ^{31}P NMR spectroscopy to show formation of the following new complexes. Complex A: ^{1}H NMR: 1.96 (d, J_{HP} = 5.4, J_{HPt} = 93 Hz); ^{31}P NMR: −120.0 (s, J_{PPt} not determined). Complex B: ^{1}H NMR: 2.03 (d, J_{HP} = 5, J_{HPt} = 91 Hz); ^{31}P NMR: −122.6 (s, J_{PPt} = 3939 Hz). Complex C: ^{1}H NMR: 3.49 (t, J_{HP} = 3.8, J_{HPt} = 45 Hz); ^{31}P NMR: −123.9 (s, J_{PPt} = 3032 Hz). A ^{31}P peak of free PPh$_3$ having an intensity comparable to that of A + B was also observed. Relative ^{31}P peak ratio for **2d**:A:B:C was 50:14:26:10. We tentatively assign complexes A and B to a pair of geometrical isomers of [Pt(μ-SPh)(CH$_2$C≡CPh)(PPh$_3$)]$_2$, and complex C to *trans*-Pt(CPh=C=CH$_2$)(SPh)(PPh$_3$)$_2$. Heating further the NMR tube resulted in a decrease of the ^{31}P resonance for **2d** and increase of those for A, B and C with a similar peak ratio to that described above.

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