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A Simple Ag(I)-Enyne Cation

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Abstract

A simple cationic Ag(I)-1,3-enyne complex was synthesized and characterized. In the solid state, single crystal X-ray crystallography showed the Ag(I) centre bonded in an asymmetric manner exclusively to the alkyne portion of the substrate. NMR spectroscopy studies showed this structure is maintained in solution over the temperature range of -90 to +60 °C.

Keywords

Silver; 1,3-enyne; X-ray crystallography; Cation.

Introduction

Gold-mediated cycloisomerization of enynes represent an important class of reactions. A plethora of gold(I) complexes and enyne substrates have been employed to access a variety of products with increased molecular complexity under very mild reaction conditions.^[1-6] The mechanism is presumed to proceed *via* initial coordination of the gold(I) moiety to the alkyne which enhances its electrophilicity allowing for subsequent nucleophilic attack from the alkene.^[7-8] However, low temperature NMR spectroscopy investigations indicated no preference between alkyne and alkene coordination, suggesting that the procedure may be kinetically rather than thermodynamically controlled.^[9] Recently, there has been some progress in isolating intermediates proposed for enyne cycloisomerization reactions. Widenhoefer and co-workers prepared the gold(I)-bicyclo[3.2.0]hept-1(7)-ene complex (by NMR spectroscopy), an actual intermediate in the cycloisomerization of 1,6-enyne (Scheme 1a).^[10] Similarly Ballesteros and co-workers detected and characterized η^1 -allylic gold(I) cation, a proposed key intermediate in 1,5-enyne cycloisomerization reaction (Scheme 1b).^[11]

Scheme 1. Experimentally observed reaction intermediates for gold(I) catalyzed; a) 1,6-enyne cycloisomerization and b) 1,5-enyne cycloisomerization reactions

Gold(I) mediated organic transformations commonly employ silver(I) salts to generate, *in situ*, cationic species of the type $[\text{LAu}][\text{X}]$ (where L = phosphine, N-heterocyclic carbenes or related ancillary ligands), rendering them more Lewis acidic and hence promoting their reactivity. On their own, the silver(I) salts and their complexes are moderately Lewis acidic in their own right and are known to promote a myriad of organic transformations.^[12-14] In some cases, the catalytic efficiency of silver(I) complexes are comparable to well established transition metal counterparts such as gold(I).^[15] Indeed, the role of silver in catalytic reactions ascribed to gold is a hotly debated topic. Given this context, it is unsurprising to find elegant examples of silver(I) catalysis. For example, Porcel and Echavarren reported the first examples of skeletal rearrangements and intramolecular cyclopropanation reactions of 1,6-enynes catalyzed by variety of silver(I) complexes bearing phosphine ligands.^[16] These reactions were proposed to proceed *via* initial selective activation alkyne unit by silver(I) complexes, in an analogous mode to their gold(I) counterparts.

In seeking to find evidence of how these coinage metal cations bind to enynes, we employed a 1,3-enyne, which prevents intramolecular rearrangement of the organic substrate on steric grounds and hence allows insight into the binding of the metal to the substrate.

Results and discussion

Reactions with gold cations proved to be extremely complicated, as shown by the study of 1-ethynylcyclohexene and an *in situ* generated gold(I) cation (generated from the mixture of a stoichiometric ration of $[P(^t\text{Bu})_2(o\text{-biphenyl})\text{AuCl}]$ and AgSbF_6 in CH_2Cl_2). After only two minutes, numerous products were observed (^1H NMR spectroscopy) which are currently unidentified, but none of which were consistent with a simple binding event. We thus turned our attention to the corresponding silver(I) complex.

Monitoring the reaction (CH_2Cl_2 , room temp, strictly in the absence of light) of the acetonitrile-ligated Ag(I) source, $[P(^t\text{Bu})_2(o\text{-biphenyl})\text{AgNCCH}_3][\text{SbF}_6]$ (**1**) with an excess of 1-ethynylcyclohexene (Scheme 2), showed, after an hour of stirring, that the ^{31}P NMR signal for the starting material, **1**, ($\delta = 46.04$ ppm) had been replaced by a marginally upfield signal for the product, **2**, at $\delta = 45.58$ ppm. Product **2** proved to be very sensitive both in solution and in the solid state (*vide infra*), decomposing rapidly (with the formation of metallic silver deposits) upon exposure to air, moisture of light.

Further insight into the composition of **2** was seen from the ^1H NMR spectrum whose acetylenic resonance (3.46 ppm) was significantly downfield shifted compared to the free enyne substrate (2.82 ppm); in comparison the alkene proton resonance remained less perturbed (6.46 ppm compared to 6.16 ppm in the starting material). Variable temperature ^1H and ^{31}P NMR studies of **2** between -90 °C to $+60$ °C remained largely unchanged. Furthermore, solution infrared spectroscopy studies on **2** showed a reduced $\text{C}\equiv\text{C}$ bond stretching frequency (2029 cm^{-1} compared to 2089 cm^{-1} in the free substrate), together with an unchanged $\text{C}=\text{C}$ bond stretching frequency. These observations support the proposition that the Ag unit binds exclusively to the alkyne moiety in solution.

Scheme 2. Synthesis of [(C₆H₉C≡CH)Ag(P(^tBu)₂(*o*-biphenyl))][SbF₆] (**2**).

This acetylinic binding is also seen in the solid state, as shown by a single crystal X-ray diffraction study using crystals grown by layering a saturated CH₂Cl₂ solution of **2** with *n*-hexane which contained additional 1-ethynylcyclohexene (~2 equiv.). The molecular structure of **2** showed the formation of an ion-separated complex with an asymmetric coordination of silver(I) across the alkyne unit (approx. 19% metal slippage in the direction of –CH end of the C≡C unit) (Figure 1). This slippage of silver moiety across the C≡C triple bond is presumably due to the stabilisation of resulting partial positive charge on C2 through the conjugation with C=C double bond. This suggestion is reinforced by the shorter C2-C3 bond distance (1.442(2) Å) and the slightly elongated C3-C4 bond (1.347(3) Å). Interestingly, the C≡C bond length (1.207(3) Å) itself is unperturbed by the binding of the silver cation when compared to a typical alkyne C≡C bond length of 1.202(5) Å,^[17-19] and also to some reported Ag(I)-alkyne complexes.^[20] In addition, the bond distances Ag1-C1 (2.2918(17) Å) and Ag1-C2 (2.4111(16) Å) in **2** are considerably longer when compared to the reported Ag(I)-alkyne complexes.^[18-21] These observations suggest a weak interaction between Ag(I) cation and the enyne substrate.

The solid-state structure also shows a strong Ag⋯arene interactions with the flanking *o*-biphenyl ring of the phosphine ligand, P(Bu^t)₂(*o*-biphenyl). The shortest Ag⋯C contacts were established with an *ortho* carbon (Ag1-C20 2.649 Å) and the *ipso* carbon (Ag1-C15 2.981 Å) of the biphenyl unit. These distances are substantially shorter than the 3.03 Å^[22-23] which has been suggested represent a significant interaction between the two units. This suggestion is reinforced by inspection of the P1-Ag1-(C≡C_{centroid}) angle, which at 154.30° is significantly deviated from linearity.

Figure. 1 Thermal ellipsoid plot of the cation of **2** shown at 50% probability level; the $[\text{SbF}_6]^-$ anion and all hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (°): Ag1-C1 2.2918(17), Ag1-C2 2.4111(16), C1-C2 1.207(3), C2-C3 1.442(2), C3-C4 1.347(3); P1-Ag1-C1 163.83(5), P1-Ag1-C2 141.85(4).

Conclusions

In conclusion, we have successfully isolated and characterized the first example of a simple silver(I)-enyne cation. Solution NMR and IR spectroscopy studies and a single crystal X-ray diffraction experiment suggest the exclusive asymmetric coordination of silver(I) across the $\text{C}\equiv\text{C}$ unit.

Experimental

Synthesis of 2: To a solution of **1** (0.071 g, 0.1 mmol) in dichloromethane (2 cm^3) was added the 1-ethynylcyclohexene (0.106 g, 1.0 mmol). The solution was stirred for 1 h in the absence of light and then filtered (porosity 3 sinter with Celite), and washed with dichloromethane ($3 \times 3\text{ cm}^3$). The volatiles were removed *in vacuo* and the solid washed with *n*-hexane ($3 \times 5\text{ cm}^3$) and dried to give **2** as a yellowy-green solid (0.054 g, 70%).

Single crystals suitable for analysis by X-ray crystallography were grown by layering CH₂Cl₂ solution (~1 cm³) of **2** with *n*-hexane (~6 cm³) at 4 °C.

‡ **Crystal data for 2:** C₂₈H₃₇AgPF₆Sb, *M* = 748.18, orthorhombic, *a* = 18.1354(7) Å, *b* = 16.0145(6) Å, *c* = 20.5280(8) Å, $\alpha = 90^\circ$, $\beta = 90^\circ$, $\gamma = 90^\circ$, *V* = 5961.9(4) Å³, *T* = 100 K, space group *Pbca*, *Z* = 8, $\mu(\text{MoK}\alpha) = 1.670 \text{ mm}^{-1}$, 96163 reflections measured, 6931 independent reflections (*R*_{int} = 0.0264). The final *R*₁ [*I* > 2σ(*I*)] was 0.0172 and the final *wR*(*F*₂) was 0.0420 (all data). The final *R*₁ values were 0.0200 (*I* > 2σ(*I*)). The final *wR*(*F*²) values were 0.0434 (*I* > 2σ(*I*)). The goodness of fit on *F*² was 1.030. CCDC 1442998

¹H NMR (300 MHz, 22 °C, CD₂Cl₂) δ 1.31 (d, *J* = 16 Hz, 18H), 1.50-1.69 (m, 4H), 2.00-2.19 (m, 4H), 3.46 (s, 1H), 6.35-6.54 (m, 1H), 7.21-7.38 (m, 3H), 7.51-7.69 (m, 5H), 7.87-8.01 (m, 1H) ppm.

¹³C{¹H} NMR (75 MHz, 22 °C, CD₂Cl₂) δ 28.52, 29.30, 31.04 (d, *J*(¹³C-³¹P) = 2 Hz), 32.12, 35.80 (d, *J*(¹³C-³¹P) = 5 Hz), 36.01, 71.41 (m, C≡CH), 90.89 (m, C≡CH), 117.89 (m, C=CH), 126.17 (d, *J*(¹³C-³¹P) = 31 Hz), 128.55, 129.10, 129.83, 130.62, 131.71, 132.38, 132.81 (d, *J*=6.49 Hz), 142.94, 149.21 ppm. One of the resonances for a quaternary carbon centre was not observed.

³¹P{¹H} NMR (162 MHz, 22 °C, CD₂Cl₂) δ 45.6 ppm.

Elemental Analysis: Found, C 43.16% H 4.97%. Calculated (for C₂₈H₃₇AgPF₆Sb): C 44.95% H 4.98%. Despite repeated attempts, satisfactory carbon content could not be obtained, presumably as a result of metal carbide formation upon attempted thermolysis.

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