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Solid-State and Dynamic Solution Behavior of a Cationic, Two-Coordinate Gold(I) π-Allene Complex

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Summary: The cationic gold π-allene complex $\{[P(t\text{-}Bu)_2o\text{-}biphenyl]Au[\eta^2\text{-}H_2C{=}C{=}C(CH_3)_2]\}^+SbF_6^-$ *was isolated in 98% yield from reaction of 3-methyl-1,2-butadiene with a mixture of* $[P(t\text{-}Bu)_2o\text{-}biphenyl]AuCl$ *and* $AgSbF_6$ *and was characterized by X-ray crystallography and variable-temperature NMR spectroscopy. These studies revealed preferential binding of gold to the less substituted C=C bond of the allene in both the solid state and solution and also revealed fluxional behavior consistent with π-face exchange of the allene ligand via an η^1-C2 allene intermediate or transition state.*

Over the past 10 years considerable progress has been made in the utilization of soluble gold complexes, in particular cationic gold(I) complexes, as catalysts for the electrophilic activation of C–C multiple bonds.[1] Allenes have played a central role in the development of this chemistry, not only as substrates but also as intermediates and products.[1] Although it is widely assumed that gold π-allene complexes are generated as reactive intermediates in these transformations, no well-defined gold π-allene complex has been documented.[2] As such, information regarding the structure and behavior of gold π-allene complexes is limited to that provided by recent computational studies[3,4] or gleaned from related transition metal π-allene complexes[5–10] and gold π-complexes.[11,12] Here we report the synthesis, X-ray crystal structure, and fluxional behavior of a cationic, two-coordinate gold(I) π-allene complex.

Reaction of 3-methyl-1,2-butadiene with a mixture of $[P(t\text{-}Bu)_2o\text{-}bipheny]AuCl$ (**1**) and $AgSbF_6$ (1:1) employing a procedure similar to that used for the synthesis of cationic gold(I) π-alkene complexes[12] (excess allene, room temperature, ~12 h) led to formation of black suspensions that contained only traces of $\{[P(t\text{-}Bu)_2o\text{-}biphenyl]Au[\eta^2\text{-}H_2C{=}C{=}C(CH_3)_2]\}^+SbF_6^-$ (**2**) as determined by ^1H NMR analysis.

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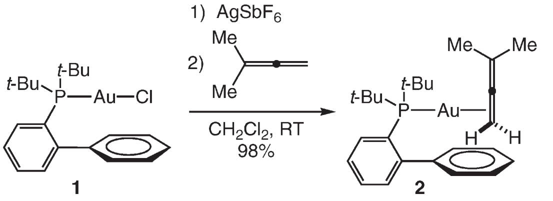

(1)

Key to the isolation of pure **2** was lower allene concentration coupled with shorter reaction time. For example, treatment of a methylene chloride suspension of **1** and $AgSbF_6$ (1:1) with 3-methyl-1,2-butadiene (1.5 equiv) at room temperature for 15 min led to isolation of **2** in 98% yield as an air and thermally stable white solid that was characterized by spectroscopy, elemental analysis, and X-ray crystallography (eq 1).[13,14]

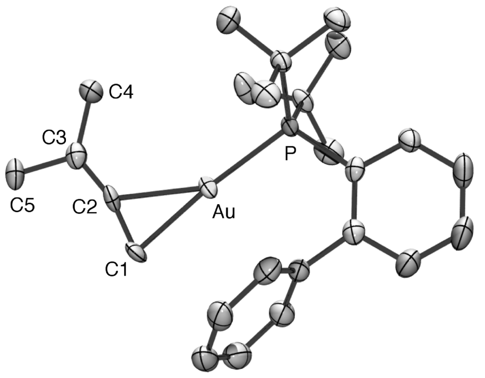

Figure 1. ORTEP diagram of $\mathbf{2}\cdot{}^1/_2CH_2Cl_2$. Ellipsoids are shown at 50% probability. Solvent, counterion, and hydrogen atoms are omitted for clarity. Key bond lengths (Å) and bond angles (deg): C1−C2 = 1.340, C2−C3 = 1.311, Au−C1 = 2.191, Au−C2 = 2.306, C1−C2−C3 = 165.0, P−Au−C1=C2$_{(cent)}$ = 167.3.

Slow diffusion of hexanes into a CH_2Cl_2 solution of **2** at 4 °C gave colorless crystals of $\mathbf{2}\cdot{}^1/_2CH_2Cl_2$ suitable for X-ray analysis (Figure 1).[14] In the solid state, the 3-methyl-1,2-butadiene ligand of **2** is bound unsymmetrically to gold through the less substituted C1=C2 π-bond with a shorter Au−C1 and a longer Au−C2 interaction (Δd = 0.116 Å). Complex **2** adopts a distorted linear conformation with a P−Au−C=C$_{(cent)}$ angle of 167° and with the uncomplexed portion of the allene directed away from the protruding phenyl group of the *o*-biphenyl moiety. Within the allene ligand, the coordinated C1=C2 bond is elongated by ~0.03 Å relative to the uncomplexed C2=C3 bond, and the allene unit is bent with a C1−C2−C3 angle of 165° (Figure 1).

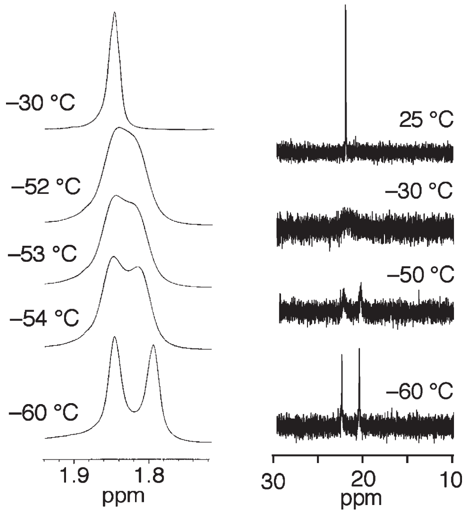

Figure 2. Partial variable-temperature ^1H (left) and ^{13}C (right) NMR spectra of **2** in CD_2Cl_2.

π-Complexation of the 3-methyl-1,2-butadiene group of **2** to gold through the less substituted C1=C2 bond in solution was established by ^{13}C and ^1H NMR spectroscopy at −60 °C. In particular, the ^{13}C NMR chemical shifts of the allenyl carbon atoms of **2** [δ 105.6 (CMe$_2$), 197.0 (=C=), 63.1 (CH_2)] were shifted significantly from those of free 3-methyl-1,2-butadiene [δ 94.4, 205, 72.6], and resonances corresponding to diastereotopic allenyl methyl groups were observed in both the ^{13}C (δ 22.3 and 20.3) and ^1H (δ 1.85 and 1.80) NMR spectra (Figure 2). The presence of a single allenyl proton resonance in the ^1H NMR spectrum of **2** at δ 4.07 indicates that the allenyl protons adopt either a static or time-averaged orientation about the pseudo-mirror plane that reflects the two *tert*-butyl groups, as was observed in the solid state. As the temperature was raised, the allenyl methyl resonances broadened and coalesced, forming single time-averaged resonances in both the ^{13}C (δ 21.9 at 25 °C) and ^1H (δ 1.85 at −30 °C) NMR spectra (Figure 2). The allenyl proton resonance in the ^1H NMR spectrum shifted slightly with increasing temperature, but was otherwise unchanged. An energy barrier of $\Delta G^{\ddagger}_{220K}$ = 11.0 kcal mol^{-1} for interconversion of the allenyl methyl groups of **2** was determined from a peak separation of $\Delta\nu$ = 26 Hz and coalescence temperature of −53 °C in the ^1H NMR spectrum [$k = \pi(\Delta\nu)/\sqrt{2}$].

The rate of methyl group interconversion of **2** was independent of concentration (25−50 mM), which argues against an intermolecular exchange mechanism. Rather, the minimal intramolecular process that accounts for interconversion of the allenyl methyl groups of **2** involves migration of gold between orthogonal allene π-faces via an η^1-C2 allene intermediate or transition state in which gold is positioned 45° relative to the orthogonal π-faces (Scheme 1). Similar π-face exchange processes have been documented for Fe(0),[5] Fe(II),[6] and Pt(II)[7,8] π-allene complexes, and the involvement of η^1-allene complexes in these processes is supported by both experimental observation[6,7,9] and computational analyses.[3] Although an η^1-allyl cation intermediate or transition state would also account for the observed π-face exchange behavior of **2**, analysis of the fluxional behavior of cationic Fe(II) π-allyl complexes ruled out the involvement of an

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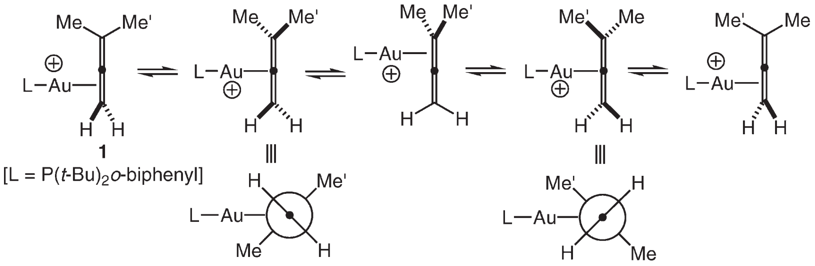
[13] Experimental details for **2**: 3-Methyl-1,2-butadiene (7.7 mg, 0.11 mmol) was added via syringe to a stirred suspension of **1** (40 mg, 0.075 mmol) and $AgSbF_6$ (26 mg, 0.075 mmol) in CH_2Cl_2 (2 mL), and the reaction mixture was stirred at room temperature for 15 min. The resulting suspension was filtered through a pad of Celite, which was flushed with additional CH_2Cl_2. The filtrate was concentrated to ~2 mL, diluted with one volume of hexanes, and cooled at 4 °C for 24 h to form **2** (59 mg, 98%) as a white solid. ^1H NMR (500 MHz, 25 °C): δ 7.95−7.87 (m, 1H), 7.68−7.59 (m, 2H), 7.54−7.47 (m, 3H), 7.33−7.20 (m, 3H), 4.21 (sept, J = 2.8 Hz, 2H), 1.90 (t, J = 2.8 Hz, 6H), 1.44 (d, J = 16.4 Hz, 18H). $^{13}C\{^1H\}$ NMR (126 MHz, 25 °C): δ 197.0, 148.8, 143.6 (d, J = 6.9 Hz), 134.4 (d, J = 33.3 Hz), 133.7, 132.2, 130.2, 129.7, 129.5, 128.4, 124.6 (d, J = 43.9 Hz), 105.6, 63.1, 39.3 (d, J = 23.8 Hz), 31.3 (d, J = 6.8 Hz), 21.9. $^{31}P\{^1H\}$ NMR (202 MHz, 25 °C): δ 66.5. Anal. Calcd (found) for $C_{25}H_{35}PF_6AuSb$: H, 4.41 (4.44); C, 37.57 (37.72).

[14] X-ray data for **2**: triclinic, $P\bar{1}$, T = 173 K, a = 7.8865(11) Å, b = 11.4932(16) Å, c = 16.466(2) Å, α = 98.452(8)°, β = 94.196(8)°, γ = 96.769(8)°, V = 1459.8(3) Å^3, Z = 2, $R[F^2 > 2\sigma(F^2)]$ = 0.032, w$R(F^2)$ = 0.077.

Scheme 1



η^1-allyl cation species in the lowest energy π-face exchange process,[6] a conclusion that is supported by the computational studies of Malacria and co-workers.[3] Also worth noting is that the computational analysis of Malacria and co-workers suggests that the allene moiety of Au(I), Au(III), and Pt(II) η^1-allene complexes adopts a bent conformation (C1−C2−C3 = 129−140°) and that the η^1-allene complexes of $(PMe_3)Au^+$ exist as transition states rather than as local minima.[3]

In summary, we have synthesized $\{[P(t\text{-Bu})_2o\text{-biphenyl}]Au[\eta^2\text{-}H_2C{=}C{=}C(CH_3)_2]\}^+SbF_6^-$ (**2**), which represents the first example of a gold π-allene complex. Solution and solid-state analysis of **2** established preferential binding of gold to the less substituted C=C bond of the allene. Variable-temperature NMR analysis revealed fluxional behavior consistent with facile π-face exchange of the allene ligand via an η^1-allene intermediate or transition state. More thorough studies regarding the structure, fluxional behavior, and reactivity of cationic gold π-allene complexes will be reported in due course.

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Supporting Information Available: X-ray crystallographic data. This material is available free of charge via the Internet at http://pubs.acs.org.