## Synthesis and Study of Cationic, Two-Coordinate Triphenylphosphine– Gold-π Complexes

### Rachel E. M. Brooner, Timothy J. Brown, and Ross A. Widenhoefer\*<sup>[a]</sup>

**Abstract:** Cationic, two-coordinate triphenylphosphine–gold(I)– $\pi$  complexes of the form [(PPh<sub>3</sub>)Au( $\pi$  ligand)]<sup>+</sup> SbF<sub>6</sub><sup>-</sup> ( $\pi$  ligand=4-methylstyrene, **1**·SbF<sub>6</sub>), 2-methyl-2-butene (**3**·SbF<sub>6</sub>), 3-hexyne (**6**·SbF<sub>6</sub>), 1,3-cyclohexadiene (**7**·SbF<sub>6</sub>), 3-methyl-1,2-butadiene (**8**·SbF<sub>6</sub>), and 1,7-diphenyl-3,4-heptadiene (**10**·SbF<sub>6</sub>) were generated in situ from reaction of [(PPh<sub>3</sub>)AuCl],

AgSbF<sub>6</sub>, and  $\pi$  ligand at -78 °C and were characterized by low-temperature, multinuclear NMR spectroscopy without isolation. The  $\pi$  ligands of these complexes were both weakly bound and kinetically labile and underwent

**Keywords:** alkene ligands  $\cdot$  allenes  $\cdot$  diene ligands  $\cdot$  gold  $\cdot \pi$  complexes

### Introduction

The utilization of soluble, gold(I) complexes as catalysts for organic transformations has increased significantly over the last decade.<sup>[1-4]</sup> In particular, cationic gold(I) complexes have been applied extensively as catalysts for the electrophilic activation of C–C  $\pi$  bonds. Included in this family of transformations are the gold(I)-catalyzed hydrofunctionalization of C-C multiple bonds with carbon and heteroatom nucleophiles and the gold(I)-catalyzed cycloaddition of enynes and related substrates.<sup>[3,4]</sup> Although a number of sterically hindered, electron-rich supporting ligands, such as Nheterocyclic carbenes (NHCs) and dialkyl o-biphenylphosphines, have been employed to good effect in gold(I) catalysis, the simplest triarylphosphine, triphenylphosphine, remains the workhorse ligand in gold(I) catalysis. In addition, axially chiral bis(triarylphosphines) remain the most common ligands utilized in enantioselective gold π-activation catalysis.<sup>[2]</sup>

Although direct experimental evidence is limited,<sup>[5-7]</sup> the mechanisms most often invoked for gold(I)  $\pi$ -activation catalysis involve activation of the C–C multiple bond through coordination to the carbophilic gold(I) center followed by outer-sphere addition of the nucleophile to the  $\pi$  ligand.<sup>[6]</sup> Due to the central role of gold– $\pi$  complexes in these mechanisms, there has been recent interest in the synthesis and

[a]	R. E. M. Brooner, Dr. T. J. Brown, Prof. R. A. Widenhoefer
	Department of Chemistry, Duke University
	French Family Science Center
	Durham, NC 27708 (USA)
	Fax: (+1)919-660-1605
	E-mail: rwidenho@chem.duke.edu

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free ligand ( $\Delta G^{\pm} \approx 9 \text{ kcal mol}^{-1}$  in the case of **6**·SbF<sub>6</sub>) and competitive displacement by weak  $\sigma$  donors, such as trifluoromethane sulfonate. Triphenylphosphine–gold(I)– $\pi$  complexes were thermally unstable and decomposed above –20 °C to form the bis(triphenylphosphine) gold cation [(PPh<sub>3</sub>)<sub>2</sub>Au]<sup>+</sup> SbF<sub>6</sub><sup>-</sup> (**2**·SbF<sub>6</sub>).

facile intermolecular exchange with

study of cationic, two-coordinate gold– $\pi$  complexes.<sup>[7]</sup> From these efforts, a number of mononuclear, cationic gold(I) complexes containing a  $\pi$  alkene,<sup>[8,9]</sup> alkyne,<sup>[10,11]</sup> allene,<sup>[12]</sup> conjugated diene,<sup>[13,14]</sup> or arene<sup>[15,16]</sup>  $\pi$  ligand and a sterically hindered, electron-rich supporting ligand, such as 1,3-bis-(2,6-diisopropylphenyl)-1,3-dihydro-2H-imidazol-2-ylidene (IPr), P(*t*Bu)<sub>3</sub>, or P(*t*Bu)<sub>2</sub>-*o*-biphenyl, have been isolated and characterized both in the solid state and in solution. Conversely, mononuclear, cationic, two-coordinate gold– $\pi$  complexes containing a triphenylphosphine ligand have not been isolated.<sup>[17]</sup>

Although monomeric triphenylphosphine-gold- $\pi$  complexes have escaped isolation, a number of these complexes have been purportedly generated in situ from reaction of a  $\pi$  ligand with either a mixture of [(PPh<sub>3</sub>)AuCl] and silver salt or with a single-component gold complex, such as [(PPh<sub>3</sub>)AuNTf<sub>2</sub>].<sup>[18-23]</sup> However, there are a number of inconsistencies in the reported spectroscopy and solution behavior of these complexes that warrant further investigation. In most cases, characterization of the purported triphenylphosphine-gold- $\pi$  complex rests solely on <sup>31</sup>P NMR analysis recorded at or above room temperature with reported chemical shifts ranging from  $\delta = 28$  to 45 ppm. We found the broad range of chemical shifts disconcerting given the narrow range of phosphorous chemical shifts ( $\delta = 65 \pm$ 3 ppm) observed for a family of more than 30 complexes of the form {[P(tBu)<sub>2</sub>-o-biphenyl]Au( $\pi$  ligand)}+SbF<sub>6</sub><sup>-.[9,11-15]</sup> Furthermore, the lower frequency value of  $\delta = 28 \text{ ppm}$  is similar to that of weak  $\sigma$  complexes, such as [(PPh<sub>3</sub>)AuOTf]<sup>[24]</sup> and [(PPh<sub>3</sub>)AuNTf<sub>2</sub>],<sup>[25]</sup> whereas the higher frequency value of  $\delta = 45$  ppm is similar to the bis(phosphine) cation  $[(PPh_3)_2Au]^+$  (2) (Table 1), complexes that could be envisioned as byproducts or decomposition products in the generation of triphenylphosphine-gold- $\pi$  complexes.<sup>[26,27]</sup> Perhaps best characterized of these tri-

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Table 1.  $^{31}\text{P}$  NMR chemical shifts of relevant triphenylphosphine–gold–  $\pi$  complexes in CD\_2Cl\_2.

σ Complex	δ at 25 °C [ppm]	$\delta$ at -90 °C [ppm]
[(PPh <sub>3</sub> )AuCl]	32.7	30.6
[(PPh <sub>3</sub> )AuOTf]	30.6	28.0
[(PPh <sub>3</sub> )AuNTf <sub>2</sub> ]	29.9	27.8
[PPh <sub>3</sub> —Au—Ph <sub>3</sub> P]	45.5	41.8
$\left[(PPh_3)Au \oplus Au(Ph_3P)\right]$	30.7	28.5

phenylphosphine–gold– $\pi$  complexes is the 4-methylstyrene complex [(PPh<sub>3</sub>)Au( $\eta^2$ -H<sub>2</sub>C=CH-4-C<sub>6</sub>H<sub>4</sub>CH<sub>3</sub>)]<sup>+</sup>BF<sub>4</sub><sup>-</sup> (1•BF<sub>4</sub>), which was interrogated by variable-temperature, multinuclear, one- and two-dimensional NMR analysis.<sup>[23]</sup> However, significant broadening of the reported <sup>31</sup>P NMR resonance of 1•BF<sub>4</sub> ( $\delta$ =37.6 ppm,  $\nu_{1/2}\approx$ 250 Hz at -20 °C) suggested the possibility of a rapidly equilibrating mixture of complexes.

Due to the apparent inconsistencies and discrepancies in the extant reports of two-coordinate triphenylphosphinegold– $\pi$  complexes, we sought to develop a more detailed understanding of the spectroscopy and solution behavior of these complexes. To this end, a family of gold complexes of the form  $[(PPh_3)Au(\pi \text{ ligand})]^+$  ( $\pi \text{ ligand} = \text{ alkene, vinyl}$ arene, alkyne, conjugated diene, allene) was generated and characterized without isolation, employing low-temperature, multinuclear NMR spectroscopy. Key observations made in the course of our investigation include the following: 1) the  $\pi$  ligands of cationic triphenylphosphine–gold– $\pi$  complexes are considerably more labile than the  $\pi$  ligands of related gold NHC and *o*-biphenylphosphine  $\pi$  complexes; 2) careful control of reaction stoichiometry and employment of a weakly coordinating counterion, such as  $SbF_6^-$ , was required to generate solutions of cationic triphenylphosphine-gold- $\pi$  complexes free from byproducts; 3) all of the gold- $\pi$  complexes generated in this study are thermally unstable and decompose above -20°C to form the bis(triphenylphosphine) gold cation  $[(PPh_3)_2Au]^+$  (2); and 4) the <sup>31</sup>P NMR resonance of these complexes falls within the range of  $\delta =$  $37.1 \pm 1.7$  ppm.

### **Results and Discussion**

**Triphenylphosphine–gold–\pi-alkene complexes**: Addition of 2-methyl-2-butene (1 equiv) to a 1:1 mixture of [(PPh<sub>3</sub>)AuCl] and AgSbF<sub>6</sub> in CD<sub>2</sub>Cl<sub>2</sub> at -78 °C for 5 min led to formation of thermally unstable {(PPh<sub>3</sub>)Au[ $\eta^2$ -Me(H)C= CMe<sub>2</sub>]}+SbF<sub>6</sub><sup>-</sup> (**3**-SbF<sub>6</sub>; Figure 1), which was characterized without isolation by NMR spectroscopy. The <sup>31</sup>P NMR spectrum of **3**-SbF<sub>6</sub> at -85 °C displayed a sharp resonance at  $\delta$  = 36.8 ppm consistent with the presence of a single organometallic complex (see below). Complexation of the alkene to gold was established by the downfield shift of the C2 alkene carbon resonance ( $\delta$ =145.4 ppm) and the upfield shift of the C3 alkene carbon resonance ( $\delta$ =111.8 ppm, d,  $J_{CP}$ =



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Figure 1. Synthesis and  $^{31}P\,NMR$  chemical shifts of triphenylphosphine–gold– $\pi\text{-}complexes$  in  $CD_2Cl_2$ .

10.5 Hz) relative to free 2-methyl-2-butene (C2,  $\delta = 132.0$ ; C3,  $\delta = 118.0$  ppm) in the <sup>13</sup>C NMR spectrum of **3**·SbF<sub>6</sub> at -85 °C and by the large downfield shift of the vinylic proton resonance at  $\delta = 5.96$  ppm relative to free 2-methyl-2-butene  $(\delta = 5.12 \text{ ppm})$  in the <sup>1</sup>H NMR spectrum of **3**·SbF<sub>6</sub> at  $-85 \degree$ C. Although the <sup>13</sup>C NMR chemical shifts of the alkenyl carbon atoms of  $3-SbF_6$  are quite similar to those observed  $[P(tBu_2)-o-biphenyl]Au[\eta^2-Me(H)C=CMe_2]]^+SbF_6^$ for (4-SbF<sub>6</sub>;  $\delta = 146.1$ , 111.4 ppm), the vinylic proton of 4-SbF<sub>6</sub>  $(\delta = 4.20 \text{ ppm})$  was shifted upfield relative to free 2-methyl-2-butene, as opposed to the strong downfield shift observed for 3-SbF<sub>6</sub>.<sup>[9]</sup> A similar relationship was observed in the spectra of triphenylphosphine and di(tert-butyl)-o-biphenylphosphine- $\pi$ -allene complexes (see below). Warming a CD<sub>2</sub>Cl<sub>2</sub> solution of 3.SbF<sub>6</sub> at 0 °C led to decomposition ( $t_{1/2} \approx 90$  min) with concomitant formation of  $[(PPh_3)_2Au]^+SbF_6^-$  (2-SbF<sub>6</sub>), as was evidenced by the appearance of the sharp, diagnostic resonance at  $\delta = 43.8$  ppm in the <sup>31</sup>P NMR spectrum and by comparison to an authentic sample.

Effect of reaction stoichiometry: To explore the effect of reaction stoichiometry on the composition and solution behavior of 3, complex 3 was generated: in situ 1) with a deficiency of 2-methyl-2-butene; 2) with a deficiency of  $AgSbF_6$ ; and 3) with the more strongly coordinating anions,  $NTf_2$ and OTf<sup>-</sup>. When an equimolar mixture of [(PPh<sub>3</sub>)AuCl], and AgSbF<sub>6</sub> was treated with a deficiency of 2-methyl-2butene (0.5 equiv) at -78 °C, the <sup>31</sup>P NMR spectrum of the resulting solution at -94°C displayed an approximately 2:1 ratio of sharp resonances at  $\delta = 36.8$  and 28.2 ppm (Figure 2). Although the  $\delta = 36.8$  ppm resonance can be confidently assigned to  $3 \cdot \text{SbF}_6$ , the composition of the complex (A·SbF<sub>6</sub>) that gives rise to the  $\delta = 28.2$  ppm resonance remains unclear; the free gold cation [(PPh<sub>3</sub>)Au]<sup>+</sup>SbF<sub>6</sub><sup>-</sup>, the solvated cation  $[(PPh_3)Au(CD_2Cl_2)]^+SbF_6^-$ , or the gold/ silver heterobimetallic complex [(PPh<sub>3</sub>)Au(µ-Cl)Ag]<sup>+</sup>SbF<sub>6</sub><sup>-</sup> represent possible structures. In any case, reaction of a 1:1 mixture of [(PPh<sub>3</sub>)AuCl] and AgSbF<sub>6</sub> at -78°C in the ab-



Figure 2. Variable-temperature <sup>31</sup>P NMR spectra of the solutions generated from reaction of 1) a 2:2:1 mixture of [(PPh<sub>3</sub>)AuCl], AgSbF<sub>6</sub>, and 2-methyl-2-butene in CD<sub>2</sub>Cl<sub>2</sub> at -78 °C (left); and 2) a 2:1:2 mixture of [(PPh<sub>3</sub>)AuCl], AgSbF<sub>6</sub>, and 2-methyl-2-butene in CD<sub>2</sub>Cl<sub>2</sub> at -78 °C (right). Vertical amplitude is not consistent between spectra.

sence of alkene likewise displays a broad resonance at  $\delta \approx 28$  ppm. Warming the aforementioned solution above -50 °C resulted in broadening of the resonance of  $\mathbf{A} \cdot \mathbf{SbF}_6$  at  $\delta \approx 28$  ppm without detectable broadening of the phosphorous resonance of  $\mathbf{3} \cdot \mathbf{SbF}_6$  below the onset of decomposition at -20 °C (Figure 2), which argues against intermolecular alkene exchange between  $\mathbf{3} \cdot \mathbf{SbF}_6$  and  $\mathbf{A} \cdot \mathbf{SbF}_6$ . Supporting this contention, the <sup>1</sup>H NMR spectrum of this 2:1 mixture of  $\mathbf{3} \cdot \mathbf{SbF}_6$  and  $\mathbf{A} \cdot \mathbf{SbF}_6$  displayed no broadening or shifting of the alkene resonances of  $\mathbf{3} \cdot \mathbf{SbF}_6$  over the temperature range -94 to 0 °C.

To evaluate the effect of a deficiency of silver salt on the formation of 3-SbF<sub>6</sub>, a 2:1:2 mixture of [(PPh<sub>3</sub>)AuCl], AgSbF<sub>6</sub>, and 2-methyl-2-butene was combined in CD<sub>2</sub>Cl<sub>2</sub> at -78°C. The <sup>31</sup>P NMR spectrum of this mixture at -90°C displayed a large broad resonance at  $\delta = 29$  and a small broad peak at  $\delta \approx 35$  ppm (Figure 2). When the temperature was raised, these resonances coalesced to form a single peak at  $\delta = 30.6$  ppm ( $\nu_{1/2} = 84$  Hz) at -50 °C, which sharpened further upon warming the solution to 25 °C ( $\delta$  = 30.0 ppm  $(v_{1/2}=11 \text{ Hz})$ ; Figure 2); at this temperature, no formation of  $2 \cdot \text{SbF}_6$  was detected after 5 h. Likewise, the <sup>1</sup>H NMR spectrum of the same mixture at -90 °C revealed extremely broad resonances in the vinylic ( $\delta = 5.7-4.7$  ppm) and aliphatic ( $\delta = 2.4-0.9$  ppm) regions, which sharpened upon warming to -50 °C, forming one vinylic resonance at  $\delta =$ 5.27 and three methyl resonances at  $\delta = 1.75$ , 1.68, and 1.60 ppm. These spectra are consistent with a rapidly interconverting mixture of  $\pi$ -alkene complex  $3 \cdot \text{SbF}_6$  ( $\delta = 36.8 \text{ ppm}$ ), [(PPh<sub>3</sub>)AuCl] ( $\delta = 30.6 \text{ ppm}$ ), the chloride-bridged bis(gold) cation [((PPh<sub>3</sub>)Au)<sub>2</sub>( $\mu$ -Cl)]<sup>+</sup>SbF<sub>6</sub><sup>-</sup> ( $5 \cdot \text{SbF}_6$ ) ( $\delta = 28.5 \text{ ppm}$ )<sup>[28]</sup>, and free 2-methyl-2-butene, which favors  $5 \cdot \text{SbF}_6$  and free alkene (Scheme 1). The thermal stability of the mixture presumably reflects the low equilibrium concentration of  $3 \cdot \text{SbF}_6$  present under these conditions.



Scheme 1. Low-temperature reaction of a 2:1:2 mixture of [(PPh<sub>3</sub>)AuCl], AgSbF<sub>6</sub>, and 2-methyl-2-butene in CD<sub>2</sub>Cl<sub>2</sub>; chemical-shift values refer to the diagnostic <sup>31</sup>P NMR resonances at -90 °C in CD<sub>2</sub>Cl<sub>2</sub>.

Effect of counterion: The effect of the more strongly coordinating counterions, bistriflimide and triflate, on the formation and solution behavior of alkene complex 3 was also investigated. For example, when an equimolar mixture of [(PPh<sub>3</sub>)AuNTf<sub>2</sub>] and 2-methyl-2-butene (73 mM) was combined in CD<sub>2</sub>Cl<sub>2</sub> at -78°C [Eq. (1)], the <sup>31</sup>P NMR spectrum of the resulting mixture at -90°C displayed an approximately 4:1 ratio of broad resonances at  $\delta = 37 (\nu_{1/2} = 105 \text{ Hz})$ and  $\delta = 28 \text{ ppm} (\nu_{1/2} = 38 \text{ Hz})$ , consistent with an equilibrating mixture of  $\pi$ -alkene complex 3-NTf<sub>2</sub> and bistriflimide complex [(PPh<sub>3</sub>)AuNTf<sub>2</sub>]. Both the <sup>1</sup>H and <sup>13</sup>C NMR spectra of the solution at -90°C displayed broad, time-averaged resonances for bound and free alkene, consistent with rapid exchange of alkene and bistriflimide on the NMR time scale. Similarly, when an equimolar mixture of [(PPh<sub>3</sub>)AuCl], AgOTf, and 2-methyl-2-butene was combined in  $CD_2Cl_2$  at -78 °C [Eq. (2)], the <sup>31</sup>P NMR spectrum at -90°C displayed an approximately 6:1 ratio of broad resonances at  $\delta = 38$  ( $\nu_{1/2} \approx 100 \text{ Hz}$ ) and 30 ppm ( $\nu_{1/2} \approx 400 \text{ Hz}$ ), consistent with an equilibrating mixture of 3-OTf and [(PPh<sub>3</sub>)AuOTf].



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 $[(PPh_3)Au(\eta^2-H_2C=CH-4-C_6H_4Me)]^+X^-$  (X = BF<sub>4</sub> (1-BF<sub>4</sub>),  $\mathbf{SbF}_{6}$  (1· $\mathbf{SbF}_{6}$ )): The reported spectroscopy for 1· $\mathbf{BF}_{4}$ ,<sup>[23]</sup> in particular the significant perturbation of the vinylic proton resonances of bound 4-methylstyrene relative to free 4methylstyrene, leave little doubt that complex  $1-BF_4$  is generated in solution from mixtures of [(PPh<sub>3</sub>)AuCl], AgBF<sub>4</sub>, and 4-methystyrene. However, as was noted in the introduction, broadening in the <sup>31</sup>P NMR spectrum (-20 °C) suggested the presence of a mixture of complexes, presumably including the free or solvated cationic species A-BF<sub>4</sub>, which may be more prevalent than was  $\mathbf{A} \cdot \mathbf{SbF}_6$  in the formation of 3-SbF<sub>6</sub> owing both to the weaker ligating ability of 4-methylstyrene to gold(I) relative to 2-methyl-2-butene and the stronger coordination of BF<sub>4</sub><sup>-</sup> relative to SbF<sub>6</sub><sup>-.[29]</sup> Indeed, the <sup>31</sup>P NMR spectrum of a 1:1:1.15 mixture of [(PPh<sub>3</sub>)AuCl], AgBF<sub>4</sub>, and 4-methylstyrene in CD<sub>2</sub>Cl<sub>2</sub> at -20 °C displayed a single broad resonance at  $\delta = 33.9$  ppm  $(\nu_{1/2} = 112 \text{ Hz})$ .<sup>[30]</sup> However, when the temperature was lowered, this resonance broadened significantly ( $v_{1/2} > 1000 \text{ Hz}$ ; Figure 3), indicating the presence of a mixture of complexes in solution.

Unable to resolve the  ${}^{31}$ P NMR spectrum of the solution generated from reaction of [(PPh<sub>3</sub>)AuCl], AgBF<sub>4</sub>, and 4-methylstyrene into its constituent resonances, a similar ex-



Figure 3. Variable-temperature <sup>31</sup>P NMR spectra of the solutions generated from reaction of 1) a 1:1:1.15 mixture of [(PPh<sub>3</sub>)AuCl], AgBF<sub>4</sub>, and 4-methylstyrene in CD<sub>2</sub>Cl<sub>2</sub> at -78 °C (left); and 2) a 1:1:1 mixture of [(PPh<sub>3</sub>)AuCl], AgSbF<sub>6</sub>, and 4-methylstyrene in CD<sub>2</sub>Cl<sub>2</sub> at -78 °C (right). Vertical amplitude is not consistent among the spectra.

periment employing the less coordinating SbF<sub>6</sub><sup>-</sup> counterion was performed. To this end, an equimolar mixture of [(PPh<sub>3</sub>)AuCl], AgSbF<sub>6</sub>, and 4-methylstyrene in CD<sub>2</sub>Cl<sub>2</sub> was mixed at -78°C for 5 min. The <sup>1</sup>H NMR spectrum of the resultant solution at -70 °C displayed a 1:1 ratio of doublets at  $\delta = 5.84$  and 5.51 ppm, corresponding to the terminal vinylic protons of bound 4-methylstyrene, whereas the internal vinylic proton was shifted downfield to the extent that it was obscured by the aromatic resonances. The <sup>31</sup>P NMR spectrum of this solution at -30°C displayed a broad resonance at  $\delta = 38.0$  ppm ( $\nu_{1/2} = 260$  Hz), which broadened further upon cooling to -50 °C ( $v_{1/2}=310$  Hz). However, as the temperature was lowered to -90°C, the resonance sharpened and shifted downfield slightly to  $\delta = 38.8 \text{ ppm}$  ( $\nu_{1/2} =$ 120 Hz) with the appearance of a second broad resonance at  $\delta = 33-25$  ppm, just visible above the baseline, consistent with a mixture of  $1 \cdot \text{SbF}_6$  and  $A \cdot \text{SbF}_6$  (Figure 3).

 $[(PPh_3)Au(\eta^2-CH_3CH_2C\equiv CCH_2CH_3)]^+SbF_6^-$  (6.SbF<sub>6</sub>): Reaction of an equimolar mixture of [(PPh<sub>3</sub>)AuCl], AgSbF<sub>6</sub>, and 3-hexyne at -78°C led formation of the thermally sensitive 3-hexyne complex  $[(PPh_3)Au(\eta^2-CH_3CH_2C)]$ (6-SbF<sub>6</sub>). The  ${}^{31}$ P NMR spectum of  $CCH_2CH_3)]^+SbF_6^-$ 6-SbF<sub>6</sub> at -70 °C displayed a single sharp resonance at  $\delta =$ 36.1 ppm ( $v_{1/2}$ =5.7 Hz), indicating the presence of a single organometallic complex. Coordination of 3-hexyne to gold was established by the downfield shift and carbon-phosphorous coupling of the sp-carbon resonance of  $6 \cdot \text{SbF}_6$  at  $\delta =$ 91.9 ppm (d,  $J_{\rm CP}$  = 8.6 Hz) relative to free 1-hexyne ( $\delta$  = 81.7 ppm) in the  ${}^{13}$ C NMR spectrum at -90 °C. Similarly, the <sup>1</sup>H NMR spectrum of 6·SbF<sub>6</sub> at -85 °C displayed a quartet at  $\delta = 2.79$  and a triplet at 1.26 ppm corresponding to equivalent ethyl groups of the 3-hexyne ligand, both of which were shifted to higher frequency relative to free 3-hexyne  $(\delta = 2.29 \text{ and } 1.12 \text{ ppm}, \text{ respectively, at } -90 \,^{\circ}\text{C})$ . Warming a  $CD_2Cl_2$  solution of 6-SbF<sub>6</sub> at -20 °C for 20 min led to approximately 15% decomposition to form  $2 \cdot \text{SbF}_6$ .

Mixtures of 6-SbF<sub>6</sub> and free 3-hexyne displayed well-resolved resonances for free ( $\delta = 2.79$  ppm) and bound ( $\delta =$ 2.24 ppm) 3-hexyne in the <sup>1</sup>H NMR spectrum at -85 °C. This peak separation was exploited to analyze the kinetics of intermolecular ligand exchange employing spin-saturation techniques. To this end, the rate of intermolecular 3-hexyne exchange with  $6-SbF_6$  (80 mm) was recorded as a function of [3-hexyne] from 18 to 60 mM in  $CD_2Cl_2$  at -85 °C. A plot of  $k_{obs}$  versus [3-hexyne] was linear and established the secondorder rate law for intermolecular 3-hexyne exchange with **6**·SbF<sub>6</sub> of rate =  $k_2$ [**6**·SbF<sub>6</sub>][3-hexyne], in which  $k_2 = 100 \pm$  $14 \,\mathrm{m}^{-1} \mathrm{s}^{-1}$  ( $\Delta G^{+}_{188\mathrm{K}} = 9.10 \pm 0.05 \,\mathrm{kcal \, mol^{-1}}$ ; Figure 4). These data support an associative pathway for 3-hexyne exchange via the cationic bis(alkyne) intermediate [(PPh<sub>3</sub>)Au( $\eta^2$ -CH<sub>3</sub>CH<sub>2</sub>C=CCH<sub>2</sub>CH<sub>3</sub>)<sub>2</sub>]\*SbF<sub>6</sub><sup>-</sup>. It is worth noting that the energy barrier for intermolecular 3-hexyne exchange with **6**·SbF<sub>6</sub> is  $\geq 6$  kcal mol<sup>-1</sup> lower than the energy barriers determined for the intermomolecular  $\pi$ -ligand exchange with [P- $(tBu)_{2}$ -o-biphenyl]Au( $\pi$  ligand) complexes.<sup>[9,12]</sup> This difference presumably reflects both the diminished steric environ-

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Figure 4. Plot of  $k_{obs}$  versus [3-hexyne] for the intermolecular exchange of the 3-hexyne ligand of **6**·SbF<sub>6</sub> ([**6**·SbF<sub>6</sub>]=80 mM) from 18 to 60 mM at -85 °C in CD<sub>2</sub>Cl<sub>2</sub>.

ment about gold and the weaker gold– $\pi$  ligand bond of **6**·SbF<sub>6</sub> relative to that of the P(*t*Bu)<sub>2</sub>-*o*-biphenyl–gold– $\pi$  complexes.

The effect of a deficiency of alkyne on the formation and solution behavior of **6**·SbF<sub>6</sub> was analogous to the effect of a deficiency of 2-methyl-2-butene on the formation of **3**·SbF<sub>6</sub>. When a 2:2:1 ratio of [(PPh<sub>3</sub>)AuCl], AgSbF<sub>6</sub>, and 3-hexyne was mixed thoroughly in CD<sub>2</sub>Cl<sub>2</sub> at -78 °C, subsequent <sup>31</sup>P NMR analysis at -90 °C revealed a 1.5:1 ratio of sharp resonances at  $\delta = 35.1$  and 28.2 ppm corresponding to **6**·SbF<sub>6</sub> and **A**·SbF<sub>6</sub>, respectively. When the solution was warmed above -50 °C, the <sup>31</sup>P NMR resonance at  $\delta = 28$  ppm, corresponding to **A**·SbF<sub>6</sub>, broadened without detectable broadening of the  $\delta = 35$  ppm resonance, corresponding to **6**·SbF<sub>6</sub>. Warming the solution above -20 °C led to rapid decomposition of **6**·SbF<sub>6</sub> (ca. 30% decomposition after 25 min) with concomitant formation of bis(phosphine) complex **2**·SbF<sub>6</sub>.

**[(PPh<sub>3</sub>)Au(η<sup>2</sup>-1,3-cyclohexadiene)]<sup>+</sup>SbF<sub>6</sub><sup>-</sup>** (7·SbF<sub>6</sub>): Reaction of an equimolar mixture of [(PPh<sub>3</sub>)AuCl], AgSbF<sub>6</sub>, and 1,3-cyclohexadiene in CD<sub>2</sub>Cl<sub>2</sub> at -78 °C led to formation of the thermally unstable η<sup>2</sup>-diene complex 7·SbF<sub>6</sub>, which displayed a single sharp resonance at  $\delta = 36.3$  ppm in the <sup>31</sup>P NMR spectrum at -90 °C. Binding of gold to one of the two C=C bonds of the cyclohexadiene ligand was established by low-temperature <sup>13</sup>C and <sup>1</sup>H NMR analysis, notably by the presence of four alkenyl resonances ( $\delta = 137.9$ , 121.7, 119.8, 117.9 ppm) and two aliphatic resonances (25.0, 22.2 ppm) corresponding to the six chemically inequivalent carbon atoms of the cyclohexadiene ligand in the <sup>13</sup>C NMR spectrum of 7·SbF<sub>6</sub> at -90 °C.

Complex **7**·SbF<sub>6</sub> displayed fluxional behavior consistent with facile interconversion of the complexed and uncomplexed C=C bonds of the cyclohexadiene ligand. For example, the <sup>1</sup>H NMR spectrum of **7**·SbF<sub>6</sub> at -94 °C displayed a 1:1:1:1 ratio of four broad vinylic resonances at  $\delta = 6.89$ , 6.50, 6.41, and 6.31 and a broad multiplet at 2.8–2.3 ppm, corresponding to the allylic protons (Figure 5). When the temperature was raised, the pairs of resonances at  $\delta$ =6.50 and 6.41, and at 6.89 and 6.31 ppm broadened and coalesced



Figure 5. Temperature dependence of the alkenyl and aliphatic <sup>1</sup>H NMR resonances of  $7 \cdot \text{SbF}_6$  from -94 to  $-25 \,^{\circ}\text{C}$  in  $\text{CD}_2\text{Cl}_2$ .

independently forming a 1:1 ratio of resonances at  $\delta = 6.48$ and 6.62 ppm at -25 °C (Figure 5). Over the same temperature range, the broad allylic multiplet collapsed to form a single sharp peak at  $\delta = 2.65$  ppm at -25 °C (Figure 5). Lineshape analysis of the vinyl resonances at  $\delta = 6.50$  and 6.41 ppm near the coalescence temperature provided an energy barrier for exchange of the complexed and uncomplexed C=C bonds of the 1,3-cyclohexadiene ligand of **7.**SbF<sub>6</sub> of  $\Delta G^{+}_{185K} \leq 9.0$  kcal mol<sup>-1</sup>.<sup>[31]</sup>

The presence of a single aliphatic resonance in the fast-exchange spectrum of 7-SbF<sub>6</sub> points to an intermolecular pathway for interconversion of the complexed and uncomplexed C=C bonds of the cyclohexadiene ligand. Because an intramolecular pathway for exchange would occur without exchange of the two faces of the 1,3-cyclohexadiene ligand, the fast-exchange spectrum should display two allylic resonances for the time-averaged allylic protons positioned *cis* 

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and trans to the gold-phosphine moiety, barring accidental equivalence. Indeed, we have previously established an intramolecular mechanism for the interconversion of the complexed and uncomplexed C=C bonds of  $\{[P(tBu)_2-o-biphe$ nyl]Au( $\eta^2$ -1,3-cyclohexadiene)}+SbF<sub>6</sub><sup>-</sup> with an energy barrier of  $\Delta G^{+}_{233\mathrm{K}} = 10.4 \text{ kcal mol}^{-1}$ .<sup>[14]</sup> Conversely, an intermolecular pathway for exchange would necessarily occur with concomitant exchange of the two faces of the 1,3-cyclohexadiene ligand, producing a single, time-averaged allylic resonance in the fast-exchange spectrum, as was observed for 7.SbF<sub>6</sub>. Supporting this contention, the <sup>1</sup>H NMR spectrum of a solution of 7.SbF<sub>6</sub> (42 mM) that contained a trace of free 1,3-cyclohexadiene (ca. 4 mM) at -90 °C displayed only two alkenyl ( $\delta = 6.56$  and 6.42 ppm) and one allylicproton resonance ( $\delta = 2.61$  ppm), which established rapid, intermolecular exchange of bound and free 1,3-cyclohexadiene.

**Triphenylphosphine-gold** $-\pi$ -allene complexes: We have previously reported the synthesis of gold– $\pi$  allene complexes of the form  $[{P(tBu)_2-o-biphenyl}Au(\pi allene)]^+SbF_6^{-}$ .<sup>[12]</sup> Solution-phase analysis of these complexes established  $\eta^2$ -allene ground state species that underwent facile ( $\Delta G^{\pm} = 8.9$ -11.4 kcalmol<sup>-1</sup>)  $\pi$ -face exchange through staggered  $\eta^2$ -allene transition states. Solution-state analysis of gold complexes containing a chiral allene ligand, such as the gold 4,5-nonadiene complex { $[P(tBu)_2-o-biphenvl]Au[\eta^2-CH_3CH_2CH_2 (H)C=C=C(H)CH_2CH_2CH_3]$ <sup>+</sup>SbF<sub>6</sub><sup>-</sup>, was further complicated by the presence of both *cis*- and *trans*-diastereomers ( $\Delta G$  $\approx 0.4 \text{ kcal mol}^{-1}$ ), which underwent  $\pi$ -face exchange and *cis*/ *trans* isomerization through multiple, diastereomeric  $\eta^{1}$ allene transition states. Building from these studies, we extended our analysis of triphenylphosphine-gold– $\pi$  complexes to include  $\pi$ -allene complexes. In one experiment, reaction of an equimolar mixture of [(PPh<sub>3</sub>)AuCl], AgSbF<sub>6</sub>, and 3methyl-1,2-butadiene in CD<sub>2</sub>Cl<sub>2</sub> at -78 °C for 5 min generated the  $[(PPh_3)Au(\eta^2-H_2C=C=CMe_2)]^+SbF_6^-$  (8-SbF<sub>6</sub>), which displayed a single sharp resonance at  $\delta = 36.3$  ppm in the <sup>31</sup>P NMR at -90 °C.  $\pi$  Complexation of 3-methyl-1,2-butadiene to gold was established by <sup>1</sup>H and <sup>13</sup>C NMR spectroscopy at -90 °C. Notably, the <sup>13</sup>C NMR chemical shifts of the allenyl carbon atoms of 8-SbF<sub>6</sub> [ $\delta$  = 105.3 (CMe<sub>2</sub>), 198.2 (=C=), 62.6 ppm  $(CH_2)$ ] were shifted significantly from those of free 3-methyl-1,2-butadiene [ $\delta = 94.4$ , 205, 72.6 ppm] and were similar to those observed for the related  $\pi$ -allene complex {[P(tBu)\_2-o-biphenyl]Au[ $\eta^2$ -H<sub>2</sub>C=C=C- $(CH_3)_2]^+SbF_6^-$  (9-SbF<sub>6</sub>) [ $\delta = 105.6$  (CMe<sub>2</sub>), 197.0 (=C=),  $63.1 \text{ ppm} (CH_2)$ ]. In comparison, the allenvel proton of 8.SbF<sub>6</sub> ( $\delta$  = 5.23 ppm) was shifted downfield relative to the allenvl resonance of both free 3-methyl-1,2-butadiene ( $\delta =$ 4.46 ppm) and (9.SbF<sub>6</sub>) ( $\delta$  = 4.07 ppm).<sup>[12]</sup> Selective binding of the 3-methyl-1,2-butadiene ligand of 8-SbF<sub>6</sub> through the less substituted allenyl C=C bond was established by the presence of a pair of diastereotopic allenyl methyl resonances in both the <sup>13</sup>C ( $\delta$ =21.4, 20.2 ppm) and the <sup>1</sup>H NMR spectrum ( $\delta = 1.93$ , 1.87 ppm) of 8.5bF<sub>6</sub> at -90 °C (Figure 6). When the temperature was raised, the proton resonances

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Figure 6. Temperature dependence of the allenyl methyl <sup>1</sup>H NMR resonances of 8-SbF<sub>6</sub> in CD<sub>2</sub>Cl<sub>2</sub>. Amplitude is not consistent between spectra.

broadened and coalesced, forming a single resonance at  $\delta = 1.93 \text{ ppm}$  at  $-30 \,^{\circ}\text{C}$ , with an energy barrier of  $\Delta G^{+}_{215\text{K}} = 10.9 \text{ kcal mol}^{-1}$ , as was determined from line-shape analysis. Although this value is similar to the energy barrier determined for intramolecular  $\pi$ -face exchange of the 3-methyl-1,2-butadiene ligand of gold–allene complex {[P(*t*Bu)<sub>2</sub>-*o*-biphenyl]Au( $\eta^2$ -H<sub>2</sub>C=C=CMe<sub>2</sub>)}+SbF\_6^- ( $\Delta G^{+}_{220\text{K}} = 11.0 \text{ kcal mol}^{-1}$ ),<sup>[12]</sup> we could not distinguish between intra- and intermolecular pathways for interconversion of the diastereotopic methyl groups of 8-SbF<sub>6</sub> (see below). Warming a solution of 8-SbF<sub>6</sub> at 0 °C for 1.5 h led to 90 % decomposition to form the bis(triphenylphosphine)–gold cation 2-SbF<sub>6</sub>.

Both the <sup>31</sup>P NMR chemical shift and thermal instability of  $8 \cdot \text{SbF}_6$  appeared incongruent with the data reported for gold– $\pi$  allene the related complex  $[(PPh_3)Au(\eta^2 -$ PhCH<sub>2</sub>CH<sub>2</sub>(H)C=C=C(H)CH<sub>2</sub>CH<sub>2</sub>Ph)]<sup>+</sup>X<sup>-</sup>  $[X = NTf_2]$ (10·NTf<sub>2</sub>),  $BF_4^-$  (10·BF<sub>4</sub>)].<sup>[21]</sup> Complex 10 was reportedly generated in situ from reaction of 1,7-diphenylhepta-3,4diene with either [(PPh<sub>3</sub>)AuNTf<sub>2</sub>] or a mixture of [(PPh<sub>3</sub>)AuCl] and AgBF<sub>4</sub> in CD<sub>3</sub>NO<sub>2</sub> and/or CD<sub>2</sub>Cl<sub>2</sub> and was characterized solely on the basis of sharp resonance at  $\delta = 45.2 \text{ ppm}$  in CD<sub>3</sub>NO<sub>2</sub> (44.8 ppm in CD<sub>2</sub>Cl<sub>2</sub>) in the <sup>31</sup>P NMR spectrum at 25–45 °C. Although the chemical shift reported for 10 is not within the range defined by triphenylphosphine-gold- $\pi$  complexes 1, 3, and 6-8 ( $\delta = 36.1$ -38.1 ppm, Figure 1), it is near the value expected for the bis(triphenylphosphine)-gold cation 2, and the rapid decom-

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position of 10 to form 2 at or above room temperature is in accord with the observed thermal stability of 8.

To gain insight into the spectroscopy and solution behavior of gold- $\pi$  allene complex 10, the reaction of an equimolar mixture of [(PPh<sub>3</sub>)AuCl], AgSbF<sub>6</sub>, and 1,7-diphenyl-3,4heptadiene was investigated in  $CD_2Cl_2$  at -78 °C for 5 min. Low-temperature one- and two-dimensional NMR analysis of the resulting solution was most consistent with an equilibrating approximately 1:2.5 mixture of diastereomeric  $\eta^2$ allene complexes, presumably cis-10-SbF<sub>6</sub> and trans-10-SbF<sub>6</sub>, although we have no information that would allow assignment of the major and minor isomers and little information regarding the structure of the minor isomer. For example, the <sup>31</sup>P NMR spectrum of **10**·SbF<sub>6</sub> at -89 °C displayed an approximately 1:2.5 ratio of resonances at  $\delta = 36.5$  and 35.4 ppm, whereas the <sup>1</sup>H NMR spectrum of 10-SbF<sub>6</sub> at -89°C displayed an approximately 1:2.5 ratio of broad allenvl resonances at  $\delta = 6.14$  and 6.03 ppm; assignment of the 6.03 ppm resonance to both allenyl protons (time-averaged or coincidental) of the major diastereomer was further supported by <sup>1</sup>H-<sup>1</sup>H COSY and heteronuclear multiple-quantum-coherence (HMQC) analysis at -90°C (see below, Figures S1 and S2 in the Supporting Information). When the temperature was raised, the approximately 1:2.5 ratio of <sup>1</sup>H and <sup>31</sup>P NMR resonances broadened and coalesced, forming single resonances in both the <sup>31</sup>P ( $\delta$  = 36.6 ppm at -50 °C) and <sup>1</sup>H ( $\delta = 6.06$  ppm at -60 °C) NMR spectra, with an energy barrier for interconversion of the major and minor diastereomers of 10·SbF<sub>6</sub> of  $\Delta G^{+}_{215K} = 9.5 \text{ kcal mol}^{-1}$ , as was determined from <sup>31</sup>P NMR line-shape analysis (Figure 7).

Assignment of the major diastereomer of  $10-SbF_6$  as an  $\eta^2$ -allene complex was further supported by low-temperature  $^{13}$ C NMR analysis. The  $^{13}$ C NMR spectrum of **10**-SbF<sub>6</sub> at -90 °C displayed a resonance at  $\delta = 190.2$  ppm (d,  $J_{CP} =$ 6.9 Hz), an approximately 1:1 ratio of resonances at  $\delta =$ 100.0 and 86.0 ppm (d,  $J_{CP}$ =6.7 Hz), and an approximately 1:1:1:1 ratio of resonances at  $\delta = 34.8$ , 33.7, 32.5, and 31.8 ppm, assigned to the allenyl sp-carbon atom, the allenyl sp<sup>2</sup>-carbon atoms, and the methylene-carbon atoms, respectively, of the allene ligand of the major diastereomer of 10 under conditions of slow exchange.<sup>[32]</sup> Corroborating this assignment, HMQC analysis of 10-SbF<sub>6</sub> at -90°C revealed a strong correlation between the allenyl sp<sup>2</sup>-carbon resonances at  $\delta = 100.0$  and 86.0 with the <sup>1</sup>H NMR resonance at  $\delta =$ 6.03 ppm assigned to the allenyl protons of the major diastereomer (Figure S2 in the Supporting Information). In addition to these resonances, the <sup>13</sup>C NMR spectrum of **10**-SbF<sub>6</sub> at -90 °C displayed a resonance at  $\delta = 188.6$  ppm, which was approximately half the intensity of the 190.2 ppm resonance and was assigned to the allenvl sp-carbon atom of the minor diastereomer. The associated allenyl sp<sup>2</sup>-carbon resonances and methylene-carbon resonances of the minor diastereomer were not observed, presumably due to more facile  $\pi$ -face exchange of this diastereomer and failure to realize the slow-exchange regime in the <sup>13</sup>C NMR spectrum at -90 °C. Warming a solution of 10-SbF<sub>6</sub> at 0 °C for 75 min led to 37% decomposition to form  $2 \cdot \text{SbF}_{6}$ .



Figure 7. Temperature dependence of the <sup>31</sup>P resonances (left) and allenyl <sup>1</sup>H resonances (right) of **10**-SbF<sub>6</sub> in  $CD_2Cl_2$ . Amplitude is not consistent between spectra.

We performed some additional experiments that evaluated the spectroscopy and solution behavior of 10 a function of counterion and solvent. In one experiment, an equimolar mixture of [(PPh<sub>3</sub>)AuNTf<sub>2</sub>] and 1,7-diphenyl-3,4-heptadiene was mixed at -78 °C in CD<sub>2</sub>Cl<sub>2</sub> for 5 min. The <sup>31</sup>P NMR spectrum of the resulting solution at -90 °C displayed an approximately 2.5:1 ratio resonances at  $\delta = 35.2$  and 27.8 ppm, assigned to the time-averaged resonance of cis- and trans-10-NTf<sub>2</sub> and [(PPh<sub>3</sub>)AuNTf<sub>2</sub>], respectively. When the temperature was raised, these resonances collapsed to form a single resonance  $\delta = 28.4$  ppm at -30 °C. In contrast to 10-SbF<sub>6</sub>, warming this solution to 25°C led to only about 9% conversion to the bis(triphenylphosphine) cation 2.NTf<sub>2</sub> after 12 h, which is perhaps due to low concentration of 10-NTf<sub>2</sub> in solution. In comparison, when an equimolar mixture of [(PPh<sub>3</sub>)AuNTf<sub>2</sub>] and 1,7-diphenyl-3,4-heptadiene was combined in CD<sub>3</sub>NO<sub>2</sub> at -25°C, the <sup>31</sup>P NMR spectrum obtained within 10 min of mixing displayed an approximately 1:5 ratio of a sharp resonance at  $\delta = 42.4$  ppm, corresponding to 2.NTf<sub>2</sub>, and a broad resonance at  $\delta = 36.1$  ppm ( $\nu_{1/2} =$ 150 Hz), corresponding either to 10·NTf<sub>2</sub> or to an equilibrating mixture of 10-NTf<sub>2</sub> and [(PPh<sub>3</sub>)AuNTf<sub>2</sub>]. Warming this mixture above -20°C resulted in rapid disappearance of the  $\delta = 36.1$  ppm resonance with concomitant increase in the 42.4 ppm resonance of 2.NTf<sub>2</sub> (Table 1). From these experiments, we conclude that the spectroscopy and solution behavior previously attributed to 10 correspond instead to the bis(triphenylphosphine)-gold complex 2 generated through decomposition of **10** under the conditions employed for its synthesis and spectroscopic analysis.<sup>[21]</sup>

#### Conclusion

Monomeric, cationic triphenylphosphine-gold(I) complexes that contain a  $\pi$ -alkene, vinyl arene, internal alkyne, conjugated diene, or allene ligand were synthesized and characterized without isolation by low-temperature NMR spectroscopy. Each of these triphenylphosphine-gold(I)- $\pi$  complexes is thermally unstable and decomposes above -20 °C in CD<sub>2</sub>Cl<sub>2</sub> to form the bis(triphenylphosphine)-gold cation  $[(Ph_3P)_2Au]^+$  (2). The  $\pi$  ligands of these complexes undergo rapid intermolecular exchange with free ligand and are competitively displaced by weak  $\sigma$  donors, such as OTf<sup>-</sup>. One of the key ramifications of the weak gold- $\pi$ -ligand interaction of these complexes is that careful control of reaction stoichiometry and employment of a weakly coordinating counterion, such as SbF<sub>6</sub><sup>-</sup>, is required to generate pure triphenylphosphine–gold– $\pi$  complexes. In many cases, the presence of rapidly equilibrating impurities was revealed only by lowtemperature <sup>31</sup>P NMR spectroscopy ( $\leq -80$  °C). The <sup>31</sup>P NMR resonance of these triphenylphosphine-gold- $\pi$  complexes was diagnostic and fell within the range  $\delta =$  $37.1 \pm 1.7$  ppm.

### **Experimental Section**

 $\{(PPh_3)Au[\eta^2\text{-}Me(H)C\!=\!CMe_2]\}^+SbF_6^-$ (3-SbF<sub>6</sub>): A solution of [(PPh<sub>3</sub>)AuCl] (22 mg,  $4.4 \times 10^{-2}$  mmol) in CD<sub>2</sub>Cl<sub>2</sub> (0.50 mL) was added to an NMR tube containing  $AgSbF_6$  (15 mg,  $4.4 \times 10^{-2}$  mmol); the mixture was shaken vigorously, and the resultant suspension was cooled to -78 °C. To this suspension was added 2-methyl-2-butene (3.1 mg, 4.4×  $10^{-2}$  mmol) at -78 °C. The contents of the tube were thoroughly mixed by inverting the tube repeatedly over about 2 min period while maintaining temperature at -78°C, causing a fine white powder to precipitate from solution. Low-temperature <sup>1</sup>H and <sup>31</sup>P NMR analyses of the resulting solution revealed complete conversion of the starting materials to **3**·SbF<sub>6</sub>. <sup>1</sup>H NMR (500 MHz,  $-85^{\circ}$ C):  $\delta = 7.68-7.24$  (m, 15 H), 5.98-5.90 (m, 1H), 2.32 (s, 3H), 2.27 (s, 3H), 2.03 ppm (d, J=1.5 Hz, 3H); <sup>13</sup>C{<sup>1</sup>H} NMR (125 MHz,  $-85^{\circ}$ C):  $\delta = 145.4$ , 133.5 (d, J = 13.4 Hz), 132.4, 129.2 (d. J=11.7 Hz), 125.1 (d, J=62.7 Hz), 111.8 (d, J=10.5 Hz), 28.5, 21.5, 16.0 ppm;  ${}^{31}P{}^{1}H$  NMR (202 MHz, -70 °C):  $\delta = 36.8$  ppm.

Complexes 1·SbF<sub>6</sub>, 6·SbF<sub>6</sub>–8·SbF<sub>6</sub>, and 10·SbF<sub>6</sub> were generated in solution by employing a procedure similar to that used to generate 3·SbF<sub>6</sub>.

[(PPh<sub>3</sub>)Au(η<sup>2</sup>-CH<sub>3</sub>CH<sub>2</sub>CC=CCCH<sub>2</sub>CH<sub>3</sub>)]\*SbF<sub>6</sub><sup>-</sup> (6·SbF<sub>6</sub>): <sup>1</sup>H NMR (500 MHz, -70°C):  $\delta$ =7.65 (t, J=7.4 Hz, 3H), 7.57 (dt, J=1.5, 7.1 Hz, 6H), 7.48–7.40 (m, 6H), 2.80 (q, J=7.0 Hz, 4H), 1.27 ppm (t, J=7.2 Hz, 6H); <sup>13</sup>C{<sup>1</sup>H} NMR (125 MHz, -90°C):  $\delta$ =133.4 (d, J=13.6 Hz), 132.4 (d, J=2 Hz), 129.2 (d, J=12.2 Hz), 125.0 (d, J=63.7 Hz), 91.9 (d, J= 8.6), 15.0, 14.0 ppm; <sup>31</sup>P{<sup>1</sup>H} NMR (202 MHz, -70°C):  $\delta$ =36.1 ppm.

**[(PPh<sub>3</sub>)Au(η<sup>2</sup>-1,3-cyclohexadiene)]**<sup>\*</sup>**SbF**<sub>6</sub><sup>-</sup> (**7**-**SbF**<sub>6</sub>): <sup>1</sup>H NMR (500 MHz, -94 °C):  $\delta$ =7.62 (t, *J*=7.5 Hz, 3 H), 7.54 (dt, *J*=1.4, 7.2 Hz, 6 H), 7.43-7.36 (m, 6 H), 6.89 (br s, 1 H), 6.50 (br s, 1 H), 6.41 (br s, 1 H), 6.31 (br s, 1 H), 2.82–2.32 ppm (m, 4 H); <sup>13</sup>C{<sup>1</sup>H} NMR (125 MHz, -90 °C):  $\delta$ = 137.9 (br), 133.5 (br), 132.4, 129.2 (d, *J*=12.1 Hz), 125.2 (d, *J*=62.0 Hz), 121.7 (br), 119.8 (br), 117.9 (br), 25.0 (br), 22.2 ppm (br); <sup>31</sup>P{<sup>1</sup>H} NMR (202 MHz, -90 °C):  $\delta$ =36.3 ppm.

[(PPh<sub>3</sub>)Au(η<sup>2</sup>-H<sub>2</sub>C=C=CMe<sub>2</sub>)]<sup>\*</sup>SbF<sub>6</sub><sup>−</sup> (8·SbF<sub>6</sub>): <sup>1</sup>H NMR (500 MHz, −90 °C):  $\delta$ =7.64 (t, J=7.1 Hz, 3H), 7.59–7.52 (m, 6H), 7.49–7.40 (m,

6H), 5.23 (br s, 2H), 1.93 (s, 3H), 1.87 ppm (s, 3H);  ${}^{13}C[{}^{1}H]$  NMR (125 MHz, -90 °C):  $\delta$ =198.2, 133.5 (d, J=13.3 Hz), 132.4, 129.3 (d, J=11.9 Hz), 125.0 (d, J=62.6 Hz), 105.3, 62.6 (d, J=10.4 Hz), 21.4, 20.2 ppm;  ${}^{31}P[{}^{1}H]$  NMR (202 MHz, -90 °C):  $\delta$ =36.3 ppm.

**[(PPh<sub>3</sub>)Au(η<sup>2</sup>-PhCH<sub>2</sub>CH<sub>2</sub>(H)C=C = C(H)CH<sub>2</sub>CH<sub>2</sub>Ph)]<sup>+</sup>SbF<sub>6</sub><sup>-</sup> (10-SbF<sub>6</sub>):** Approximately 2.5:1 mixture of diastereomers; <sup>1</sup>H NMR (500 MHz, -89 °C):  $\delta$  = 7.75–7.36 (m, 29 H), 7.36–6.86 (m, 45 H), 6.78 (br s, 9 H), 6.42 (br d, J=7.4 Hz, 4H), [6.14 (br s), 6.03 (br s), ca. 1:2.5, 2 H] 3.15–2.16 ppm (m, 26 H); <sup>13</sup>C{<sup>1</sup>H} NMR (125 MHz, -85 °C):  $\delta$ =[190.2 (d, J= 6.9 Hz), 187.8 (d, J=7.2 Hz), ca. 2.5:1], 139.4, 139.0, 133.5 (d, J= 13.5 Hz), 132.5 (m), 129.1 (d, J=12.0 Hz), 128.5, 128.1, 127.9, 126.0, 125.7, [124.8 (d, J=62.5 Hz), 124.5 (d, J=62.5 Hz), 1:2.5], 100.0, 86.0 (d, J=6.7 Hz), 34.0, 32.9, 31.6, 31.4 ppm; <sup>31</sup>P{<sup>1</sup>H} NMR (202 MHz, -89 °C):  $\delta$ =36.5, 35.4 ppm (ca. 1:2.5).

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- [30] The discrepancy between the chemical shift reported by Macchoni  $(\delta = 37.8 \text{ ppm})$  and in this work  $(\delta = 34.3 \text{ ppm})$  appears to be due to the different referencing systems employed in the two studies (85% H<sub>3</sub>PO<sub>4</sub> versus (PPh<sub>3</sub>)O in CD<sub>2</sub>Cl<sub>2</sub>). Supporting this contention, Macchoni reported the <sup>31</sup>P NMR chemical shift of the decomposition product **2**·[BF<sub>4</sub>] at  $\delta = 45.4 \text{ ppm}$  (253 K), whereas we observed this resonance at 43.3 ppm.<sup>[23]</sup>
- [31] Due to the width of the peaks at low temperature, line-shape simulation of the proton NMR spectra provided an upper limit of the energy barrier for interconversion of vinyl protons of  $\Delta G^*_{185\text{K}} \leq 9.0 \text{ kcal mol}^{-1}$ .
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