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Syntheses, X-ray Crystal Structures, and Solution Behavior of Monomeric, Cationic, Two-Coordinate Gold(I) π -Alkene Complexes

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Cationic gold(I) complexes have recently emerged as effective catalysts for the functionalization of C–C multiple bonds.¹ With few exceptions, mechanisms involving outer-sphere attack of a nucleophile on a transient cationic gold π -complex have been invoked for these transformations.¹ However, although gold π -complexes have been known for over 40 years, examples of the cationic, two-coordinate gold(I) π -complexes germane to π -activation catalysis are exceedingly rare and monomeric gold(I) π -alkene complexes are unknown.^{2–5} Echvarren⁶ and Bertrand⁷ have reported the X-ray crystal structures cationic, two coordinate gold π -arene complexes. Sadighi⁸ and Bertrand⁷ have reported monomeric, cationic gold(I) π -alkyne complexes, but high-resolution X-ray analysis has not been reported.⁹ Toste has reported the X-ray crystal structures of multimeric, cationic, two-coordinate gold(I) π -alkyne and π -alkene complexes; however, no evidence supports the integrity of the gold(I) π -alkene bond in solution.¹⁰ Here we report the syntheses, X-ray crystal structures, and solution behavior of monomeric, cationic, two-coordinate gold π -alkene complexes.

Treatment of a methylene chloride suspension of (IPr)AuCl [IPr = 1,3-bis(2,6-diisopropylphenyl)imidazol-2-ylidene] and AgSbF₆ (1:1) with isobutylene at room temperature for 20 min led to isolation of [(IPr)Au(η^2 -H₂C=CMe₂)]⁺ SbF₆[–] (**1a**) in 98% yield as an air- and thermally-stable white solid that was characterized by NMR, MALDI-MS, combustion analysis, and X-ray crystallography (see below). Complexation of isobutylene to gold in solution was established by NMR, in particular by the large difference in the ¹³C NMR shifts of the olefinic carbon atoms of bound [δ 155.2 (s), 88.2 (t)] and free [δ 142.4 (s), 110.5 (t)] isobutylene. The ¹J_{C=C} coupling constant of the isobutylene ligand of the ¹³C-isotopomer (IPr)Au(η^2 -H₂¹³C=CMe₂) (**1a**-¹³C₁) (¹J_{C=C} = 66 Hz) was diminished only slightly relative to free isobutylene (¹J_{C=C} = 71 Hz), pointing to minimal deviation of the bound isobutylene from ideal sp² hybridization.¹¹

In addition to **1a**, gold π -alkene complexes [(IPr)Au(η^2 -alkene)]⁺ SbF₆[–] [alkene = norbornene (**1b**), 2-methyl-2-butene (**1c**), methylenecyclohexane (**1d**), 2,3-dimethyl-2-butene (**1e**), *cis*-2-butene (**1f**), 1-hexene (**1g**), and 4-methylstyrene (**1h**)] were isolated in >80% yield and were fully characterized (Chart 1).

Slow diffusion of hexane into a CH₂Cl₂ solution of **1a** at 4 °C gave colorless crystals of **1a**·2CH₂Cl₂ suitable for X-ray analysis (Figure 1, Table 1). Complex **1a** adopts a slightly distorted linear conformation with a C_(carbene)–Au–alkene_(centroid) angle of 172 °. The C=C bond of the isobutylene is rotated 52 degrees out of the carbene N–C–N plane, which positions

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Supporting Information Available: Experimental procedures, spectroscopic data, and X-ray crystallographic data. This material is available free of charge via the Internet at <http://pubs.acs.org>.

one isobutylene methyl group near the carbene plane and the second in the quadrant opposing the methylene group across the carbene plane (Figure 1). There is no significant elongation of the isobutylene C=C bond, but isobutylene is bound unsymmetrically to gold with a short Au-CH₂ and a long Au-CMe₂ interaction ($\Delta d = 0.116 \text{ \AA}$) (Table 1).

In addition to **1a**·2CH₂Cl₂, crystals of the norbornene complex **1b** and the 2,3-dimethylbutene solvate complex **1c**·2CH₂Cl₂ were analyzed by X-ray crystallography (Figure 1, Table 1). In comparison to isobutylene complex **1a**, complexes **1b** and **1c** displayed less deviation from linearity and more symmetric binding of the alkene to gold ($\Delta d < 0.03 \text{ \AA}$) (Table 1, Figure 1). In contrast to **1a**, the C=C bond of coordinated norbornene in complex **1b** is positioned perpendicular (88.5°) to the carbene N-C-N plane whereas the C=C bond of coordinated 2,3-dimethyl-2-butene of **1c**·2CH₂Cl₂ lies very near ($<5^\circ$) the carbene plane. These variations indicate that alkene orientation is controlled by steric, rather than by electronic factors, in accord with a strong σ -donating/weak π -backbonding Au-(π -alkene) interaction.

Although the relative binding strength of alkenes has been compiled for a number of transition metal complexes,¹² cationic gold(I) complexes are not among them. To evaluate the relative binding affinity of alkenes to the twelve-electron gold fragment [(IPr)Au]⁺, we determined the equilibrium constants for displacement of NCAr_F [NCAr_F = N≡C-3,5-C₆H₃(CF₃)₂] from [(IPr)Au(NCAr_F)]⁺ SbF₆⁻ (**2**) with alkenes in CD₂Cl₂ at -60°C employing ¹H NMR analysis. K_{eq} decreased by a factor of ~ 13 in the order methylenecyclohexane > isobutylene $\approx$ 2-methyl-2-butene > 2,3-dimethylbutene > *cis*-2-butene > 1-hexene > *trans*-2-butene > propene (Table 2). To isolate the effect of alkene electron density on binding affinity to [(IPr)Au]⁺, we determined K_{eq} for the displacement of NCAr_F from **2** with 4-substituted styrene derivatives H₂C=CH-4-C₆H₄X (X = OMe, Me, H, Br, CF₃). K_{eq} decreased with decreasing electron density by a factor of $\sim 8 \times 10^2$ (Table 2). A plot of $\log(K_X/K_H)$ versus the Hammett σ -parameter was linear with $\rho = -2.4 \pm 0.2$ (Figure S2). This value is considerably more negative than are the values obtained for the binding of substituted styrenes to Ag⁺ ions ($\rho = -0.77$)¹³ and for cationic, 16-electron Pt(II) ($\rho = -1.32$)¹⁴ and Pd(II) ($\rho \approx -1.4$)¹⁵ complexes, which points to the predominant σ -donating nature of the gold π -alkene bond.

Because ligand exchange reactions often play a key role in catalysis, we studied the kinetics of isobutylene exchange with **1a** as a function of [isobutylene] in CDCl₃ at 45°C employing ¹H NMR line broadening techniques. A plot of k_{obs} versus [isobutylene] over the concentration range 20-140 mM was linear with a second-order rate constant for isobutylene exchange of $k_{\text{ex}} = 64 \pm 3 \text{ M}^{-1}\text{s}^{-1}$ ($\Delta G^\ddagger = 16 \pm 1 \text{ kcal mol}^{-1}$) (Figure S3). Second-order rate constants for isobutylene exchange with **1a** were also determined at 26 and 65°C . An Eyring plot of these data provided the activation parameters: $\Delta H^\ddagger = 8 \pm 1 \text{ kcal mol}^{-1}$ and $\Delta S^\ddagger = -27 \pm 4 \text{ eu}$ (Figure S4).¹⁶ These data support an associative pathway for isobutylene exchange with an energy barrier that is comparable to the values obtained for the associative exchange of substituted alkenes at square planar Pt(II) complexes.¹⁷

In summary, we have synthesized a family of cationic, linear gold π -alkene complexes that contain an *N*-heterocyclic carbene ligand and we have fully characterized these complexes in solution and, in three cases, by X-ray crystallography. All of our experimental observations, most notably the large $^1J_{\text{C}=\text{C}}$ of coordinated isobutylene and the large negative ρ value for vinyl arene binding point to a gold-(π -alkene) interaction that is dominated by σ -donation with negligible π -backbonding. These experimental observations are in accord with the strong σ -donating/weak π -backbonding Au-(π -alkene)⁺ interaction predicted through computational analysis, which was attributed to both the low electron density and the relativistic nature of the gold.⁵

Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

Acknowledgments

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Figure 1. ORTEP diagrams of **1a**·2CH₂Cl₂ (top structure), **1b** (middle structure), and **1c**·2CH₂Cl₂. Ellipsoids are shown at 50%. Solvent, counterion, and hydrogen atoms are omitted for clarity.

Chart 1.
Synthesis of (IPr)gold π -alkene complexes.

Table 1
Selected Bond Lengths (Å) and Bond Angles (°) for (**1a**·2CH₂Cl₂), (**1b**), and (**1c**·2CH₂Cl₂).

complex	C1-C2	Au-Cl	Au-C2	Au-C _(NHC)	C=C _(centroid) -Au-C _(NHC)
1a • 2CH ₂ Cl ₂	1.331	2.199	2.285	2.006	171.8
1b	1.374	2.224	2.248	1.996	174.8
1c • 2CH ₂ Cl ₂	1.346	2.239	2.230	1.998	176.8

Table 2Equilibrium constants for reaction of alkenes and vinyl arenes with **2** in CD₂Cl₂ at -60 °C.
$$\text{IPr}-\overset{\oplus}{\text{Au}}-\text{NCAr}_\text{F} + \text{alkene} \xrightleftharpoons[-60\text{ }^\circ\text{C}]{\text{CD}_2\text{Cl}_2} \text{IPr}-\overset{\oplus}{\text{Au}}-(\eta^2\text{-alkene}) + \text{NCAr}_\text{F}$$

alkene	K_{eq}^a	vinyl arene	K_{eq}^a
methylene cyclohexane	90 ± 7	H ₂ C=CH-4-C ₆ H ₄ OMe	5.8 ± 0.2
isobutylene	67 ± 4	H ₂ C=CH-4-C ₆ H ₄ Me	2.7 ± 0.3
2-methyl-2-butene	64 ± 4	H ₂ C=CH-4-C ₆ H ₄ H	1.7 ± 0.4
2,3-dimethylbutene	50 ± 3	H ₂ C=CH-4-C ₆ H ₄ Br	0.27±0.03
<i>cis</i> -2-butene	38 ± 2	H ₂ C=CH-4-C ₆ H ₄ CF ₃	0.07 ± 0.01
1-hexene	25 ± 1		
<i>trans</i> -2-butene	12.5 ± 0.4		
propene	6.8 ± 0.3		

^a K_{eq} determined by ¹H NMR spectroscopy.