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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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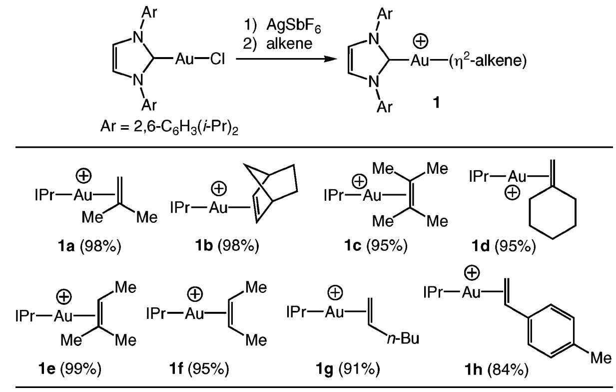
Cationic gold(I) complexes have recently emerged as effective catalysts for the functionalization of C−C multiple bonds with carbon and heteroatom nucleophiles.[1] With few exceptions, mechanisms involving outer-sphere attack of the nucleophile on a cationic gold(I) π-complex have been invoked for these transformations.[1] However, although gold π-complexes have been known for over 40 years,[2−5] examples of the cationic, two-coordinate gold(I) π-complexes germane to catalysis remain scarce.[6−13] As a result, little is known about the structure and reactivity of these important complexes. A small number of monomeric, cationic, two-coordinate gold(I) π-alkyne[7,8] and π-alkene[9] complexes have recently appeared, but no fully refined X-ray structures have been reported.[10−12] Alternatively, Toste has recently reported the X-ray crystal structures of multimeric, cationic, two-coordinate gold(I) π-alkyne and π-alkene complexes, but solution-state analysis, particularly in the case of the π-alkene complex, was complicated by facile disproportionation.[13] Here we report the syntheses, X-ray crystal structures, and solution behavior of monomeric, cationic, two-coordinate gold(I) π-alkene complexes.

Treatment of a methylene chloride suspension of (IPr)AuCl [IPr = 1,3-bis(2,6-diisopropylphenyl)imidazol-2-ylidine] and $AgSbF_6$ (1:1) with isobutylene at room temperature for 12 h led to isolation of $[(IPr)Au(\eta^2\text{-}H_2C{=}CMe_2)]^+\ SbF_6^-$ (**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 ^{13}C 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 ^{13}C-isotopomer $(IPr)Au(\eta^2\text{-}H_2{}^{13}C{=}CMe_2)$ (**1a**-$^{13}C_1$) ($^1J_{C=C}$ = 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 sp^2 hydbridization.[14]

In addition to **1a**, gold π-alkene complexes $[(IPr)Au(\eta^2\text{-alkene})]^+\ SbF_6^-$ [alkene = norbornene (**1b**), 2,3-dimethyl-2-butene (**1c**), methylenecyclohexane (**1d**), 2-methyl-2-butene (**1e**), *cis*-2-butene (**1f**), 1-hexene (**1g**), and 4-methylstyrene (**1h**)] were isolated in ≥84% yield and were fully characterized (Chart 1).

Slow diffusion of hexane into a CH_2Cl_2 solution of **1a** at 4 °C gave colorless crystals of $\mathbf{1a}\cdot 2CH_2Cl_2$ 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 ligand is rotated 52° relative to the carbene N−C−N plane, which positions 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 $Au{-}CH_2$ and a long $Au{-}CMe_2$ interaction (Δd = 0.086 Å) (Table 1).

Chart 1. Synthesis of Gold π-Alkene Complexes



Crystals of the norbornene complex **1b** and the 2,3-dimethylbutene solvate complex $\mathbf{1c}\cdot 2CH_2Cl_2$ were also analyzed by X-ray diffraction (Figure 1, Table 1). In comparison to isobutylene

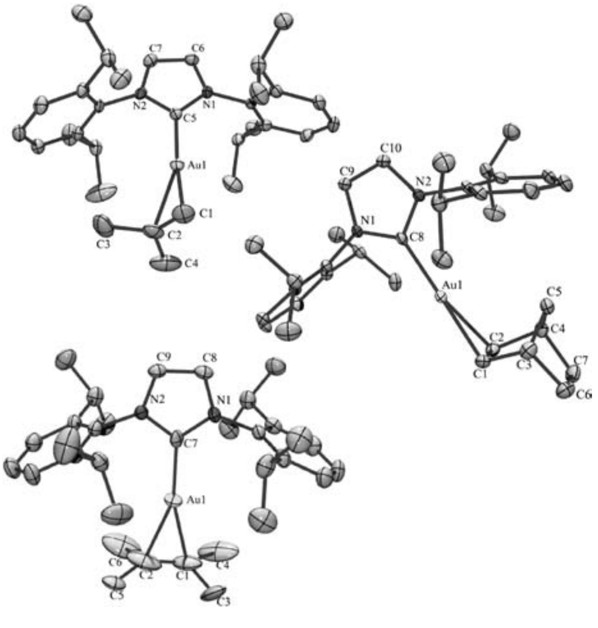


Figure 1. ORTEP diagrams of $\mathbf{1a}\cdot 2CH_2Cl_2$ (top structure), **1b** (middle structure), and $\mathbf{1c}\cdot 2CH_2Cl_2$. Ellipsoids are shown at 50%. Solvent, counterion, and hydrogen atoms are omitted for clarity.

Table 1. Selected Bond Lengths (Å) and Bond Angles (deg) for $\mathbf{1a}\cdot 2CH_2Cl_2$, **1b**, and $\mathbf{1c}\cdot 2CH_2Cl_2$

complex	C1−C2	Au−C1	Au−C2	$Au{-}C_{(NHC)}$	$C{=}C_{(centroid)}{-}Au{-}C_{(NHC)}$
$\mathbf{1a}\cdot 2CH_2Cl_2$	1.331	2.199	2.285	2.006	171.8
1b	1.374	2.224	2.248	1.996	174.8
$\mathbf{1c}\cdot 2CH_2Cl_2$	1.346	2.239	2.230	1.998	176.8

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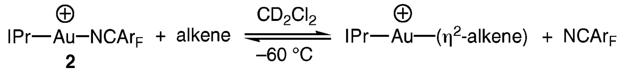
complex **1a**, complexes **1b** and **1c** displayed less deviation from linearity and more symmetric binding of the alkene to gold ($\Delta d <$ 0.025 Å) (Table 1, Figure 1). In contrast to **1a**, the C=C bond of coordinated norbornene in complex **1b** is positioned perpendicular (88.5°) to the carbene N—C—N plane, whereas the C=C bond of coordinated 2,3-dimethyl-2-butene in **1c**$\cdot 2CH_2Cl_2$ lies very near (<5°) the carbene plane. These variations suggest that alkene orientation is controlled largely by steric factors.

Although relative binding affinities of alkenes have been compiled for a number of transition metal complexes,[15] cationic gold(I) complexes are not among them. To evaluate the relative binding affinity of alkenes to the 12-electron gold fragment $[(IPr)Au]^+$, we determined the equilibrium constants for the displacement of $NCAr_F$ [$NCAr_F$ = N≡C-3,5-$C_6H_3(CF_3)_2$] from $[(IPr)Au(NCAr_F)]^+\ SbF_6^-$ (**2**) with alkenes in CD_2Cl_2 at −60 °C employing ^1H NMR analysis. K_{eq} decreased by a factor of ~13 in the order methylenecyclohexane > isobutylene ≈ 2-methyl-2-butene > 2,3-dimethylbutene > *cis*-2-butene > 1-hexene > *trans*-2-butene > propene (Table 2). To evaluate the effect of alkene electron density on binding affinity, we determined K_{eq} for the displacement of $NCAr_F$ from **2** with 4-substituted styrene derivatives $H_2C{=}CH$-4-C_6H_4X (X = OMe, Me, H, Br, CF_3). K_{eq} decreased with decreasing electron density by a factor of ~80 (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 S1), which is considerably more negative than the values obtained for the binding of 4-substituted styrenes to Ag^+ ions ($\rho = -0.77$)[16] or cationic, 16-electron Pt(II) ($\rho = -1.32$)[17] or Pd(II) ($\rho = -1.44$)[18] complexes. These data are consistent with the more pronounced σ-donating nature of the gold−(π-alkene) bond relative to these related electrophilic complexes.

Table 2. Equilibrium Constants for Reaction of Alkenes and Vinyl Arenes with **2** in CD_2Cl_2 at −60 °C



$$\underset{\mathbf{2}}{IPr{-}\overset{\oplus}{Au}{-}NCAr_F} + \text{alkene} \underset{-60\ ^\circ C}{\overset{CD_2Cl_2}{\rightleftharpoons}} IPr{-}\overset{\oplus}{Au}{-}(\eta^2\text{-alkene}) + NCAr_F$$

alkene	K_{eq}[a]	vinyl arene	K_{eq}[a]
methylene cyclohexane	90 ± 7	$H_2C{=}CH$-4-C_6H_4OMe	5.8 ± 0.2
isobutylene	67 ± 4	$H_2C{=}CH$-4-C_6H_4Me	2.7 ± 0.3
2-methyl-2-butene	64 ± 4	$H_2C{=}CH$-4-C_6H_4H	1.7 ± 0.4
2,3-dimethylbutene	50 ± 3	$H_2C{=}CH$-4-C_6H_4Br	0.27 ± 0.03
cis-2-butene	38 ± 2	$H_2C{=}CH$-4-$C_6H_4CF_3$	0.07 ± 0.01
1-hexene	25 ± 1		
trans-2-butene	12.5 ± 0.4		
propene	6.8 ± 0.3		

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

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 $CDCl_3$ 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 $k_{ex} = 64 \pm 3\ M^{-1}\ s^{-1}$ ($\Delta G^\ddagger = 16.0 \pm 0.1$ kcal mol^{-1}) (Figure S2). Second-order rate constants for isobutylene exchange with **1a** were also determined at 26 and 63 °C. An Eyring plot of these data provided the activation parameters: $\Delta H^\ddagger = 8 \pm 1$ kcal mol^{-1} and $\Delta S^\ddagger = -27 \pm 4$ eu (Figure S3).[19] 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.[20]

In summary, we have synthesized a family of cationic, linear gold π-alkene complexes that contain an *N*-heterocyclic carbene ligand and fully characterized these complexes in solution and, in three cases, by X-ray crystallography. All of our experimental observations, most notably the large $^1J_{C=C}$ of coordinated isobutylene and the pronounced effect of alkene electron density on binding affinity, point to nominal contribution of π-backbonding to the Au−alkene bonding interaction.

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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.

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