

## Reaction of gold(III) oxo complexes with alkenes. Synthesis of unprecedented gold alkene complexes, $[\text{Au}(\text{N},\text{N})(\text{alkene})][\text{PF}_6]$ . Crystal structure of $[\text{Au}(\text{bipy}^{\text{ip}})(\eta^2\text{-CH}_2=\text{CHPh})][\text{PF}_6]$ ( $\text{bipy}^{\text{ip}} = 6\text{-isopropyl-2,2'-bipyridine}$ )<sup>†</sup>

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Gold alkene complexes  $[\text{Au}(\text{bipy}^{\text{R}})(\eta^2\text{-alkene})][\text{PF}_6]$  ( $\text{bipy}^{\text{R}} = 6\text{-alkyl-2,2'-bipyridine}$ ) have been obtained by reaction of gold(III) oxo complexes  $[\text{Au}_2(\text{bipy}^{\text{R}})_2(\mu\text{-O})_2][\text{PF}_6]_2$  with alkenes. The crystal structure of the styrene adduct  $[\text{Au}(\text{bipy}^{\text{ip}})(\eta^2\text{-CH}_2=\text{CHPh})][\text{PF}_6]$  ( $\text{bipy}^{\text{ip}} = 6\text{-isopropyl-2,2'-bipyridine}$ ) has been solved by X-ray analysis.

Gold(III) oxo complexes<sup>1</sup> are a new entry into the relatively small family of late transition metal oxo complexes.<sup>2</sup> The chemistry of this class of compounds has been of interest for many years. Among the various aspects of the reactivity displayed by metal oxo complexes is the capability of transferring oxygen atoms to organic and inorganic substrates.<sup>2,3</sup>

In the course of our investigations of the reactivity of the oxo complexes  $[\text{Au}_2(\text{bipy}^{\text{R}})_2(\mu\text{-O})_2][\text{PF}_6]_2$  ( $\text{bipy}^{\text{R}} = 6\text{-alkyl-2,2'-bipyridine}$ ) we found that  $\text{PPh}_3$  is stoichiometrically converted into  $\text{OPPh}_3$ ; the gold(I) complex  $[\text{Au}(\text{PPh}_3)_2][\text{PF}_6]$  and the free bipyridine ligand are also quantitatively obtained from the reaction.<sup>1a</sup> In view of these encouraging results we decided to extend this reaction to alkenes. Alkene oxidation by oxygen atom transfer reaction from late transition metal oxo complexes is, at present, an objective of particular interest.

The  $\mu$ -oxo complexes  $[\text{Au}_2(\text{bipy}^{\text{R}})_2(\mu\text{-O})_2][\text{PF}_6]_2$  ( $\text{R} = \text{Me}$  **a**,  $\text{CH}_2\text{Me}$  **b**,  $\text{CHMe}_2$  **c**,  $\text{CH}_2\text{CMe}_3$  **d**) react with excess alkene in acetone or acetonitrile solution under different experimental conditions to give, albeit in low yield, unexpected alkene adducts,  $[\text{Au}(\text{bipy}^{\text{R}})(\text{alkene})][\text{PF}_6]$  (alkene = styrene **2**,  $\alpha$ -methylstyrene, ethylene and norbornene).<sup>4,5</sup> Few examples of alkene complexes obtained by reaction of a late transition metal oxo complex have been reported.<sup>6</sup>

The reaction with styrene was used as a model and studied with all the complexes in order to assess the possible influence of the alkyl substituent at the 6 position on the reactivity of the oxo complexes.<sup>†</sup> In no case is the reaction quantitative—average yield is in the range 15–45%. Most of the starting material is recovered when the reaction is carried out in anhydrous solvents, while complete conversion of the oxo complexes is accomplished in the presence of water, after a long reaction time.<sup>‡</sup> Variable amounts of metallic gold and organic products arising from oxidation of alkenes are also formed in all cases.<sup>4,5</sup> To the best of our knowledge, alkene oxidation by an isolated late transition metal oxo complex is still rare.<sup>6b,7</sup>

The thermally stable styrene adducts  $[\text{Au}(\text{bipy}^{\text{R}})(\eta^2\text{-CH}_2=\text{CHPh})][\text{PF}_6]$  (**2a–d**)<sup>†</sup> give satisfactory elemental analyses and their molecular ions  $M^+$  have been detected by FAB mass spectrometry. The <sup>1</sup>H NMR spectra at room temperature, recorded in various solvents, show that both the CH and CH<sub>2</sub> resonances are shifted upfield compared to free styrene. For example, in CDCl<sub>3</sub> the methyne proton resonates at  $\delta$  5.43 ( $\Delta\delta$  –1.29) and the methylene protons at  $\delta$  4.07 ( $\Delta\delta$  –1.68 ppm) and 4.03 ( $\Delta\delta$  –1.21 ppm). The

resonances of the corresponding carbon atoms are likewise shifted upfield with coordination-induced shift  $\Delta\delta$  –52.4 ppm for the methyne and –56.4 ppm for the methylene carbon. These upfield shifts are similar to those found in the comparable three-coordinate copper(I) olefin complexes supported by chelating nitrogen ligands ( $\Delta\delta(\text{H})$  –0.1 to –2.0 ppm;  $\Delta\delta(\text{C})$  –40 to –50 ppm).<sup>8,9</sup> Addition of one equivalent of styrene to a CD<sub>2</sub>Cl<sub>2</sub> solution of **2a** causes broadening of the vinylic protons of the coordinated styrene, indicating fast intermolecular exchange at room temperature.

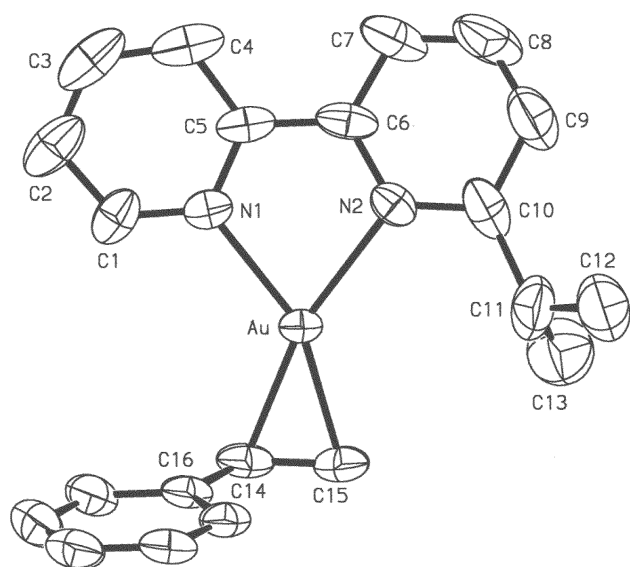
Variable temperature <sup>1</sup>H NMR spectra of complex **2c** indicate at room temperature a dynamic process involving rotation of the coordinated styrene around the metal–olefin bond. The calculated  $\Delta G_{\text{rot}}^\ddagger$  value (50.3 kJ mol<sup>–1</sup> at 243 K)<sup>†</sup> is in the range previously reported for similar d<sup>10</sup> olefin complexes with  $\alpha$ -diimine ligands.<sup>8e,9a,b,10</sup>

Olefin gold complexes have been known for many years,<sup>11</sup> however, only a small number of isolable complexes have been reported<sup>12</sup> and only a few of them have been structurally characterized.<sup>13</sup> Furthermore the available X-ray data are relevant to species incomparable to compounds **2a–2d**.

The structure of **2c**§ consists of the packing of  $[\text{Au}(\text{bipy}^{\text{ip}})(\eta^2\text{-styrene})]^+$  cations, PF<sub>6</sub><sup>–</sup> anions and MeCN molecules in the molar ratio 2 : 2 : 1. Fig. 1 shows an ORTEP view of the cation, and principal bond parameters are reported in the figure caption. The orientation of the olefin is coplanar with the bipyridine backbone, which chelates the gold centre with a bite angle of 75.1(2)°. The dihedral angle between the metal coordination plane and the C(14)–C(15)–C(16) plane is 77.2(3)° which means that there is a bending back angle of 12.8(3)° of the phenyl ring with respect to the ideal orthogonal coordination. Gold–carbon distances, Au–C(14) 2.114(6) and Au–C(15) 2.098(5) Å, are slightly shorter or similar to those found in two gold(I) alkene complexes (2.21(2), 2.15(2) Å<sup>13c</sup> and 2.14(4), 2.11(4) Å<sup>13b</sup>) (consider the high standard deviations of the four latter distances). The bond length between Au and the CH carbon atom, 2.114(6) Å, is slightly longer than that of the other Au–C contact, 2.098(5) Å. This is a common feature of metal-coordinated styrene, compare with e.g. Cu–C distances of 2.014(5) and 1.985(6) Å in the cationic Cu(I) styrene complex  $[\text{Cu}(\text{bipy})(\eta^2\text{-styrene})][\text{ClO}_4]$  **3**.<sup>8b</sup> The C(14)–C(15) distance, 1.384(8) Å, is slightly longer than in free styrene (1.346(20) Å)<sup>14</sup> and in **3** (1.358(10) Å)<sup>8b</sup> and comparable to that found in the neutral  $\beta$ -diketiminato complex  $[\text{Cu}(\text{Me}_2\text{NN})(\eta^2\text{-CH}_2=\text{CHPh})]$  (1.373(6) Å).<sup>8e</sup> The Au–N distances, 2.150(3) and 2.217(5) Å are very long, probably because of the *trans*-influence of the styrene molecule. The elongation of the Au–N(2) bond, 2.217(5) Å, compared to the Au–N(1) bond, 2.150(3) Å, is probably due to the steric hindrance of the bulky isopropyl substituent. A similar effect has been found previously, for instance, in **1d**.<sup>1c</sup>

The coordinated styrene is readily displaced from **2d** by triphenylphosphine, as shown by a proton spectrum recorded straight after the addition of one equivalent of PPh<sub>3</sub>.  $[\text{Au}(\text{PPh}_3)_2][\text{PF}_6]$  is quantitatively isolated from the reaction with two equivalents of PPh<sub>3</sub>.

<sup>†</sup> Electronic supplementary information (ESI) available: experimental details. See <http://www.rsc.org/suppdata/cc/b4/b404890c/>



**Fig. 1** ORTEP view of the  $[\text{Au}(\text{bipyridine})(\eta^2\text{-styrene})]^+$  cation. Ellipsoids are drawn at the 30% probability level. Selected bond distances (Å) and angles ( $^\circ$ ): Au–N(1) 2.150(3), Au–N(2) 2.217(5), Au–C(14) 2.114(6), Au–C(15) 2.098(5), C(14)–C(15) 1.384(8), C(14)–C(16) 1.488(6) Å, N(1)–Au–N(2) 75.1(2), N(1)–Au–C(14) 119.6(2), N(1)–Au–C(15) 157.8(2), N(2)–Au–C(14), 165.4(2), N(2)–Au–C(15) 127.0(2), C(14)–Au–C(15) 38.4(2), C(15)–C(14)–C(16) 126.3(5) $^\circ$ .

On the whole the spectroscopic and structural data, taken together, point to a non negligible  $\pi$  contribution in the olefin–gold bond.

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## Notes and references

† Reactions of compounds **1a–1d** with styrene. *Anhydrous solvent*: styrene (2 mmol) was added to a solution of **1** (0.2 mmol) in acetonitrile (40 cm<sup>3</sup>) (**1a** and **1b**) or acetone (40 cm<sup>3</sup>) (**1c** and **1d**). The resulting yellow solution was stirred for 3 days at room temperature and then filtered through Celite. The solution was evaporated to dryness and the residue extracted with CHCl<sub>3</sub> (3 × 15 cm<sup>3</sup>). The combined chloroform extracts were filtered and concentrated to a small volume. Addition of diethyl ether gave a whitish precipitate of compound **2** (**2a**, 15%; **2b**, 20%; **2c** 25%; **2d**, 45%). Unreacted complex **1** was recovered from the insoluble residue (**1a**, 66%; **1b**, 61%; **1c**, 50%; **1d**, 30%).

*Aqueous solvent*: to a solution of **1a** (0.320 g, 0.3 mmol) in acetonitrile (50 cm<sup>3</sup>) styrene (6 mmol) and water (5 cm<sup>3</sup>) were added. The resulting solution was stirred under Ar for 7 days at room temperature. Concentration of the filtered solution gave a white precipitate of **2a** which was recovered by filtration under vacuum. Recrystallization from dichloromethane gave the analytical sample (0.130 g, 35%). Compounds **2c** and **2d** were obtained similarly from **1c** and **1d**, respectively. In contrast to **2a**, **2c** and **2d** were extracted with CHCl<sub>3</sub> (3 × 15 cm<sup>3</sup>) after evaporation to dryness of the filtered solution. (**2c**, 31%; **2d**, 46%).

§ Crystal data for **2c**·0.5MeCN: C<sub>22</sub>H<sub>23.5</sub>Au<sub>1</sub>F<sub>6</sub>N<sub>2.5</sub>P, *M<sub>r</sub>* = 664.88, monoclinic, space group *P*2<sub>1</sub>/*c* (no. 14), *a* = 13.717(1), *b* = 12.833(1), *c* = 15.272(2) Å,  $\beta$  = 114.15(1) $^\circ$ , *U* = 2453.1(4) Å<sup>3</sup>, *Z* = 4, *d<sub>c</sub>* = 1.800 g cm<sup>-3</sup>, *T* = 223 K,  $\mu$  = 61.1 cm<sup>-1</sup>, *F*(000) = 1284. Reflections measured 33327, independent 5027 with *R<sub>int</sub>* = 0.027. Final *R<sub>2</sub>* (*F<sup>2</sup>*, all reflections) = 0.054, *R<sub>2w</sub>* = 0.090, conventional *R<sub>1</sub>* = 0.032 for 291 variables. Bruker SMART CCD area-detector, Mo–K $\alpha$  radiation ( $\lambda$  = 0.71073 Å),  $\omega$  scan mode,  $\theta_{\text{min}}$  = 3 $^\circ$ ,  $\theta_{\text{max}}$  = 26 $^\circ$ . Structure solved by direct methods and refined by full-matrix least squares. Atom C(13) is disordered and split into two half atoms, C(13a) and C(13b), with occupancy factors = 0.50; only C(13a) has been drawn in Fig. 1. The half MeCN molecule is disordered around an inversion centre. The programme used was Personal SDP on a

Pentium III computer. CCDC 236738. See <http://www.rsc.org/suppdata/cc/b4/b404890c/> for crystallographic data in .cif or other electronic format.

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