

Synthesis and properties of gold alkene complexes. Crystal structure of $[\text{Au}(\text{bipy}^{\text{oXyl}})(\eta^2\text{-CH}_2=\text{CHPh})](\text{PF}_6)$ and DFT calculations on the model cation $[\text{Au}(\text{bipy})(\eta^2\text{-CH}_2=\text{CH}_2)]^{\dagger}$

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Unprecedented 16-electron gold(I) olefin complexes of general formula $[\text{Au}(\text{bipy}^{\text{R,R'}})(\eta^2\text{-olefin})](\text{PF}_6)$ and $[\text{Au}_2(\text{bipy}^{\text{R,R'}})_2(\mu\text{-}\eta^2\text{:}\eta^2\text{-diolefin})](\text{PF}_6)_2$ ($\text{bipy}^{\text{R,R'}}$ = 6-substituted-2,2'-bipyridine) have been prepared by reaction of dinuclear gold(III) oxo complexes $[\text{Au}_2(\text{bipy}^{\text{R,R'}})_2(\mu\text{-O})_2](\text{PF}_6)_2$ with the appropriate olefin. The X-ray crystal structures of two mononuclear complexes (olefin = styrene) show in-plane coordination of the olefin and a C=C bond distance considerably lengthened with respect to the free olefin. The spectroscopic properties of the complexes are discussed and compared with those of analogous d^{10} metal derivatives. Both structural and spectroscopic information indicate a substantial contribution of π -back-donation to the Au–olefin bond in the three-coordinate species. Theoretical calculations carried out at the hybrid-DFT level on the model compound $[\text{Au}(\text{bipy})(\eta^2\text{-CH}_2=\text{CH}_2)]^{\dagger}$ show excellent agreement with the experimental findings giving in addition an estimate of a π -back-bonding contribution higher than that of the σ -bonding.

Introduction

The binding of unsaturated hydrocarbons to transition metals is a topic of paramount importance in organometallic chemistry for various reasons.¹ A great number of studies have concerned π -coordination complexes of Group 9–11 elements due to their involvement in a number of chemical, industrial and natural processes.^{1,2} As for Group 11 metal–olefin π -complexes, the wide variety of copper(I) and silver(I) derivatives has not been matched by analogous gold(I) species.³ Indeed, only few gold(I) olefin complexes have been reported: mostly they are monomers (olefin)AuCl,⁴ synthesized many years ago, which tend to have poor thermal and solution stabilities. Evidence for these species mainly rests on spectroscopic information. Only in a few cases could X-ray diffraction analysis be performed and their structure established:⁵ they are typical linear 14-electron derivatives where AuCl is coordinated to the mid-point of the olefin. A different environment around a gold atom was first observed in a complex tetranuclear species where an S_2Au fragment is coordinated to a C=C bond inside the backbone of a diphosphine ligand: an X-ray study⁶ demonstrated that in-plane coordination of the olefin is preferred as in the case of analogous d^{10} $\text{L}_2\text{M}(\text{olefin})$.⁷

Recently we preliminarily communicated the synthesis of the first cationic olefin complexes supported by 6-substituted-bipyridines and the structural characterization of the styrene derivative $[\text{Au}(\text{bipy}^{\text{iPr}})(\eta^2\text{-CH}_2=\text{CHPh})](\text{PF}_6)$ (bipy^{iPr} = 6-isopropyl-2,2'-bipyridine).⁸ This and other olefin complexes were obtained by reactions of a series of dinuclear gold(III) oxo complexes⁹ $[\text{Au}_2(\text{bipy}^{\text{R,R'}})_2(\mu\text{-O})_2](\text{PF}_6)_2$. In the course of our studies we isolated also the unprecedented oxauracyclobutane $[\text{Au}(\text{bipy}^{\text{Me}})(\kappa^2\text{-O,C-2-oxynorbornyl})](\text{PF}_6)$ ¹⁰ and established that the alkene complexes are formed, together with oxygenated organic products, by reaction of the auraoxetane species with excess olefin. Indeed, in the case of norbornene, *exo*-2,3-epoxynorbornane and the norbornene complex were obtained from the isolated auraoxetane.

Herein we describe a series of new alkene complexes, $[\text{Au}(\text{bipy}^{\text{R,R'}})(\eta^2\text{-olefin})](\text{PF}_6)$ and $[\text{Au}_2(\text{bipy}^{\text{R,R'}})_2(\mu\text{-}\eta^2\text{:}\eta^2\text{-diolefin})](\text{PF}_6)_2$, obtained by reaction of gold(III) oxo species. Their synthesis, analytical and spectroscopic characterization is reported in detail. The structure of $[\text{Au}(\text{bipy}^{\text{oXyl}})(\eta^2\text{-CH}_2=\text{CHPh})](\text{PF}_6)$ [$\text{bipy}^{\text{oXyl}}$ = 6-(2,6-dimethylphenyl)-2,2'-bipyridine] as obtained by means of X-ray diffraction analysis is also described. The nature of the olefin–gold(I) bond will be discussed on the basis of spectroscopic and structural information as well as on theoretical calculations carried out at the hybrid-DFT level on the model compound $[\text{Au}(\text{bipy})(\eta^2\text{-CH}_2=\text{CH}_2)]^{\dagger}$.¹¹

Further insight into the structural features and electronic properties of these still rare gold olefin derivatives can be of interest, for example, in the design of new catalysts. In the last two decades, the activation of C–C multiple bonds by gold catalysts has received considerable attention.¹² Most of the applications have concerned the addition of carbon-, nitrogen- and

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† The HTML version of this article has been enhanced with colour images.

oxygen-nucleophiles to the multiple bond of alkynes^{12b,c,f,13} while the activation of the allene¹⁴ and the alkene bonds¹⁵ for the addition of these nucleophiles has been far less undertaken. In most cases, gold-unsaturated molecule adducts and cyclic organogold species have been suggested to be key intermediates in C–E bond formation (E = C, N, O). Alkene–gold intermediates have also been proposed in the gold(I) catalyzed oxidative cleavage of C–C double bonds in water.¹⁶

Results and discussion

Synthesis of the complexes

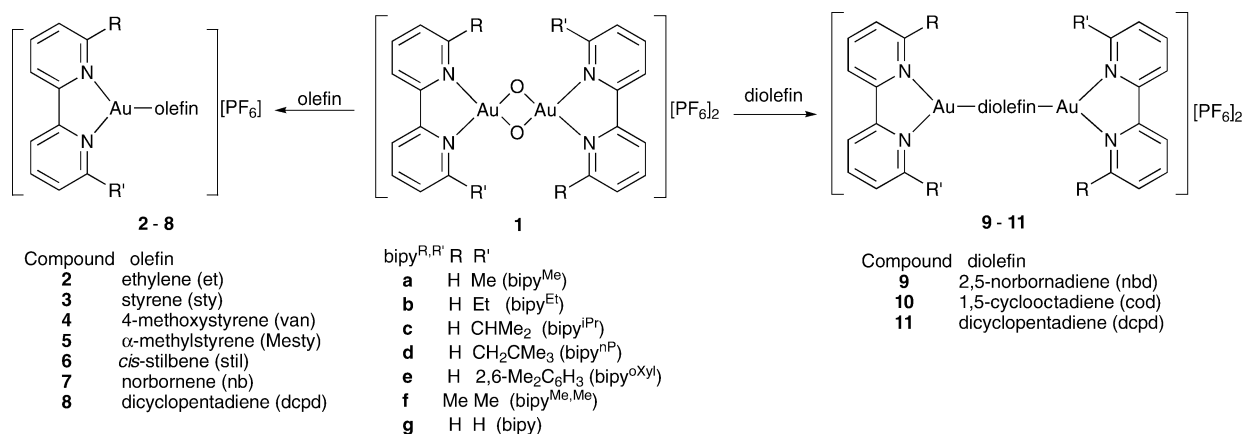
Novel cationic gold(I) alkene complexes, stabilized by 6-substituted-bipyridines, have been obtained by reaction of a series of dinuclear gold(III) oxo complexes $[\text{Au}_2(\text{bipy}^{\text{R,R}'})_2(\mu\text{-O})_2](\text{PF}_6)_2$, **1a–1f** ($\text{bipy}^{\text{R,R}'}$ = 6-R- or 6,6'-R₂-2,2'-bipyridine; see Scheme 1 for R). The reaction has been carried out with various linear and cyclic mono- and diolefins to give mononuclear $[\text{Au}(\text{bipy}^{\text{R,R}'})_2(\eta^2\text{-alkene})](\text{PF}_6)$, **2–8**, {alkene = ethylene (et), **2**; styrene (sty), **3**; 4-methoxystyrene (van), **4**; α -methylstyrene (Mesty), **5**; *cis*-stilbene (stil), **6**; norbornene (nb), **7**; dicyclopentadiene (dcpd), **8**} and dinuclear $[\text{Au}_2(\text{bipy}^{\text{R,R}'})_2(\mu\text{-}\eta^2\text{:}\eta^2\text{-dialkene})](\text{PF}_6)_2$, **9–11** {diolefin = 2,5-norbornadiene (nbd), **9**; 1,5-cyclooctadiene (cod), **10**; dicyclopentadiene (dcpd), **11**} alkene complexes, respectively (Scheme 1). The oxo complexes **1** treated with an excess of the appropriate olefin in Me₂CO or MeCN give the olefin complexes **2–11** in low to moderate yields—*e.g.* the yield for the styrene derivatives **3a–3f** is in the range 15–55% (see Experimental section). Metallic gold and organic products arising from oxidation of alkenes are also formed in all cases.¹⁷ In the case of α -methylstyrene and norbornene, unprecedented auroxetanes $[\text{Au}(\text{bipy}^{\text{R,R}'})_2(\kappa^2\text{-O,C-2-oxoalkyl})](\text{PF}_6)$ (alkyl = α -methylstyryl **4O**, norbornyl **7O**) are also formed in variable amounts depending on the olefin, the bipyridine ligand and the preparative conditions; *e.g.* significant amounts of **7O** are obtained by reaction of nb with **1a** in MeCN–H₂O.¹⁰ Evidence was also provided for the formation of the olefin complex **7a** and 2,3-epoxynorbornane from the isolated auroxetane **7Oa** and excess nb.¹⁰ An analogous reaction pathway is thus assumed for the formation of the other olefin complexes and of the oxygenated olefin derivatives.

Dinuclear species, featuring a bridging dialkene, have been obtained with nbd¹⁰ and cod, while with dcpd a mixture of the dinuclear **11** and mononuclear **8** species is formed, from which only the mononuclear complex **8** could be isolated in a pure form.

The alkene adducts **2–10** have good thermal stability and are stable in various solvents and in the presence of water. They can be dried at 10^{–1} mbar at ambient temperature without decomposition. Melting points are well above 100 °C, the bipy^{Me} derivatives being the most stable in each series; *cf.* for example: **7a**, mp 206–207 °C, and **7d**, mp 114–115 °C. Satisfactory elemental analyses have been obtained in all cases and the molecular ions of most of the complexes detected by FAB mass spectrometry. The mononuclear derivatives **2–8** give the molecular ions $[\text{Au}(\text{bipy}^{\text{R,R}'})_2(\text{olefin})]^+$; very low intensity peaks ($\leq 5\%$) corresponding to $[\text{Au}(\text{olefin})]^+$ and low to medium intensity peaks at $[M + 16]$, due to auroxetanes, have been detected in most of the spectra. Peaks corresponding to the mononuclear species are also present in the spectra of the dinuclear derivatives **9** and **10**. The molecular ions $[\text{Au}_2(\text{bipy}^{\text{R,R}'})_2(\text{diolefin})(\text{PF}_6)]^+$ have been observed in the case of **10c** and **11a** (mixture of **8a** and **11a**); low intensity peaks corresponding to M/2 have been found for all the dinuclear species.

Spectroscopic characterization

Compounds **2–11** have been characterized by standard 1D multinuclear NMR spectroscopy (Table 1). Dissociation of the olefin is not observed even in coordinating solvents such as CD₃CN. Nevertheless, addition of one equivalent of the corresponding olefin causes broadening of the signals of the coordinated olefin, indicating fast intermolecular exchange at room temperature: a dynamic process, involving free rotation of the coordinated olefin around the metal–olefin bond, gives rise to a single set of signals in all complexes; *e.g.* the four ethylene protons give a singlet. Variable temperature ¹H NMR spectroscopy carried out on complex **3c** shows that the process is frozen at low temperature as shown by the spectrum at 193 K, where, owing to the unsymmetrical nature of ligand **c**, two well-separate sets of signals (molar ratio 1.3 : 1) are observed for the olefin protons as well as for the CH and the diastereotopic CH₃ of the isopropyl group. The calculated $\Delta G_{\text{rot}}^\ddagger$ value (50.3 kJ mol^{–1} at 243 K) is in the range previously reported for d¹⁰ olefin complexes with α -diimine ligands.¹⁸



Scheme 1 Oxo complexes **1a–1g** (**1a**, **1b** and **1c** are mixtures of the *cis* and *trans* isomer) and olefin complexes **2–8** and **9–11**.

Table 1 ^1H and ^{13}C NMR shifts δ (ppm) of the coordinated olefins^a in selected $[\text{Au}(\text{bipy}^{\text{R,R}})(\text{olefin})](\text{PF}_6)$ and $[\text{Au}_2(\text{bipy}^{\text{R,R}})_2(\mu\text{-diolfin})](\text{PF}_6)_2$ and coordination-induced upfield shifts $\Delta\delta = \delta_{\text{free}} - \delta_{\text{coord}}$ (ppm)^b

Compound	Solvent	$=\text{CH}_2$			$=\text{CH}$			$=\text{C}$			
		δH	$\Delta\delta(\text{H})$	δC	$\Delta\delta(\text{C})$	δH	$\Delta\delta(\text{H})$	δC	$\Delta\delta(\text{C})$	δC	$\Delta\delta(\text{C})$
2a	CD_3CN	3.81	1.6	61.7	55.7						
2d	CD_2Cl_2	3.87	1.6								
2e	CD_2Cl_2	3.09	2.3	61.6	55.2						
3a	CD_2Cl_2	4.09, 4.16	1.2, 1.6			5.41	1.4				
3a	CD_3CN	4.06, 4.20	1.2, 1.6	54.7	59.8	5.44	1.3	80.9	56.9		
3d	CDCl_3	4.03, 4.08	1.2, 1.7			5.43	1.3				
3d	CD_2Cl_2	4.09, 4.15	1.2, 1.6			5.46	1.3				
3d	CD_3CN	4.06, 4.20	1.2, 1.6			5.44	1.3				
3d	$(\text{CD}_3)_2\text{CO}$	4.25, 4.41	1.0, 1.4	55.6	57.8	5.71	1.1	82.8	54.4		
3e	CD_2Cl_2	2.97 ^c	2.3, 2.8			5.11	1.7	81.9	55.3		
3e	$(\text{CD}_3)_2\text{CO}$	3.02 ^e	2.2, 2.8	53.6	59.8	5.29	1.5	81.6	55.6		
3f	CD_2Cl_2	4.20, 4.10	1.1, 1.7			5.31	1.5				
4a	CD_2Cl_2	4.01, 4.08	1.1, 1.6	53.3	58.3	5.43	1.3	83.0	53.5		
4a	$(\text{CD}_3)_2\text{CO}$	4.16, 4.33	0.9, 1.3			5.66	1.0				
5a	CD_2Cl_2	3.97, 4.23	1.2, 1.2	57.8	54.6					95.8	47.9
5e	CD_2Cl_2	2.79, 3.00	2.3, 2.4							95.2	46.7
5e	$(\text{CD}_3)_2\text{CO}$	2.87, 3.03	2.2, 2.4	55.9	56.7						
6a	CD_2Cl_2					5.77	0.7	79.2	51.4		
7a	CD_2Cl_2					4.22	1.8	83.3	52.3		
7a	$(\text{CD}_3)_2\text{CO}$					4.36	1.6				
7d	CD_2Cl_2					4.23	1.8	84.1	51.5		
7e	CD_2Cl_2					3.48	2.5	83.9	51.7		
8a	CD_2Cl_2					4.17, 4.38;	1.6, 1.8;	80.6, 84.9;	51.7, 48.4;		
9a	CD_3CN					5.71 ^f	(-0.2)	131.3, 132.7 ^g	(1.4, 3.6)		
9c	$(\text{CD}_3)_2\text{CO}$					4.59	2.2	85.2	59.0		
9d	CD_2Cl_2					4.84	2.0				
10a	CD_3CN					4.68	2.1				
10a	$(\text{CD}_3)_2\text{CO}$					4.72	0.8				
10c	CD_2Cl_2					4.94	0.7				
10c	CD_2Cl_2					4.79	0.6	80.5	48.4		
11a	CD_2Cl_2					4.54, 4.60;	1.4, 1.4;	81.2, 82.6;	50 ^h		
						4.84, 5.02	0.7, 0.5	83.8, 85.8 ^h			

^a Spectra recorded at 293 K and 300.0 (^1H) or 75.4 (^{13}C) MHz; for more data, see Experimental section. ^b For δH and δC of the free olefins, see Experimental section. ^c Centre of a second order multiplet. ^d Obscured by the solvent. ^e Centre of a doublet. ^f Uncoordinated $=\text{CH}_{2,3}$ of depd . ^g Not attributed. ^h Average value.

With few exceptions—which will be discussed later—the signals of the olefin protons are sharp and show a typical pattern; in all cases they are significantly shifted to high field with respect to those of the free alkenes, with $\Delta\delta(\text{H})$ [$\Delta\delta = \delta(\text{H})_{\text{free}} - \delta(\text{H})_{\text{coord}}$] in the range 0.8–2.2 ppm: the low value corresponds to the cod adducts **10**, the high to the nbd adducts **9**. The chemical shifts of the olefin protons show some dependence on the solvent (see Experimental section and Table 1). At variance, in a given solvent the chemical shift is independent of the bipyridine ligand, with the exception of the **e** and **f** derivatives (Table 1).¹⁹ Compounds **9** and **10** display only one set of signals for the protons of the bridging diolefin: these are sharp singlets in **9** while in **10** they are broad; in both cases upfield shifts are observed.

The resonances of the olefin carbon atoms of **2–11** are likewise shifted upfield with coordination-induced shift $\Delta\delta(\text{C})$ [$\Delta\delta(\text{C}) = \delta(\text{C})_{\text{free}} - \delta(\text{C})_{\text{coord}}$] in the range 47.5–61.7 ppm (Table 1); the following general trend is observed: $\Delta\delta(\text{CRR}') < \Delta\delta(\text{CHR}) < \Delta\delta(\text{CH}_2)$ with differences $\Delta\delta\delta = \Delta\delta(\text{CH}_2) - \Delta\delta(\text{CHR})$ and $\Delta\delta(\text{CHR}) - \Delta\delta(\text{CRR}')$ of ca. 5 ppm. As observed for the proton resonances, the corresponding methynic carbons of the coordinated cod and nbd are less and more shielded respectively compared to those of the other olefins.

The ¹H and ¹³C NMR data of **2–11**, in particular the extent of the upfield shift of the olefinic protons and carbons, can be compared with those of various d¹⁰ olefin complexes. Comparison with the 14-electron (olefin)AuCl⁴ complexes, for which, *inter alia*, only the proton spectra have been reported,^{4c–g,i} underlines the different bonding mode of the coordinated alkene; indeed, in these complexes the olefin protons feature small (either low- or upfield) shifts: e.g. in {CH₂=CH(CH₂)_nMe}AuCl the methylenic protons are shifted 0.1 ppm upfield and the methynic proton 0.1 ppm downfield.^{4d} More meaningful is the comparison with other tricoordinate d¹⁰ metal ion complexes. A number of comparable copper(I) derivatives [(N[∞]N)Cu(olefin)]^{m+}, both cationic (*n* = 1; N[∞]N = bipy, phen and their derivatives, HN(2-py)₂, O=C(2-py)₂)²⁰ and neutral (*n* = 0; N[∞]N = H₂B[3,5-(CF₃)₂pz]₂)^{3a,d} have been reported which exhibit $\Delta\delta(\text{H})$ values in the range 0.1 to 0.8 ppm. Larger $\Delta\delta(\text{H})$ (0.9–2.3 ppm) are found for Cu(I) olefin complexes supported by diamines^{20d,21} or electron-rich anionic ligands, such as β -diketiminato^{18a} and iminophosphoramidate.²² Carbon spectra have also been reported for the compounds supported by diamines²¹ and anionic ligands:^{3a,d,18a,22} these feature upfield shift of the olefinic carbons with the same trend observed for the proton resonances. For example, the ethylene complexes supported by the diamines or the electron-rich anionic ligands exhibit $\Delta\delta(\text{C})$ of 42 and 50 ppm, respectively; lower values have been found in the other cases. Silver(I) mainly forms isoleptic complexes such as the trigonal planar ethylene complex [Ag(CH₂=CH₂)₃]⁺,²³ this shows downfield shift of the olefin protons and a very small upfield shift ($\Delta\delta$ 6.9 ppm) of the carbons; a slightly larger shift ($\Delta\delta$ 20.1 ppm) of the ethylene carbons was exhibited by the trigonal complex [Ag(N[∞]N)(CH₂=CH₂)]⁺ supported by a chelating diamine.^{3e} Substantially larger high-field shift [$\Delta\delta(\text{H})$ 3.0–3.5 ppm, $\Delta\delta(\text{C})$ 90–120 ppm] of both olefin protons and carbons was observed for several palladium(0) and platinum(0) complexes of the type [(N[∞]N)M(olefin)] (N[∞]N = diamine, diimine) with electron accepting olefins,^{18b,c,24} as well as for some five-coordinate Pt(II)²⁵ complexes of electron-rich olefins.

Alkene adducts **2–11** are unprecedented in the chemistry of gold: they are the first 16-electron gold olefin complexes and the first isolated cationic species.²⁶

It is widely acknowledged that the NMR parameters give useful insight into the nature of the metal–olefin bond; in particular the extent of the shift featured by the coordinated olefin carbons gives an estimate of the electronic density around the olefinic carbon nuclei.^{18b,27} According to the model originally proposed by Chatt, Dewar and Duncanson, both σ -donation from the olefin to the metal and π -back-donation from the metal to the olefin contribute to the metal–olefin bond.²⁸ Several studies have been addressed to evaluate the magnitude of these contributions; most have concerned platinum compounds, due to their chemical inertness and to the wide variety of olefins and coordination environments. A number of theoretical¹¹ and experimental (in the gas phase)²⁶ studies have also been performed on the ethylene adducts of Group 11 metals; it was established that in the cationic species [M(η^2 -CH₂=CH₂)]⁺ σ -donation is by far more important than π -back-donation.^{11a–d} Structural data in the case of copper(I) compounds support this trend; on the other hand, on the basis of thermodynamic and spectroscopic data, π -back-donation is suggested to be a weak but important factor in stabilizing these olefin complexes.^{20e,3a–c}

According to the acknowledged trend that the high-field coordination shift of the olefin protons and carbons increases on increasing π -back-donation contribution,^{18b,27} a remarkable π -contribution to the olefin–gold bond in compounds **2–11** is suggested on the basis of the NMR parameters, notwithstanding the positive charge expected to considerably decrease the π -back-donation.^{27a} The spectral features on which this statement is based can be summarized as follows:

- (i) High-field coordination shift of the olefin protons $\Delta\delta(\text{H})$ and carbons $\Delta\delta(\text{C})$ in the range 0.8–2.2 and 48–62 ppm, respectively. The high-field shift of the olefin protons, although less meaningful than that of the carbons, has been used as a probe of the extent of π -back-donation also in palladium and platinum complexes.²⁹
- (ii) In the styrene complexes **3** and **4**, small differences in the upfield shift $\Delta\delta(\text{C})$ are observed between the olefinic carbons ($\Delta\Delta\delta = 4.0$ ppm in **3** and 4.9 ppm in **4**); a small difference ($\Delta\Delta\delta = 7.0$ ppm) is also found in the α -methylstyrene derivatives **5** between the methylenic and quaternary carbon. These data indicate a low polarization of the C=C double bond and, as a consequence, a high degree of π -back-donation.²⁷
- (iii) A small value for $\delta(\text{CHR}) - \delta(\text{CH}_2)$ of coordinated styrene is also considered diagnostic of high π -back-donation.^{27b,30} For complexes **3** and **4** this difference is small, 27.5 and 29.7 ppm, respectively; in the free olefins it is 23.2 (sty) and 24.8 ppm (van).

Structural characterization

The structure of **3e** consists of the packing of [Au(bipy^{oxy}yl)(η^2 -styrene)]⁺ cations, **3e'**, PF₆[−] anions and CH₂Cl₂ molecules in the molar ratio 1 : 1 : 1 with normal van der Waals contacts. Fig. 1 shows an ORTEP view of the cation **3e'**; principal bond parameters are reported in Table 2, together with corresponding distances and angles in cation **3e'**. The orientation of the olefin is coplanar with the pyridine backbone, which chelates the gold centre with a bite angle of 75.1(1)°. The gold atom is in a square planar environment with a slight tetrahedral distortion, maximum

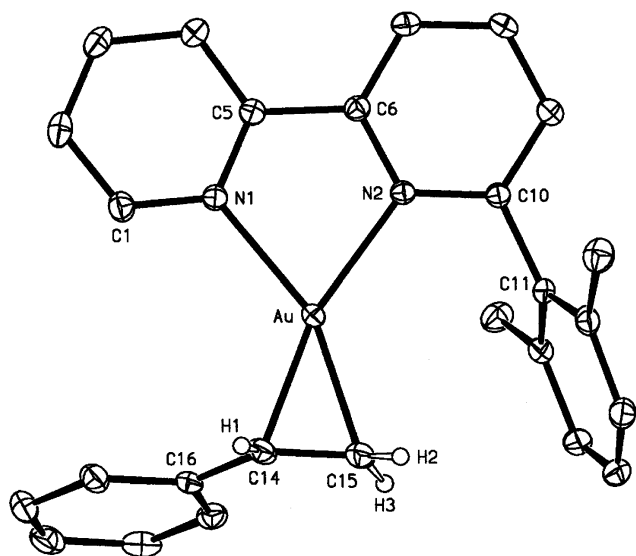


Fig. 1 ORTEP view of cation $3e'$. Ellipsoids are drawn at the 30% probability level.

Table 2 Selected bond lengths (Å) and angles (°) in $3e'^8$ and $3e'$, with estimated standard deviations (e.s.d.s) on the last figure in parentheses

	$3e'$	$3e'$
Au–N(1)	2.150(3)	2.176(2)
Au–N(2)	2.217(5)	2.204(2)
Au–C(14)	2.114(6)	2.118(2)
Au–C(15)	2.098(5)	2.105(3)
C(14)–C(15)	1.384(8)	1.409(4)
C(14)–C(16)	1.488(6)	1.484(4)
N(1)–Au–N(2)	75.1(2)	75.1(1)
N(1)–Au–C(14)	119.6(2)	119.7(1)
N(1)–Au–C(15)	157.8(2)	158.6(1)
N(2)–Au–C(14)	165.4(2)	165.2(1)
N(2)–Au–C(15)	127.0(2)	126.2(1)
C(14)–Au–C(15)	38.4(2)	39.0(1)
C(15)–C(14)–C(16)	126.3(5)	125.5(2)

distances from the best plane being +0.030(3) and $-0.031(3)$ Å for C(14) and C(15), respectively. The dihedral angle between the Au–N(1)–N(2) and Au–C(14)–C(15) planes is $3.2(1.1)^\circ$, that between the metal coordination plane and the C(14)–C(15)–C(16) plane is $78.6(2)^\circ$, which means that there is a bending back angle of $11.4(2)^\circ$ of the phenyl ring with respect to an ideal orthogonal coordination. As can be seen in Table 2 all bond lengths and angles in $3e'$ are in good agreement with those found in $3e'$ and previously discussed.⁸ In particular, the C(14)–C(15) distance in $3e'$ is even slightly longer than that found in $3e'$ (1.409(4) vs. 1.384(8) Å). The distances of H2 and H3 from the centroid of the xylyl ring are 3.12(4) and 3.09(4) Å, respectively, suggesting some kind of non-covalent interaction with the aromatic ring. It is worth noting that, in agreement, in the ^1H NMR the same protons are remarkably upfield shifted as previously commented.¹⁹

Theoretical calculations

In order to verify the actual relationship between the spectroscopic and structural features and the extent of π -back-donation, an investigation was undertaken at density functional theory (DFT)³¹

level on the model cationic complex $[\text{Au}(\text{bipy})(\eta^2\text{-CH}_2=\text{CH}_2)]^+$ ($2g'$), differing from $3e'^8$ and $3e'$ in having unsubstituted bipyridine (bipy) and ethylene as ligands at the gold(I) metal centre. With the aim of evaluating a proper computational set-up, calculations have been carried out on the complex $[\text{Au}(\eta^2\text{-CH}_2=\text{CH}_2)]^+$ with different functionals and basis sets (BS's). In particular, we have focussed on hybrid-DFT calculations (with both Becke3LYP³² and mPW1PW³³ functionals) considering the 6-31+G*³⁴ and Ahlrichs pVDZ³⁵ BS's for the organic framework and three different BS's with relativistic effective core potentials (RECP) for the metal ion (LanL2DZ,³⁶ Stuttgart RSC,³⁷ CRENBL³⁸),³⁹ An examination of the results of our calculations (Table 3) allows us to deduce that: 1) the two BS's used for C and H yield very similar results, which are comparable to those reported previously on the same system^{11a,c} and can be considered reliable based on the calculation on free ethylene (for example, the C–C distance $d_{\text{C-C}}$ is calculated in the range 1.330–1.335 Å, to be compared to the solid-state experimental value of 1.339 Å)⁴⁰; 2) in agreement with the results reported previously,⁴¹ the Becke3LYP functional yields slightly overestimated $d_{\text{Au-C}}$ lengths (in the range 2.214–2.253 Å), reflected in lower bond dissociation energy (BDE) values (55.9–61.1 kcal mol⁻¹), as compared to those obtained with the mPW1PW functional ($d_{\text{Au-C}}$ in the range 2.176–2.213 Å; BDE 56.8–63.3 kcal mol⁻¹);^{11a,c,26a,42,43} 3) within each series, the Stuttgart BS gives the poorest estimates of the BDE values,⁴² corresponding to the highest $d_{\text{Au-C}}$ and the lowest $d_{\text{C-C}}$ distances. In all cases, as expected on the basis of the Dewar–Chatt–Duncanson bond model,²⁸ the interaction between Au⁺ and ethylene results in a lengthening $\Delta d_{\text{C-C}}$ of the C–C ethylene bond distance $d_{\text{C-C}}$, corresponding to a lowering in the C–C bond order. This can be evaluated through the Wiberg bond index $\text{WBI}_{\text{C-C}}$, whose variation $\Delta \text{WBI}_{\text{C-C}}$ with respect to free ethylene is not sensibly affected by the level of theory (0.442–0.487). As pointed out by Lee and co-workers,^{11a} the degree of σ -donation (from the filled π -bonding orbital of ethylene to an empty orbital centred on the metal) and π -back-donation (from a filled d orbital of the metal to the unoccupied antibonding π^* orbital of ethylene) can be separately evaluated by the electron populations P_π and P_{π^*} of the involved natural bonding orbitals (NBO's)⁴⁴ localised on the olefin in the complex $[\text{Au}(\eta^2\text{-CH}_2=\text{CH}_2)]^+$. In agreement with the values reported previously for the same complex,^{11a} the variation in the electron population on the π -bonding orbital of ethylene is higher than that on the π^* -antibonding orbital, confirming that the extent of donation is higher than that of back-donation.

Based on the results obtained for $[\text{Au}(\eta^2\text{-CH}_2=\text{CH}_2)]^+$, we have performed DFT calculations on $2g'$ with the Becke3LYP and mPW1PW functionals, using the Ahlrichs pVDZ BS's for the ligands, and the LanL2DZ and CRENBL basis sets with RECP's for the central metal ion. In concordance with the calculations on the $[\text{Au}(\eta^2\text{-CH}_2=\text{CH}_2)]^+$ moiety, a comparison of the optimised bond lengths and angles with the average structural values collected for $3e'^8$ and $3e'$ clearly indicates that the mPW1PW functional yields more reliable results (Table 4). In fact, geometry optimisations performed with Barone's functional perfectly reproduce the experimental bond lengths, especially when the CRENBL BS is used for the gold centre. The C–C distance of the ethylene ligand is only slightly overestimated in all the explored combinations of functionals and BS's (1.404–1.412 Å), the C–C elongation with respect to free ethylene resulting

Table 3 Optimised Au–C ($d_{\text{Au-C}}$, Å) bond distance, C–C ($d_{\text{C-C}}$, Å) bond distance and variation with respect to free ethylene ($\Delta d_{\text{C-C}}$, Å), C–C Wiberg bond index ($\text{WBI}_{\text{C-C}}$) and variation with respect to free ethylene ($\Delta \text{WBI}_{\text{C-C}}$), population of the π natural bond orbital (P_{π} , e) and variation with respect to free ethylene (ΔP_{π} , e), population of the π^* natural bond orbital (P_{π^*} , e), and bond dissociation energies (BDE, kcal mol⁻¹) calculated at DFT level with different hybrid functionals and basis sets (BS's) on the [Au(CH₂=CH₂)]⁺ model complex

Functional	C,H BS	Au BS	$d_{\text{Au-C}}$	$d_{\text{C-C}}$	$\Delta d_{\text{C-C}}$	$\text{WBI}_{\text{C-C}}$	$\Delta \text{WBI}_{\text{C-C}}$	P_{π}	ΔP_{π}	P_{π^*} ^m	BDE ⁿ
B3LYP	Ahlrichs pVDZ	LanL2DZ	2.242	1.400	0.067 ^a	1.600	0.443 ^e	1.631	0.368 ⁱ	0.131	58.2
		CRENBL	2.214	1.402	0.069 ^a	1.559	0.484 ^e	1.587	0.412 ⁱ	0.142	61.1
		Stuttgart RSC 1997	2.253	1.397	0.064 ^a	1.594	0.449 ^e	1.611	0.388 ⁱ	0.119	55.9
	6-31 + G*	LanL2DZ	2.239	1.403	0.068 ^b	1.586	0.455 ^f	1.619	0.381 ^j	0.137	59.9
		CRENBL	2.219	1.403	0.068 ^b	1.557	0.484 ^f	1.585	0.415 ^j	0.142	60.9
		Stuttgart RSC 1997	2.249	1.399	0.064 ^b	1.587	0.454 ^f	1.605	0.395 ^j	0.123	56.4
mPW1PW	Ahlrichs pVDZ	LanL2DZ	2.201	1.397	0.067 ^c	1.602	0.442 ^g	1.647	0.352 ^k	0.145	59.6
		CRENBL	2.176	1.399	0.069 ^c	1.560	0.484 ^g	1.599	0.400 ^k	0.154	62.9
		Stuttgart RSC 1997	2.213	1.394	0.064 ^c	1.600	0.444 ^g	1.628	0.371 ^k	0.130	56.8
	6-31 + G*	LanL2DZ	2.199	1.400	0.068 ^d	1.560	0.482 ^h	1.628	0.372 ^l	0.130	62.1
		CRENBL	2.180	1.400	0.068 ^d	1.555	0.487 ^h	1.594	0.406 ^l	0.154	63.3
		Stuttgart RSC 1997	2.209	1.396	0.064 ^d	1.588	0.454 ^h	1.619	0.381 ^l	0.135	58.0

^a $d_{\text{C-C}} = 1.333$ Å for free ethylene. ^b $d_{\text{C-C}} = 1.335$ (b) Å for free ethylene. ^c $d_{\text{C-C}} = 1.330$ (c) Å for free ethylene. ^d $d_{\text{C-C}} = 1.332$ (d) Å for free ethylene. ^e $\text{WBI}_{\text{C-C}} = 2.043$ for free ethylene. ^f $\text{WBI}_{\text{C-C}} = 2.041$ for free ethylene. ^g $\text{WBI}_{\text{C-C}} = 2.044$ for free ethylene. ^h $\text{WBI}_{\text{C-C}} = 2.042$ for free ethylene. ⁱ $P_{\pi} = 1.999$ e for free ethylene. ^j $P_{\pi} = 2.000$ e for free ethylene. ^k $P_{\pi} = 1.999$ e for free ethylene. ^l $P_{\pi} = 2.000$ e for free ethylene. ^m The NBO π^* is unoccupied in free ethylene. ⁿ Calculated with unscaled ZPE corrections.

Table 4 Au–N ($d_{\text{Au-N}}$, Å) and Au–C ($d_{\text{Au-C}}$, Å) bond distances, C–C ($d_{\text{C-C}}$, Å) bond distances and variation with respect to free ethylene ($\Delta d_{\text{C-C}}$, Å), N–Au–N ($\alpha_{\text{N-Au-N}}$, °) and C–Au–C ($\alpha_{\text{C-Au-C}}$, °) angles optimized at DFT level for the model complex **2g'**, as compared to the corresponding experimental average values derived from the XRD data collected for **3e** and **3e**

	Functional	Au BS	$d_{\text{Au-N}}$	$d_{\text{Au-C}}$	$d_{\text{C-C}}$	$\Delta d_{\text{C-C}}$	$\alpha_{\text{N-Au-N}}$	$\alpha_{\text{C-Au-C}}$
DFT ^a	B3LYP	LanL2DZ	2.276	2.181	1.404	0.071 ^b	73.09	37.55
		CRENBL	2.245	2.142	1.411	0.078 ^b	73.94	38.47
	mPW1PW	LanL2DZ	2.237	2.141	1.405	0.075 ^c	73.81	38.30
		CRENBL	2.210	2.109	1.412	0.082 ^c	71.59	39.10
Experimental			2.186	2.109	1.396	0.057 ^d	75.09	38.67

^a Ahlrichs pVDZ BS's for C, H, and N. ^b $d_{\text{C-C}} = 1.333$ Å calculated for free ethylene. ^c $d_{\text{C-C}} = 1.330$ Å calculated for free ethylene. ^d $d_{\text{C-C}} = 1.339$ Å for free ethylene (ref. 40).

anyway in an agreement within 0.02 Å with the experimental average value. The nature of the bonding between the closed-shell fragments [Au(bipy)]⁺ and ethylene in **2g'**, for which a BDE value of 64.5 kcal mol⁻¹ was calculated {BDE = 62.9 kcal mol⁻¹ for [Au(η^2 -CH₂=CH₂)]⁺ at the same level of theory, Table 3}, can be rationalised in terms of a fragment molecular orbital (FMO)⁴⁵ approach (Fig. 2). In agreement with the Dewar–Chatt–Duncanson bond model,²⁸ the ethylene filled π orbital is symmetry allowed to σ -interact with the lowest unoccupied orbital of the [Au(bipy)]⁺ moiety, which is centred on the metal ion and is mainly 6p_y in nature, resulting in the HOMO–2 and LUMO+5 of **2g'**. The back-bonding occurs between the unoccupied π^*

orbital on ethylene with the highest occupied molecular orbital of [Au(bipy)]⁺, which features a very large contribution from the 5d_{xy} Au atomic orbital, to give HOMO–1 and LUMO+3 in the **2g'** cation. Interestingly enough, all calculations agree in evaluating a slight but significant negative NBO charge $Q_{\text{C}_2\text{H}_4}$ (of about –0.1 e) on the η^2 -coordinating ethylene, the positive charge of the cationic complex being entirely concentrated on the [Au(bipy)]⁺ fragment (Table 5). This suggests that, contrary to what was calculated for the [Au(η^2 -CH₂=CH₂)]⁺ model complex, the extent of π -back-bonding would be higher than that of the σ -bonding, as previously observed for complexes of the type [L₂M(η^2 -CH₂=CH₂)] (M = Ni, Pd, Pt; L = PH₃, PMe₃).⁴³ Accordingly, the electron population

Table 5 Calculated NBO charges (Q_{Au} , Q_{bipy} , and $Q_{\text{C}_2\text{H}_4}$, e) on the Au centre and on the bipy and ethylene ligands, respectively, population of the π natural bond orbital (P_{π} , e) and variation with respect to free ethylene (ΔP_{π} , e), population of the π^* natural bond orbital (P_{π^*} , e), C–C Wiberg bond index ($\text{WBI}_{\text{C-C}}$) and variation with respect to free ethylene ($\Delta \text{WBI}_{\text{C-C}}$), calculated at DFT level on model complex **2g'**^a

Functional	Au BS	Q_{Au}	Q_{bipy}	$Q_{\text{C}_2\text{H}_4}$	P_{π}	ΔP_{π}	P_{π^*} ^c	$\text{WBI}_{\text{C-C}}$	$\Delta \text{WBI}_{\text{C-C}}$
B3LYP	LanL2DZ	0.797	0.258	–0.073	1.741	0.258 ^b	0.312	1.547	0.496 ^d
	CRENBL	0.778	0.298	–0.076	1.699	0.300 ^b	0.352	1.487	0.556 ^d
mPW1PW	LanL2DZ	0.839	0.256	–0.110	1.743	0.256 ^b	0.341	1.405	0.639 ^e
	CRENBL	0.803	0.303	–0.098	1.697	0.303 ^b	0.375	1.412	0.632 ^e

^a Ahlrichs pVDZ BSs for C, H, and N. ^b $P_{\pi} = 1.999$ e for free ethylene. ^c The NBO π^* is unoccupied in free ethylene. ^d $\text{WBI}_{\text{C-C}} = 2.043$ for free ethylene. ^e $\text{WBI}_{\text{C-C}} = 2.044$ for free ethylene.

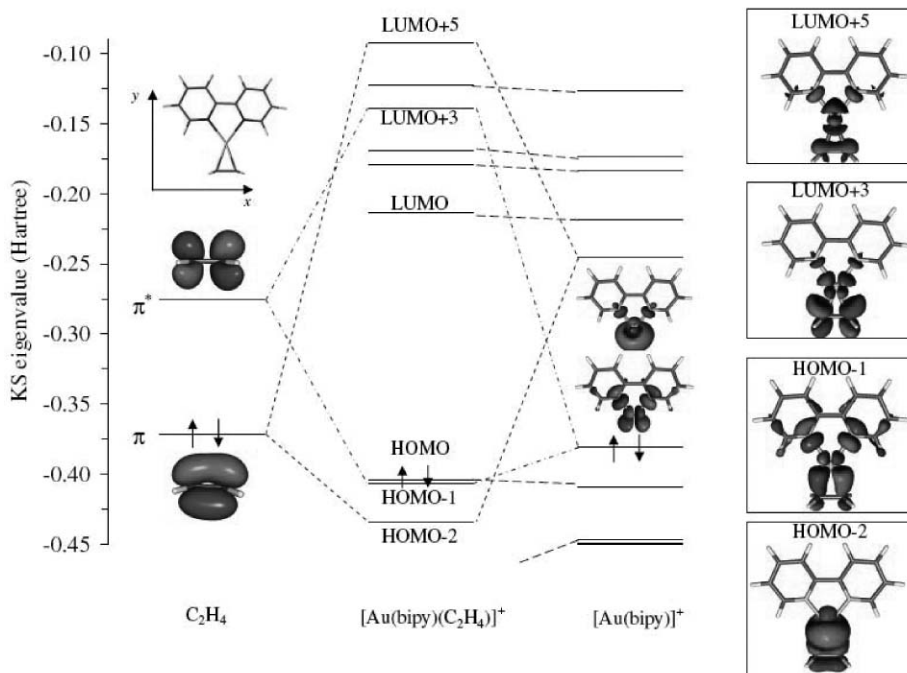


Fig. 2 MO diagram showing the interaction between the $[\text{Au}(\text{bipy})]^+$ and $\eta^2\text{-CH}_2=\text{CH}_2$ moieties in the model complex $[\text{Au}(\text{bipy})(\text{CH}_2=\text{CH}_2)]^+$ (**2g'**), calculated at DFT level (mPW1PW functional, Ahlrichs pVDZ BS's for C and H, LanL2DZ BS with RECP for Au). The MOs HOMO, LUMO+1, LUMO+2, and LUMO+4 are centred on the bipy ligand.

P_{π^*} on the π^* natural orbital of the coordinated olefin is slightly higher than the variation of the population ΔP_{π} on the π orbital (0.375 and 0.303 e , respectively, at mPW1PW/CRENBL level). The increased back-bonding on passing from $[\text{Au}(\eta^2\text{-CH}_2=\text{CH}_2)]^+$ to **2g'** is reflected not only in the optimised C–C bond distances, but also in the Wiberg bond indexes, lower for the latter model complex (1.560 and 1.412, respectively, at mPW1PW/CRENBL level).

Exchange reactions of the alkene complexes. Some aspects of the reactivity of the new gold alkene complexes have been explored. As discussed before, the intermolecular exchange between the coordinated and the free styrene was found to be very fast for complexes **3** on the NMR time scale at room temperature, as shown by broadening of the signals of the coordinated styrene on addition of an equimolar amount of styrene to a solution of the complex; the exchange reaction between coordinated and free norbornene is fast also for complexes **7**. At variance, no broadening was observed for the coordinated ethylene protons when a solution of complex **2a** in $(\text{CD}_3)_2\text{CO}$ was saturated with ethylene. From complex **3a** the coordinated styrene was readily displaced by excess ethylene and norbornene to give **2a** and **7a**, respectively; the reverse reaction in the case of complex **2a** affords an equilibrium mixture of **2a** and **3a** (**2a** : **3a** = 1 : 1), free styrene and ethylene. Addition of ethylene to a dichloromethane solution of **3e** resulted in the partial displacement of the coordinated styrene to give a 2 : 1 mixture of **3e** and **2e**. Norbornene was not displaced by other olefins; the relatively higher stability of the norbornene complexes **7**, compared to **3**, is consistent with the larger values of $\Delta\delta$ which suggest a stronger π -bond of this strained alkene to gold. An analogous behaviour has been observed in a cationic platinum(II) complex,^{27c}

and explained by the pyramidalization effect occurring in strained cyclic alkenes, which results in a stronger metal–olefin bond.⁴⁶ In agreement, addition of excess dicyclopentadiene to the dinuclear dcpd complex **11a** (the major component of the mixture obtained by reaction of **1a** with dcpd) results in the ready displacement of the less strong π -bond, *i.e.* that to the C=C of the cyclopentene ring, with formation of the mononuclear species **8a**, where the gold atom is bonded to the C=C bond of the norbornene ring.

The coordinated styrene in complex **3a** is not displaced by CO, at least at one atmosphere pressure. It is worth noting that addition of excess olefin to a gold carbonyl complex has been used to synthesize alkene complexes of type (olefin)AuCl (olefin = norbornene, *cis*-cyclooctene, dcpd).⁵ As a consequence of the greater Cu→CO back donation, the opposite behaviour has been observed for most of the copper(I) olefin complexes supported by chelating anionic O- and N-donor ligands, for which the olefin/CO exchange reaction has been thoroughly studied.^{3a-c}

Conclusion

Unprecedented 16-electron gold(I) cationic olefin complexes have been successfully obtained by reaction of dinuclear gold(III) oxo complexes, through auraoxetane intermediates.¹⁰ Owing to their novelty, they have been thoroughly studied both in solution, mainly by ¹H and ¹³C NMR spectroscopy, and in the solid state, by X-ray diffraction analysis. Excellent correlation has been found between spectroscopic and structural parameters which point to a significant contribution of π -donation from the metal to the alkene. These findings have also been corroborated by theoretical calculations carried out at hybrid-DFT level on the model cation $[\text{Au}(\text{bipy})(\eta^2\text{-CH}_2=\text{CH}_2)]^+$; these give an estimate of a

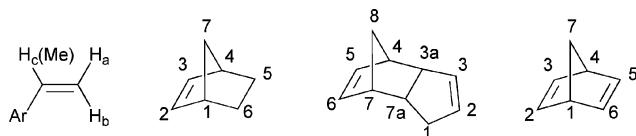
π -back-bonding contribution higher than that of the σ -bonding. A few analogies, such as the upfield shift of the ^1H and ^{13}C resonances of the coordinated olefin, have been observed with analogous complexes of other d^{10} metal ions of Groups 10 and 11. In contrast, it is worth underlining the differences with the copper(I) derivatives, for which a weak π -back-donation was suggested on the basis of thermodynamic and spectroscopic data and by theoretical calculations as well. A different behaviour between the gold and copper derivatives was also found in the CO/olefin exchange reaction; indeed, the coordinated olefin, e.g. styrene, is not displaced by CO, at least at atmospheric pressure.

Experimental

General experimental details

Compounds **1a–1f** were synthesized according to ref. 9. Ethylene (et) was purchased from SAPIO, styrene (sty), 4-vinylansole (van), α -methylstyrene (Mesty), *cis*-stilbene (stil), norbornene (nb), 2,5-norbornadiene (nbd), 1,5-cyclooctadiene (cod) and dicyclopentadiene (dcpd) were obtained from Aldrich Chimica. Solvents were purchased from Carlo Erba Reagents and distilled prior to use, while anhydrous MeCN ($\text{H}_2\text{O} \leq 0.001\%$; acidity $\leq 0.002\%$) was used as received. Elemental analyses were performed with a Perkin-Elmer Elemental Analyzer 240B by Mr A. Canu (Dipartimento di Chimica, Università di Sassari). Conductivity measurements were performed with a Philips PW 9505 conductivity meter. Infrared spectra were recorded with a Jasco FTIR-480 Plus spectrophotometer using Nujol mulls. ^1H and $^{13}\text{C}\{^1\text{H}\}$ NMR spectra were recorded with a Varian VXR 300 spectrometer operating at 300.0 and 75.4 MHz, respectively, at 293 K or at a different temperature (specified in the text); the ^1H NMR shifts were referenced to the resonance of the residual protons of the solvents ($\delta = 7.27$, CDCl_3 ; 5.35, CD_2Cl_2 ; 2.05, $(\text{CD}_3)_2\text{CO}$; 1.95, CD_3CN), the ^{13}C NMR shifts to the solvent resonance ($\delta = 77.0$, CDCl_3 ; 53.8, CD_2Cl_2 ; 29.8, $(\text{CD}_3)_2\text{CO}$; 1.3, CD_3CN). Mass spectra were recorded with a VG 7070 instrument operating under FAB conditions, with 3-nitrobenzyl alcohol as supporting matrix.

^1H and ^{13}C NMR shifts of the free olefins in various solvents



$\text{CH}_2=\text{CH}_2$ (et). (CD_2Cl_2): δ_{H} 5.43; δ_{C} 116.8; (CD_3CN): δ_{H} 5.42; δ_{C} 117.4.

$\text{CH}_2=\text{CHPh}$ (sty). (CDCl_3): δ_{H} 5.24 (dd, $J = 1.0$, 11.0 Hz, 1H, H_a), 5.75 (dd, $J = 1.0$, 17.6 Hz, 1H, H_b), 6.72 (dd, $J = 11.0$, 17.6 Hz, 1H, H_c); δ_{C} 113.7 ($=\text{CH}_2$), 137.0 ($=\text{CH}$); (CD_2Cl_2): δ_{H} 5.28 (dd, $J = 1.0$, 10.9 Hz, 1H, H_a), 5.79 (dd, $J = 1.0$, 17.6 Hz, 1H, H_b), 6.76 (dd, $J = 10.9$, 17.6 Hz, 1H, H_c); δ_{C} 113.9 ($=\text{CH}_2$), 137.2 ($=\text{CH}$); (CD_3CN): δ_{H} 5.26 (dd, $J = 1.0$, 11.2 Hz, 1H, H_a), 5.81 (dd, $J = 1.0$, 17.6 Hz, 1H, H_b), 6.77 (dd, $J = 11.2$, 17.6 Hz, 1H, H_c); δ_{C} 114.5 ($=\text{CH}_2$), 137.8 ($=\text{CH}$); $\{(\text{CD}_3)_2\text{CO}\}$: δ_{H} 5.23 (dd, $J = 1.0$, 11.0 Hz, 1H, H_a), 5.81 (dd, $J = 1.0$, 17.7 Hz, 1H, H_b), 6.76 (dd, $J = 11.0$, 17.7 Hz, 1H, H_c); δ_{C} 113.4 ($=\text{CH}_2$), 137.2 ($=\text{CH}$).

$\text{CH}_2=\text{CHC}_6\text{H}_4\text{OMe-4}$ (van). (CD_2Cl_2): δ_{H} 5.15 (dd, $J = 0.9$, 11.0 Hz, 1H, H_a), 5.64 (dd, $J = 0.9$, 17.6 Hz, 1H, H_b), 6.70 (dd, $J = 11.0$, 17.6 Hz, 1H, H_c); δ_{C} 111.6 ($=\text{CH}_2$), 136.5 ($=\text{CH}$); $\{(\text{CD}_3)_2\text{CO}\}$: δ_{H} 5.08 (dd, $J = 1.1$, 10.9 Hz, 1H, H_a), 5.64 (dd, $J = 1.1$, 17.6 Hz, 1H, H_b), 6.68 (dd, $J = 10.9$, 17.6 Hz, 1H, H_c); δ_{C} 111.6 ($=\text{CH}_2$), 137.3 ($=\text{CH}$).

$\text{CH}_2=\text{C}(\text{Me})\text{Ph}$ (Mesty). (CD_2Cl_2): δ_{H} 5.12 (quint, $J = 1.6$ Hz, 1H, H_a), 5.41 (m, $J = 1.6$ Hz, 1H, H_b); δ_{C} 112.4 ($=\text{CH}_2$), 143.7 ($=\text{C}$); $\{(\text{CD}_3)_2\text{CO}\}$: δ_{H} 5.09 (quint, $J = 1.5$ Hz, 1H, H_a), 5.39 (m, $J = 1.5$ Hz, 1H, H_b); δ_{C} 112.6 ($=\text{CH}_2$), 141.9 ($=\text{C}$). **PhCH=CHPh (stil)** (CD_2Cl_2): δ_{H} 6.65 (s, $=\text{CH}$); δ_{C} 130.6 ($=\text{CH}$).

Norbornene (nb). (CD_2Cl_2): δ_{H} 6.02; δ_{C} 135.6; $\{(\text{CD}_3)_2\text{CO}\}$: δ_{H} 5.97; δ_{C} 135.9.

Dicyclopentadiene (dcpd). (CD_2Cl_2): δ_{H} 5.51 (m, $=\text{CH}_{2,3}$), 5.95 (m, $J_{\text{AB}} = 5.8$ Hz, $J_{\text{AX}} = 3.0$ Hz, $=\text{CH}_6$), 6.01 (m, $J_{\text{BA}} = 5.8$ Hz, $J_{\text{BY}} = 3.0$ Hz, $=\text{CH}_5$); δ_{C} 132.3 ($=\text{CH}_{5,6}$), 132.7 ($=\text{CH}_3$), 136.3 ($=\text{CH}_2$).

2,5-Norbornadiene (nbd). (CD_2Cl_2): δ_{H} 6.78; δ_{C} 143.6; (CD_3CN): δ_{H} 6.77; δ_{C} 144.2; $\{(\text{CD}_3)_2\text{CO}\}$: δ_{H} 6.85; δ_{C} 144.0.

1,5-Cyclooctadiene (cod). (CD_2Cl_2): δ_{H} 5.59; δ_{C} 128.9; (CD_3CN): δ_{H} 5.55; δ_{C} 129.5; $\{(\text{CD}_3)_2\text{CO}\}$: δ_{H} 5.51; δ_{C} 129.2.

Synthesis and characterisation

$[\text{Au}(\text{bipy}^{\text{R,R'}})(\text{olefin})](\text{PF}_6)$ (2–8) and $[\text{Au}_2(\text{bipy}^{\text{R,R'}})_2(\mu\text{-diolefin})](\text{PF}_6)_2$ (9–11). Reactions of compounds **1a–1d** with sty and of compounds **1a–1e** with nb and nbd to give **3a–3d**, **7a–7e** and **9a–9d** have been reported in detail in ref. 8 and in ref. 10, respectively. **2a**, **2c–2e**, **3f**, **4a**, **4c–4e**, **5a**, **8a**, **10a**, **10c**, **11a** were synthesized according to the following general procedure: to 25–30 mL of a MeCN solution of **1** (0.2 mmol), 4 mmol (10 equiv.) of the respective alkene and 3–5 mL of water were added; in the case of ethylene the solution was saturated with the gas. The resulting mixture was stirred for 10–15 d at 10–15 °C, filtered through Celite, evaporated to dryness and the residue extracted with CH_2Cl_2 (3 \times 15 mL). The combined chloroform extracts were filtered and concentrated to a small volume; addition of Et_2O gave a whitish solid product which was recovered by filtration under vacuum. In most cases the analytical sample was obtained by recrystallization from dichloromethane–diethyl ether. A pure sample of **7a** as a white solid was obtained by adding MeOH to a CH_2Cl_2 solution of a mixture of **7a** and **70a** cooled to -20 °C. At variance, after an analogous workup of the mixture (**7c** + **70c**) a pure sample of **7c** could not be separated. Some **8a** was extracted with CHCl_3 from the mixture containing **11a**; the residue was still a mixture (**11a** : **8a** = 2 : 1; NMR criterion) from which more **8a** was obtained on addition of dcpd to a CH_2Cl_2 solution.

Molar conductivity, Λ_{M} , of compounds **2–8** (5×10^{-4} mol dm^{-3} , Me_2CO) is in the range 115–120 Ω^{-1} cm^2 mol^{-1} ; that of compounds **9–10** (5×10^{-4} mol dm^{-3} , Me_2CO) 170–180 Ω^{-1} cm^2 mol^{-1} .

$[\text{Au}(\text{bipy}^{\text{Me}})(\text{et})](\text{PF}_6)$ (2a). Yield: 15%; mp 143–144 °C (decomp.). Anal. Calcd. for $\text{C}_{13}\text{H}_{14}\text{AuF}_6\text{N}_2$: C, 28.90; H, 2.61; N, 5.19%. Found C, 28.85; H, 2.56; N, 5.18%. Selected IR bands: (ν/cm^{-1} , Nujol mull): 1597s, 1569m, 1030m, 842vs(br), 780s, 725m. ^1H NMR (CD_3CN): δ 2.91 (s, 3H; Me), 3.81 (s, 4H; $=\text{CH}_2$), 7.80–8.52 (m, 6H; ArH), 8.88 (d, $J = 5.1$ Hz, 1H; H_6 bipy^{Me}); $^{13}\text{C}\{^1\text{H}\}$ NMR (CD_3CN): δ 28.6 (Me), 61.7 ($=\text{CH}_2$), 122.0, 125.0,

127.6, 128.6, 128.7, 128.9, 142.7, 152.7, 152.9, 153.7, 161.1. MS data (FAB+): m/z 395 (55%) (M^+), 367 (37%) ($M - CH_2=CH_2$), 171 (100%) ($bipy^{Me} + H$).

$[Au(bipy^{iPr})(et)](PF_6)$ (**2c**). Yield: 18%; mp 131–132 °C (decomp.). Anal. Calcd. for $C_{15}H_{18}AuF_6N_2P$: C, 31.70; H, 3.19; N, 4.93%. Found C, 31.41; H, 2.98; N, 4.85%. Selected IR bands: (ν/cm^{-1} , Nujol mull): 1597vs, 1574s, 1491vs, 1308m, 1262m, 1169m, 1031s, 1006m, 842vs(br), 641m. 1H NMR (CD_3CN): δ 1.45 (d, $J = 7.0$ Hz, 6H; Me), 3.58 (sept, $J = 7.0$ Hz, 1H; CH), 3.83 (s, 4H; $=CH_2$), 7.74–8.59 (m, 6H; ArH), 8.88 (d, $J = 5.2$ Hz, 1H; $H_{6'}$ $bipy^{iPr}$).

$[Au(bipy^{nPr})(et)](PF_6)$ (**2d**). Yield: 25%; mp 134–135 °C. Anal. Calcd. for $C_{17}H_{22}AuF_6N_2P$: C, 34.24; H, 3.72; N, 4.70%. Found C, 34.09; H, 3.65; N, 4.62%. Selected IR bands: (ν/cm^{-1} , Nujol mull): 1605s, 1573s, 1497s, 1310m, 1225m, 1025m, 840vs(br), 781vs, 740m. 1H NMR (CD_2Cl_2): δ 1.06 (s, 9H; Me), 3.26 (s, 2H; CH_2), 3.87 (s, 4H; $=CH_2$), 7.85–8.57 (m, 6H; ArH), 8.83 (d, $J = 5.2$ Hz, 1H; $H_{6'}$ $bipy^{nPr}$).

$[Au(bipy^{oXyl})(et)](PF_6)$ (**2e**). Yield: 20%; mp 134–135 °C (decomp.). Anal. Calcd. for $C_{20}H_{20}AuF_6N_2P$: C, 38.11; H, 3.20; N, 4.44%. Found C, 38.01; H, 3.05; N, 4.36%. Selected IR bands: (ν/cm^{-1} , Nujol mull): 1601s, 1574s, 1238m, 1029m, 996m, 842vs(br), 780s. 1H NMR (CD_2Cl_2): δ 2.07 (s, 6H; Me), 3.09 (s, 4H; $=CH_2$), 7.26–8.61 (m, 9H; ArH), 8.81 (ddd, $J = 5.2$; 1.7; 0.9 Hz, 1H; $H_{6'}$ $bipy^{oXyl}$); $^{13}C\{^1H\}$ NMR (CD_2Cl_2): δ 20.3 (Me), 61.6 ($=CH_2$), 122.4, 124.4, 128.2, 128.5, 128.8, 130.4, 136.2, 141.3, 142.1, 142.9, 152.1, 152.4, 152.8, 161.3.

$[Au(bipy^{Me})(sty)](PF_6)$ (**3a**). Yield: 15%; mp 136 °C (decomp.). Anal. Calcd. for $C_{19}H_{18}AuF_6N_2P$: C, 37.02; H, 2.94; N, 4.55%. Found C, 37.39; H, 2.74; N, 4.64%. Selected IR bands: (ν/cm^{-1} , Nujol mull): 1600s, 1565m, 1223m, 1030m, 848vs(br), 785s, 700m. 1H NMR (CD_2Cl_2): δ 2.85 (s, 3H; Me), 4.09 (dd, $J_{ab} = 2.1$, $J_{ac} = 9.0$ Hz, 1H; H_a), 4.16 (dd, $J_{ba} = 2.1$, $J_{bc} = 13.5$ Hz, 1H; H_b), 5.41 (dd, $J_{ca} = 9.0$, $J_{cb} = 13.5$ Hz, 1H; H_c), 7.33–8.44 (m, 11H; ArH), 8.57 (d, broad, 1H; $H_{6'}$ $bipy^{Me}$); (CD_3CN): δ 2.80 (s, 3H; Me), 4.06 (dd, $J_{ab} = 2.0$, $J_{ac} = 9.1$ Hz, 1H; H_a), 4.20 (dd, $J_{ba} = 2.0$, $J_{bc} = 13.5$ Hz, 1H; H_b), 5.44 (dd, $J_{ca} = 9.1$, $J_{cb} = 13.5$ Hz, 1H; H_c), 7.32–8.46 (m, 11H; ArH), 8.60 (d, broad, 1H; $H_{6'}$ $bipy^{Me}$); $^{13}C\{^1H\}$ NMR (CD_3CN): δ 27.5 (Me), 54.7 ($=CH_2$), 80.9 ($=CH$), 121.5, 123.9, 125.1, 127.46, 128.4, 129.4, 130.0, 138.0, 142.7, 143.2, 152.0, 153.7, 169.2. MS data (FAB+): m/z 487 (<5%) ($M + O$), 471 (100%) (M^+), 367 (92%) ($M - PhCH=CH_2$), 301 (5%) ($M - bipy^{Me}$), 171 (57%) ($bipy^{Me} + H$).

$[Au(bipy^{Et})(sty)](PF_6)$ (**3b**). Yield: 20%; mp 130–131 °C. Calcd for $C_{20}H_{20}AuF_6N_2P$: C, 38.11; H, 3.20; N, 4.45%. Found C, 37.95; H, 3.08; N, 4.48%. Selected IR bands: (ν/cm^{-1} , Nujol mull): 1595s, 1568m, 1227m, 1027m, 842vs(br), 777s, 698m. 1H NMR $\{(CD_3)_2CO\}$: δ 1.36 (t, $^3J = 7.7$ Hz, 3H; Me), 3.20 (dq, $^2J = 11.2$, $^3J = 7.7$ Hz, 2H; CH_2), 4.23 (dd, $J_{ab} = 2.0$, $J_{ac} = 9.1$ Hz, 1H; H_a), 4.40 (dd, $J_{ba} = 2.0$, $J_{bc} = 13.7$ Hz, 1H; H_b), 5.64 (dd, $J_{ca} = 9.1$, $J_{cb} = 13.7$ Hz, 1H; H_c), 7.33–8.79 (m, 11H; ArH), 8.85 (d, $^3J = 3.6$ Hz, 1H; $H_{6'}$ $bipy^{Et}$); (CD_2Cl_2): δ 1.37 (t, $J = 7.7$ Hz, 3H; Me), 3.11 (dq, $^2J = 11.2$, $^3J = 7.7$ Hz, 2H; CH_2), 4.09 (dd, $J_{ab} = 2.1$, $J_{ac} = 9.1$ Hz, 1H; H_a), 4.16 (dd, $J_{ba} = 2.1$, $J_{bc} = 13.6$ Hz, 1H; H_b), 5.42 (dd, $J_{ca} = 9.1$, $J_{cb} = 13.6$ Hz, 1H; H_c), 7.34–8.45 (m, 11H; ArH), 8.58 (d, $^3J = 5.4$ Hz, 1H; $H_{6'}$ $bipy^{Et}$).

$[Au(bipy^{iPr})(sty)](PF_6)$ (**3c**). Yield: 25%; mp 140–141 °C. Calcd for $C_{21}H_{22}AuF_6N_2P$: C, 39.14; H, 3.44; N,

4.35%. Found C, 39.01; H, 3.38; N, 4.24%. Selected IR bands: (ν/cm^{-1} , Nujol mull): 1595s, 1567m, 1226m, 1028m, 842vs(br), 778s, 701m. 1H NMR $\{(CD_3)_2CO\}$: δ 1.18 (d, $^3J = 6.8$ Hz, 3H; CH_3), 1.51 (d, $^3J = 6.8$ Hz, 3H; CH_3), 3.55 (sept, $^3J = 6.8$ Hz, 1H; CH), 4.24 (dd, $J_{ab} = 2.0$, $J_{ac} = 9.0$ Hz, 1H; H_a), 4.41 (dd, $J_{ba} = 2.0$, $J_{bc} = 13.6$ Hz, 1H; H_b), 5.64 (dd, $J_{ca} = 9.0$, $J_{cb} = 13.6$ Hz, 1H; H_c), 7.31–8.82 (m, 11H, ArH), 8.89 (d, $^3J = 4.6$ Hz, 1H; $H_{6'}$ $bipy^{iPr}$); $^{13}C\{^1H\}$ NMR $\{(CD_3)_2CO\}$: δ 22.4 (Me), 23.0 (Me), 41.8 ($CHMe_2$), 55.6 ($=CH_2$), 83.1 ($=CH$), 122.6, 124.9, 125.3, 127.5, 128.6, 129.4, 129.9, 137.9, 142.8, 143.2, 152.2, 153.7, 169.0. MS data (FAB+): m/z 515 (5%) ($M + O$), 499 (100%) (M^+), 395 (90%) ($M - PhCH=CH_2$), 301 (<5%) ($M - bipy^{iPr}$), 154 (90%) ($bipy^{iPr}$). Crystals suitable for X-ray diffraction were obtained by slow diffusion of diethyl ether into an acetonitrile solution.

The activation barrier for styrene rotation in **2c** was calculated using the following 1H NMR data $\{(CD_3)_2CO, 193 K\}$: δ 0.73 [d, $^3J = 6.7$ Hz, 3H; $CH_3(A)$], 1.42 [d, $^3J = 7.0$ Hz, 3H; $CH_3(B)$], 1.46 [d, $^3J = 6.7$ Hz, 3H; $CH_3(A)$], 1.51 [d, $^3J = 6.7$ Hz, 3H; $CH_3(B)$], 3.10 (m, broad, 1H, CH(A)), 3.65 (m, broad, 1H; CH(B)), 4.03 [d, $J_{ac} = 8.3$ Hz, 1H; $H_a(B)$], 4.19 [d, $J_{ac} = 8.8$ Hz, 1H; $H_a(A)$], 4.35 [d, $J_{bc} = 13.4$ Hz, 1H; $H_b(A)$], 4.49 [d, $J_{bc} = 13.3$ Hz, 1H; $H_b(B)$], 5.48 (dd, $J_{ca} = 8.8$, $J_{cb} = 13.4$ Hz, 1H; $H_c(A)$], 5.60 (dd, $J_{ca} = 8.3$, $J_{cb} = 13.3$ Hz, 1H; $H_c(B)$], 7.27–9.03 (m, 24H; ArH(A) + ArH(B)) (A : B = 1 : 1.3). Coalescence of the styrene CH peaks at δ 5.48 and 5.60 ($\Delta\nu = 36$ Hz, $T_c = 243$ K) corresponds to an activation barrier $\Delta G^\ddagger = 50.3$ kJ mol $^{-1}$ at 243 K.

$[Au(bipy^{nPr})(sty)](PF_6)$ (**3d**). Yield: 45%; mp 158–159 °C. Calcd for $C_{23}H_{26}AuF_6N_2P$: C, 41.08; H, 3.90; N, 4.17%. Found C, 40.96; H, 3.87; N, 4.14%. Selected IR bands: (ν/cm^{-1} , Nujol mull): 1604s, 1567m, 1226s, 1023m, 846vs(br), 778s, 696m. 1H NMR ($CDCl_3$): δ 1.03 (s, 9H; Me), 3.13 (d, $J_{AB} = 12.8$ Hz, 1H; CH_AH_B), 3.24 [d, $J_{AB} = 12.8$ Hz, 1H; CH_AH_B], 4.03 (dd, $J_{ab} = 2.0$, $J_{ac} = 9.0$ Hz, 1H; H_a), 4.08 (dd, $J_{ba} = 2.0$, $J_{bc} = 13.4$ Hz, 1H; H_b), 5.43 (dd, $J_{ca} = 9.0$, $J_{cb} = 13.4$ Hz, 1H; H_c), 7.29–8.49 (m, 12H; ArH); (CD_2Cl_2): δ 1.08 (s, 9H; Me), 3.21 (d, $J_{AB} = 12.9$ Hz, 1H, CH_AH_B), 3.29 (d, $J_{AB} = 12.9$ Hz, 1H, CH_AH_B), 4.09 (dd, $J_{ab} = 2.0$, $J_{ac} = 9.0$ Hz, 1H; H_a), 4.15 (dd, $J_{ba} = 2.0$, $J_{bc} = 13.6$ Hz, 1H; H_b), 5.46 (dd, $J_{ca} = 9.0$, $J_{cb} = 13.6$ Hz, 1H; H_c), 7.37–8.48 (m, 12H; ArH); (CD_3CN): δ 1.02 (s, 9H; Me), 3.22 (s, 2H; CH_2), 4.06 (dd, $J_{ab} = 1.9$, $J_{ac} = 9.1$ Hz, 1H; H_a), 4.20 (dd, $J_{ba} = 1.9$, $J_{bc} = 13.6$ Hz, 1H; H_b), 5.44 (dd, $J_{ca} = 9.1$, $J_{cb} = 13.6$ Hz, 1H; H_c), 7.30–8.53 (m, 12H; ArH); $\{(CD_3)_2CO\}$: δ 1.06 (s, 9H; Me), 3.34 (s, 2H; CH_2), 4.25 (dd, $J_{ab} = 1.8$, $J_{ac} = 9.0$ Hz, 1H; H_a), 4.41 (dd, $J_{ba} = 1.8$, $J_{bc} = 13.6$ Hz, 1H; H_b), 5.71 (dd, $J_{ca} = 9.0$, $J_{cb} = 13.6$ Hz, 1H; H_c), 7.34–8.70 (m, 11H; ArH) 8.77 (d, $J = 7.8$ Hz, 1H; $H_{6'}$ $bipy^{nPr}$); $^{13}C\{^1H\}$ NMR $\{(CD_3)_2CO\}$: δ 26.9 (Me), 33.4 (CMe_3), 55.6 ($=CH_2$), 56.3 (CH_2), 82.8 ($=CH$), 122.8, 125.0, 127.5, 128.5, 129.2, 129.5, 129.9, 137.5, 141.9, 142.8, 151.9, 152.4, 154.0, 162.0. MS data (FAB+): m/z 543 (5%) ($M + O$), 527 (85%) (M^+), 423 (100%) ($M - PhCH=CH_2$), 301 (10%) ($M - bipy^{nPr}$), 227 (95%) ($bipy^{nPr} + H$).

$[Au(bipy^{oXyl})(sty)](PF_6)$ (**3e**). Yield: 55%; 118–119 °C. Calcd for $C_{26}H_{24}AuF_6N_2P$: C, 44.21; H, 3.42; N, 3.97%. Found C, 43.98; H, 3.18; N, 3.67%. Selected IR bands: (ν/cm^{-1} , Nujol mull): 1601s, 1573m, 1226s, 1028m, 996m, 842vs(br), 780vs, 697m. 1H NMR (CD_2Cl_2): δ 2.06 (s, 3H; Me), 2.13 (s, 3H; Me), 2.97 (m, 2H; $=CH_2$), 5.11 (dd, $J_{ca} = 9.5$, $J_{cb} = 13.0$ Hz, 1H; $=CH$), 7.27–8.45 (m, 15H; ArH), 8.53 (ddd, $J = 8.1$; 2.4; 0.9 Hz, 1H; $H_{6'}$ $bipy^{oXyl}$); $\{(CD_3)_2CO\}$: δ 2.07 (s, 3H; Me), 2.17 (s, 3H; Me), 3.02

(d, $J = 12.1$ Hz, 2H; =CH₂), 5.29 (pseudot, $J = 8.0, 11.2$ Hz, 1H; =CH), 7.25–8.66 (m, 15H; ArH), 8.85 (d, $J = 8.06$ Hz, 1H; H_{6'} bipy^{oxyl}); ¹³C{¹H} NMR (CD₂Cl₂): δ 20.3 (Me), 20.4 (Me), 81.9 (=CH), 122.4, 124.4, 126.4, 128.2, 128.5, 128.8, 129.1, 129.5, 136.2, 136.4, 141.3, 142.2, 142.9, 151.2, 151.9, 152.6, 161.5; {(CD₃)₂CO}: δ 20.2 (Me), 20.3 (Me), 53.6 (=CH₂), 81.6 (=CH), 123.2, 125.1, 127.06, 128.7, 128.8, 129.2, 129.3, 129.8, 130.7, 136.8, 136.9, 137.6, 142.2, 142.8, 143.6, 152.0, 152.8, 153.5, 161.6. MS data (FAB+): m/z 561 (30%) (M⁺), 457 (15%) (M – PhCH=CH₂), 261 (100%) (bipy^{oxyl} + H).

[Au(bipy^{Me,Me})(sty)](PF₆) (**3f**). Yield: 35%; mp 166–167 °C. Calcd for C₂₀H₂₀AuF₆N₂P: C, 38.11; H, 3.20; N, 4.44%. Found C, 38.23; H, 3.31; N, 4.30%. Selected IR bands: (ν /cm⁻¹, Nujol mull): 1601s, 1571m, 1245m, 1182m, 1022m, 841vs(br), 793vs, 714m, 698m. ¹H NMR (CD₂Cl₂): δ 2.81 (s, 6H; Me), 4.10 (dd, $J_{ba} = 2.0, J_{bc} = 13.4$ Hz, 1H; H_b), 4.20 (dd, $J_{ab} = 2.0, J_{ac} = 9.0$ Hz, 1H; H_a), 5.31 (dd, $J_{ca} = 9.0, J_{cb} = 13.4$ Hz, 1H; H_c), 7.35–8.27 (m, 11H, ArH). MS data (FAB+): m/z 501 (<5%) (M + 16), 485 (75%) (M⁺), 381 (70%) (M – PhCH=CH₂), 301 (<5%) (M – bipy^{Me,Me}), 185 (100%) (bipy^{Me,Me} + H).

[Au(bipy^{Me})(van)](PF₆) (**4a**). Yield: 59%; mp 144–145 °C (decomp.). Calcd for C₂₀H₂₀AuF₆N₂OP: C, 37.17; H, 3.12; N, 4.33%. Found C, 37.23; H, 3.31; N, 4.28%. Selected IR bands: (ν /cm⁻¹, Nujol mull): 1596s(br), 1530m, 1301m, 1254m, 1028m, 841vs(br), 775vs, 699m. ¹H NMR (CD₂Cl₂): δ 2.85 (s, 3H; Me), 3.83 (s, 3H; MeO), 4.01 (dd, $J_{ab} = 2.1, J_{ac} = 9.0$ Hz, 1H; H_a), 4.08 (dd, $J_{ba} = 2.1, J_{bc} = 13.7$ Hz, 1H; H_b), 5.43 (dd, $J_{ca} = 9.0, J_{cb} = 13.7$ Hz, 1H; H_c), 6.94 (d, $J = 8.8$ Hz, 2H; H_o van), 7.45 (d, $J = 8.8$ Hz, 2H; H_m van), 7.70–8.42 (m, 6H; ArH), 8.58 (d, $J = 4.8$ Hz, 1H; H_{6'} bipy^{Me}); {(CD₃)₂CO}: δ 2.94 (s, 3H; Me), 3.80 (s, 3H; MeO), 4.16 (dd, $J_{ab} = 2.0, J_{ac} = 9.0$ Hz, 1H; H_a), 4.33 (dd, $J_{ba} = 2.0, J_{bc} = 13.6$ Hz, 1H; H_b), 5.66 (dd, $J_{ca} = 9.0, J_{cb} = 13.6$ Hz, 1H; H_c), 6.95 (d, $J = 8.9$ Hz, 2H; H_o van), 7.62 (d, $J = 8.9$ Hz, 2H; H_m van), 7.91–8.78 (m, 6H; ArH), 8.84 (d, $J = 4.7$ Hz, 1H; H_{6'} bipy^{Me}); ¹³C{¹H} NMR {(CD₃)₂CO}: δ 53.3 (=CH₂), 55.7 (MeO), 83.0 (=CH), 114.9, 121.2, 124.1, 128.0, 128.1, 128.2, 128.5, 142.0, 151.3, 151.6, 152.7, 160.3, 160.6.

[Au(bipy^{Me})(Mesty)](PF₆) (**5a**). Yield: 31%; mp 93–94 °C (decomp.). Calcd for C₂₀H₂₀AuF₆N₂P: C, 38.11; H, 3.20; N, 4.44%. Found C, 37.98; H, 3.02; N, 4.32%. Selected IR bands: (ν /cm⁻¹, Nujol mull): 1601s, 1573m, 1306m, 1260m, 1028m, 842vs(br), 780vs, 697m. ¹H NMR (CD₂Cl₂): δ 2.44 (s, 3H; Me Mesty), 3.86 (s, 3H; Me bipy^{Me}), 3.97 (d, $J_{ab} = 1.8$ Hz, 1H; H_a), 4.23 (d, $J_{ab} = 1.8$ Hz, 1H; H_b), 7.34–8.44 (m, 11H; ArH), 8.55 (ddd, $J = 5.2, 1.6, 0.8$ Hz, 1H; H_{6'} bipy^{Me}); ¹³C{¹H} NMR (CD₂Cl₂): δ 24.1 (Me Mesty), 28.0 (Me bipy^{Me}), 57.8 (=CH₂), 95.8 (=CMePh), 121.3, 124.3, 125.8, 128.1, 128.4, 129.2, 129.5, 139.7, 142.0, 142.2, 150.9, 151.5, 152.8, 160.3. MS data (FAB+): m/z 501 (20%) (M + O), 485 (30%) (M⁺), 367 (50%) (M – Mesty), 171 (100%) (bipy^{Me} + H).

[Au(bipy^{iPr})(Mesty)](PF₆) (**5c**). Yield: 38%; mp 104–106 °C (decomp.). Calcd for C₂₂H₂₄AuF₆N₂P: C, 40.13; H, 3.67; N, 4.25%. Found C, 39.98; H, 3.38; N, 4.02%. Selected IR bands: (ν /cm⁻¹, Nujol mull): 1599s, 1574s, 1308m, 1261m, 1170m, 1027m, 841vs(br), 778vs, 698m. ¹H NMR (CD₂Cl₂): δ 1.23 (d, $J = 6.9$ Hz, 3H; Me), 1.48 (d, $J = 6.9$ Hz, 3H; Me), 2.42 (s, 3H; Me Mesty), 3.45 (sept, $J = 6.9$ Hz, 1H; CHMe₂), 3.97 (d, $J = 1.8$ Hz, 1H; H_a), 4.22 (d, $J = 1.8$ Hz, 1H; H_b), 7.35–8.57 (m, 12H; ArH); ¹³C{¹H} NMR (CD₃CN): δ 22.0 (Me), 22.2 (Me), 23.1 (Me), 41.0 (CH),

57.6 (=CH₂), 95.0 (=CMePh), 121.7, 123.5, 124.2, 124.5, 125.8, 127.7, 128.3, 128.6, 129.1, 141.9, 142.1, 151.0, 151.1, 152.9, 168.5. MS data (FAB+): m/z 529 (24%) (M + 16), 513 (100%) (M⁺), 395 (90%) (M – Mesty), 315 (5%) (M – bipy^{iPr}), 197 (32%) (bipy^{iPr}–H).

[Au(bipy^{nP})(Mesty)](PF₆) (**5d**). Yield: 40%; mp 131–133 °C (decomp.). Calcd for C₂₄H₂₈AuF₆N₂P: C, 41.99; H, 4.11; N, 4.08%. Found C, 41.48; H, 3.95; N, 3.96%. Selected IR bands: (ν /cm⁻¹, Nujol mull): 1598s, 1572s, 1310m, 1265m, 1168m, 1028m, 842vs(br), 780vs, 697m. ¹H NMR (CD₂Cl₂): δ 1.07 (s, 9H; Me), 2.44 (s, 3H; Me Mesty), 3.29 (s, 2H; CH₂), 3.92 (d, $J = 1.7$ Hz, 1H; H_a), 4.21 (d, $J = 1.7$ Hz, 1H; H_b), 7.39–8.44 (m, 12H; ArH). MS data (FAB+): m/z 557 (10%) (M + 16), 541 (85%) (M⁺), 423 (95%) (M – Mesty), 315 (5%) (M – bipy^{nP}), 227 (100%) (bipy^{nP} + H).

[Au(bipy^{oxyl})(Mesty)](PF₆) (**5e**). Yield: 35%; mp 140–141 °C (decomp.). Calcd for C₂₇H₂₆AuF₆N₂P: C, 45.01; H, 3.64; N, 3.87%. Found C, 44.81; H, 3.48; N, 3.66%. Selected IR bands: (ν /cm⁻¹, Nujol mull): 1600s, 1573m, 1312m, 1268m, 1170m, 1028m, 840vs(br), 788vs, 700s. ¹H NMR (CD₂Cl₂): δ 2.09 (s, 6H; Me), 2.20 (s, 3H; Me Mesty), 2.79 (d, $J = 2.4$ Hz, 1H; H_a), 3.00 (d, $J = 2.4$ Hz, 1H; H_b), 7.29–8.55 (m, 15H; ArH); {(CD₃)₂CO}: δ 2.11 (s, 6H; Me), 2.24 (s, 3H; Me Mesty), 2.87 (d, $J = 2.2$ Hz, 1H; H_a), 3.03 (d, $J = 2.2$ Hz, 1H; H_b), 7.30–8.87 (m, 15H; Ar–H); ¹³C{¹H} NMR {(CD₃)₂CO}: δ 20.3 (Me bipy^{oxyl}), 23.7 (Me Mesty), 55.9 (=CH₂), 95.2 (=CMePh), 123.1, 125.2, 126.2, 128.7, 128.8, 129.1, 129.4, 129.7, 130.7, 136.9, 140.6, 142.1, 142.8, 143.4, 147.8, 152.0, 152.6, 153.5, 161.5. MS data (FAB+): m/z 591 (5%) (M + 16), 575 (100%) (M⁺), 457 (55%) (M – Mesty), 315 (<5%) (M – bipy^{oxyl}), 259 (50%) (bipy^{oxyl}–H).

[Au(bipy^{Me})(stil)](PF₆) (**6a**). Yield: 30%; mp 139–140 °C. Calcd for C₂₅H₂₂AuF₆N₂P: C, 43.37; H, 3.20; N, 4.05%. Found C, 43.09; H, 3.11; N, 3.89%. Selected IR bands: (ν /cm⁻¹, Nujol mull): 1600s, 1573m, 1530w, 1252m, 1167m, 1029m, 842vs(br), 776vs, 703m. ¹H NMR (CD₂Cl₂): δ 2.58 (s, 3H; Me), 5.77 (s, 2H; =CH), 7.25–7.33 (m, 5H; ArH stil), 7.38–7.44 (m, 5H; ArH stil), 7.66–8.63 (m, 7H; ArH bipy^{Me}); ¹³C{¹H} NMR (CD₂Cl₂): δ 27.5 (Me), 79.2 (=CH), 121.5, 124.4, 127.4, 128.6, 129.0, 129.1, 130.1, 135.3, 142.2, 142.3, 151.1, 151.8, 153.1, 160.6.

[Au(bipy^{Me})(nb)](PF₆) (**7a**). Yield: it depends on the preparative conditions;¹⁰ mp 206–207 °C. Calcd for C₁₈H₂₀AuF₆N₂P: C, 35.65; H, 3.32; N, 4.62%. Found C, 35.71; H, 3.31; N, 4.55%. Selected IR bands: (ν /cm⁻¹, Nujol mull): 1597s, 1575m, 1561m, 1125m, 1027m, 1011m, 839vs(br), 780s, 741m. ¹H NMR (CD₂Cl₂): δ 0.81 (dt, $J = 9.7, 1.5$ Hz, 1H; CHH-7), 1.21 (2d overlapped, 3H; CHH_{5,6} + CHH₇), 1.78 (dm, 2H; CHH_{5,6}), 3.04 (s, 3H; Me), 3.22 (s, 2H; CH_{1,4}), 4.22 (s, 2H; CH=CH), 7.75–8.45 (m, 6H, ArH), 8.86 (dd, $J = 5.2, 1.7$ Hz, 1H; H_{6'} bipy^{Me}); {(CD₃)₂CO}: δ 0.77 (dt, $J = 9.8$ Hz, 1H; CHH₇), 1.18 (dm, $J = 7.8, 2.4$ Hz, 2H; CHH_{5,6}), 1.30 (dt, $J = 9.5$ Hz, 1H; CHH₇), 1.74 (dm, $J = 7.4$ Hz, 2H; CHH_{5,6}), 3.11 (s, 3H; Me), 3.25 (s, 2H; CH_{1,4}), 4.36 (s, 2H; CH=CH), 7.95–8.79 (m, 6H; ArH), 9.12 (d, $J = 4.4$ Hz, 1H; H_{6'} bipy^{Me}); ¹³C{¹H} NMR (CD₂Cl₂): δ 25.4 [2C, CH_{2(5,6)}], 28.41 (1C, Me), 42.8 (2C, CH_{1,4}), 43.6 [1C, CH₂₍₇₎], 83.3 (2C, =CH), 121.3 (1C, CH), 124.2 (1C, CH), 128.0 (1C, CH), 128.3 (1C, CH), 141.9 (1C, CH), 142.0 (1C, CH), 151.7 (1C, CH), 152.1 (1C, qC), 153.0 (1C, qC) 160.1 (1C, qC). MS data (FAB+) m/z : 461 (100%) (M⁺), 367 (68%) (M – nb), 291 (5%) (M – bipy^{Me}), 171 (60%) (bipy^{Me} + H).

$[Au(bipy^{np})(nb)](PF_6)$ (**7d**). Yield: 40%; mp 142–143 °C. Calcd for $C_{22}H_{28}AuF_6N_2P$: C, 39.89; H, 4.26; N, 4.23%. Found C, 39.71; H, 4.16; N, 4.21%. Selected IR bands: (ν/cm^{-1} , Nujol mull): 1597vs, 1573s, 1307s, 1227s, 1167m, 1128m, 1025s, 1009s, 838vs(br), 789s, 765s, 741m, 723m, 654m, 639m. 1H NMR (CD_2Cl_2): δ 0.81 (d, $J = 9.7$ Hz, 1H; CHH_{7anti}), 1.09 (s, 9H, Me), 1.18–1.23 (m, 3H; $CHH_{5,6} + CHH_{7syn}$), 1.79 (d, $J = 9.0$ Hz, 2H; $CHH_{5,6}$), 3.26 (s, 2H; $CH_{1,4}$), 3.38 (s, 2H, CH_2CMe_3), 4.23 (s, 2H; CH=CH), 7.73–8.47 (m, 6H, ArH), 8.86 (d, $J = 4.8$ Hz, 1H; $H_{\delta'}$ bipy^{np}). $^{13}C\{^1H\}$ NMR (CD_2Cl_2): δ 25.2 [2C, $CH_{2(5,6)}$], 29.7 (3C, Me), 33.2 (1C, CH_2CMe_3), 42.7 (2C, $CH_{1,4}$), 43.4 [1C, $CH_{2(7)}$], 55.9 (1C, CH_2CMe_3), 84.1 (2C, =CH), 122.0, 124.2, 127.9, 129.1, 141.0, 141.9, and 151.4 (ArCH), 152.1, 153.5, and 161.5 (ArC). MS data (FAB+) m/z : 553 (12%) (M + 16), 517 (100%) (M⁺), 423 (42%) (M – nb), 291 (5%) (M – bipy^{np}), 227 (15%) (bipy^{np} + H).

$[Au(bipy^{oxyl})(nb)](PF_6)$ (**7e**). Yield: 19%; mp 114–115 °C. Calcd for $C_{25}H_{26}AuF_6N_2P$: C, 43.12; H, 3.76; N, 4.02%. Found C, 42.91; H, 3.78; N, 4.09%. Selected IR bands: (ν/cm^{-1} , Nujol mull): 1600s, 1574m, 1167m, 1126m, 1026m, 1005m, 842vs(br), 778s, 739m, 722m. 1H NMR (CD_2Cl_2): δ 0.56 (d, $J = 9.5$ Hz, 1H; CHH_7), 0.86–0.89 (m, 3H; $CHH_{5,6} + CHH_7$), 1.54 (d, $J = 8.7$ Hz, 2H; $CHH_{5,6}$), 2.08 (s, 6H; Me), 2.67 (s, 2H; $CH_{1,4}$), 3.46 (s, 2H; CH=CH), 7.32–8.58 (m, 9H; ArH), 8.82 (dd, $J = 5.2, 1.7$ Hz, 1H; $H_{\delta'}$ bipy^{oxyl}); $^{13}C\{^1H\}$ NMR (CD_2Cl_2): δ 20.4 (2C, Me), 24.7 [2C, $CH_{2(5,6)}$], 42.6 (2C, $CH_{1,4}$), 43.5 [1C, $CH_{2(7)}$], 83.9 (2C, =CH), 122.4, 124.2, 128.2, 128.4, 128.9, 130.2, 136.2, 140.9, 141.9, 142.6, 151.6, 152.5, 152.6, 161.4. MS data (FAB+) m/z : 567 (5%) (M + O), 551 (100%) (M⁺), 457 (30%) (M – nb), 291 (5%) (M – bipy^{oxyl}), 259 (15%) (bipy^{oxyl}–H).

$[Au(bipy^{Me})(dcpd)](PF_6)$ (**8a**). Yield: 32%; mp 146–147 °C (decomp.). Calcd for $C_{21}H_{22}AuF_6N_2P$: C, 39.14; H, 3.44; N, 4.35%. Found C, 38.85; H, 3.36; N, 4.30%. Selected IR bands: (ν/cm^{-1} , Nujol mull): 1606s, 1518s, 1488s, 1255s, 1175s, 1027s, 842vs(br), 776s, 727m. 1H NMR (CD_2Cl_2): δ 1.05 (dt, $J = 9.9, 1.5$ Hz, 1H; CH, H_8), 1.44 (dt, $J = 9.9, 1.5$ Hz, 1H; CH, H_8), 2.15–2.40 [m, 2H; $CH_{2(1)}$], 2.60–2.94 (m, 1H, CH_{7a}), 3.01 (s, 3H; Me), 3.22 (broad s, 2H; $CH_{4,7}$), 3.37 (m, 1H; CH_{3a}), 4.18 (d, $J_{AB} = 4.3$ Hz, 1H; =CH₅), 4.38 (d, $J_{BA} = 4.3$ Hz, 1H; =CH₆), 5.71 (s, 2H; =CH_{2,3}), 7.72–8.45 (m, 6H; ArH), 8.84 (d, $J = 5.1$ Hz; $H_{\delta'}$ bipy^{Me}); $^{13}C\{^1H\}$ NMR (CD_2Cl_2): δ 28.4 (1C, Me), 33.0 [1C, $CH_{2(1)}$], 41.5 (1C), 45.2 (1C), 46.6 (1C), 80.6 (1C, =CH₅), 84.9 (1C, =CH₆), 121.2 (1C, CH), 124.1 (1C, CH), 128.0 (1C, CH), 128.3 (1C, CH), 131.3 (1C, =CH₂), 132.7 (1C, =CH₃), 141.9 (2C, CH), 151.7 (1C, CH), 152.0 (1C, qC), 152.9 (1C, qC), 160.0 (1C, qC).

$[Au_2(bipy^{Me})_2(\mu-nbd)](PF_6)_2$ (**9a**). Yield: 15%; mp 130 °C (decomp.). Anal. Calcd for $C_{29}H_{28}Au_2F_{12}N_4P_2$: C, 31.19; H, 2.53; N, 5.02%. Found C, 31.08; H, 2.54; N, 5.14%. Selected IR bands: (ν/cm^{-1} , Nujol mull): 1590s, 1565m, 1030m, 850vs(br), 785s, 735m. 1H NMR (CD_3CN): δ 1.38 [s, 2H; $CH_{2(7)}$], 2.99 (s, 6H; Me), 4.03 (s, 2H; $CH_{1,4}$), 4.59 (s, 4H; CH=CH), 7.80–8.49 (m, 12H; ArH), 8.91 (d, $J = 4.5$ Hz, 2H; $H_{\delta'}$ bipy^{Me}). $^{13}C\{^1H\}$ NMR (CD_3CN): δ = 28.6 (2C, Me), 49.6 (2C, $CH_{1,4}$), 55.6 [1C, $CH_{2(7)}$], 85.2 (4C, =CH), 122.1 (2C, CH), 125.0 (2C, CH), 128.7 (2C, CH), 129.0 (2C, CH), 142.8 (4C, CH) 152.8 (2C, CH), 153.0 (2C, qC), 153.8 (2C, qC), 161.0 (2C, qC). MS data (FAB+) m/z : 551 (50%) [$Au(bipy^{Me})(nbd)_2$], 457–461 \approx [$Au(bipy^{Me})(nbd)$], 367 (100%) [$Au(bipy^{Me})$].

$[Au_2(bipy^{iPr})_2(\mu-nbd)](PF_6)_2$ (**9c**). Yield: 10%; mp 141–142 °C. Calcd for $C_{33}H_{36}Au_2F_{12}N_4P_2$: C, 33.80; H, 3.09; N, 4.78%.

Found C, 33.45; H, 3.11; N, 4.65%. Selected IR bands: (ν/cm^{-1} , Nujol mull): 1585s, 1560m, 1020m, 840vs(br), 780s. 1H NMR $\{(CD_3)_2CO\}$: δ 1.52 (d, $J = 6.8$ Hz, 12H; CH_3), 1.55 [s, 2H; $CH_{2(7)}$], 3.96 (sept, $J = 6.8$ Hz, 2H; $CHMe_2$), 4.84 (s, 4H; CH=CH), 8.03–8.90 (m, 12H; ArH), 9.17 (d, $J = 5.2$ Hz, 2H; $H_{\delta'}$ bipy^{iPr}). MS data (FAB+) m/z : 487 (70%) [$Au(bipy^{iPr})(nbd)$], 395 (50%) [$Au(bipy^{iPr})$].

$[Au_2(bipy^{np})_2(\mu-nbd)](PF_6)_2$ (**9d**). Yield: 41%; mp 147–148 °C (decomp.). Calcd for $C_{37}H_{44}Au_2F_{12}N_4P_2$: C, 36.17; H, 3.61; N, 4.56%. Found C, 35.98; H, 3.33; N, 4.48%. Selected IR bands: (ν/cm^{-1} , Nujol mull): 1600s, 1573m, 1228m, 1026m, 842vs(br), 782s, 740m. 1H NMR (CD_2Cl_2): δ 1.18 (s, 18H; Me), 1.43 [s, 2H; $CH_{2(7)}$], 3.36 (s, 4H; CH_2CMe_3), 4.16 (br, 2H; $CH_{1,4}$), 4.68 (br, 4H; CH=CH), 7.75–8.41 (m, 12H, ArH), 8.98 (d, $J = 4.7$ Hz, 2H; $H_{\delta'}$ bipy^{np}).

$[Au_2(bipy^{Me})_2(\mu-cod)](PF_6)_2$ (**10a**). Yield: 30%; mp 115–116 °C (decomp.). Calcd for $C_{30}H_{32}Au_2F_{12}N_4P_2$: C, 31.82; H, 2.85; N, 4.95%. Found C, 31.75; H, 2.90; N, 4.87%. 1H NMR $\{(CD_3)_2CO\}$: δ 2.39 (broad m, 4H; CH_2), 2.70 (broad m, 4H; CH_2), 3.04 (s, 6H; Me), 4.94 (broad m, 4H; CH=CH), 7.92–8.81 (m, 12H; ArH), 9.03 (dd, $J = 5.2, 0.9$ Hz, 2H, $H_{\delta'}$ bipy^{Me}); (CD_3CN) : δ 2.56 (broad m, 4H; CH_2), 2.84 (broad m, 4H; CH_2), 2.97 (s, 6H; Me), 4.72 (broad m, 4H; CH=CH), 7.72–8.78 (m, 14H; $H_{\delta'}$ bipy^{Me}).

$[Au_2(bipy^{iPr})_2(\mu-cod)](PF_6)_2$ (**10c**). Yield: 44%; mp 109–110 °C (decomp.). Calcd for $C_{34}H_{40}Au_2F_{12}N_4P_2$: C, 34.36; H, 3.39; N, 4.71%. Found C, 34.08; H, 3.01; N, 4.58%. 1H NMR (CD_2Cl_2): δ 1.49 (d, $J = 7.0$ Hz, 6H; Me), 1.52 (d, $J = 7.0$ Hz, 6H; Me), 2.27 (broad m, 2H; CH_2), 2.52–2.83 (m, 4H; CH_2), 2.93 (broad d, $J = 12.5$ Hz, 2H; CH_2), 3.55 and 3.56 (2 sept, $J = 7.0$ Hz, 2H, CH), 4.79 (broad m, 4H; CH=CH), 7.75–8.82 (m, 14H; ArH); $^{13}C\{^1H\}$ NMR (CD_2Cl_2): δ 23.0 (2C, Me), 29.9 (2C, CH_2), 30.4 (2C, CH_2), 42.0 (2C, CH), 80.5 (4C, =CH), 121.7 (2C, CH), 124.0 (2C, CH), 124.6 (2C, CH), 128.1 (2C, CH), 141.9 (2C, CH), 142.3 (2C, CH), 151.5 (2C, CH), 151.7 (2C, qC), 152.9 (2C, qC), 168.7 (2C, qC). MS data (FAB+) m/z : 1043 (15%) (M + PF_6), 503 (65%) [M – Au(bipy^{iPr})], 449 (5%) (M/2), 395 (100%) [$Au(bipy^{iPr})$], 197 (bipy^{iPr}–H).

*Spectroscopic data of $[Au_2(bipy^{Me})_2(\mu-dcpd)](PF_6)_2$ (**11a**).* 1H NMR (CD_2Cl_2): δ 1.04 (d, $J = 10.0$ Hz, 1.5H; $CHH-8$ **8a** + **11a**), 2.00 (d, $J = 10.0$ Hz, 1H; $CHH-8$), 2.22–2.47 (m, 6H; CH_2 **8a** + **11a**), 2.68–2.95 (m, 3H; $CH-7a$ **8a** + **11a**), 3.01 (s, 3H; Me), 3.05 (s, 3H; Me), 3.27 [broad s, 1H; $CH_{4(7)}$], 3.61 (broad s, 2H; $CH_{7(4)} + CH_{7a}$), 4.54 (d, $J_{AB} = 4.3$ Hz 1H; =CH₅), 4.60 (d, $J_{BA} = 4.3$ Hz 1H; =CH₆), 4.84 (t, $J = 4.2$ Hz 1H; =CH₂), 5.02 (d, $J = 4.2$ Hz 1H; =CH₃), 7.36–8.97 (m, 35 H; ArH **8a** + **11a**); $^{13}C\{^1H\}$ NMR (CD_2Cl_2): δ 27.9 (Me), 28.6 (Me), 33.7, 43.6, 45.6, 46.3, 46.7, 81.2 (=CH), 82.6 (=CH), 83.8 (=CH), 85.8 (=CH), 121.1, 123.9, 128.3, 141.9, 151.7, 152.0, 152.2, 152.7, 160.2. MS data (FAB+) m/z : 1043 (M + PF_6 + 32), 1027 (M + PF_6 + 16), 1011 (M + PF_6), 882 (M + 16), 499 [M – Au(bipy^{Me})], 433 (M/2), 367 [$Au(bipy^{Me})$], 171 (bipy^{Me} + H).

X-Ray data collection and structure determination

Crystal data are summarised in Table 6. The diffraction experiment was carried out on a Bruker SMART CCD area-detector diffractometer at 150 K. No crystal decay was observed, so that no time–decay correction was needed. The collected frames were processed with the software SAINT,⁴⁷ and an empirical absorption correction was applied (SADABS)⁴⁸ to the collected reflections.

Table 6 Crystallographic data

Compound	3e-CH ₂ Cl ₂
Formula	C ₂₇ H ₂₆ AuCl ₂ F ₆ N ₂ P
<i>M</i>	791.36
Colour	Colourless
Crystal system	Monoclinic
Space group	<i>P</i> 2 ₁ / <i>c</i>
<i>a</i> /Å	15.011(1)
<i>b</i> /Å	13.445(1)
<i>c</i> /Å	14.603(1)
β /°	108.48(1)
<i>U</i> /Å ³	2795.3(3)
<i>Z</i>	4
<i>F</i> (000)	1536
<i>D</i> _c /g cm ⁻³	1.880
<i>T</i> /K	150
Crystal dimensions/mm	0.22 × 0.34 × 0.43
μ (Mo-K α)/cm ⁻¹	55.62
Min. and max. transmiss. factors	0.793–1.000
Scan mode	ω
Frame width/°	0.30
Time per frame/s	15
No. of frames	2770
θ -range	3–27
Reciprocal space explored	Full sphere
No. of reflections (total; independent)	42473, 6102
<i>R</i> _{int}	0.0293
Final <i>R</i> ₂ and <i>R</i> _w indices ^a (<i>F</i> ² , all reflections)	0.032, 0.056
Conventional <i>R</i> ₁ index [<i>I</i> > 2 σ (<i>I</i>)]	0.019
Reflections with <i>I</i> > 2 σ (<i>I</i>)	5373
No. of variables	379
Goodness of fit ^b	0.984

^a $R_2 = [\sum (|F_o^2 - kF_c^2| / \sum F_o^2)]$, $R_w = [\sum w / (F_o^2 - kF_c^2)^2 / \sum w (F_o^2)^2]^{1/2}$.
^b $[\sum w (F_o^2 - kF_c^2)^2 / (N_o - N_v)]^{1/2}$, where $w = 4F_o^2 / \sigma(F_o^2)^2$, $\sigma(F_o^2) = [\sigma^2(F_o^2) + (pF_o^2)^2]^{1/2}$, N_o is the number of observations, N_v the number of variables, and p , the ignorance factor, = 0.04.

The calculations were performed using the Personal Structure Determination Package⁴⁹ and the physical constants tabulated therein.⁵⁰ The structure was solved by direct methods (SHELXS)⁵¹ and refined by full-matrix least-squares using all reflections and minimising the function $\sum w(F_o^2 - kF_c^2)^2$ (refinement on *F*²). All the non-hydrogen atoms were refined with anisotropic thermal factors. Hydrogen atoms H1–H3 and those of the two CH₃ groups were refined with a fixed isotropic thermal parameter. All the other hydrogen atoms were placed in their ideal positions (C–H = 0.97 Å), with the thermal parameter *U* 1.10 times that of the carbon atom to which they are attached, and not refined. In the final Fourier map the maximum residual was 0.93(14) e Å⁻³ at 0.91 Å from Cl(1).

CCDC reference number 615695.

For crystallographic data in CIF or other electronic format see DOI: 10.1039/b610657a

Calculations

Quantum-chemical DFT³¹ calculations were carried out on the compounds [Au(η^2 -CH₂=CH₂)]⁺, [Au(bipy)(η^2 -CH₂=CH₂)]⁺ (**2g**), [Au(bipy)]⁺, and CH₂=CH₂ with the well-known three-parameters Becke3LYP³² and Barone's mPW1PW³³ functionals using the commercially available suite of programs Gaussian03.³² Although the use of all-electron basis sets provides better accuracy, pseudopotential techniques are useful when relativistic effects have to be taken into account. Thus, the Schafer, Horn, and

Ahlrichs³⁵ and the 6-31+G*³⁴ all-electron basis sets (BS's) were used for C, H, and N, while the LanL2DZ,³⁶ Stuttgart RSC 1997 (ECP60MDF)³⁷ and CRENLB³⁸ BS's with relativistic effective core potentials (RECP's) were tested for Au.³⁹ For all compounds NBO populations and Wiberg bond indexes were calculated at the optimised geometries.^{44,53} Bond dissociation energies (BDE)⁵⁴ were computed using the fully relaxed equilibrium structures and corrected for zero point energy (ZPE), evaluated from vibrational frequency calculations. Calculations were performed on a IBM SP5/512 equipped with 512 IBM Power5 1.9 GHz processors with 1.2 TB RAM running AIX 5.2, and on an Intel PIV 2.8 GHz workstation running Linux Mandriva One 2006. The programs GaussView 3.0,⁵⁵ Molekel 4.3,⁵⁶ and Molden 4.4⁵⁷ were used to investigate the NBO charge distributions and MO compositions.

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