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Gold molecular precursors and gold–silica interactions

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The gold(I) precursor $Au(O_2CNEt_2)(PPh_3)$ has been successfully employed to graft isolated $Au(PPh_3)$ fragments on amorphous silica. Molecular models of the silica surface, *i.e.* Ph_3SiOH, $(c\text{-}C_5H_9)_7Si_7O_{12}SiOH$ and $(c\text{-}C_5H_9)_7Si_7O_9(OH)_3$, have been found to react with $Au(O_2CNR_2)(PPh_3)$, R = Me, Et, yielding the corresponding silanolato molecular complexes containing the SiO–$Au(PPh_3)$ moiety. Gold nanoparticles on silica have been produced by using AuCl(CO) as precursor.

Introduction

Gold nanoparticles have attracted considerable interest both for their intrinsic properties[1] and for their implications in catalysis and as CO-sensing systems.[2] Thus, it appeared of interest to study the implantation of gold starting from molecular mononuclear gold complexes, through a specific reaction on silanol sites. The compounds $Au(O_2CNR_2)(PPh_3)$,[3] R = Me, Et, and AuCl(CO)[4] have been chosen for this purpose. Evolution of CO_2 was expected with the *N*,*N*-dialkylcarbamato complexes, with grafting of gold(I) onto the silica surface, whereas the formation of gold nanoparticles was predicted with the chlorocarbonyl derivative, in view of the reducing properties of the carbonyl ligand.

Results and discussion

Gold(I) implantation on silica

N,*N*-Dialkylcarbamato derivatives are attractive precursors for grafting well-defined metal-containing fragments on a silica surface. In principle, the primary process consists of the silanolysis of the carbamato ligand,[5] carbon dioxide being evolved in the process, see eqn. (1).

$$\#SiOH + ML_m(O_2CNR_2)_n \longrightarrow \#SiO\text{–}ML_m(O_2CNR_2)_{(n-1)} + CO_2 + NHR_2 \quad (1)$$

Further to earlier reports from these Laboratories, the mononuclear *N*,*N*-dialkylcarbamato-triphenylphosphine derivatives of gold(I) have now been found to react with amorphous silica in toluene suspension, with complete displacement of the carbamato group, as monitored by gas-volumetry. The formation of a matrix-grafted gold-silicate, displaying the Si–O–Au–P sequence [eqn. (1), $n = 1$; R = Me, Et; L = PPh_3; $m = 1$] has been confirmed by XPS, XRD and CP-MAS NMR spectroscopic data. The XPS spectrum showed a single-component $Au_{4f(7/2)}$ spin–orbit split peak centred around 84.9 eV,[6] attributed to a Au(I) species bearing a tertiary phosphine ligand, in comparison with the species $Au(OSiPh_3)(PPh_3)$ (*vide infra*) used as a reference substance. This value is to be compared with those around 85 eV reported for bicoordinated complexes of gold(I) chloride[7a] with tertiary phosphines. As expected, the XRD analysis showed a completely amorphous pattern, while the CP-MAS NMR spectra had ^{13}C resonances at 132 and 128 ppm attributed to the aryl groups of the gold-coordinated tertiary phosphine and a single ^{31}P resonance at 26.9 ppm (with respect to solid PPh_3 at −9.9 ppm), the latter being in good agreement with the resonance of the bicoordinated acetato complex $Au(O_2CMe)(PPh_3)$ (at 24 ppm in the solid state and 27 ppm in chloroform solution) and the resonances of the molecular models containing the SiO–$Au(PPh_3)$ moiety reported hereafter (see Table 1 for relevant spectroscopic data).

Molecular gold(I) silanolates

Taking advantage of the earlier finding that O_2CNR_2 is a good leaving group, the silanolato complex $Au(OSiPh_3)(PPh_3)$, **1**, has been synthesized by reacting $Au(O_2CNEt_2)(PPh_3)$ with Ph_3SiOH, see eqn. (2).

$$Au(O_2CNEt_2)(PPh_3) + Ph_3SiOH \longrightarrow Au(OSiPh_3)(PPh_3) + 0.5\ CO_2 + 0.5\ [NH_2Et_2][O_2CNEt_2] \quad (2)$$

The resulting compound showed an XPS $Au_{4f(7/2)}$ peak[6] centred at 84.8 eV and a ^{31}P NMR signal at 27.7 ppm in $CDCl_3$ solution, in good agreement with the spectroscopic data reported above (see Table 1).

Gold silanolates of formula $Au(OSiMe_3)(PR_3)$ have been previously prepared from $AuCl(PR_3)$ and Me_3SiONa (R = Me, Ph)[7c] and found to be mononuclear by cryoscopic measurements in benzene and by mass spectrometry.

In further modelling studies, we have investigated the reaction of the gold precursors $Au(O_2CNR_2)(PPh_3)$ (R = Me, Et) with molecular silsesquioxane derivatives, such as $(c\text{-}C_5H_9)_7Si_7O_{12}SiOH$ and $(c\text{-}C_5H_9)_7Si_7O_9(OH)_3$, which are regarded to model the silica surface, in as much as they mimick isolated and vicinal grafting sites of the surface, respectively.[8] A prompt reaction occurs between $Au(O_2CNMe_2)(PPh_3)$ and the monosilanol $(c\text{-}C_5H_9)_7Si_7O_{12}SiOH$ in toluene, with the release of 0.5 mol of carbon dioxide per mol of gold, to yield $(c\text{-}C_5H_9)_7Si_7O_{12}SiOAu(PPh_3)$, **2**, see eqn. (3).

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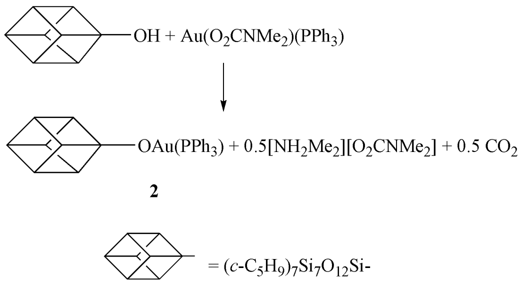
Table 1 NMR data of gold(I) derivatives containing the SiOAu linkage system[a]

Compound	^{1}H-NMR, δ^b Resonance	Assignment	^{13}C-NMR, δ^c Resonance	Assignment	^{29}Si-NMR, δ^d Resonance	Assignment	^{31}P-NMR, δ^e Resonance
Silica–(AuPPh$_3$), CP-MAS			132 (br), 128^f	C_6H_5			26.9^g
Au(PPh$_3$)(OSiPh$_3$), **1**	7.75–7.41 (m)^h	$C_6\mathit{H}_5$	140.1, 137.4, 135.4, 134.2 (d, 13), 131.2, 129.1 (d, 10), 127.5^h	C_6H_5			27.7^h
SIL-O$_3$Si[OAu(PPh$_3$)], 2	7.25–7.16, 7.04–6.97 (m)	$C_6\mathit{H}_5$	134.2 (d, 13), 131.4 (br, $\Delta_{1/2}$ 7 Hz), 129.0 (d, 11), 128.3	C_6H_5	−65.3, −65.4	(c-C$_5$H$_9$)Si	28.5
	1.97–1.52 (m)	(c-CH(CH_2)$_4$)	28.5, 28.4, 27.9, 27.8	(c-CH(CH$_2$)$_4$)	−98.2	SiOAu	
	1.47 (m)	(c-CH(CH$_2$)$_4$)	23.7, 23.5, 23.4	(c-CH(CH$_2$)$_4$			
SIL-[OAu(PPh$_3$)]$_3$, 3	7.30–7.25, 6.96 (m)	$C_6\mathit{H}_5$	134.5 (d, 13), 131.3 (br, $\Delta_{1/2}$ 6 Hz), 129.1 (d, 12), 128.3	C_6H_5	−55.8	SiOAu	28.0
	1.96–1.55 (m)	(c-CH(CH_2)$_4$)	28.7, 28.5, 28.2, 28.0	(c-CH(CH$_2$)$_4$)	−64.7, −65.9	(c-C$_5$H$_9$)Si	
	1.30 (m)	(c-CH(CH$_2$)$_4$)	24.4, 23.7, 23.5	(c-CH(CH$_2$)$_4$			
SIL-(OH)[O(AuPPh$_3$)]$_2$, **4**	9.03 (s, br)	OH	134,7 (d, 13), 131.2 (br, $\Delta_{1/2}$ 7 Hz), 129.0 (d, 11), 128.3	C_6H_5	−55.6, −58.3	SiOH, SiOAu	27.6
	7.46, 6.96 (m)	$C_6\mathit{H}_5$	28.7, 28.5, 28.1, 28.0	(c-CH(CH$_2$)$_4$)	−64.6, −65.9, −67.0	(c-C$_5$H$_9$)Si	
	1.97–1.53 (m)	(c-CH(CH_2)$_4$)	24.4, 23.8	(c-CH(CH$_2$)$_4$			
	1.26 (m)	(c-CH(CH$_2$)$_4$)					

[a] SIL = (c-C$_5$H$_9$)$_7$Si$_7$O$_9$; C$_6$D$_6$ solution, unless otherwise stated; coupling constants (J_{C-P}) in Hz. [b] With respect to C$_6$D$_5$H at 7.15 ppm. [c] With respect to C$_6$D$_6$ at 128 ppm. [d] With respect to SiMe$_4$ at 0 ppm. [e] With respect to H$_3$PO$_4$ at 0 ppm. [f] Referenced to –COOH group of solid glycine at 176.0 ppm from SiMe$_4$. [g] With respect to solid PPh$_3$ at −9.9 ppm from H$_3$PO$_4$. [h] In CDCl$_3$, ^{1}H referenced to CHCl$_3$ at 7.24 ppm, ^{13}C referenced to CDCl$_3$ at 77.0 ppm.

The formation of [NH$_2$Me$_2$][O$_2$CNMe$_2$] has been confirmed by the ^{13}C-NMR analysis of the resulting reaction mixture. The observed release of carbon dioxide under the conditions of reaction (3) can be explained by the formation of dimethylammonium dimethylcarbamate, as for earlier experiments from these laboratories showing reaction (4) to be almost completely shifted to the right.[9]



(3)

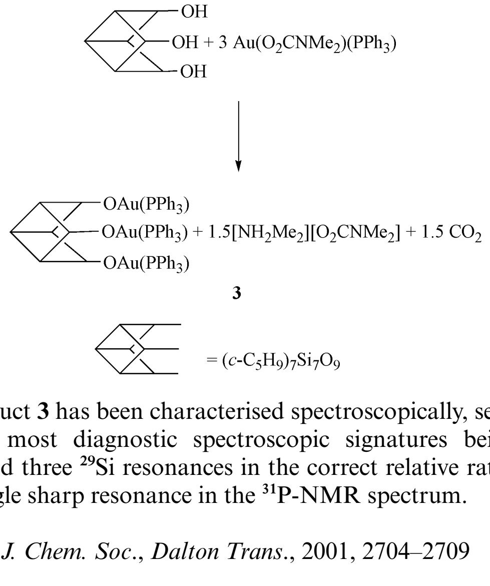
2

$$2\,NHR_2 + CO_2 \rightleftharpoons [NH_2R_2][O_2CNR_2] \qquad (4)$$

Conversely, the silica implantation reaction, see eqn. (1), releases 1 mol of CO$_2$ per mol of carbamate. This is because the unreacted silanol groups fix the secondary amine[10] shifting eqn. (4) to the left, since the silanol/gold molar ratio is ≫1.

The gold-containing compound (c-C$_5$H$_9$)$_7$Si$_7$O$_{12}$SiOAu(PPh$_3$), **2**, was recovered as a colourless substance. The product was characterised by ^{1}H-, ^{13}C-, ^{31}P-, and ^{29}Si-NMR data, as reported in Table 1. The ^{29}Si-NMR spectrum is known to be particularly diagnostic for the symmetry of the silsesquioxane-based derivatives. While complexes of C_{3v} symmetry, such as the starting silanols, show only three resonances, complexes of the lower symmetry C_2 display five resonances.[8b] The ^{29}Si-NMR spectrum of complex **2** displays the expected three resonances, the signal at −98.2 ppm being attributed to the Si–OAu(PPh$_3$) group and the other two signals, at −65.3 and −65.4 ppm of relative intensity 4 : 3 being assigned to the silicon atoms bearing the cyclopentyl substituent. Noteworthy, the signals of relative intensity 1 : 4 : 3 of the precursor SIL-O$_3$SiOH [SIL = (c-C$_5$H$_9$)$_7$Si$_7$O$_9$] are at −97.8 −65.6 and −65.2 ppm in CDCl$_3$. The ^{31}P-NMR spectrum of **2** displays a single peak at 28.5 ppm, that correlates well with the CP-MAS NMR spectrum (26.9 ppm) for the gold-derivatized silica, *vide supra*. This peak undergoes essentially no shift with respect to the ^{31}P-NMR resonances of the starting carbamato complexes Au(O$_2$CNR$_2$)(PPh$_3$), R = Me and Et, found at 28.4 and 28.7 ppm, respectively.

When Au(O$_2$CNEt$_2$)(PPh$_3$) was reacted with the tris-silanol (c-C$_5$H$_9$)$_7$Si$_7$O$_9$(OH)$_3$ in the molar ratio 3 : 1, the product (c-C$_5$H$_9$)$_7$Si$_7$O$_9$[OAu(PPh$_3$)]$_3$, **3**, was obtained, see eqn. (5).



(5)

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Product **3** has been characterised spectroscopically, see Table 1, the most diagnostic spectroscopic signatures being the expected three ^{29}Si resonances in the correct relative ratio, and the single sharp resonance in the ^{31}P-NMR spectrum.

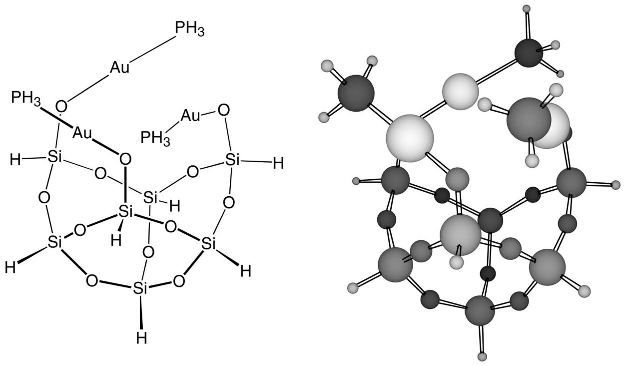

Fig. 1 Optimized geometry of model compound $H_7Si_7O_9[OAu(PH_3)]_3$.

A computer-generated space-filling model of $(c\text{-}C_5H_9)_7Si_7O_9[OAu(PPh_3)]_3$ shows that there is enough room to accommodate three $Au(PPh_3)$ groups on the silsesquioxane moiety, albeit with some steric congestion. It is interesting that in the $V(CO)_5(AuPPh_3)_3$ complex[11] the three $Au(PPh_3)$ fragments are in close proximity, the three gold atoms occupying the vertices of a substantially equilateral triangle with an average Au–Au distance of 2.817 Å.

In an attempt to assess the most probable geometry for complex **3**, we have undertaken geometry optimisation studies on the model compound $H_7Si_7O_9[OAu(PH_3)]_3$. The sets of DFT calculations were based on starting geometries for the $[Au(PH_3)]_3$ moiety derived from the atomic coordinates measured for $V(CO)_5(AuPPh_3)_3$[11] and converged to an optimised geometry with distant $Au(PH_3)$ moieties, the calculated Au–Au distance within the almost equilateral triangle being 4.119 Å, implying the absence of $Au \cdots Au$ contacts (see Fig. 1).

Reaction (3) was monitored by gas-volumetric measurements. Prompt ($t < 5$ min) evolution of 0.97 mol of CO_2 per mol of silsesquioxane upon addition of the gold derivative to the silsesquioxane solution has been observed, followed by a slow evolution of a further 0.54 mol of CO_2, the reaction being terminated in about 15 h at room temperature. Such stepwise CO_2 release is presumably due to the fact that the first two silanolysis reactions, see eqns. (6a) and (6b), occur promptly, while the third substitution requires longer reaction times, see eqn. (6c).

$$(c\text{-}C_5H_9)_7Si_7O_9(OH)_3 + Au(O_2CNEt_2)(PPh_3) \longrightarrow (c\text{-}C_5H_9)_7Si_7O_9[OAu(PPh_3)](OH)_2 + 0.5\,[NH_2Et_2][O_2CNEt_2] + 0.5\,CO_2 \qquad (6a)$$

$$(c\text{-}C_5H_9)_7Si_7O_9[OAu(PPh_3)](OH)_2 + Au(O_2CNEt_2)(PPh_3) \longrightarrow \underset{\mathbf{4}}{(c\text{-}C_5H_9)_7Si_7O_9[OAu(PPh_3)]_2(OH)} + 0.5\,[NH_2Et_2][O_2CNEt_2] + 0.5\,CO_2 \qquad (6b)$$

$$(c\text{-}C_5H_9)_7Si_7O_9[OAu(PPh_3)]_2(OH) + Au(O_2CNEt_2)(PPh_3) \longrightarrow \underset{\mathbf{3}}{(c\text{-}C_5H_9)_7Si_7O_9[OAu(PPh_3)]_3} + 0.5\,[NH_2Et_2][O_2CNEt_2] + 0.5\,CO_2 \qquad (6c)$$

The intermediate $(c\text{-}C_5H_9)_7Si_7O_9[OAu(PPh_3)]_2(OH)$, **4**, was synthesized independently from $(c\text{-}C_5H_9)_7Si_7O_9(OH)_3$ and $Au(O_2CNEt_2)(PPh_3)$ in a 1 : 2 molar ratio, 0.98 mol of CO_2 being rapidly evolved per mol of silsesquioxane. The spectroscopic data of compound **4** are reported in Table 1. Interestingly, the ^{1}H-NMR spectrum of **4** exhibits a resonance for the hydroxyl group at 9.03 ppm as a broad peak, beside the resonances for the triphenyl and cyclopentyl groups. Such assignment is in accordance with the single literature precedent for a metalla-derivative silsesquioxane presenting an unreacted silanol site close to a metalla-siloxane fragment. The complex $(c\text{-}C_5H_9)_7Si_7O_9(OSiMe_3)(O_2AlO)(OH)(OSiMe_3)Si_7(c\text{-}C_5H_9)_7$ has been reported to be synthesised by reacting $(c\text{-}C_5H_9)_7Si_7O_9(OSiMe_3)(OH)_2$ with $AlEt_3$ in the appropriate stoichiometric ratio, and found to display a similar resonance at 8.2 ppm for the hydroxyl proton.[8e] The ^{29}Si-NMR spectrum of **4** exhibits the expected five resonances, see Table 1, in agreement with a lower symmetry with respect to **3**.

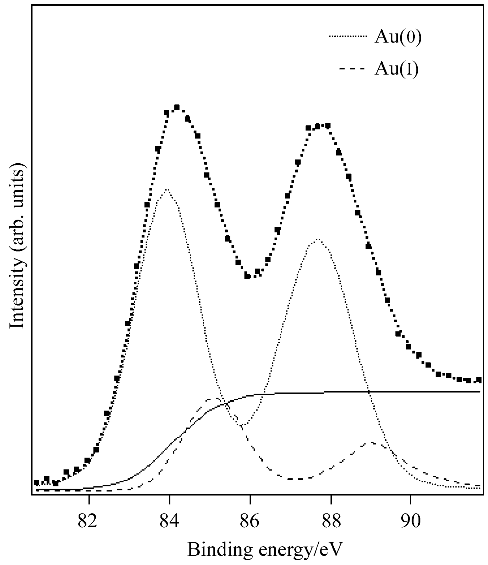

Fig. 2 XPS Au_{4f} spectrum of the sample obtained from the reaction of AuCl(CO) with amorphous silica. The contributions of Au(I) and Au(0) are shown. The deconvolution has been obtained by non-linear least-squares curve-fitting procedures.

Gold nanoparticles on silica

The choice of AuCl(CO) for gold implantation on silica stems from the observation that halo-carbonyl complexes of late transition elements undergo reduction in the presence of water, coordinated carbon monoxide being converted to carbon dioxide.[12] Thus, we expect physi-/chemi-sorption of gold(I) to be the primary process, followed by reduction in the presence of water, as such or arising from condensation of silanol groups, see eqn. (7).

$$AuCl(CO) + \tfrac{1}{2}\,H_2O \longrightarrow [Au] + \tfrac{1}{2}\,CO + \tfrac{1}{2}\,CO_2 + HCl \qquad (7)$$

The treatment of silica with AuCl(CO) produced gas evolution with formation of a violet gold-doped silica, that does not show any gold-coordinated carbonyl group by Diffuse Reflectance Fourier Transformed Infrared (DRIFT) spectra.

The gases produced in the grafting experiment were found to be CO, CO_2 and HCl, their total volume being lower than expected, see Experimental, due to the relatively high solubility of HCl and CO_2.

The presence of metallic gold on the silica support was evidenced by XPS, TEM, XRD and UV-Vis spectra. The absorption band observed around 520 nm was assigned to the surface plasmon resonance of gold clusters.[13] XPS data[6] confirmed that gold was mainly present as Au(0) with only a minor contribution of Au(I), due to incomplete reduction, gold clusters being presumably anchored to silica *via* oxygen-bridging. The more intense $Au_{4f(7/2)}$ spin–orbit split component of the Au_{4f} peak was found to be centred around 84.2 eV, which was deconvoluted to two peaks located around 84.0 and 85.1 eV, associated with Au(0) and Au(I) species, respectively, see Fig. 2.

The relative intensity of the two peaks [the Au(0)/Au(I) molar ratio was found to be approximately 4] was unaffected by the experimental conditions [fast or slow addition of the AuCl(CO) solution to the silica, ageing of the samples at room

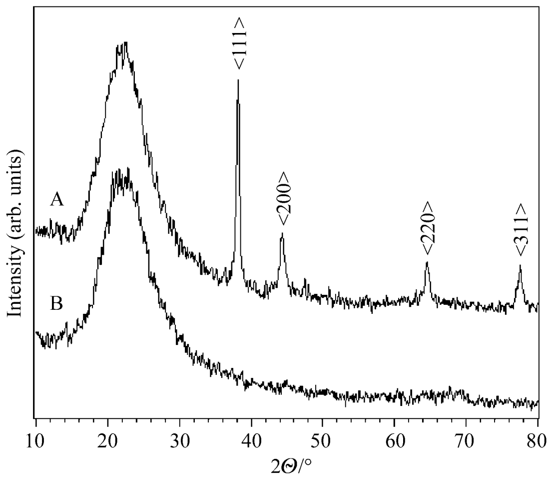

Fig. 3 XRD diffraction patterns for the gold-implanted silica samples using (A) AuCl(CO) and (B) $Au(O_2CNEt_2)(PPh_3)$ as molecular precursors. The reflections attributed to fcc gold[20] are shown.

temperature, storage at 40 °C in a water-vapour saturated atmosphere]. The Cl_{2p} region suggests the presence of Au–Cl bonds. Relevant to this point is that Au(I)–Au(0) clusters have already been prepared and structurally characterized.[14,15] The Si_{2p} (BE = 103.6 eV) and O_{1s} (BE = 532.9 eV) peaks are characteristic of SiO_2, whereas the C_{1s} line was mainly due to adventitious contamination.

Based on XRD data, the average crystallite dimension is about 11 nm, whereas by TEM analysis the estimated grain size is 100–200 nm. Similar findings are frequently encountered in the literature, since the large particles observed by TEM presumably consist of multiple nanocrystals.[15]

The XRD analysis showed diffraction patterns characterised by four peaks, attributed to fcc gold. Such a crystalline phase was absent in the sample obtained from the $Au(O_2CNEt_2)(PPh_3)$ precursor (see Fig. 3).

Conclusions

Gold-grafting on silica has been obtained under mild conditions starting with the mononuclear molecular precursors $Au(O_2CNR_2)(PPh_3)$, and AuCl(CO). The anionic ligand is eliminated during the grafting silanolysis reaction in both cases (as CO_2 and NHR_2 for the former, and as HCl for the latter). Thus, the neutral ancillary ligand influences the chemical complexity, nuclearity and morphology of the implanted fragment. In the former case, isolated grafted $Au(PPh_3)$ moieties are obtained, that do not show any tendency to undergo reduction or clustering. Conversely, deposition of gold nano-clusters, through the joint action of adsorbed water and CO is obtained with AuCl(CO). The deposition reactions from the carbamato precursor $Au(O_2CNR_2)(PPh_3)$ has been successfully modelled with triphenylsiloxane and silsesquioxane derivatives.

Experimental

General

All manipulations were performed under an atmosphere of pre-purified dinitrogen, carbon monoxide or carbon dioxide. Solvents were dried by conventional methods prior to use. AuCl(CO),[16a] and $Au(O_2CNEt_2)(PPh_3)$[3] were prepared according to the literature, while $Au(O_2CNMe_2)(PPh_3)$ was synthesised in a manner similar to that of the corresponding ethyl derivative, using dimethylamine [$Au(O_2CNMe_2)(PPh_3)$: Anal. (%) Found (Calc.): C, 45.4 (46.4); H, 3.8 (3.9); N, 1.5 (2.5); NMR (C_6D_6): ^1H: δ 7.27–7.14 (m, Ph), 6.96–6.83 (m, Ph); 3.098 (s, Me); ^{13}C: δ 163 (O_2C), 134, 131, 129, 128 (Ph), 37.5 (Me); ^{31}P: δ 28.4]. The Aldrich products $(c\text{-}C_5H_9)_7Si_7O_{12}SiOH$ and $(c\text{-}C_5H_9)_7Si_7O_9(OH)_3$ were heated at 60 °C *in vacuo* for 12 h at 10^{-2} Torr prior to use. Commercial silica (Grace, EP 17G, surface area 325 $m^2\ g^{-1}$, pore volume, 1.82 $cm^3\ g^{-1}$ was treated at 160 °C over P_4O_{10} for 12 h *in vacuo* up to constant weight and then stored in flame-sealed vials under an atmosphere of dry CO_2. The total silanol content (typically between 2.8 and 3.1 mmol g^{-1}) was estimated from the mass loss upon heating at 850 °C. Gas-volumetric measurements were carried out by using previously described equipment.[16b]

IR spectra were recorded with a 1725X FT-IR Perkin-Elmer spectrophotometer in solution or as Nujol or poly(chlorotrifluoroethylene) (PCTFE) mulls prepared under exclusion of moisture. Diffuse Reflectance Infrared Fourier Transform (DRIFT) spectra were measured with the same instrument by mixing the samples with dry KBr under an inert atmosphere and by rapid transfer to the cell (Spectra Tech). ^1H, ^{13}C, ^{31}P and ^{29}Si spectra in solution were recorded with a Varian Gemini 200 BB spectrometer; chemical shifts being reported in ppm *vs.* $SiMe_4$ for ^1H, ^{13}C and ^{29}Si and *vs.* 85% H_3PO_4 for ^{31}P. CP-MAS ^{13}C-, ^{29}Si- and ^{31}P-NMR spectra were measured at room temperature with a MSL 200 Bruker instrument operating at 50.321 (^{13}C) and 81.015 (^{31}P) MHz, chemical shifts being referenced to the –COOH group of glycine at 176.0 ppm from $SiMe_4$ and to PPh_3 at −9.9 ppm from H_3PO_4 for ^{13}C and ^{31}P, respectively.

XPS analyses were performed with a Perkin-Elmer Φ 5600-ci spectrometer using non mono-chromated Mg-Kα radiation (1253.6 eV). Samples were analysed as pellets and introduced directly, by a fast-entry lock system, into the XPS analytical chamber. The working pressure was $<5 \times 10^{-8}$ Pa and the spectrometer was calibrated assuming the binding energy (BE) of the $Au_{4f(7/2)}$ line at 83.9 eV with respect to the Fermi level. A low-energy electron flood gun was used for charge compensation. The reported BE's (±0.15 eV) were corrected by assigning the BE value of 285.0 eV[17] to the C_{1s} line of adventitious carbon. Survey scans were run in the 0–1100 eV range. Detailed scans were recorded for the Au_{4f}, Si_{2p}, C_{1s}, O_{1s}, Cl_{2p} and P_{2p} regions.[6] The analyses involved Shirley-type background subtraction,[18] and non-linear least-squares curve fitting, adopting Gaussian–Lorentzian peak shapes and peak area determination by integration. The atomic compositions were evaluated by using sensitivity factors supplied by the spectrometer manufacturer, taking into account the geometric configuration of the apparatus.

XRD measurements were performed using a Philips PW 1820 diffractometer (Cu-Kα radiation, 40 kV, 50 mA). Selected angular ranges were step-scanned (0.05°) several times until a satisfactory signal-to-noise ratio was reached. The average crystallite size was calculated by using the Scherrer equation, taking into account the instrumental broadening. The optical absorption spectra were recorded in the 200–1000 nm range using a double-beam CARY 5E UV-Vis spectrophotometer with a spectral bandwidth of 1 nm. DRIFT spectra were recorded with a Perkin-Elmer 1725X spectrophotometer by mixing the samples with dry KBr in the absence of air with a SpectraTech cell. TEM measurements were carried out with a Jeol JEM 2010 instrument operating at 200 kV. A small amount of specimen was ground in a mortar to a very fine powder, which was deposited on a lacy carbon film supported on a standard copper grid. The whole sequence of operations was carried out under a N_2 atmosphere. The time required for sample preparation was minimized in order to avoid deterioration or contamination.

All calculations[19] were performed using Gaussian-94.[19a] The LanL2DZ set was employed to perform complete geometry optimisation with a Density Functional Theory (DFT) approach. The three-parameter form of the Becke, Parr, Lee, and Yang functional (B3LYP)[19b] was employed.[19c] The LanL2DZ basis set includes both Dunning and Hay's D95 sets for H, and the relativistic Electron Core Potential (ECP) sets of Hay and Wadt for the heavy atoms.[19c–f]

Interaction of $Au(O_2CNEt_2)(PPh_3)$ with silica

A solution of $Au(O_2CNEt_2)(PPh_3)$ (0.440 g, 0.76 mmol) in toluene (50 cm^3) was added to a suspension of the silica (7.2 g, corresponding to 22.3 mmol of silanols) in toluene (50 mL). After 6 h stirring, the suspension was filtered, and the substantially colourless solid was washed with toluene (25 cm^3), and dried *in vacuo*. CP-MAS NMR: ^{31}P δ 26.9, ^{13}C δ 132 and 128. XPS analysis (sample AM2-118), BE: $Au_{4f(7/2)}$ peak centred at 84.9 eV, assigned to Au(I).

In a gas-volumetric experiment carried out at 20.3 °C in toluene, $Au(O_2CNEt_2)(PPh_3)$ (0.268 g, 0.47 mmol) was treated with excess silica (4.2 g, corresponding to 11.76 mmol of silanols) and an evolution of CO_2 was measured corresponding to a Au/CO_2 molar ratio of 1.0.

Synthesis of $Au(OSiPh_3)(PPh_3)$

The carbamato complex $Au(O_2CNEt_2)(PPh_3)$ (1.02 g, 1.8 mmol) was treated in toluene (100 cm^3) with Ph_3SiOH (0.46 g, 1.7 mmol). After 10 h stirring in the dark, the solution was concentrated to dryness and the residue was treated with toluene (5 cm^3). Heptane (50 cm^3) was added to the resulting solution. After 24 h at −30 °C, the colourless solid was filtered and dried *in vacuo* (0.80 g, 64%). Found: C, 58.4; H, 4.3. Calc. for $C_{36}H_{30}AuOPSi$: C, 58.9; H, 4.1%. ^{31}P-NMR: δ 28.4. XPS analysis, BE (eV): $Au_{4f(7/2)}$: 84.8, O_{1s}: 532.4, Si_{2p}: 102.3, P_{2p}: 131.8.

Reaction of $(c\text{-}C_5H_9)_7Si_7O_{12}SiOH$ with $Au(O_2CNMe_2)(PPh_3)$ (1 : 1 molar ratio)

By operating in gas-volumetric apparatus, a flame-sealed fragile glass vial containing the complex $Au(O_2CNMe_2)(PPh_3)$ (136 mg, 0.250 mmol) was introduced under carbon dioxide into a reactor containing a toluene (20 cm^3) solution of $(c\text{-}C_5H_9)_7Si_7O_{12}SiOH$ (229 mg, 0.249 mmol). After breaking the vial, 0.126 mol of carbon dioxide were evolved. NMR analysis of the supernatant solution of **1** gave the results in Table 1. An authentic sample of $[NH_2Me_2][O_2CNMe_2]$ in C_6D_6 at room temperature shows two resonances: 161.4 ppm (O_2CN) and 32.5 ppm (CH_3).

The mother solution was evaporated to dryness. The resulting residue was washed with heptane (2 × 5 mL) and the suspension was filtered, thus allowing product **1** to be isolated as a colourless solid (32% yield).

Reaction of $(c\text{-}C_5H_9)_7Si_7O_9(OH)_3$ with $Au(O_2CNEt_2)(PPh_3)$ (1 : 3 molar ratio) with production of $(c\text{-}C_5H_9)_7Si_7O_9[OAu(PPh_3)]_3$, 3

Complex $Au(O_2CNEt_2)(PPh_3)$ (407 mg, 0.71 mmol), was sealed in a glass vial under carbon dioxide and introduced into a reactor containing a toluene (35 cm^3) solution of $(c\text{-}C_5H_9)_7Si_7O_9(OH)_3$ (223 mg, 0.24 mmol) saturated with carbon dioxide and connected to a gas-volumetric apparatus. A prompt evolution of 0.23 mmol of carbon dioxide was measured, followed by a slow release of further gas (*ca.* 0.1 cm^3 h^{-1}). Upon stirring overnight, additional CO_2 was evolved (0.11 mmol) corresponding to a final CO_2/Au molar ratio of 1.5. The resulting pink supernatant solution was evaporated to dryness and the residue was washed with pentane (2 × 5 cm^3) and then dried *in vacuo* (24% yield). The NMR spectroscopic data are reported in Table 1.

Reaction of $(c\text{-}C_5H_9)_7Si_7O_9(OH)_3$ with $Au(O_2CNEt_2)(PPh_3)$ (1 : 2 molar ratio)

In a gas-volumetric experiment carried out by adding $Au(O_2CNEt_2)(PPh_3)$ (189 mg, 348 mmol) to a toluene (40 mL) solution of $(c\text{-}C_5H_9)_7Si_7O_9(OH)_3$ (148 mg, 0.169 mmol), the evolution of 0.166 mmol of carbon dioxide was measured. Part of the resulting colourless supernatant solution was evaporated to dryness and the residue was dissolved in C_6D_6 and transferred to an NMR tube, for spectroscopic characterisation, see Table 1. The mother solution was evaporated to dryness and the residue was extracted with pentane (2 × 25 mL); upon concentration to about 2 mL, a colourless solid separated out (26% yield), which was identified as $(c\text{-}C_5H_9)_7Si_7O_9(OH)[OAu(PPh_3)]_2$, **4**.

Implantation of gold with AuCl(CO)

In a typical experiment, a solution of AuCl(CO) (0.21 g, 0.8 mmol, $\nu_{CO} = 2151\ cm^{-1}$) in toluene (100 cm^3) was added to pre-treated silica (AM2-80; silanol groups: 3.1 mmol g^{-1}; 8.4 g corresponding to 26.04 mmol of SiOH). After 20 h stirring the suspension was filtered and the violet solid was dried *in vacuo*. Anal.: Au 1.4%. DRIFT: no bands attributable to CO stretching vibrations. XPS analysis, BE: the peak centred at 84.2 eV [$Au_{4f(7/2)}$] was deconvoluted to two peaks at 84.0 and 85.1 eV, associated to Au(0) (≅80%) and Au(I) (≅20%), respectively; further peaks were observed at 103.6 eV [Si_{2p}] and 532.9 eV [O_{1s}] typical of silica. XRD: gold nanoparticles show a diffraction pattern characterized by four peaks at $2\theta = 38.18°$ (⟨111⟩), 44.39° (⟨200⟩), 64.58° (⟨220⟩) and 77.55° (⟨311⟩), attributed to fcc gold (JCPDS card no. 4-784).[20] The estimated average particle size is 11 ± 3 nm for all samples. The broad band located at about 21.5° is due to amorphous silica. UV-VIS: band at around 520 nm, associated with the surface plasmon resonance of gold clusters.[13] An IR spectrum of the gases produced in the grafting experiment showed bands due to CO, CO_2 and HCl, while 1.5 mol of gas per mol of gold were measured under carbon monoxide.

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