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Radical Trapping by Gold Chlorides Forming Organogold Intermediates

Carmela Aprile, Mercedes Boronat, Belén Ferrer, Avelino Corma,* and Hermenegildo García*

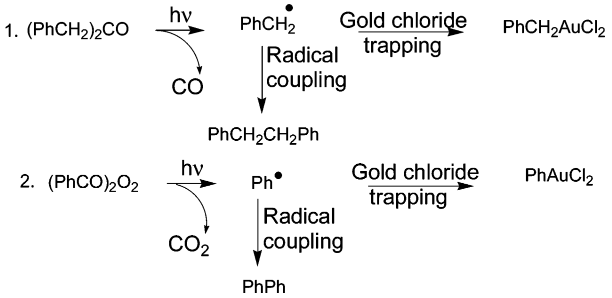
Instituto de Tecnología Química CSIC−UPV and Departamento de Química, Universidad Politécnica de Valencia,
Avda de los naranjos s/n, 46022 Valencia, Spain

Received March 23, 2006; E-mail: hgarcia@qim.upv.es

Homogeneous and heterogeneous gold species are attracting increasing interest due to their unique properties as catalysts for oxidation reaction,[1−3] water−gas shift reaction,[4] carbon−carbon formation,[5] enantioselective aldol condensation, and hydrogenation.[6] Very recently it has been reported[7] that the presence of a radical initiator promotes the gold-catalyzed epoxidation of cyclohexene by air, giving rise to a mixture of epoxide, cyclohexanol, and cyclohexanone in high selectivity. Such a process should require the formation of radicals that will be stabilized by gold trapping, reacting then with hydrocarbons. If this is so, gold species can be used either to quench radicals and stop undesiderable parasite reactions or to stabilize formed radicals increasing their average lifetime while acting as intermediates for a desired catalytic reaction. Thus, it becomes important to determine the reactivity of gold compounds with carbon-centered radicals. In the present work, we provide firm preparative and time-resolved evidence for the reaction of carbon-centered radicals with gold chlorides. Quantum chemical calculations predict a low activation barrier for this reaction. Our study is relevant in gold catalysis because it proves the ability of gold to trap radicals. This opens the possibility to consider some organogold compounds as an efficient source of long-lived radicals. These radicals derived from the organogold would then react with other adsorbed species.

Gold halides have shown to be active catalysts for coupling reactions,[5,8] and they constitute an excellent model to study the interaction of radicals with gold of different oxidation states and the type of organogold compound formed if such interaction occurs. Thus, to learn whether gold chloride could react with organic radicals, we have performed the photolysis and thermolysis of well-established radical precursors such as dibenzyl ketone and benzoyl peroxide in the presence of gold chlorides. The anticipated mechanism of the process is illustrated in Scheme 1.

Scheme 1. Expected Trapping of Radicals by Gold Halides



The course of the photochemical reaction to generate benzyl radicals was followed by optical spectroscopy. Upon irradiation of dibenzyl ketone, the absorption band corresponding to the gold halides at λ_{max} 325 nm (see inset of Figure 1) decreases, while a new absorption band with a lower extinction coefficient appears at 360 nm. These two facts suggest that the radicals have been trapped by gold and that new organogold compounds are being formed during the photolysis. The final UV/vis spectrum was coincident for the three gold halides and is shown in Figure 1.

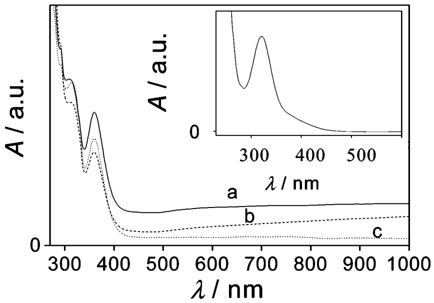


Figure 1. UV/vis spectra after 5-h lamp irradiation under N_2 of 1,3-diphenylacetone (2.9×10^{-2} M) in CH_3CN and AuCl (a), $AuCl_3$ (b), and $HAuCl_4$ (c). The inset shows the UV/vis spectrum of $AuCl_3$ in CH_3CN.

Blank experiments where solutions containing a gold salt ($AuCl_3$, $HAuCl_4$, or AuCl) were irradiated in the absence of 1,3-diphenylacetone show that gold chlorides are stable under these conditions. On the other hand, irradiation of 1,3-diphenylacetone in the absence of gold chlorides gives 1,2-diphenylethane, which is formed by recombination of the free organic radicals.[9] 1,2-Diphenylethane exhibits in UV/vis spectroscopy a band at 270 nm. Therefore, only when 1,3-diphenylacetone is irradiated in the presence of gold chlorides are the changes in the optical spectrum described above observed.

The progress of the photochemical reaction and the formation of organometallic gold compounds were also followed by ^{1}H NMR. Thus, when 1,3-diphenylacetone (3.0×10^{-2} M) was irradiated in CD_3CN, but in the presence of $AuCl_3$ (3.2×10^{-2} M) in addition to starting material (singlet at 3.8 ppm) and diphenylethane (singlet at 2.9 ppm), formation of a new singlet in the aliphatic region appearing at 4.71 ppm was observed (see Figure S1 of Supporting Information). Analogous experiments where $AuCl_3$ was replaced by AuCl or $HAuCl_4$ showed identical behavior, giving a peak exactly at the same chemical shift. We attributed this new singlet to an organogold compound, where a positive gold atom is bonded to the benzyl groups. This organogold compound could be purified through $D_2O/CDCl_3$ liquid extraction. ^{1}H NMR spectrum (inset of Figure S1) of the aqueous phase shows only the signals corresponding to the organogold compound. ^{13}C NMR spectra of the pure organogold compound confirmed the appearance of a deshielded methylene carbon common for $AuCl_3$, AuCl, and $AuCl_4^-$ characterized by a peak at 47.2 ppm. HETCOR experiments indicate that the carbon at 47.2 ppm in ^{13}C NMR corresponds to the 4.71 ppm signal in the ^{1}H NMR. High-resolution mass spectrometry (HRMS) gives a molecular formula $C_{14}H_{16}AuOH^+$ (HRMS = 397.248; theoretical mass = 397.243) for this compound. A likely structure that is compatible with all the available spectroscopic data would be $(PhCH_2)_2AuClOH$, which, according to Scheme 1, corresponds to the expected product when two benzyl radicals have been trapped by gold. Chlorine atoms are frequently not observed

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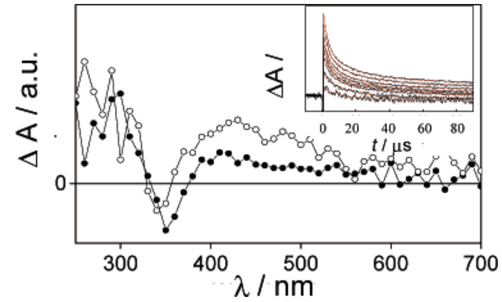

Figure 2. UV/vis transient absorption spectra recorded 4 μs after 266-nm laser excitation of a N_2-purged CH_3CN solution of 1,3-diphenylacetone (1.1×10^{-3} M) and $AuCl_3$ (○) and $HAuCl_4$ (●; 1×10^{-3} M). The inset shows the decay monitored at 290 nm of a N_2-purged CH_3CN solution of 1,3-diphenylacetone (1.1×10^{-3} M) upon the addition of increasing amounts of $HAuCl_4$.

in MS and apparently a second one has been replaced by OH during workup or in the preparation of the MS matrix. Also, the MS peak corresponds to the protonated form of the dibenzylgold species. This compound is the same irrespective of the initial gold oxidation state. In all cases, photochemical irradiation of dibenzyl ketone in the presence of gold chlorides led also to the reduction of gold either as nanoparticles ($AuCl_3$ and $HAuCl_4$) or as a metallic mirror (AuCl). In the case of AuCl, dismutation of Au^I to Au^{III} and Au^0 would explain why the same organogold compound is formed by reaction of benzyl radicals with Au^I or Au^{III} chlorides. When benzoyl peroxide is used as a radical source instead of dibenzyl ketone, analogous behavior was observed. ^{1}H and ^{13}C NMR and MS data corresponding to these experiments also support the formation of the diphenylgold halide. (Figure S2).

To understand the mechanism for the electrophilic substitution of chloride by carbon-centered radicals in the gold salts, we have performed quantum chemical calculations for the reaction of $AuCl_3$, with phenyl radicals as a model process (Figures S3 and S4). Because the HOMO of the phenyl radical (−6.47 eV) is higher than the LUMO of $AuCl_3$ (−6.82 eV), both species interact rapidly and without activation energy to give $AuCl_2Ph$ in a highly exothermic process. Calculations indicate that there is no activation energy barrier for the electrophilic substitution of chloride by phenyl radicals while leading to the formation of stable phenylgold compounds. The energy profile shows that subsequent additions of phenyl radicals should be very fast and always downhill from the energetic point of view, in agreement with the multiple radical substitution observed experimentally.

To obtain direct spectroscopic evidence of the trapping of benzyl radicals generated in the photolysis of 1,3-diphenylacetone by the gold chlorides, a laser flash photolysis study has been performed. As can be expected, photolysis of dibenzyl ketone in the absence of gold halides gives benzyl radicals that decay in the microsecond time scale (Figure S5). Laser flash photolysis shows that benzyl radicals are quenched by the presence of sufficiently high concentrations of any of the three gold salts (Figure 2). The observation of this quenching process is firm evidence that benzyl radicals interact with gold halides. The Stern−Volmer constants obtained from the relative signal intensity decrease (I_0/I) at zero delay time measured at 290 nm for the three gold salts are the following: K_{sv} ($AuCl_3$) $= 9.6 \times 10^3$ M^{-1}; K_{sv} ($HAuCl_4$) $= 1.4 \times 10^4$ M^{-1}; and K_{sv} (AuCl) $= 4.1 \times 10^3$ M^{-1}. UV/vis spectroscopy shows that absorbance at 266 nm of the cell before and after flash photolysis does not change significantly. To determine the nature of the species arising from the interception of benzyl radical by gold halides, we have recorded the transient absorption spectrum of the 1,3-diphenylacetone upon quenching with the three different gold salts (Figure 2). The transient absorption spectrum shows three common characteristic features: (i) an absorption at wavelengths below 300 nm, corresponding to a residual population of benzyl radicals, (ii) bleaching at about 360 nm, indicating the disappearance of gold chlorides, and (iii) a broad absorption band from 400 to 700 nm, corresponding to the surface Au^0 plasmon, which decreases with time, indicating that it is at least partially reacting with benzyl radicals. The broadness of the plasmon band and its unusual λ_{max} may indicate that gold nanoparticles still contain a variable positive charge density. The most likely fate of gold nanoparticles is the reaction with benzyl radicals to form benzylgold species. This has been confirmed by performing the in situ radical formation in the presence of pre-prepared gold colloid. In this case, ^{1}H NMR shows a new signal at 2.42 ppm, which can be assigned to the surface-bound benzyl radical (Figure S6). We have ascertained that Cl^- ions accompanying Au are not responsible for the quenching by observing that 3-methylimidazolium chloride is not a quencher of benzyl radicals (see Figure S7).

At this point, it is clear that the gold salts as well as gold nanoparticles are able to trap the in situ formed radicals and to form well-defined organogold compounds. The room-temperature air stability of these organogold compounds has been studied by purging the solution with O_2 for 5 and 15 min at room temperature after the in situ formation of the organogold compound. The recorded ^{1}H NMR spectra are coincident with the one performed before flowing O_2, thus showing the air stability of the photogenerated organogold. An organogold compound decomposes at 50 °C or at room temperature in the presence of HCl, whereas a new ^{1}H NMR peak at 2.2 ppm appears probably due to the formation of toluene as product.

In conclusion, we have shown that gold chlorides as well as gold nanoparticles are able to trap radicals, forming well-defined organogold compounds that have not been observed up to now. These organogold compounds are stable at room temperature in the presence of O_2 but decompose at higher temperature or in the presence of acids, generating potentially reactive surface species. These organogold species are probably responsible for the remarkable catalytic activity enhancement of gold species in the presence of radical initiators.[7]

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Supporting Information Available: Experimental details, ^{1}H NMR spectra, and diagrams of energy levels of the new species and of the steps of the proposed mechanism. This material is available free of charge via the Internet at http://pubs.acs.org.

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