Generation and reactivity of electron–rich carbenes on the surface of catalytic gold nanoparticles

Judit Oliver–Meseguer,‡ Mercedes Boronat,‡ Alejandro Vidal–Moya,‡ Patricia Concepción,‡ Miguel Ángel Rivero–Crespo,‡ Antonio Leyva–Pérez,*‡ and Avelino Corma,*‡

1Instituto de Tecnología Química (UPV–CSIC), Universitat Politècnica de València–Consejo Superior de Investigaciones Científicas, Avda. de los Naranjos s/n, 46022 Valencia, Spain.

Supporting Information Placeholder

ABSTRACT: The reactive nature of carbenes can be modulated, and ultimately reversed, by receiving additional electron density from a metal. Here, it is shown that Au nanoparticles (NPs) generate an electron–rich carbene on surface after transferring electron density to the carbonyl group of an in situ activated diazoacetate, as assessed by Fourier transformed infrared (FT–IR) spectroscopy, magic angle spinning nuclear magnetic resonance (MAS NMR) and Raman spectroscopy. Density functional theory (DFT) calculations support the observed experimental values and reveal the participation of at least three different Au atoms during carbene stabilization. The surface stabilized carbene shows an extraordinary stability against nucleophiles, and rather react with electrophiles to give new products. These findings showcase the ability of catalytic Au NPs to inject electron density in energetically high but symmetrically allowed valence orbitals of sluggish molecules.

Carbenes are divalent C–atoms, often generated in situ with catalytic metals to program their reactivity towards nucleophiles. However, carbenes can reverse their reactivity if the catalytic metal transfers a significant amount of electron density to unoccupied bonding orbitals. This has been achieved so far by spontaneous one electron oxidation of soluble Co2+ and Fe2+/3+ carbene complexes. The latter feature suitable quasi-planar ligands that not only furnish an appropriate chemical environment for the electron–rich carbene, but also provide the energetically and spatially suitable valence orbitals to engage the empty anti-bonding orbitals of the carbene, since a direct electron transfer from the metal to the carbene is severely restricted. It would be of interest to have metals able to do so on solid surfaces, thus enabling heterogeneous catalysis and avoiding ligands.

Au is able to bind carbenes as a metal complex in solution and also as NPs,3,5 The latter reacts in a classical way, probably on unsaturated Au atoms present in the boundaries, corners and vertexes of the NP.5 It may occur that bulk Au atoms would inject electron density into the symmetrically matching unoccupied valence orbitals of a suitable carbene, if efficiently formed on the NP surface. This is not more what occurs during the activation on Au NPs of relatively inert molecules such as H2,5 O2,5 HCl5 and benzenes and alkenes,5 which coordinate on unsaturated Au atoms and then receive electron density from the NP bulk. The electron–rich intermediates are stable enough to be detected6 and used in productive catalytic processes.6,9

Figure 1 shows the temperature programmed FT–IR spectrum of a sample of commercially-available, homogeneously dispersed 3 nm Au NPs on TiO2 (1 wt%), degassed at 200 °C under vacuum, and treated with ethyl diazoacetate (EDA, 1) at 25 °C. According to blank experiments with 1 adsorbed on TiO2 (Fig S1–3), the peaks at 2115 and 1640 cm−1 corresponds to unreacted 1, and the peaks at 1736, 1679 and 1568 cm−1 correspond to the hydration product ethyl glycolate 2, as also assessed by the disappearance of hydroxyl groups of Au–TiO2 after adsorption of 1. However, new peaks at 1704 and 1549 cm−1 rise in intensity after 1 dosing, remaining quite stable to evacuation. These peaks can be ascribed to the strongly blue-shifted C=O of an electron–rich carbene that receives electron density from Au (1549 cm−1, 3A) and the free C=O of a classical Au carbene (1704 cm−1, 3B). Increasing temperature to 150 °C triggers formation of ethyl fumarate and ethyl maleate 4, as assessed by the peaks at 1711, 1667 and 1524 cm−1 (see Fig S2). Benzyl diazoacetate gives also blue-shifted C=O signals in the presence of Au–TiO2 (Fig S3).

Figure 1 Temperature programmed FT–IR spectra of 1 adsorbed on Au–TiO2 at increasing dosing (black lines), after evacuation at 10−6 mbar (blue lines) at 25 °C, and after increasing temperature to 150 °C (red line). Figure 2A shows the 13C CP/MAS NMR spectra of isotopically labelled EtOOCH3CHN2 (1–13C) adsorbed on Au–TiO2 (sur-
face Au atoms/1 = 1), and sealed in an ampule (see Fig S4 for full spectra). The mixture at RT shows the original signal of 1-13C centered at 46 ppm (Fig S4) together with three new signals centered at 41, 77 and 132 ppm (broad), the two latter corresponding to 2 and 4, respectively. Notice that, under these conditions, the dimerization reaction has been completed. After heating at 80 °C during 30 min, the signal of 1-13C completely disappears and the signal ranging from ~30 to ~50 ppm, with a maximum at 41 ppm, persists, without further changes in the spectrum for longer heating times. Notice that surface heterogeneity broadens signals in the spectrum. A very recent work reports a nucleophilic Au carbene complex resonating at 18.2 ppm in 13C liquid NMR, which strongly suggests that the signal at 41 ppm may correspond to an electron-rich C carbene atom. Please note that a carbene can persist after heating since the experiment is made in the gas phase with very low covering level, thus bimolecular reactions are hampered. 1-13N was also prepared by co-adsorbed with 1-13C, and the combined 13N and 13C CP/MAS NMR spectra confirm that the peak at 41 ppm only forms after N2 release (Fig S5). Please notice the difficulties associated in characterizing nucleophilic metal carbene by NMR, since they usually feature paramagnetic metals. Figure 2B shows the corresponding time-resolved Raman spectra, and two new peaks at ~290-320 and 445 cm⁻¹ appear, which could be assigned to Au-N and Au-O vibrations of carbene 3, respectively, beside the Raman bands at 197, 396, 514 and 639 cm⁻¹ corresponding to TiO2.

Figure 3 DFT calculations of the most probable configurations of carbene 3 on Au NPs, including bond lengths (black) and net atomic charges (blue).

The Au-TiO2 (0.1 mol%) catalyzed reaction of 1, in toluene at 70 °C, gives an equimolecular mixture of dimers 4, up to 90% yield.13 Au-ZnO and Au-Al2O3 were also effective, and Au-TiO2 could be reused up to 10 times without depletion in the final yield of 4. For all Au NPs, the equation rate for the formation of 4 was r = kexp[1]c[Au], which is the expected equation rate for a classical Lewis-acid catalyzed reaction and dimerization of 1 (Fig S6).14 The Lewis base Bu3N (0.01 mol%) severely stopped the formation of 4, while a similar amount of NaI had no effect. Besides, the cross dimerization between ethyl (1) and tert-butyl diazoacetate, which possess a bulky group that impedes a good coordination on the bulk Au atoms and thus hamper metal catlysis on planar surfaces (Taft effect),14b proceeds very well (Fig S7), which supports that 1 transforms to 3B at unsaturated Au atoms. This process may run in parallel and be co-operative with the formation of 3A on bulk Au atoms, with an electronic flow from the unsaturated to the bulk (Fig S8). Notice that products in solution differ from species observed by in-situ IR, NMR and Raman techniques, since the latter mainly correspond to species remaining adsorbed on surface (Fig S9).

The reactivity of 3A and other potential electron-rich Au carbenes was then studied. Table 1 shows the results with Au-TiO2. Au+ complexes and some representative catalysts. In general, the reactivity of 1 drastically decreases in the presence of Au-TiO2. For instance, toluene, n-hexane and ethanol (entry 1) can be used as a reaction solvent since they do not react in the presence of Au-TiO2, in clear contrast with Au+ complexes15,16 and classical metal species.17-23 The electron-
Table 1 Reactivity of carbene−forming substrates in the presence of different catalysts.

<table>
<thead>
<tr>
<th>Entry</th>
<th>Reaction*</th>
<th>Catalyst / products (catalyst loading, product yield and reference)</th>
<th>Other representative catalysts</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Insertion reagents 70°C, 24 h 10-25 mol%, no reaction</td>
<td>Au−TiO2</td>
<td>Rh(CO)3C≡CPh (5 mol%)/R (95%)</td>
</tr>
<tr>
<td></td>
<td>2a</td>
<td>7a (10%), 7b (27%), 7c-f (35-24%)</td>
<td>Au complexes</td>
</tr>
<tr>
<td>3</td>
<td>8</td>
<td>9 (58-82%)</td>
<td>Au−TiO2/AgBF4</td>
</tr>
<tr>
<td>4</td>
<td>12</td>
<td>10 (50%)</td>
<td>Au−TiO2/AgBF4</td>
</tr>
</tbody>
</table>

* Reaction conditions for Au−TiO2 catalyst, Au−ZnO and Au−Al2O3 catalysts gave similar results in most cases. Blank experiments with Au−TiO2 show only marginal yields of the nucleophile carbene products 7a−d 13 and 14. See detailed reaction conditions in references. IPr: 1,3-cyclopentane 1014d,28–29 and ether 1130 after intra−or inter−rearrangements or alcohol insertion reactions, which gives oxo−carbenes with metal catalysts, including products 1532a and 16.32b When Au−TiO2 was used as a catalyst, neither 15 nor 16 were formed, but just isatin 13 and indigo dye 14. These products come from rearrangements and radical oxidation of carbene atoms, as previously observed with Cu+32c, which suggests the formation of electron−rich carbene 12.32d

In conclusion, combined experimental and theoretical evidences strongly support that Au NPs generate and stabilize electron−rich carbene on surface, after electronic transfer to the anti−bonding valence orbitals of the C=O group of RCOH:N: molecules. This carbene umpolung avoids participation in insertion reactions but rather enables the carbene to act as a nucleophile in addition reactions.33

ASSOCIATED CONTENT

Supporting Information
Experimental section, compound characterization and additional Figures S1−15 and Table S1−3. This material is available free of charge via the Internet at http://pubs.acs.org.

AUTHOR INFORMATION

Corresponding Author
E-mail: anleyva@ltq.upv.es, acorma@ltq.upv.es; phone: +34 963 77 800; fax: +34 963 77 809.

Notes
The authors declare no competing financial interests.

ACKNOWLEDGMENT

The rich nature of 3A is also seen during the cyclopropanation of alkynes (entry 2). In contrast to classical cyclopropanation reactions where electron-rich alkynes are much more reactive, 16,23,24 3A reacts worse with electron-rich 1-hexene 6a than with electron-poor styrenes 6b-f. The similar reactivity trend found with Co2+ porphyrin radical carbene catalysts. A Hamnett plot confirms this tendency (Fig S10). The higher reactivity of the Co2+ complex respect Au−TiO2 catalyst correlates with the more electron density transferred by the former (ca. 1 e−) than by the latter (0.2 e− according to DFT). Different Au−TiO2 samples with average sizes of 7, 12, 17 and 21 nm, respectively, were prepared, characterized, and tested as catalysts for the cyclopropanation of 6d (Fig S11−15), and the results clearly showed that the cyclopropanation rate increases linearly with the amount of exposed bulk Au atoms in the NP, and not with the amount of unsaturated Au atoms.

Other representative carbene-forming substrates were tested. Dimedone 827 (entry 3) is a typical reagent for Wolff rearrangements or alcohol insertion reactions, which gives cyclopentane 1014d,28–29 and ether 1130 under intra− or inter−molecular nucleophilic attack to the carbene of 8 in ethanol solvent, respectively, under metal or microwave catalyzed conditions. In clear contrast, coupled bis-dione 9 was the only product obtained with Au−TiO2 catalyst, in up to 82% yield, irrespective of the presence of light or not, and without any trace of Wolff rearrangement or alcohol insertion products. An electron−rich carbene of 8 on Au−TiO2 can be involved as intermediate of the reaction, since blank experiments showed that Au−TiO2 does not oxidize ethanol to acetaldehyde in the absence of 8 under identical reaction conditions, and a very active aerobic oxidation catalysis of alcohols such as Au−CeO2 gives a similar yield of 9 (57%).31c

Ortho-nitro phenylacetylene 12 (entry 4) generates oxo−carbenes with metal catalysts, including products 1532a and 16.32b. When Au−TiO2 was used as a catalyst, neither 15 nor 16 were formed, but just isatin 13 and indigo dye 14. These products come from rearrangements and radical oxidation of carbene atoms, as previously observed with Cu+32c, which suggests the formation of electron−rich carbene 12.32d
Financial support by MINECO through the Severo Ochoa program, RETOS program (CTQ2014–55178–R) and Ramón y Cajal Program (A.-L.P.) is acknowledged. J. O.-M. thanks ITQ for the concession of a contract. We thank to the Electron Microscopy Service of the UPV.

REFERENCES


