Title

Permalink
https://escholarship.org/uc/item/0s31z3h3

Journal
Journal of the American Chemical Society, 140(9)

ISSN
0002-7863

Authors
Oliver-Meseguer, Judit
Boronat, Mercedes
Vidal-Moya, Alejandro
et al.

Publication Date
2018-03-01

DOI
10.1021/jacs.7b13696

Peer reviewed
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*†

Instituto 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

**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 unveil the participation of at least three different Au atoms during carbene stabilization. The surface stabilized carbene shows an extraordinary stability against nucleophiles and reacts 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 toward 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 Fe³⁺ 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 antibonding 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. The latter reacts in a classical way, probably on unsaturated Au atoms present in the boundaries, corners, and vertexes of the NP. 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, O₂, HCl, and benzenes and alkynes, which coordinate on unsaturated Au atoms and then receive electron density from the NP bulk. The electron-rich intermediates are stable enough to be detected and used in productive catalytic processes.

Figure 1 shows the temperature-programmed FT−IR spectrum of a sample of commercially-available, homogeneously dispersed 3 nm Au NPs on 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 $^{13}$C CP/MAS NMR spectra of isotopically labeled EtOOC$^{13}$CHN$_2$ (1−$^{13}$C), adsorbed on Au−TiO$_2$ (surface Au atoms/1 = 1), and sealed in an ampule (see Figure S4 for full spectra). The mixture at RT shows the original signal of 1−$^{13}$C centered at 46 ppm (Figure 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−$^{13}$C 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 $^{13}$C liquid NMR, which strongly supports the electronic transfer from the Au surface to the carbene atom of 0.7 e (see Table S3 for validation). These results, together, strongly support the electronic transfer from the Au surface to the antibonding orbitals of the C=O bond to generate the electron-rich carbene 3A.

The Au−TiO$_2$ (0.1 mol %) catalyzed reaction of 1, in toluene at 70 °C, gives an equimolecular mixture of dimers 4, up to 90% yield. Au−ZnO and Au−Al$_2$O$_3$ were also effective, and Au−TiO$_2$ 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 $r_0 = k_{eq}[1][Au]$, which is the expected equation rate for a classical Lewis acid-catalyzed activation and dimerization of 1 (Figure S6). The Lewis base Bu$_3$N (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 possesses a bulky group that impedes a good coordination on the bulk Au atoms and thus hampers metal catalysis on planar surfaces (Taft effect), proceeds very well (Figure S7), which supports that 1 transforms to 3B at unsaturated Au atoms. This process may run in parallel and be cooperative with the formation of 3A on bulk Au atoms, with an electronic flow from the unsaturated to the bulk (Figure S8).

Figure 3 shows the calculated interaction energies, net atomic charges, bond lengths, and NMR shifts for the carbene C atom in structure A, B, and C, and the combined $^{15}$N and $^{13}$C CP/MAS NMR spectra for 1, 2, 4, and 4A. 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 the surface (Figure S9).

The reactivity of 3A and other potential electron-rich Au carbene was then studied. Table 1 shows the results with Au−TiO$_2$. Au$^+$ complexes, and some representative catalysts. In general, the reactivity of 1 drastically decreases in the presence of Au−TiO$_2$. 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-rich nature of 3A is also seen during the cyclopropanation of alkenes (entry 2). In contrast to classical cyclopropanation reactions where electron-rich alkenes are much more reactive,16,23,24 the higher reactivity of the Co2+ complex with intermediate of the reaction31a,b since blank experiments showed that 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 carbones of 12,32d. In conclusion, combined experimental and theoretical evidence strongly support that Au NPs generate and stabilize carbene umpolung avoids participation in insertion reactions but rather enables the carbene to act as a nucleophile in addition reactions.13

<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</td>
<td>1−2 mol%, no reaction</td>
<td>Rhy(BCDC)CO2 (2 mol%) / 6b (95%)15−19 Ag(0.5−CF3)(PyPy) (5 mol%) / 6c (55%, mixture of isomers)19−22 RhyO[η6]O2C (0.2 mol%) / 5d (88%)23−25 IPnCuCl (4 mol%) / 8d (93%)26−29</td>
</tr>
<tr>
<td>2</td>
<td>RCOCHN2 molecules</td>
<td>5 mol%; 7a (10%), 7b (27%), 7c-f (35−24%)</td>
<td>Tp³Ac2 (2 mol%) / 7a-b (84−99%)24 IPnCuCl (4 mol%) / 7b (99%)23 Co2+-porphyrin (1 mol%) / 7b (&gt;90%)22</td>
</tr>
<tr>
<td>3</td>
<td>10−25 mol%,</td>
<td>9 (58−62%)</td>
<td>Rh[η6]O2C (2 mol%) / 9 (40%)30</td>
</tr>
<tr>
<td>4</td>
<td>Toluen 100 °C, 24 h</td>
<td>10 mol%, 53%</td>
<td>Rpy[η6]O2C (2 mol%) / 10 (50%)31</td>
</tr>
</tbody>
</table>

*Reaction conditions for Au−TiO2, 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, 9, 13, and 14. See detailed reaction conditions in references. IPr: 1,3-bis(disopropylphenyl)imidazol-2-ylidene. BAr₆-tetrakis(3,5-bis(trifluoromethyl)phenyl)borate. PyrPy: 2,2′-pyridylpyrrolid ligand. Tp³H-hydrotetrakis(3,5-(2,4,6-trimethylphenyl)pyrazolyl)borate. ba: benzylideneacetone. R²= n-But, R² = H 6a; R² = Ph, R² = Me 6b; R² = 4-R-Ph (R = CF₃, Br, H, Me), R² = H 6c-f. Mass balances account for >95% in entries 1−3 and ca. 80% in entry 4.

## ASSOCIATED CONTENT

### Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/jacs.7b13696. Experimental section, compound characterization, and additional Figures S1−15 and Table S1−3 (PDF)

### AUTHOR INFORMATION

**Corresponding Authors**
*anleyva@itq.upv.es*  
*acorma@itq.upv.es*

**ORCID**
Antonio Leyva-Pérez: 0000-0003-1063-5811  
Avelino Corma: 0000-0002-2232-3527
Notes
The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

Financial support by MINECO through the Severo Ochoa program, RETOS program (CTQ2014-55178-R), and Ramón y Cajal Program (to A.L.-P.) is acknowledged. J.O.-M. thanks ITQ for the concession of a contract. We are thankful for the electron microscopy service of UPV.

■ REFERENCES


