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The chemistry of gold and its catalytic applications, with Antonio Echavarren

"In the chemistry of gold, human resources are the most expensive"

Antonio Echavarren directs a research group at the Catalan Institute of Chemistry Research (ICIQ) of Tarragona, studying the catalytic activity of gold in the synthesis of molecules, research which is of great importance to the pharmaceutical industry. He has been invited to the conference series "Chemists diffusing Chemistry" and recently shared his impressions about the current state of his discipline and explained his principal contributions to UABDivulga.

Antonio Echavarren is director of a research group at the Catalan Institute of Chemistry Research of Tarragona since 2004. In 1992 he was named professor of Organic Chemistry at University of Madrid. His research includes the invention of new reactions catalysed by transition metals, especially gold and palladium, as well as the synthesis of natural products and polyarenes related to graphene and fullerens.

-Your line of research is centered in catalyst reactions utilizing gold. What advantages does this have?

-We work in homogeneous catalysis with gold, palladium, ruthenium, and other metals. In the homogeneous catalysis, the catalyst is in the same phase as the substrate. The case of gold is that it is an inert metal, which makes it difficult to react with, and thus it came to be ignored by chemists who work in the synthesis of complex molecules. After 2003 and 2004, various groups discovered that gold actually works fantastic to activate some small molecules. We were the pioneers, along with two other groups (one in the United States and the other in Germany). It was a project that we developed in the Universidad Autónoma de Madrid and that we continued with when we moved to the Institut Català d'Investicació Química in Tarragona, converting it into the primary research area of the group. Currently there are literally hundreds of groups working on the chemistry of gold worldwide, as well as in Spain, where we find the Universidad Autónoma de Barcelona with Gregori Ujaque's group working on theoretic studies of this particular chemistry. It is one of the most current fields, one labeled a "hot topic."

-It does not seem that working with gold is a type of chemistry affordable to everyone.

-Contrary to what people think, gold is cheap! Of course it's much cheaper than platinum o rhodium. Gold is abundant, there are large gold reserves, and it is easily recyclable. Platinum, however, is much more expensive. We started working with platinum and after we switched to gold, hoping that the results would be similar. In the end, it turned out that gold was much more reactive and selective, and so we decided to stick with it.

-Was your group the first to develop catalysis with gold?

-We have been working with this metal for seven years, but all of this didn?t come from nothing. In science, it is very difficult to say who was first in something. There had been a previous project, in 1998, an isolated investigation that, in its moment, was seen as something interesting without much use, but for us it served as an inspiration. It was Teles' group from the BASF in Germany, and there were fundamentals in that project that were key to the rest of the later investigations that have demonstrated that gold is the best catalyst.

-And that's how the so-called "gold fever" in catalysis started?

-We completed our research in 2003 and we published it in 2004, and a few months later two more publications appear on the same subject. In the last few years, hundreds of publication and hundreds of groups have appeared which indicates how competitive this field is. Every day new articles come out about the chemistry of gold as a catalyst, such that if you go one week without consulting the latest publications, you're out of the game.

Our work was selected in 2003 and published in 2004, although we could have published it months before. There was a publication delay because we were chosen to be on the front page of the *Angewandte Chemie*, with an image of the Madrid mountains (possibly the first Madrid and Spanish motif to appear in that magazine), and the layout process slowed everything down. This year we have published in *Chemistry - A European Journal* and on the front page, we have used a Catalan motif showing the monument to the *castellers* on the Rambla Nova in Tarragona. It is a metaphor for the verticality of group 11, with the metals copper, silver, and gold. Stretching the simile a bit, we have introduced something as characteristic of Tarragona as the *castellers* to the front page of a prestigious magazine.

-Do these catalysts generate new molecules for the creation of C-C bonds?

-Not always. The first reaction that was published by Teles' group in the BASF was the addition of water to acetylenes, and gold is the best catalyst that exists for these hydrations, which are a formation of C-O bonds. But we have focused on the creation of C-C bonds, though gold is also able to carry out other types of additions such as hydration, about which theoretic studies are conducted in the molecular modeling group in the area of Physical Chemistry, here in the UAB.

As far as the creation of C-C bonds go, the versatility of gold doesn?t stop to surprise us. We call the bonds "molecular acrobatics" because they complete reactions produced at room temperature, in only minutes, in a clean and almost quantitative manner.

-And what is the key to these peculiarities in gold?

-Gold is tremendously electrophile, its atom is small, and it moderates reactions in a more controllable and selective way than the protons of acids, thanks to a question of its orbits and how it forms bonds. We have tried to substitute it for silver, copper, or platinum, but the reactivity isn't comparable. We would have liked to substitute it for copper now that, even though it's not as sexy, it's much cheaper than gold. Although there are more expensive alternatives.

The chemistry that we develop is more applicable in pharmaceutical laboratories and, as the resulting molecules are products of a higher added value, the cost of the reagents is not as important. The pharmaceutical industry is willing to utilize more expensive palladium and rhodium products and in whatever quantity, in order to obtain the final product. But in other more industrial processes, the cost of the catalyst can pose a problem, and for that reason, gold can be an affordable alternative.

-But this does not pose a problem, now that the catalyst is recovered at the end of the process.

-The truth is that we don't worry much about recycling gold. Every catalyst molecule has one atom of gold and the weight quantity of the catalyst to obtain one gram of final product is really insignificant. In fact, the amount of the dissolvent, silica gel, and above all the amount of time that the students and post-docs have invested is more expensive; all of that costs more money than gold. In fact, although we could recover the catalyst of gold, we prefer not to do so because very small quantities are used and also because of it?s an area that we don?t usually put much emphasis on. Gold needs ligands in order to be stabilized and these molecules that stabilize gold are more expensive than gold itself.

One of my old PhD students studied the possibility of recovering it, and now in collaboration with another ICIQ group, lead by Miquel Pericàs ?director of the institute? we have generated a catalyst around a polymer support that can be recycled and used repeatedly until, apart from the ninth use, a certain deactivation is noticeable.

-What are the medical applications of the resulting products?

-One of the more important medical applications can be found in our method of the artificial synthesis of the englerine, an antitumoral product for kidney cancer that is actually more potent than those products that have been discovered for these types of tumors. There have been five groups that have dedicated themselves to the synthesis of this molecule; of them, two have utilized the chemistry of gold, obtaining optimum results. One was our team, and the other was a Chinese group, in Shanghai, that was based in the chemistry that we develop in the ICIQ. Curiously, we finished the synthesis the same week: we finished ours on Friday, and on Sunday we received a letter from them saying that they had finished and that they would wait for us if we were behind. For this reason, we sent in the results together, in spite of the fierce competition in the field.

-And what about the heterogeneous catalysis of gold?

-In the catalyst field there are two pretty much unlimited fields: heterogeneous catalysis and homogeneous catalysis, which is what we work with. None the less, the heterogeneous catalysis is as exciting as what our group develops, and it has industrial applications to the oxidation of carbon monoxide, and to the activation of small molecules in heterogeneous phases. Gold is as fantastic in heterogeneous catalysis as it is in homogenous catalysis, and by chance, the reasons for which it is successful in both fields are different.

-What group does the use of nanoparticles of gold in catalysis pertain to?

-It is associated with heterogeneous catalysis, though there have been doubts about whether there are chemical similarities between some systems. In fact, we know that the nanoparticles are able to catalyze certain reactions but, surely, smaller nanoparticles would be able to develop a fundamentally new type of chemistry.

-Does the chemistry of gold prosper in Spain?

- There's a fair amount of activity. Apart from collaborating with other groups from the ICIQ, we have also worked circumstantially with the Huelva group (that is also centered on homogeneous catalysis using copper, silver, and gold), and with another group in Valladolid. Furthermore, there are other groups like the one at UAB directed by Gregori Ujaque, another in Valencia, in Santiago de Compostela, in Oviedo, also in Burgos... so we could say that we are living in a good time for such studies on a state level. For years, organometallic chemistry in Spain has come mainly from developments made by groups from the Universidad de Zaragoza. That's were we can find Antonio Laguna who, working on the chemistry of gold, nonetheless has focused on issues very far from catalysis. The catalytic activity of gold went unperceived by him and by many others.

-It does not seem like the first time that this facet of gold has been ignored.

-It's true. For example, in a publication in *Organometallics* a few years ago, there was a comparison made between the catalytic activities of copper, silver, and gold, which said that a part from a few interesting aspects related to bonds, not much truly important catalytic activity could be expected from the latter metal. It's a fantastic sentence! (laughs). Another case would be that of a known organic chemist who, in an arrogant attitude characteristic of scientists overly sure of themselves (though it should be exactly the contrary) referred to palladium as a "fat proton." Metalic centers are more than fat protons: they are larger and more "intelligent." Protons are dull; they don't even have electrons! And chemistry is the science of electrons.

A physicist friend of mine used to tell me that we chemists have taken the best of the atom: they've been stuck with the nucleus and we've got the electrons. In fact, more and more physicists are moving full speed towards chemistry, and one example of this is the latest Nobel prize in physics which is definitely more chemistry-related than ever. However, this case is an exception, not the rule: traditionally chemistry has been very generous with the other sciences. Nevertheless, now thanks to interdisciplinary work and inter-area collaboration, the boarders between disciplines are already disappearing.

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