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Structural Preferences in Phosphanylthiolato Platinum(II) Complexes



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Invited for this month's cover picture are the groups of Prof. Alfonso Polo and Dr. Albert Poater at the Universitat de Girona, as well as their collaborators from the Universitat Autònoma de Barcelona and the Institute of Chemical Research of Catalonia. The cover picture shows phosphanylthiolate ligand coordination on a platinum(II) center to give only the bischolate *cis*-P,P isomer when the ligand/Pt ratio is 2, whereas a trinuclear unexpected complex is achieved with a ligand/Pt ratio of 1. Here, the synthesis and structural determination is combined with density functional theory (DFT) calculations to rationalize the reaction mechanistically and through conceptual DFT. The exciting point of this study is that it opens the door to test new experimental pathways to monitor the preferred *cis* or *trans* arrangement of bidentate ligands to platinum. (Legend: H-white, C-black, P-purple, S-yellow, Cl-green, Pt-blue.) For more details, see the Full Paper on p. 51 ff.

What prompted you to investigate this topic?

These compounds have applications in some interesting reactions, and the stereochemistry of these complexes has particular importance, as different stereoisomers could present a different behavior in a given process. The main goal of the study was to unravel the mechanism of phosphanylthiol coordination to platinum(II).

How did each team member/collaborator contribute to the work?

The team was made of members belonging to three different institutions: We benefited from the expertise in crystallography of Dr. Jordi Benet-Buchholz, at the Institute of Chemical Research of Catalonia (ICIQ), whereas Dr. Julio Real from the Universitat Autònoma de Barcelona (UAB), together with Dr. Josep Duran and Dr. Alfonso Polo from the University of Girona (UdG), carried out all the experiments. Also from the UdG, Prof. Miquel Solà and Dr. Albert Poater contributed their broad computational knowledge in organometallic and inorganic chemistry.

What do you consider exciting developments in this field?

The knowledge on ligand-based stereoelectronic effects in determining the stereochemistry of complexes is pretty exciting. This awareness is of great importance to improve the selectivity of processes catalyzed by transition-metal complexes. A second feature of the field which is just as exciting is that it opens the door to test new experimental pathways to get selectively new *cis*-platinum species, known to have an active role as drugs against various types of cancer.

What is in your opinion an upcoming research theme likely to become one of the 'hot topics' in the near future?

First of all, the possibility to master the selectivity of a catalytic reaction by controlling the stereochemistry of the catalyst. Secondly, the trinuclear species mentioned here is a potential catalyst to be linked with multicatalysis. For years now, most reactions have been thought to be catalytically activated by means of just a monometal catalyst, whereas recent insights into either carbon dioxide fixation by niobium (*Chem. Eur. J.* 2014, 20, 11870–11882) or iridium-based (*Eur. J. Inorg. Chem.* 2015, 4653–4657) catalysts or functionalization of alkynes by gold catalytic moieties (*Chem. Eur. J.* 2016, 22, 1125–1132) have unraveled the necessity of having different metal catalysts co-operating.

