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BOOK REVIEW

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Book Review of Computational Mechanisms of Au and Pt Catalyzed Reactions

Computational Mechanisms of Au and Pt Catalyzed Reactions. Edited by Elena Soriano and José Marco-Contelles (Instituto de Química Orgánica General, Madrid, Spain). From the series, Topics in Current Chemistry, 302. Springer: Heidelberg, Dordrecht, London, New York. 2011. xiv + 252 pp. $309. ISBN 978-3-642-21082-2.

This book is a collection of seven chapters on the use of Au and Pt homogeneous catalysts for reactions of unsaturated precursors. The focus is on the development of mechanisms using theoretical approaches, specifically in terms of the types of reactions under consideration, with an emphasis on the various authors' own work. A positive feature of the book is the extensive discussion by knowledgeable authors of the experimental work and its connection to computational mechanistic studies. The question of how general the results are and how they can be applied to other areas of homogeneous catalysis remains to be seen.

A critical issue that I have with the book is that it deals with computational studies of complex reactions, and yet there is not a chapter on the quality of the methods nor are there any real details of the calculations. The authors lightly touch on computational methods and issues, but essentially the book is devoted to density functional theory (DFT) studies of the mechanisms of these catalytic reactions at a modest level. There is a lack of discussion on the quality of the DFT exchange-correlation functionals, basis sets, and issues dealing with relativistic effects. Most of the calculations were done with the B3LYP functional, the polarized double-ζ 6-31G* basis set for the lighter elements, and an effective core potential and basis set (LANL2DZ) for the heavy element transition metals. These are typically the easy choices to make when using the defaults of the Gaussian-XX program. In some cases, self-consistent reaction-field approaches are used to estimate solvent effects. There is no real discussion of computational issues in terms of the size of the system, the quality of DFT for such treatments, and the role of the solvent environment. It would have been helpful to have a chapter focusing on what methods are currently in use and their deficiencies, which are many in terms of accurate predictions of potential-energy surfaces for transition-metal reactions in solution. For example, there is no discussion of the need for polarization functions for transition metals or the role of the $n-1$ core electrons, no coverage of full relativistic treatments and the potential for spin orbit effects, and no mention of the accuracy of the functional and why B3LYP might be acceptable for potential energy surfaces with third-row transition metals. Issues with DFT in terms of nonbonded interactions and how methods such as B3LYP begin to degrade as the size of the system increases are also not covered. It would have been helpful to have some focus on the method that is being used rather than a mere litany of results. Furthermore, I have issues with the use of the term a "DFT calculation" here and elsewhere in the literature. Such a term has no meaning without the exchange-correlation functional and the basis set because the accuracy of a "DFT calculation" cannot be determined without such information. DFT is not a panacea for all computations, and a discussion of this is critically needed in this book.

There are a number of other problems as well. There are energy values in figures without units, for example, and the referencing in the book was not always helpful: for example, only the final chapter had all of the titles for the references with initial and final page numbers.

In summary, this book is for people interested in the mechanisms of homogeneous catalytic reactions of gold and platinum organometallic catalysts. It has a strong computational perspective, but the reliability of the results is not put into any context and a nonexpert in computational chemistry could be easily led astray in terms of the reliability of the predicted mechanisms.

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