MEMÓRIAS
DA
ACADEMIA DAS CIÊNCIAS
DE
LISBOA

CLASSE DE CIÊNCIAS

TOMO XLVIII

Celebratory Symposium

A – Catalysis and the Periodic Table

Mechanistic Studies on Rhodium and Iridium Homogeneous Catalysts

Luis A. Oro

ACADEMIA DAS CIÊNCIAS
DE LISBOA

LISBOA • 2022

Mechanistic Studies on Rhodium and Iridium Homogeneous Catalysts

Luis A. Oro[6]

Luis A. Oro obtained his Ph. D. from the University of Zaragoza in 1970. He was postdoctoral fellow at Cambridge University from 1972 to 1973. He has served on the faculties of the Universities of Zaragoza, Madrid Complutense, and Santander. He became full professor of Inorganic Chemistry in Zaragoza in 1982 and served as head and founder of the Homogeneous Catalysis Institute (2004-2013).

His main research interests are in organometallic chemistry and homogeneous catalysis of platinum group metals. He has co-authored well over 650 scientific papers and several books. His research has been recognized with numerous awards including Humboldt Forschungspreise, Sacconi Medal, National Research Prize for Chemistry, Lourenço-Madinaveitia Award, Lord Lewis Prize from the Royal Society of Chemistry and Honoris Causa Doctorates from the Universities of Rennes, Rovira i Virgili, San Jorge and Madrid Complutense.

He has been President of the European Chemical Society (EuChemS) (2008-11). He has also served in high-level positions in the Spanish public administration with responsibilities for science, as well as being vice-president of the European Science Foundation.

The catalysis field began in the nineteenth century with the work on heterogeneous platinum group metals. This background influences the first homogeneous platinum metal catalysts, where rhodium and iridium have been key elements on the understanding of homogeneous catalysts.[1-2]

Precise determination of the mechanism of a catalytic process is essential in order to control the selectivity outcome. In particular, we have studied the mechanism and activity of a set of rhodium and iridium complexes with N-heterocyclic carbene (NHC) ligands in some specific homogeneous reactions. The high steric hindrance and powerful electron-donor capacity of the bulky NHC´s used, along with ancillary N-donor ligands, seems to be determinant to get selective transformations and to facilitate useful information about the reaction mechanisms.[3]

[6] Departamento de Química Inorgánica, Instituto de Síntesis Química y Catálisis Homogénea, Universidad de Zaragoza-CSIC, 50010-Zaragoza, España

H/D exchange reactions are valuable transformations for the preparation of isotopically labelled compounds that have found practical applications on mechanistic investigations, spectroscopic analysis, or the monitoring of drug metabolism.[4] In particular, we have studied the catalytic activity of a set of rhodium and iridium complexes with N-heterocyclic carbene (NHC) ligands as catalysts in deuterium labeling of α–olefins, choosing styrene as model for the evaluation of catalytic activity and selectivity.[5] The [RhClH(κ^2-O,N-C_9H_6NO)(IPr)] catalyst, bearing a 8-quinolinolate ligand and an electron-donor and bulky N-heterocyclic carbene as 1,3-bis-(2,6-diisopropylphenyl)imidazol-2-carbene (IPr), showed very high selectivity for the β-vinylic positions (Figure 1).

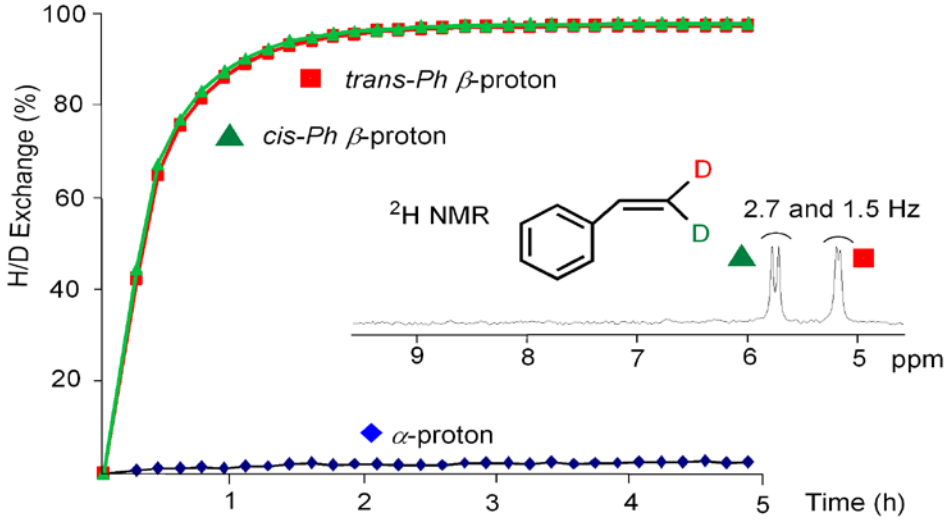

Figure 1.
H/D exchange in styrene catalyzed by [RhClH(κ^2-O,N-C_9H_6NO)(IPr)] at 25.ºC.

The bulky 1,3-bis-(2,6-diisopropylphenyl)imidazol-2-carbene (IPr) ligand is responsible of the controlled steric induction for selective H/D exchange because the required rotation around the C1-C2 axis of the alkyl ligand is required to exchange the proton and deuterium positions as shown in Figure 2. The first step could be deuteration of the hydride ligand in [RhClH(κ^2-O,N-C_9H_6NO)(IPr)] catalyst by CD_3OD to produce **a**. NMR observations suggest that only the deuterium atom from the O-D group are responsible for the exchange. The disposition of the chelating quinolinate ligand directs the coordination of the alkene to the equatorial position. Two orientations (**b** and **c**) are possible for olefin coordination and the Markovnikov insertion is kinetically favored, and according with DFT calculations the liner alkyl species **d** is more stable than the branched alkyl derivative **f**, but the steric hindrance imposed by the bis-isopropylphenyl substituents of IPr restricts the C1-C2 rotation due to repulsion with the phenyl group of the alkyl ligand. Subsequent *β*–elimination reforms the starting olefin but with a deuterium atom at the *β*–position in either a *cis* o *trans* disposition, thereby explaining the similar rate observed for H/D exchange for both *cis* and *trans* protons.

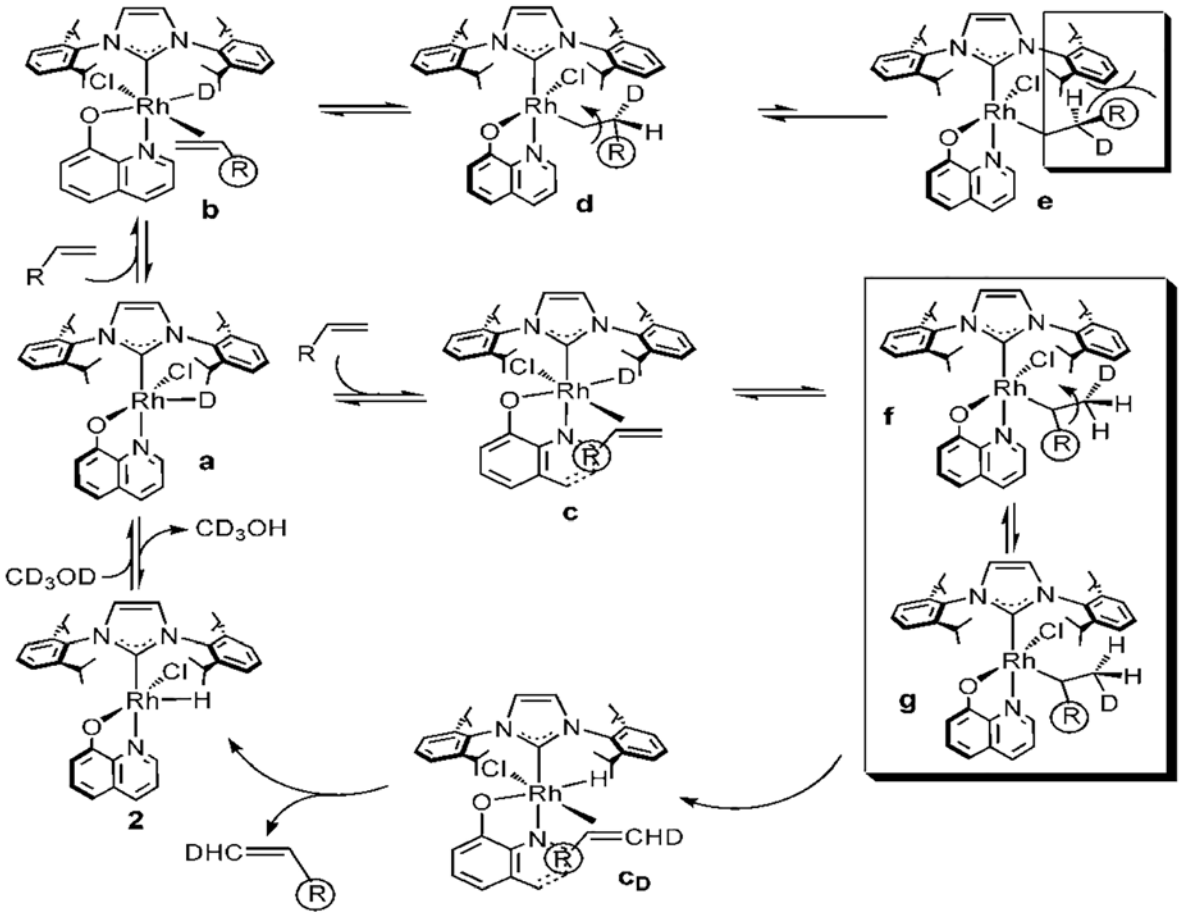

Figure 2.
IPr-controlled steric induction for selective H/D exchange.

Taking into account that tricyclohexylphosphine ligand is also a bulky and basic ligand the related rhodium-quinolinate-hydride complex of formula [RhClH(κ^2-O,N-C_9H_6NO)(PCy_3)(CH_3CN)] was studied. It catalyzes the H/D exchange of styrene but with lower activity because their substituents are disposed in a conical fashion pointing out of the equatorial plane of the coordination sphere, whilst IPr adopts an umbrella type disposition with the isopropylphenyl substituents pointing towards the equatorial plane. Thus. the different selectivity is due to the different steric hindrance exerted by the two ligands. NHC ligand has a higher electron releasing capacity than PCy_3 (Figure 3).

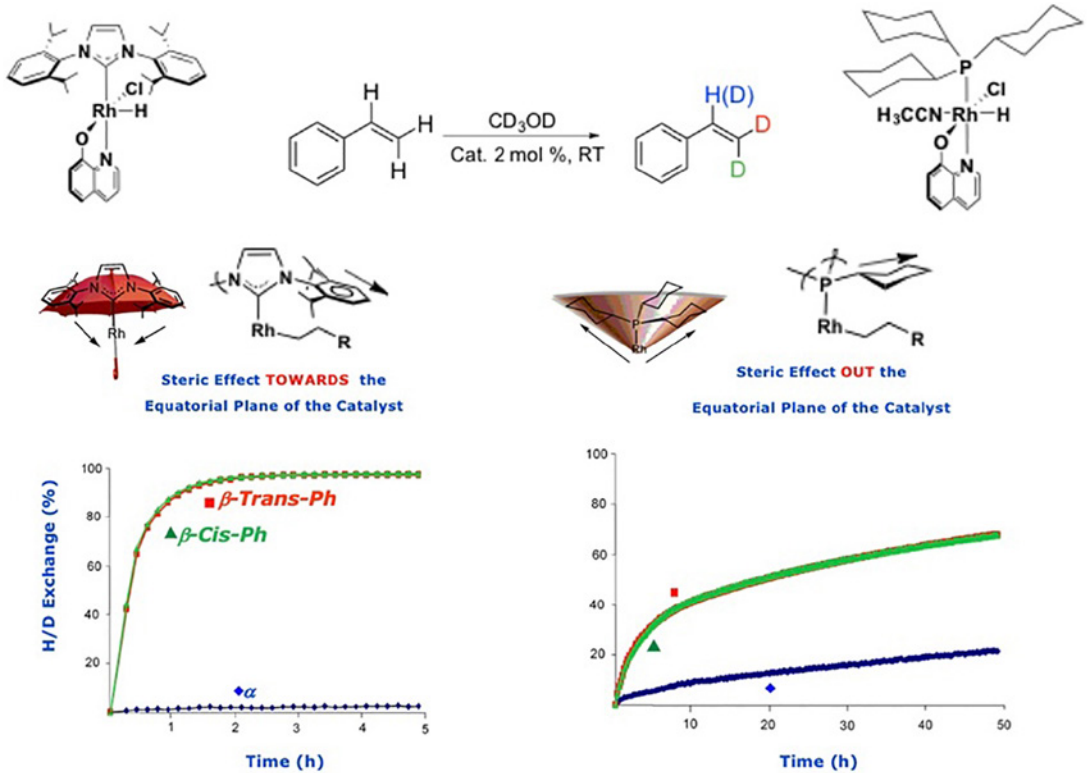

Figure 3.
Comparative H/D exchange in styrene at 25 .ºC.

These studies[5] contribute to the understanding of the catalytic mechanism of H/D exchange reactions, allowing for the design of better performing catalysts.

Concerning iridium catalysts, we have been particularly interested on hydrosilylation and silylation reactions.[6] In this line, hoping to shed some light on the effect of heterotopic ligands of hemilabile character in the generation of latent coordination sites, we envisaged a 14-electron bis-NHC iridium(III) fragment stabilised by two hemilabile side arms, which would allow ready accessible coordination sites and concomitant protection of the active catalyst for selective catalyzed hydrosilylation of terminal alkynes to vinylsilanes (Figure 4).

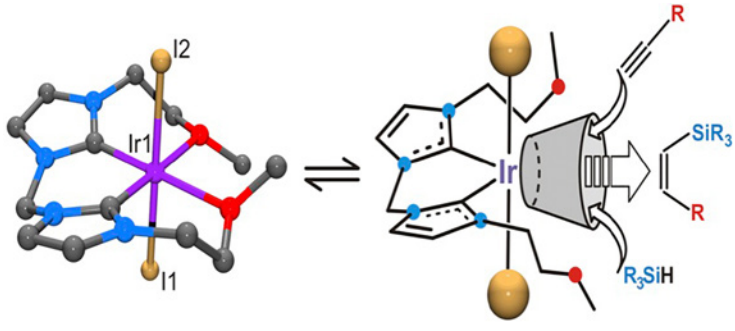

Figure 4.
The cation $[Ir(I)_2\{\kappa\text{-}C,C,O,O\text{-bis(NHC)}\}]^+$

Interestingly, the $[Ir(I)_2\{\kappa\text{-C,C,O,O-bis(NHC)}\}]BF_4$ (bis-NHC = methylenebis(N-2-methoxyethyl) imidazole-2-ylidene)) complex shows to be very effective for the hydrosilylation of a range of terminal alkynes, employing different silanes. The reactions proceed with excellent yields and selectivities to their corresponding *β*–(Z)-vinylsilanes, but only when acetone was used as solvent. The specificity of acetone for the success of the hydrosilylation reaction is based on Si-O interactions between the silane and the acetone solvent, favouring a metal-ligand bifunctional outer-sphere mechanism.[7]

The proposed stepwise outer-sphere mechanism is based on the initial heterolytic splitting of the silane molecule by the metal centre in such way that the acetone molecule facilitate the transfer of the R_3Si^+ moiety from the silane to the terminal alkyne by means of an oxocarbenium ion. In the next step the resulting oxocarbenium ion ($[R_3Si–O(CH_3)_2]^+$) reacts with the corresponding alkyne to give the silylation product ($[R_3Si–CH=C–R]^+$), followed by the selective nucleophilic attack of the hydrido ligand over $[R_3Si–CH=C–R]^+$. The excellent *β*–(*Z*)-selectivity of the reaction could be explained as a consequence of the higher steric interaction resulting from the geometry of the approach that leads to *β*–(*E*)-vinylsilanes (Figure 5).[7a]

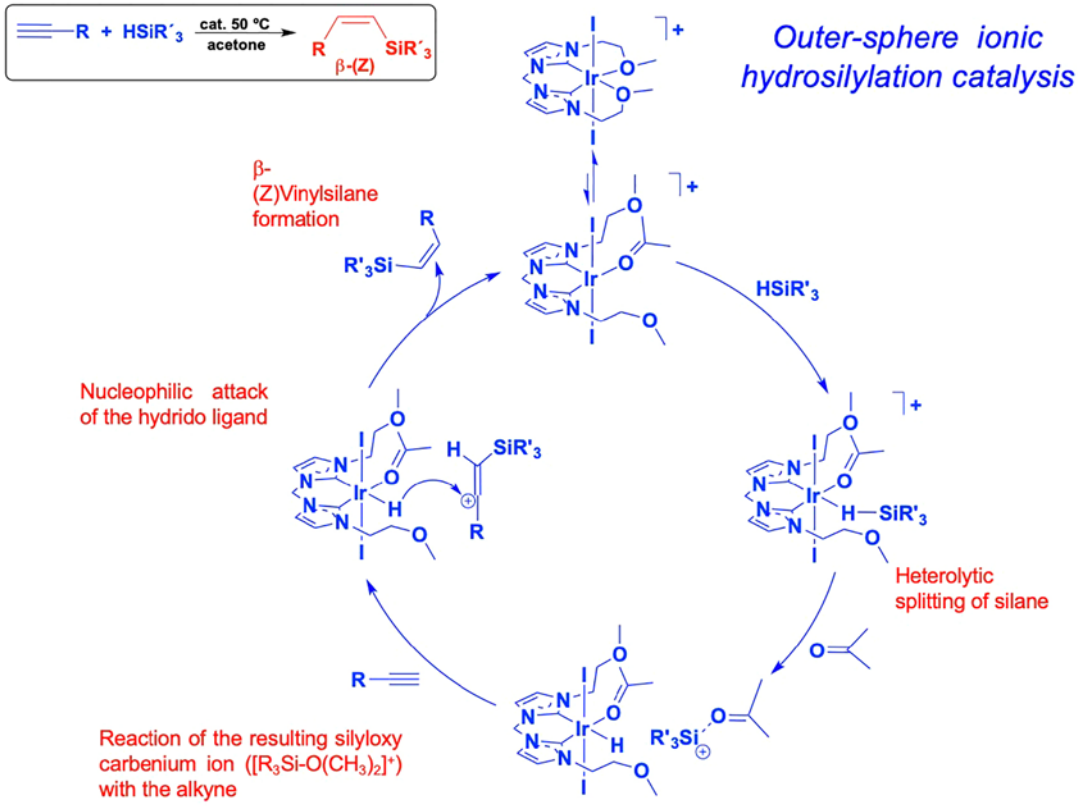

Figure 5.
Outer-sphere ionic hydrosilylation catalysis

The mechanism proposal represents the first example of an outer-sphere mechanism for the hydrosilylation of terminal alkynes, in which the acetone acts as a silane shuttle transferring the silyl moiety from the silane to the alkyne. It is noteworthy to mention that while the presence of ionic and

concerted outer-sphere mechanisms is well established in hydrogenation catalysis,[8] the development of new hydrosilylation catalysts that operate by ionic or concerted outer-sphere mechanism should be expected.[7b]

REFERENCES

1 *Rhodium Catalysis*, in Topics on Organometal Chemistry, Vol. 61, ed. C. Claver, Springer Verlag (2018).

2 (*a*) *Iridium Catalysis,* in Topics on Organometal Chemistry, Vol. 34, ed. P. G. Andersson, Springer-Verlag (2011); (*b*) *Iridium Complexes in Organic Synthesis*, ed. L. A. Oro and C. Claver, Wiley-VCH Verlag GmbH & Co, Weinheim (2008).

3 (*a*) E. Peris. Smart N-Heterocyclic Carbene Ligands in Catalysis. *Chem. Rev.* 2018, **118**, 9988-10031; (*b*) M. Iglesias and L.A. Oro. A Leap Forward in Iridium-NHC Catalysis: New Horizons and Mechanistic Insights. *Chem. Soc. Rev.*, 2018, 47, 2772-2808.

4 (*a*) A. Di Giuseppe, R. Castarlenas and L. A. Oro. Mechanistic Considerations on Catalytic H/D Exchange Mediated by Organometallic Transition Metal Complexes. *C.R. Chimie*, 2015, **18**, 713-741.

5 (*a*) A. Di Giuseppe, R. Castarlenas, J. J. Pérez-Torrente, F. J. Lahoz and L. A. Oro. Rhodium(III) Hydride Complexes Bearing NHC Ligands as Catalysts in the Selective H/D Exchange Reaction of α-Olefins: A Structure-Activity Study. *Chem. Eur. J.*, 2014, **20**, 8391-8403; (*b*) A. Di Giuseppe, R. Castarlenas, J. J. Pérez-Torrente, F. J. Lahoz, V. Polo, and L. A. Oro. Mild and Selective H/D Exchange at the β-Position of Aromatic α-Olefins by N-Heterocyclic Carbene-Hydride-Rhodium Catalysts. *Angew. Chem. Int. Ed*., 2011, **50**, 3938-3942.

6 (*a*) M. Iglesias, F. J. Fernández-Alvarez and L. A. Oro. Non-classical hydrosilane mediated reductions promoted by transition metal complexes. *Coord. Chem. Rev.*, 2019, **386**, 240-266; (*b*) L. Rubio-Pérez, M. Iglesias, J. Munárriz, V. Polo, V. Passarelli, J. J. Pérez-Torrente and L. A. Oro. A well-defined NHC–Ir(III) catalyst for the silylation of aromatic C–H bonds: substrate survey and mechanistic insights. *Chem. Sci.*, 2017, **8**, 4811-4822.

7 (*a*) M. Iglesias, P. J. Sanz Miguel, V. Polo, F. J. Fernández-Alvarez, J. J. Pérez-Torrente and L. A. Oro. An Alternative Mechanistic Paradigm for the sym-Z Hydrosilylation of Terminal Alkynes: The Role of Acetone as a Silane Shuttle. *Chem. Eur. J.*, 2013, **19**, 17559-17566; (*b*) M. Iglesias, F. J. Fernández-Alvarez and L. A. Oro. Outer-Sphere Ionic Hydrosilylation Catalysis. *ChemCatChem*, 2014, **6**, 2486-2489.

8 O. Eisenstein and R.H. Crabtree. Outer sphere hydrogenation catalysis. *New J. Chem*., 2013, 37, 21-27