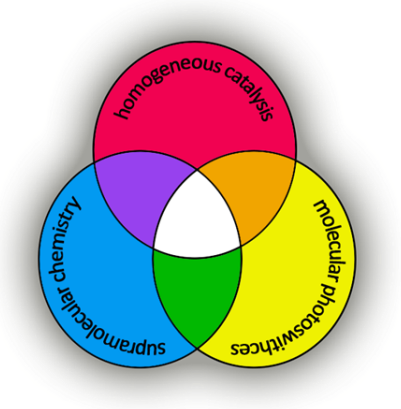
Dr Zoraida Freixa

Ikerbasque Research Professor
Universidad del País Vasco (UPV-EHU)
ORCID: 0000-0002-2044-2725
Researcher ID: K-4294-2014



Education.

2000 **PhD (Catalysis).** Universitat Autònoma de Barcelona, Spain.
Title: New ligands for rhodium catalyzed asymmetric hydroformylation.
Supervisor: Prof. Dr. J.C. Bayón (*cum laude*).

1997 **Master (Catalysis)**, Universitat Autònoma de Barcelona, Spain.
Main subject: Synthesis and catalytic applications of dithiolates: rhodium catalyzed hydroformylation. Supervisor Prof. Dr. J.C. Bayón.

1994 **Bachelor of Science (Chemistry – Inorganic Chemistry).**
Universitat Autònoma de Barcelona, Spain.

Professional experience.

11.2010 / current **Ikerbasque Research Professor**
Universidad del País Vasco (UPV-EHU), San Sebastián

04.2010 / 09.2010 **Lecturer**
Universitat de Barcelona (UB)

03.2004 / 11.2009 **Group manager & "Ramón y Cajal" fellow**
Institut Català d'Investigació Quimica (ICIQ), Tarragona, Spain.

01.2001 / 12.2003 **Post-doctoral researcher**
Universiteit van Amsterdam (UvA), Amsterdam, The Netherlands.

04.2000 / 12.2000 **Docent**
Escola Superior de Tecnología de Castelo Branco, Portugal.

10.1999 / 11.2000 **Researcher and Docent**
Universidade de Coimbra (UdC), Coimbra, Portugal.

09.1994 / 09.1999 **Lecturer Y2, Predoctoral fellow, Lecturer Y3**
Universitat Autònoma de Barcelona (UAB), Bellaterra, Spain.

Current research line.

The long-term goal of the research line that I pursue since I started my independent career is the development of **light-tunable organometallic compounds**, for a wide range of applications, being catalysis the main focuss. After some initial explorative years, we have a set of synthetic tools to readily incorporate azobenzene derivatives in a wide range of compounds, and we are expanding them to the synthesis of DTE-based photoswitches. Along these years we have synthesized more than 60 new azobenzene-appended organometallic complexes, and studied them for several applications: iridium(III) triscyclometalated for **phosphors** in OLEDs, ruthenium(II) and iridium(III) half-sandwich complexes to be used as **photoswitchable catalysts**, are the first examples we worked on. In this area, our current challenge is the development of a new generation of compounds displaying **photo-induced amplification of the chirality**.

Additionally, in recent years we start working in the development of organometallic compounds as highly sensitive **luminescent sensors** for cations.

Expanding the range of compounds, and applications together with gaining a better **understanding and control of their interaction with light** is our daily task that should bring us through a path of amazing discoveries.

phone: +34 635638132
e-mail: Zoraida_freixa@ehu.eus
www. freixagroup.com

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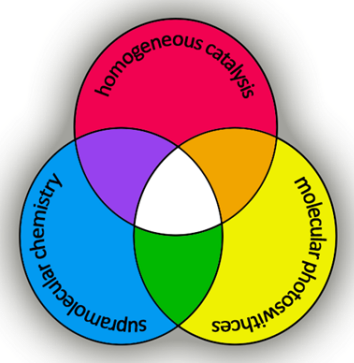

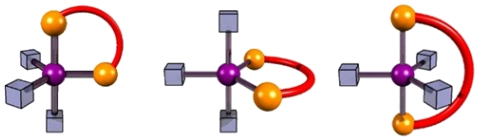

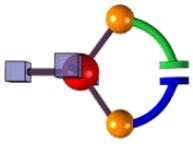

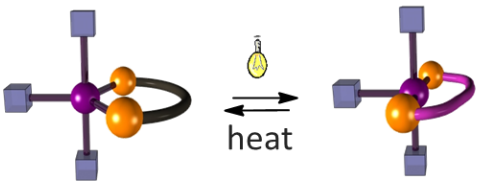

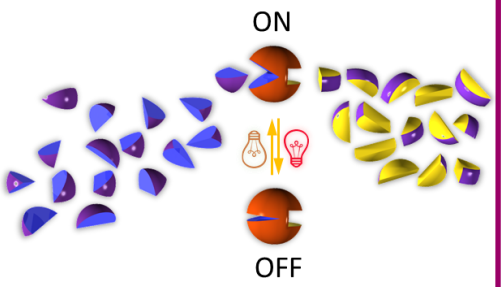

phone: +34 635638132
e-mail: Zoraida_freixa@ehu.eus
www. freixagroup.com

Research background.

After obtaining the Bachelor in Chemistry from the Universitat Autónoma de Barcelona (UAB) in 1994 I enrolled as PhD student at the group of Prof. J.C. Bayón. Within that period I spent 18 months at the University of Coimbra as a contracted researcher, obtaining the PhD in Chemistry by the UAB in 2000. Afterward, I moved to the University of Amsterdam where I spent 3 years as a postdoctoral researcher in the group of Prof. van Leeuwen (2001–2003). In 2004 I returned to Spain, joining the Institute of Chemical Research of Catalonia (ICIQ) as Ramón y Cajal researcher and Group Manager of Prof. van Leeuwen's group. During that period (2004–2009) I co-leaded all the research projects of the group (both academic and industrial). Our main focus was on Supramolecular Catalysis. After a short period as a Lecturer at the University of Barcelona, in 2010, I accepted the position I am currently holding as Ikerbasque Research Professor at the University of the Basque Country (UPV-EHU).

Since I started my independent career, and always looking for new challenges in research, I drove my interest toward developing photo-switchable organometallic complexes. The use of that stimuli-responsive entities in catalysis to create photo-switchable catalysts is one of the most promising possibilities, but those unique compounds can also encounter many other fascinating applications. In my group we explore several of them, such as their use as phosphors for photo-switchable OLEDs, as luminescent, sensors, as photo-sensitizers for solar cells, or as (photo-activatable)metalodrugs.
The most relevant achievements in the different areas I explored along my career are:

Homogeneous catalysis: Together with Prof. van Leeuwen, we developed a unique ligand, SPANphos, which has been considered the first truly trans-spanning diphosphine ligand. Some of its organometallic complexes presented unique properties, as for instance extraordinary activity in methanol carbonylation processes (ACIE 2003, ACIE 2005, Dalton 2006, OM 2005).
More rencently, I have also unravelled the mechanism operating in metal-catalyzed processes for the hydrogen generation by hydrolysis of amineborane adducts (ACS Cat. 2017, Organometallics 2020) and imine hydrosilylation (Catal. Sci & Tech 2018), using half-sandwich ruthenium and iridium complexes. In collaboration with Dr. Huertos and Dr.Matxain, we identified a unique example of an organometallic catalyst working through hydrogen tunneling (Angew. Chem. Int. Ed., 2022).

Supramolecuar catalysis: Together with Prof. van Leeuwen we developed bifunctional ligands which permitted us to create large libraries of supramolecularly-build ligands, very effective in both non-enantioselective and asymmetric catalytic processes (ACIE 2007, JACS 2011). We also established, for the first time, the possibility to use ionic interactions as driving force for the construction of supramolecular catalysts (Chem. Eur. J. 2007, patent WO 2008031889 for BASF).

Photoswitchable catalysis: Recently, I developed the first example of a photo-tunable catalyst for the generation of hydrogen by hydrolysis of amino-borane adducts. (Eur.JIC 2010, Dalton 2017, Catal. Sci. Technol. 2020).

Luminescent sensors: In the last years, and as part of our participation in the NEXT-collaboration, we are focusing on the development of luminescent sensor for cations (Nature 2020, Phys. Chem. Chem. Phys. 2021).

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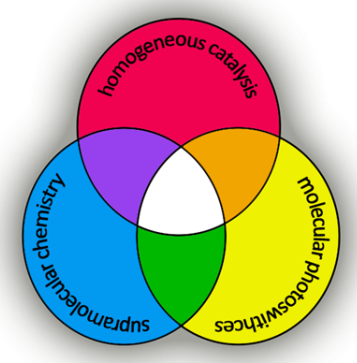

phone: +34 635638132
e-mail: Zoraida_freixa@ehu.eus
www. freixagroup.com

Funded Research Projects (2011-2022).

2022 / 2025 **Basque-Government, Grupos Consolidados (IT 1553-22).** PI F.P. Cossío. Total funding 346500 €.

2021 / 2027 **ERC-synergy grant (H2020-ERC-SyG20/01)** PI: Prof. F.P. Cossío, Prof. J.J. Gómez-Cadenas and Prof. R. Guenette. Total funding 9 M€ .

2020 / 2022 **MINECO (PID2019-111281GB-I00).** PI: Z. Freixa. Total funding 84700€ .

2019 / 2021 **Basque-Government, Grupos Consolidados (IT1180-19).** PI Z. Freixa. Total funding 87536 €.

2017 / 2019 **UPV-EHU (GIU16/25).** PI MA Garralda. Total funding 35000 €.

2016 / 2018 **MINECO (CTQ2015-65268-C2-1P).** Coordinated project. PI: Z. Freixa (coordinator), M.A. Garralda, M.A. Huertos. Total funding 98000€ .

2014 / 2016 **UPV-EHU Research group (GIU13/06).** PI MA Garralda. Total funding 35000 €.

2014 / 2015 **ICIQ/ IKERBASQUE** collaboration agreement. PIs Z. Freixa, PWNM van Leeuwen. Total funding 18000 €.

2014 / 2015 **Basque-Government, Network Program "Comunidad de Trabajo de los Pirineos (CTP13-R03).** Consortium: Prof. K. Philippot (Toulouse), Prof. N. McClenahan (Bordeaux), Dr. X. Sala (UAB), Dr. Z. Freixa (UPV-EHU). Local funding 6900 €.

2013 **Basque Government Saiotek Program, (S-PE13UN020).** PI Z. Freixa. Total funding 5092 €.

2012 /2013 **Basque Government Saiotek Program, (S-PE12UN044).** PI Z. Freixa. Total funding 18600€ .

2011 /2012 **Basque Government Saiotek Program, (SPE11UN029).**PI Z. Freixa. Total funding 14114 €.

2011 / 2013 **MINECO (CTQ2011-23333).** PI Z. Freixa. Total funding 30000 €

Research supervision.(2011-2022)

PHD THESIS:

Ongoing: A.I. Aranburu, A. Centeno, U. Prieto., A. Pazos.

2022 F.B. Urquiola "*Chiral-at-metal Iridium(III) Complexes Containing Dithienylethene-Based Photoswitchable Ligands*"

2017 J. Pérez Miqueo "*Complejos ciclometalados de Ir(III) derivados de azobenceno. Estudio de aplicaciones* "

2016 A. Telleria "*Photo-switchable organometallic compounds. Screening of applications*"

2010 D.M. Rivillo "*Metal-templated self-assembled diphosphines* "

2010 M.D. Segarra "*Switchable and tunable ligands for homogeneous catalysis* "

MASTER THESIS:

2020 P. Agueda "Towards supramolecular flavin-based gold complexes for photoredox catalysis"

2019 A. Pazos "Catalizadores híbridos MOF-organometálicos"

2017 F. Borja Urquiola "Catalizadores de iridio para generación de hidrógeno"

2014 M. Muñoz "Deshidrogenación de aductos amino-borano con catalizadores de rutenio"

2012 A. Telleria "*Complejos organometálicos de rutenio(II) e iridio(III) que incorporan la unidad azobenceno como fotosensibilizador*"

2012 A. Ibarnavarro "*Preparación de materiales híbridos grafeno-complejos de iridio*"

FINAL DEGREE PROJECTS: 2020 (E. Fraile) 2019 (E. Galarraga, N. Dadie); 2018 (M. Sanz, P. Corral); 2017 (B. Patino, G. Galarraga); 2016 (M. Vázquez; F.B. Urquiola; O. Hernández).

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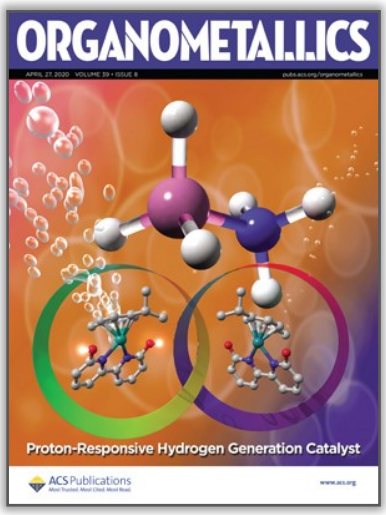

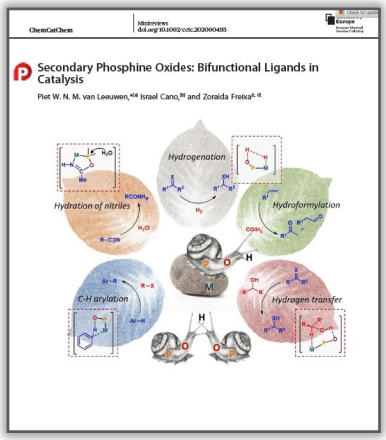

Publications.

RESEARCH PAPERS:

"Hydrogen Tunneling in Catalytic Hydrolysis and Alcoholysis of Silanes"
Angew. Chem. Int. Ed., **2022**, *e202201558*
Almenara N., Garralda M.A., López X., Matxain J.M., Freixa Z, Huertos M.A.

"Measurement of the Xe-136 two-neutrino double-beta-decay half-life via direct background subtraction in NEXT"
Phys. Rev. C, **2022**, *105, 055501*
NEXT Collaboration

"Phosphonium-based ionic liquids: Economic and efficient catalysts for the solvent-free cycloaddition of CO_2 to epoxidized soybean vegetable oil to obtain potential bio-based polymers precursors"
Molecular Catalysis, 2021, 515, 11889
Centeno-Pedrazo A., Perez-Arce J., Prieto-Fernández S., Freixa Z., García-Suárez E.J.

"Sensitivity of a tonne-scale NEXT detector for neutrinoless double-beta decay searches"
J. High Energy Phys. **2021**, *8*, 164
NEXT Collaboration

"Boosting background suppression in the NEXT experiment through Richardson-Lucy deconvolution"
J. High Energy Phys. **2021**, *7*, 146
NEXT Collaboration

"Bicolour fluorescent molecular sensors for cations: design and experimental validation"
Phys. Chem. Chem. Phys., **2021**, *23*, 15440-15457
Freixa Z, Rivilla I., Monrabal F., Gómez-Cadenas J.J., Cossío F.P.

"Efficient Homogeneous Hydridoirida-beta-Diketone-Catalyzed Methanolysis of Ammonia-Borane for Hydrogen Release in Air. Mechanistic Insights"
Eur. J. Inorg. Chem., **2021**, *31*, 3131-3138.
Bustos I., Freixa Z., Pazos A., Mendicute-Fierrro C., Garralda M.A.

"Steric Effects in the Catalytic Tandem Isomerization-Hydrosilylation Reaction"
CHEMCATCHEM, **2021**, *13*, 1403-1409.
Prieto U. Azpeitia S., san Sebastián E., Freixa Z., Garralda M.A., Huetos M.A.

"Proton-responsive Ruthenium(II) Catalysts for the Solvolysis of Ammonia-Borane "
Organometallics, **2020**, 39, 1238–1248.
San Nacianceno V., Garralda M.A., Matxain J.M., Freixa Z.

"Fluorescent bicolour sensor for low-background neutrinoless double beta decay experiments"
Nature, **2020**, 583, 48–54.
Rivilla I., Aparicio B., Bueno J. M. Casanova D., Tonnelé C., Freixa Z., Herrero P., Rogero C., Miranda J.I., Martínez-Ojeda R.M., Monrabal F., Olave B., Schäfer T., Artal P., Nygren D., Cossío F.P., Gómez-Cadenas, J.J.

"Photoswitchable catalysis using organometallic complexes"
Catal. Sci. Technol, **2020**, 10, 3122–3139.
Freixa Z.

"Secondary Phosphine Oxides: Bifunctional Ligands in Catalysis "
ChemCatChem, **2020**, 12, 3982–3994.
Van Leeuwen P.W.N.M., Cano I., Freixa Z.

"Revisiting the iridacycle-catalyzed hydrosilylation of enolizable imines"
Catal. Sci. Tech., **2018**, 23, 6316–6329
Pérez-Miqueo J., San Nacianceno V., Urquiola F.B., Freixa Z.

Ikerbasque Research Professor
Universidad del País Vasco (UPV-EHU)
ORCID: 0000-0002-2044-2725
Researcher ID: K-4294-2014

"Light-driven water oxidation using hybrid photosensitizer-decorated Co_3O_4 nanoparticles"
Materials Today Energy, **2018**, *9*, 506–515.
de Tovar J., Romero N., Denisov S.A., Bofill R., Gimbert-Surinach C., Ciuculescu-Pradines D., Drouet S., Llobet A., Lecante P., Colliere V., Freixa Z., McClenaghan N,. Amiens C., Garcia-Anton J,. Philippot K., Sala X.

"Experimental Evidence Supporting Related Mechanisms for Ru(II)-Catalyzed dehydrocoupling and Hydrolysis of Amine-Boranes"
ACS Catalysis, **2017**, *7(12)*, 8394–8405.
Telleria A. , Vicent C. , San Nacianceno V. , Garralda M.A. , Freixa Z.

"Azobenzene-based ruthenium(II) catalysts for light-controlled hydrogen generation"
Dalton Trans. **2017**, *46, 3569–3578.*
Telleria A., van Leeuwen, P.W.N.M., Freixa Z.

"Photoswitchable azobenzene-appended iridium(III) complexes"
Dalton Trans. **2016**, 13726–13741.
Pérez-Miqueo J., Altube A., García-Lecina E., Tron A., McClenaghan N.D., Freixa Z.

"Synthesis and characterization of diethylphosphonate and carboxylate-appended iridium complexes for application on dye-sensitized solar cells"
Chemistry Select. **2016**, 1, 2842–2848.
Telleria A., Kohlrausch E.C., Duarte RdC., Rodembusch F.S., Dupont J., Freixa Z., Santos M.J.L.

"Azobenzene-Appended Bis-Cyclometalated Iridium(III) Bipyridyl Complexes"
Organometallics, **2015**, *34*, 5513–5529.
Telleria A., Peŕez-Miqueo J., Altube A., García-Lecina E., deCoźar A., Freixa Z.

"Highly active, chemo- and enantioselective Pt-SPO catalytic systems for the synthesis of aromatic carboxamides"
Cat. Sci. Tech., **2015**, *5*, 3822–3828.
Gulyás H., Rivilla I., Curreli S., Freixa Z., van Leeuwen P.W.N.M.

"Palladium catalyzed oxidative carbonylation of alcohols: effects of diphosphine ligands"
Catal. Sci. Tech., **2015**, *5*, 2856–2864.
Amadio E., Freixa Z., van Leeuwen P.W.N.M., Toniolo L.

"Insights into the use of [Ru(p-Cym)(bipy)Cl]Cl as precatalyst for solvolytic dehydrogenation of ammonia-borane"
Inorg. Chim. Acta, **2015**, *431*, 184–189.
Freixa Z., Garralda M.A.

"A readily accessible ruthenium catalyst for the solvolytic dehydrogenation of amine–borane adducts"
Dalton Trans., **2014**, *43*, 11404–11409.
Muñoz-Olasagasti M., Telleria A., Pérez-Miqueo J,. Garralda M.A., Freixa Z.

"Strong π-Acceptor Ligands in Rhodium Catalyzed Hydroformylation of Ethene and 1-Octene: Operando Catalysis"
ACS Catalysis, **2013**, *3*, 128–137.
Diebolt O., Tricas H, Freixa Z., van Leeuwen P.W.N.M.

"N-Tetradentate SPANamine Derivatives and Their MnII 1 - Complexes as Catalysts for Epoxidation of Alkenes"
Eur. J. Inorg. Chem., **2013**, *7*, 1213–1224
Rich R., Rodríguez M., Romero I., Fontrodona X., van Leeuwen P.W.N.M., Freixa Z., Sala X., Poater A., Solà M.

Ikerbasque Research Professor
Universidad del País Vasco (UPV-EHU)
ORCID: 0000-0002-2044-2725
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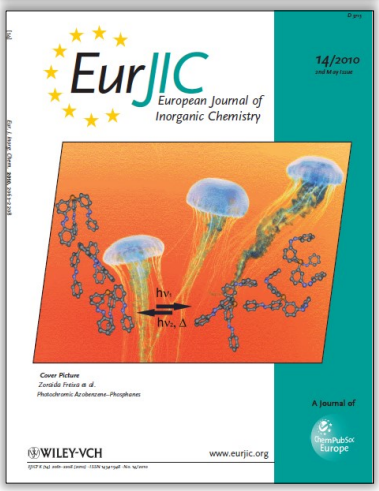

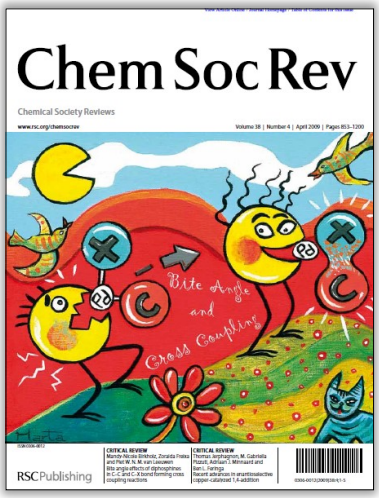

phone: +34 635638132
e-mail: Zoraida_freixa@ehu.eus
www. freixagroup.com

"Bidentate ligands templated by a convex trimetallic bis(salphen) platform"
Supramolecular Chemistry, **2012**, 1, 1–8.
Ponsico S., Frischmann P.D., MacLachlan M.J., Martínez-Belmonte M., Escudero-Adan E.C., Freixa Z., van Leeuwen P.W.N.M.

"Relationship Between Conformational Flexibility and Chelate Cooperativity"
J. Org. Chem., **2011**, *76*, 2723–2732.
Misuraca M.C., Grecu T., Freixa Z., Garavini V., Hunter C.A., van Leeuwen P.W.N.M., Segarra-Maset M.D., Turega S.M.

"SPOs as new ligands in Rh(III) catalyzed enantioselective transfer hydrogenation"
Catal. Sci. Tech., **2011**, *1*, 401–407.
Castro P.M., Gulyás H., Benet-Buchholtz J., Bo C., Freixa Z., van Leeuwen P.W.N.M.

"Zn(II) Robson macrocycles as templates for chelating diphosphines"
Dalton Trans., **2011**, *40*, 10686–10697
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"SPANamine derivatives in the catalytic asymmetric a-fluorination of β-keto esters"
Tetrahedron Asymmetry, **2011**, *22*, 1490–1498.
Jacquet O. Clément N.D., Freixa Z., Ruiz A., Claver C., van Leeuwen P.W.N.M.

"Enantioselective Supramolecular Catalysis Induced by Remote Chiral Diols"
J. Am. Chem. Soc., **2011**, *133*, 18562–18565.
van Leeuwen P.W.N.M., Rivillo D., Raynal M., Freixa Z.

"Large P–P distance diphosphines and their monophosphine analogs as ligands in the Pd-catalyzed telomerization of 1,3-butadiene and methanol"
Organometallics, **2011**, 30, 792-799.
Tschan M.J-L., López-Valbuena J.M., Freixa Z., Launay H., Hagen H., Benet-Buchholz J., van Leeuwen P.W.N.M.

"Efficient Bulky Phosphines for the Selective Telomerization of 1,3-Butadiene with Methanol"
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Tschan M.J-L., García-Suárez E.J., Freixa Z., Launay H., Hagen H., Benet-Buchholz J., van Leeuwen P.W.N.M.

"An approach to bimetallic catalysts by ligand design"
Dalton Trans., **2010**, 8560–8574.
López-Valbuena J.M., Escudero-Adan E.C., Benet-Buchholz J., Freixa Z., van Leeuwen P.W.N.M.

"Light Switches the Ligand! Photochromic Azobenzene–Phosphanes"
Eur. J. Inorg. Chem., **2010**, 2075–2078.
Segarra-Maset M.D., van Leeuwen P.W.N.M., Freixa Z.

"Bite angle effects of diphosphines in C-C and C-X bond forming reactions"
Chem. Soc. Rev., **2009**, 1099–1118.
Birkholz M-N., Freixa Z., van Leeuwen P.W.N.M.

"Modular Spiro Bidentate Nitrogen Ligands: Synthesis, Resolution and Application in Asymmetric Catalysis"
Eur. J. Org. Chem., **2008**, 6197–6205.
Sala X., García Suárez E.J., Freixa Z., Benet-Buchholz J., van Leeuwen P.W.N.M.

"Trans-chelating diphosphines, the elusive ligands!"
Coord. Chem. Rev., **2008**, *252(15–17)*, 1755–1786.
Freixa Z., van Leeuwen P.W.N.M.

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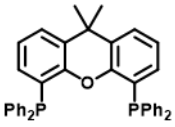

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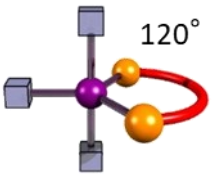
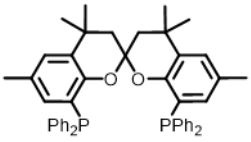
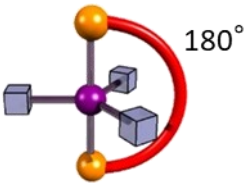




spanphos



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phone: +34 635638132
e-mail: Zoraida_freixa@ehu.eus
www. freixagroup.com

Ikerbasque Research Professor
Universidad del País Vasco (UPV-EHU)
ORCID: 0000-0002-2044-2725
Researcher ID: K-4294-2014

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phone: +34 635638132
e-mail: Zoraida_freixa@ehu.eus
www. freixagroup.com

Dr Zoraida Freixa

Ikerbasque Research Professor
Universidad del País Vasco (UPV-EHU)
ORCID: 0000-0002-2044-2725
Researcher ID: K-4294-2014

BOOK CHAPTERS:

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"Novel phosphine-based catalysts useful for the telomerization of butadiene"
van Leeuwen PWNM, Tschan M, Freixa Z, Hagen H **DOW Global Technologies Inc.** ES201/070086

phone: +34 635638132
e-mail: Zoraida_freixa@ehu.eus
www. freixagroup.com

Dr Zoraida Freixa

Ikerbasque Research Professor
Universidad del País Vasco (UPV-EHU)
ORCID: 0000-0002-2044-2725
Researcher ID: K-4294-2014

Scholarships/recognitions.

2020	**Profesor Titular de Universidad** accreditation from the Agencia Nacional de Evaluación de Calidad y Acreditación (ANECA)
2019	**Advanced Research** accreditation from the Catalan Agency for the Quality of the University (AQU).
2019	**IKERTRAMO (2012-2017)** 6 years of research recognition by the Basque Agency for the Quality of the University (UNIBASQ).
2009	**I3P** accreditation from the Spanish Ministry of Science and Innovation in recognition to an outstanding research trajectory.
2009	**Associate Professor** accreditation by the Catalan Agency for the Quality of the University (AQU)
2004 / 2009	**Ramon y Cajal** fellow from the Spanish Ministry of Science and Innovation.
2003	**Lecturer** accreditation by the the Catalan Agency for the Quality of the University (AQU).
1995 / 1999	**DGR** fellowship to conduct the PhD studies from the Catalan Government.

Commissions of trust.

- Member of the ANECA Commission for the EUROLABEL European accreditation for Bachelor and Master Degrees in Chemistry since 2019.
- Member of the panel of experts for the evaluation of National Research Projects (2016, 2017, 2022), and Juan de la Cierva contracts (2020).
- Member of the panel of experts for the evaluation Evaluation of senior, junior, and principal contracts FCT-Portugal (2021, 2022)
- External evaluator for AIE (2009, 2011, 2012, 2014, 2018. 2020, 2021, 2022).
- External evaluator for FONCYT (Argentina), 2017.
- External evaluator for ANR (France) 2017, 2018, 2020, 2022.
- External evaluator for Fundación Séneca Projects (2018)
- PhD thesis committees: E. Guimet (URV-2005), L. Crespi (UAB-2007), X. Sala (UdG-2007), E.M. Guillamón (UJI, 2009), A. García (UdZ, 2009), A Barrios (UJI, 2013), D Peral, (UAB, 2013), J Aguiló (UAB, 2013), E. Mercade (URV, 2015), E. Ruggiero (UPV-EHU, 2016), I. Zumeta (UPV-EHU, 2016), P. Clavero (UB, 2016), L. Pisciottani (Bordeaux, 2018), A Forero (StAndrews, 2018), L. Sotorrios (UPV/EHU, 2020), J. de la Cuesta (UPV/EHU, 2021), A. Gutiérrez Blanco (UJI, 2021).
- Vice-president of the Organometallic Chemistry Group (GEQO) of the RSEQ (2014–2018).

Organization of scientific events.

Workshop "From Bioinorganic Chemistry to Catalysis", Donostia International Physics Center, 23 November 2018, Donostia (Spain).

"Organometallic Chemistry day", Alcalá de Henares, 22 Sept 2017.

S19 Symposium "Reacciones de formación y ruptura de enlaces inducidas por metales. Diseño de ligandos" at the XXXVI Reunión bienal de la Sociedad Española de Química, Sitges, 25-29 Jun 2017.

Workshop "From Bioinorganic Chemistry to Catalysis", Donostia International Physics Center, 6 June 2017, Donostia (Spain).

XXXIII Meeting of the Specialized Group on Organometallic Chemistry (GEQO) of the RSEQ, Madrid, 14 May 2015.

phone: +34 635638132
e-mail: Zoraida_freixa@ehu.eus
www. freixagroup.com