



HAL
open science

Pierre Dixneuf: A Pioneering Career in Organometallic Chemistry Highlighting Ruthenium as a Star Metal in Homogeneous Catalysis

Jean-François Soulé, Christian Bruneau, Christophe Darcel

► **To cite this version:**

Jean-François Soulé, Christian Bruneau, Christophe Darcel. Pierre Dixneuf: A Pioneering Career in Organometallic Chemistry Highlighting Ruthenium as a Star Metal in Homogeneous Catalysis. *Organometallics*, 2021, 40 (11), pp.1551-1554. 10.1021/acs.organomet.1c00254 . hal-03269561

HAL Id: hal-03269561

<https://univ-rennes.hal.science/hal-03269561>

Submitted on 28 Jun 2021

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.

Pierre Dixneuf: A Pioneering Career in Organometallic Chemistry Highlighting Ruthenium as a Star Metal in Homogeneous Catalysis

With this virtual issue, *Organometallics* celebrates the career of Professor Pierre H. Dixneuf. Pierre is an internationally renowned chemist who has devoted his scientific life to organometallic chemistry and catalysis with ruthenium as a favorite transition metal. Before introducing the content of this issue, it is appropriate to dedicate a few lines to describe Pierre's career.



Figure 1. Photography of Professor Pierre H. Dixneuf, taken in 2014 in the Loire Valley area. Reproduced with permission. Copyright 2014 Christian Bruneau.

PIERRE DIXNEUF'S FIRST CAREER

Pierre H. Dixneuf was born in Coron, a village located on the Loire valley's west side. Because of its mild climate and peaceful countryside, this area was selected by the kings of France to establish their wonderful castles during the Renaissance period. It is also a place where it feels good to live with good food and pleasant wines, which Pierre considers the best province in France.

Very early, a very enthusiastic and enthralling primary school teacher triggered his passion for sciences. After his first years at the University of Brest and Rennes, he undertook doctorate studies on ferrocene chemistry under the supervision of Prof. René Dabard, a former student of Prof. Jean Tirouflet, both of

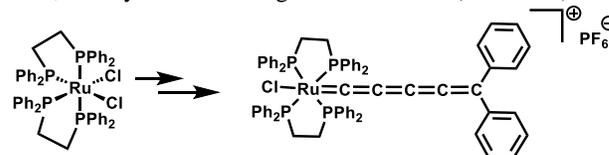
them pioneers of organometallic chemistry in France. After obtaining his doctorate in sciences in 1971, he spent a post-doctoral period (1971-72) in the laboratory of Prof. Michael F. Lappert in Brighton (UK) working on pioneering transition metal carbene complexes generated in the presence of electron-rich olefins. Then he began his academic career at the University of Rennes where he got a Professor of Chemistry position in 1978 and was subsequently promoted 1st class in 1988 and exceptional class in 1994.



Figure 2. left - Pierre with Prof. Jean Tirouflet, his *grandfather* in Chemistry and right - with Prof. René Dabard, his PhD director. Reproduced with permission. Copyright 2005 Christophe Darcel, and 2000 Christian Bruneau.

FROM ORGANOMETALLIC CHEMISTRY: RUTHENIUM AS A STAR

He initially developed his laboratory in the field of organometallic and coordination chemistry and rapidly oriented his research on topics dedicated to *Organometallics and Catalysis* in the 1980s. At that period, he intensively developed the domain of stoichiometric activation of terminal alkynes at ruthenium centers, essentially from $\text{RuCl}_2(\text{arene})(\text{phosphine})$ and $\text{RuCl}_2(\text{dppf})_2$ precursors, and provided a huge innovative contribution to the field of ruthenium-alkoxycarbenes, -vinylienes, -allenylidenes and higher -cumulenes (Scheme 1)¹⁻³

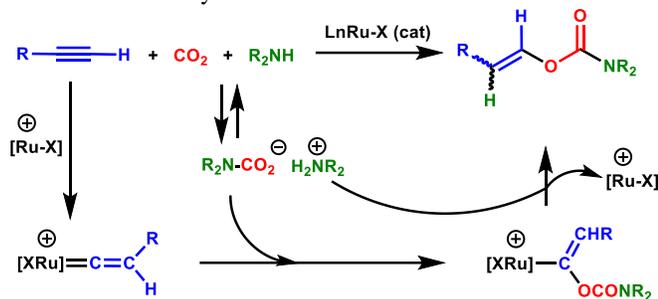


Scheme 1- First isolable pentatetraenylidene metal complex

ORGANOMETALLIC CHEMISTRY AS A MAIN INSPIRATION FOR THE DEVELOPMENT OF HOMOGENEOUS CATALYSIS

At the same time, he looked at the possibility of applying these new unsaturated organometallic species in catalysis. This constant exchange of ideas between stoichiometry and catalysis in

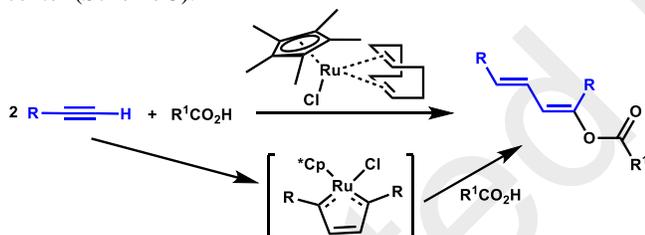
the same research team led to the discovery of the *anti*-Markovnikov addition of *O*-nucleophiles to terminal alkynes and the proposal for the first time of the involvement of a ruthenium-vinylidene in a catalytic cycle.^{4,5} This period corresponded to the development of catalytic reactions from terminal alkynes, more precisely the synthesis of vinylcarbamates directly from carbon dioxide and amines, (Scheme 2) and the preparation of the two regioisomers of enol esters depending on the nature of the ruthenium catalyst.



Scheme 2 – Valorization of carbon dioxide for the synthesis of vinylcarbamates involving a ruthenium vinylidene species

At the same period, the preparation of cyclic carbonates from carbon dioxide and propargylic substrates catalyzed by a phosphine, and their reactivity in the presence of palladium catalysts contributed to the development of the topic on carbon dioxide valorization.

Catalytic transformations of alkynes and alkenes with the electron-rich $\text{RuClCp}^*(\text{cod})$ complex provided unprecedented coupling reactions *via* oxidative coupling of alkynes at the metal center (Scheme 3).⁶⁻⁷



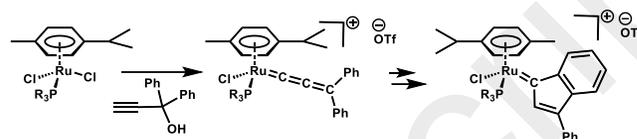
Scheme 3 – Activation of alkynes *via* oxidative coupling of CC and C=C bonds.



Figure 3 – the pioneering team, 1980s, left to right, Bernard Demerseman, Christian Bruneau, Hubert Le Bozec, and Daniel Touchard. Reproduced with permission. Copyright 2002.

FROM ORGANOMETALLIC CHEMISTRY OF ALLENYLIDENE RUTHENIUM TO METATHESIS CATALYSIS

At the end of the 1990s, when well-defined ruthenium carbene complexes were developing as efficient olefin metathesis catalysts, cationic ruthenium allenylidene complexes were also introduced in catalysis for the first time as efficient olefin metathesis catalysts in Pierre's team.⁸ Mechanistic studies revealed that the ruthenium allenylidene entity was transformed into a metathesis active ruthenium indenylidene species under catalytic conditions, which provided an entry to stoichiometric preparation of this type of complexes, another example of back and forth movement between stoichiometry and catalysis (Scheme 4).⁹

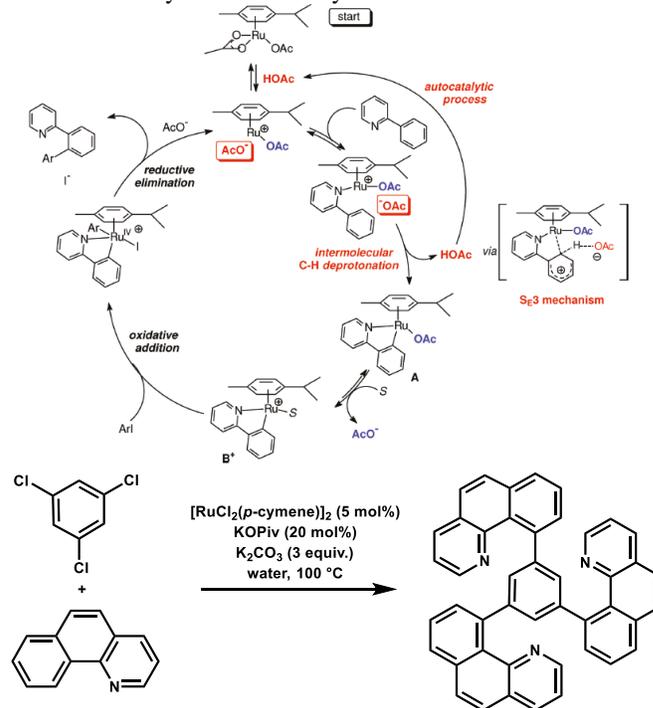


Scheme 4 – New allenylidene to indenylidene arene ruthenium catalysts for metathesis reactions

Later on, in the same vein, transformations of natural products such as fatty acid derivatives, terpenes and phenylpropenoids *via* cross-metathesis were exploited towards industrial targets.¹⁰

RUTHENIUM AND C-H ACTIVATION

At the dawn of the 21st century, due to seminal results obtained with various transition metal catalysts, the interest of researchers for C-H bond activation/functionalization all around the world increased considerably. With his expertise in ruthenium catalysis, the future impact of ruthenium catalysis in this field was obvious to Pierre Dixneuf. He developed this topic using mainly $[\text{RuCl}_2(p\text{-cymene})]_2$ as catalyst precursor in a strategy of directed *ortho*-functionalization of arenes in water. In collaboration with Dr. Anny Jutand he evidenced an autocatalytic process during the C-H bond activation in the catalytic arylation of arenes (Scheme 5).¹¹ He applied such methodology to prepared a trisbenzoquinoline motif, representing a Triskell, one of the famous Celtic symbol in Brittany.¹²⁻¹³



Scheme 5 – Ru(II)-catalyzed C-H activation – From mechanism involving an autocatalysis process to Breton application. [Mechanism reproduced with permission from reference *J. Am. Chem. Soc.* **2011**, *133*, 10161-10170. Copyright 2011, ACS].

Very recently, he turned his attention to photoredox catalysis and wrote a review article on this topic.¹⁴

HIS ENERGY DEDICATED TO NATIONAL AND INTERNATIONAL ACTIVITIES

Besides his prolific research activities, which have led to about 500 publications, including 25 review articles, 21 book chapters, and 7 edited books, Pierre has been strongly involved in the national and local administration of research. He spent 3 years as vice scientific director at CNRS (The National Centre for Scientific Research) in Paris from September 1996 to December 1999 and 3 years as vice-President for Research at the University of Rennes from 2001 to 2004. He played an important role in the creation of the Institute of Chemistry at the University of Rennes, gathering in the same Institute most of the local chemists and became the first director.

In recognition of his many contributions, Pierre Dixneuf has been a member of the Institut Universitaire de France since 2000, and has received numerous awards, including national prizes from the French Chemical Society, the Le Bel Prize (2000), from the Academy of Sciences, de la Charlonie Prize (1994) and IFP Grand Prix (2006), and international awards, the A. von Humboldt Foundation Prize (Germany 1990), Grignard-Wittig Award of the GDCh (Germany 2001), The Sacconi medal (Italy 2006), Catalan Award of the Spanish Chemistry Society (Spain 2014), Prize of the Chinese Chemical Society (China 2014), the Asima Chatterjee Award (India, 2020). He has been elected member of The European Academy of Sciences (2014), the Academy of Sciences of Portugal (2017), and the National Academy of Science, India (2020) and has been honored as Honoris Causa Doctor of the University of Waterloo (Canada) and Honorary professor in foreign universities (China: Anhui Normal - 2006; Jinan - 2017; Nanjing Tech. - 2018; Taiwan: Tsinghua - 2009).

Following the motto “no one is a prophet in his own country”, Pierre initiated many collaborations with chemists all around the world either with invited professor positions in Rennes, participation in European Research networks, the creation of an Erasmus student exchange network, and organization of international workshops.



Figure 3. First international conference organized by Pierre Dixneuf in Rennes in May 1981 (NSF-CNRS). Reproduced with permission. Copyright 1981.

This special issue is thus timely for celebrating the busy scientific life of Pierre H. Dixneuf. It contains a selection of papers published by Pierre in the ACS journals (*Acc. Chem. Res.* (1), *ACS Catal.* (1), *J. Org. Chem.* (2), *J. Am. Chem. Soc.* (7), *Organometallics* (12)). It should be underlined that *Organometallics* is one of the journals where he often published (more than 50 papers). Its content has been ranged in chronological order within the main topics that have punctuated his research. We have concentrated our efforts to introduce all the permanent coworkers of his research team, many of his foreign collaborators and friends and as much as possible of his students and post-doctors.

AUTHOR INFORMATION

Corresponding Authors

Jean-François Soulé, Christian Bruneau, Christophe Darcel
UnivRennes, CNRS ISCR (Institut des Sciences Chimiques de Rennes) UMR 6226, F-35000, Rennes, France

REFERENCES

(1) Touchard, D.; Haquette, P.; Daridor, A.; Toupet, L.; Dixneuf, P. H. First Isolable Pentatetraenylidene Metal Complex Containing the Ru:C:C:C:C:CPH₂ Assembly. A Key Intermediate To Provide Functional Allenylidene Complexes. *J. Am. Chem. Soc.* **1994**, *116*, 11157-11158.

(2) For selection of other contributions on stoichiometric activation of alkynes, see: (a) Kucukbay, H.; Cetinkaya, B.; Guesmi, S.; Dixneuf, P. H. New (Carbene)ruthenium-Arene Complexes: Preparation and Uses in Catalytic Synthesis of Furans. *Organometallics* **1996**, *15*, 2434-2439; (b) Demerseman, B.; Guilbert, B.; Renouard, C.; Gonzalez, M.; Dixneuf, P. H.; Masi, D.; Mealli, C. Synthesis and reactivity of (η⁶-arene)(phosphino enolato)ruthenium(II) complexes, their coupling reaction with phenylacetylene and thermal rearrangement to a phosphametalacyclopropane. X-ray crystal structures of [cyclic] {Ru[η³-CH:C(Ph)CH(PPh₂)C(Bu-tert):O](p-cymene)}(PF₆), of [cyclic] {Ru[η³-CH:C(Ph)C(Me)-(PPh₂)C(Et):O](mesitylene)}(BF₄), and of [cyclic] {Ru[η³-CH(PPh₂)CPh:C(H)C(Bu-tert):O](mesitylene)}(BF₄). *Organometallics* **1993**, *12*, 3906-3917; (c) Dussel, R.; Pilette, D.; Dixneuf, P. H.; Fehlhammer, W. P. Isocyanide arene-ruthenium(II) complexes and activation of alkenylacetylenes: synthesis and characterization of isocyanide carbene- and mixed carbene-ruthenium compounds. *Organometallics* **1991**, *10*, 3287-3291.

(3) For selection of other contributions on Metal-carbene, Metal-vinylidene, Metal-cumulene, see: (a) Sun, Y.; Chan, H.-S.; Dixneuf, P. H.; Xie, Z. Reaction of [η⁵:s-Me₂C(C₅H₄)(C₂B₁₀H₁₀)]Ru(NCCH₃)₂ with Me₃SiC≡CR. Synthesis and Structural Characterization of Mononuclear Ruthenium Bis(vinylidene) and Vinylvinylidene Complexes. *Organometallics* **2006**, *25*, 2719-2721; (b) Lavastre, O.; Plass, J.; Bachmann, P.; Guesmi, S.; Moinet, C.; Dixneuf, P. H. Ruthenium or Ferrocenyl Homobimetallic and RuPdRu and FePdFe Heterotrimetallic Complexes Connected by Unsaturated, Carbon-Rich -C≡CC₆H₄C≡C-Bridges. *Organometallics* **1997**, *16*, 184-189; (c) Touchard, D.; Pirio, N.; Dixneuf, P. H. Synthesis of Di- and Mono- Substituted Allenylidene-Ruthenium [(Ph₂PCH₂PPh₂)₂ClRu:C:C:C(Y)R]PF₆ and Acetylidene Complexes by Activation of Prop-2-yn-1-ols. *Organometallics* **1995**, *14*, 4920-4928; (d) Le Lagadec, R.; Roman, E.; Toupet, L.; Müller, U.; Dixneuf, P. H. (C₅Me₅)Ru-vinylidene complexes from terminal alkynes and propargyl alcohol derivatives. *Organometallics* **1994**, *13*, 5030-5039; (e) Pilette, D.; Ouzzine, K.; Le Bozec, H.; Dixneuf, P. H.; Rickard, C. E. F.; Roper, W. R. Activation of 2-propyn-1-ol derivatives by (arene)ruthenium(II) complexes: new route to (alkenylcarbene)- and (polyenylcarbene)-metal complexes. *Organometallics* **1992**, *11*, 809-817.

(4) Sasaki, Y.; Dixneuf, P. H. A novel catalytic synthesis of vinyl carbamates from carbon dioxide, diethylamine and alkynes in the presence of $\text{Ru}_3(\text{CO})_{12}$. *J. Chem. Soc. Chem. Commun.* **1986**, 790-791.

(5) Mahé R., Sasaki Y., Bruneau C., Dixneuf P. H. Catalytic Synthesis of Vinylcarbamates from Carbon Dioxide and Alkynes with Ruthenium Complexes. *J. Org. Chem.* **1989**, *54*, 1518-1523.

(6) Le Paih, J.; Monnier, F.; Derien, S.; Dixneuf, P. H.; Clot, E.; Eisenstein, O. Biscarbene-Ruthenium Complexes in Catalysis: Novel Stereoselective Synthesis of (1*E*,3*E*)-1,4-Disubstituted-1,3-dienes via Head-to-Head Coupling of Terminal Alkynes and Addition of Carboxylic Acids. *J. Am. Chem. Soc.* **2003**, *125*, 11964-11975.

(7) For additional examples of the use of alkynes in catalysis, see: (a) Bianchini, C.; Meli, A.; Peruzzini, M.; Zanobini, F.; Bruneau, C.; Dixneuf, P. H. Activation of 1-alkynes at tripodal (polyphosphine)rhodium systems. Regioselective synthesis of enol esters from 1-alkynes and carboxylic acids catalyzed by rhodium(I) monohydrides. *Organometallics* **1990**, *9*, 1155-1160; (b) Monnier, F.; Vovard-Le Bray, C.; Castillo, D.; Aubert, V.; Derien, S.; Dixneuf, P. H.; Toupet, L.; Ienco, A.; Mealli, C. Selective ruthenium-catalyzed transformations of enynes with diazoalkanes into alkenylbicyclo[3.1.0]hexanes. *J. Am. Chem. Soc.* **2007**, *129*, 6037-6049.

(8) Fürstner, A.; Picquet, M.; Brunbeau, C.; Dixneuf, P. H. Cationic ruthenium allenylidene complexes as a new class of performing catalysts or ring closing metathesis. *Chem. Commun.* **1998**, 1315-1316.

(9) Castarlenas, R.; Vovard, C.; Fischmeister, C.; Dixneuf, P. H. Allenylidene-to-Indenylidene Rearrangement in Arene-Ruthenium Complexes: A Key Step to Highly Active Catalysts for Olefin Metathesis Reactions. *J. Am. Chem. Soc.* **2006**, *128*, 4079-4089.

(10) For additional representative examples of ruthenium catalyzed metathesis transformation, see: (a) Masoud, S. M.; Mailyan, A. K.; Dorcet, V.; Roisnel, T.; Dixneuf, P. H.; Bruneau, C.; Osipov, S. N. Metathesis catalysts with fluorinated unsymmetrical NHC ligands. *Organometallics* **2015**, *34*, 2305-2313; (b) Bassetti, M.; Centola, F.; Sémeril, D.; Bruneau, C.; Dixneuf, P. H. Rate Studies and Mechanism of Ring-

Closing Olefin Metathesis Catalyzed by Cationic Ruthenium Allenylidene Arene Complexes. *Organometallics* **2003**, *22*, 4459-4466.

(11) Ferrer-Flegeau, E.; Bruneau, C.; Dixneuf, P. H.; Jutand, A. Autocatalysis for C-H Bond Activation by Ruthenium(II) Complexes in Catalytic Arylation of Functional Arenes. *J. Am. Chem. Soc.* **2011**, *133*, 10161-10170.

(12) Arockiam, P. A.; Fischmeister, C.; Bruneau, C.; Dixneuf, P. H. C-H Bond Functionalization in Water Catalyzed by Carboxylato Ruthenium(II) Systems. *Angew. Chem. Int. Ed.* **2010**, *49*, 6629-6632).

(13) For additional representative examples of ruthenium catalyzed C-H bond activation, see: (a) Arockiam, P. B.; Bruneau, C.; Dixneuf, P. H. Ruthenium(II)-Catalyzed C-H Bond Activation and Functionalization. *Chem. Rev.* **2012**, *112*, 5879-5918; (b) Özdemir, I.; Demir, S.; Cetinkaya, B.; Gourlaouen, C.; Maseras, F.; Bruneau, C.; Dixneuf, P. H. Direct Arylation of Arene C-H Bonds by Cooperative Action of NHCarbene-Ruthenium(II) Catalyst and Carbonate via Proton Abstraction Mechanism. *J. Am. Chem. Soc.* **2008**, *130*, 1156-1157; (c) Li B., Bheeter C. B. Darcel C., Dixneuf P. H. Sequential Catalysis for the Production of Sterically Hindered Amines: Ru(II)-Catalyzed C-H Bond Activation and Hydrosilylation of Imines. *ACS Catal.* **2011**, *1*, 1221-1224; (d) Yan, T.; Chen, L.; Bruneau, C.; Dixneuf, P. H.; Doucet, H. Synthesis of Heteroarylated Polyfluorobiphenyls via Palladium-Catalyzed Sequential sp^2 C-H Bonds Functionalizations. *J. Org. Chem.* **2013**, *78*, 4177-4183.

(14) Wang, C.-S.; Dixneuf, P. H.; Soulé, J.-F. Photoredox catalysis for building C-C bonds from C(sp^2)-H bonds. *Chem. Rev.* **2018**, *118*, 7532-7585.

Authors are required to submit a graphic entry for the Table of Contents (TOC) that, in conjunction with the manuscript title, should give the reader a representative idea of one of the following: A key structure, reaction, equation, concept, or theorem, etc., that is discussed in the manuscript. Consult the journal's Instructions for Authors for TOC graphic specifications.

Insert Table of Contents artwork here
