

## Dmitry A. Valyaev, Chargé de Recherche CNRS

Laboratoire de Chimie de Coordination du CNRS

205 route de Narbonne, 31077 Toulouse Cedex 4, France

Born on 11/02/1982 in Orehovo Zouevo (Moscow region)

Tel. : +33 (0)5 61 33 31 71 ; E-mail : [dmitry.valyaev@lcc-toulouse.fr](mailto:dmitry.valyaev@lcc-toulouse.fr)

ORCID iD : [0000-0002-1772-844X](https://orcid.org/0000-0002-1772-844X)



### Education

- 1998-2004 **Master of Science** (Chemistry, diploma with honors) in Higher Chemical College of Russian Academy of Sciences (Moscow, Russia)
- 2004-2007 **PhD in Organometallic and Organic Chemistry**, A. N. Nesmeyanov Institute of Organoelement Compounds of Russian Academy of Sciences (Moscow, Russia)  
Supervisors: *Prof. Dr Nikolai A. Ustynyuk, Dr. Oleg V. Semeikin*  
"Reactions of transition metal vinylidene and carbyne complexes for selective formation of carbon-carbon and carbon-heteroatom bonds"
- 2018 **Habilitation (HDR)**, Université Paul Sabatier (Toulouse, France)  
Committee: *Dr. A. Marinetti, Dr. S. Chardon-Noblat, Pr. D. Prim, Dr. Noël Lugan, Pr. J.-C. Hierso, Pr. E. Benoist*  
"Chemistry of manganese carbene complexes: from fundamental studies to applications in organic synthesis and homogeneous catalysis"

### Professional background

- 2013- **CNRS researcher / Chargé de recherche CNRS**  
Laboratoire de Chimie de Coordination du CNRS, Toulouse
- 2012-2013 **Post-doctoral fellow (CDD CNRS)**  
Laboratoire de Chimie de Coordination du CNRS, Toulouse  
Supervisor: *Dr. Noël Lugan*
- 2011-2012 **Post-doctoral fellow (Grant of PACA region then CDD CNRS)**  
Institut des Sciences Moléculaire de Marseille, Marseille  
Institut Matériaux Microélectroniques Nanosciences de Provence, Marseille  
Supervisors: *Dr. Olivier Chuzel and Dr. Jean-Luc Parrain*
- 2009-2010 **Post-doctoral fellow (CDD CNRS then PICS CNRS/Russie)**  
Laboratoire de Chimie de Coordination du CNRS, Toulouse  
Supervisor: *Dr. Noël Lugan*
- 2008-2011 **Researcher** in A.N. Nesmeyanov Institute of Organoelement Compounds (INEOS) of Russian Academy of Sciences, Moscow.

## Research interests

Manganese organometallic chemistry for organic synthesis; Organophosphorous chemistry; N-heterocyclic carbenes; Homogeneous catalysis; Supramolecular interligand interactions; Redox-induced reactions of organometallic compounds.

## Awards and Honors

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|------|---|
| 2017 | Invited professor in People's Friendship University of Russia (RUDN University)   |
| 2011 | Allocation d'Accueil de la Ville de Marseille   |
| 2009 | Laureate of the scientific competition "Academia Europaea Prize"  |
| 2007 | Winner of competition "Best PhD students of Russian Academy of Sciences" organized by Russian Science Support Foundation                            |
| 2006 | Participation in the Lindau Nobel Laureate Meetings in Chemistry (Germany)  |
| 2005 | INTAS Young Scientist Fellowship (Grant no. 05-109-4753)  |
| 2004 | DuPont de Nemours Corporation scholarship   |
| 2003 | Award for outstanding poster presentation in XV <sup>th</sup> FECEM Conference on Organometallic Chemistry, August 10-15, 2003, Zurich, Switzerland |

## Scientific record

32 publications in peer reviewed journals (average IF 5.8) including 2 in *Coord. Chem. Rev.*, 3 in *Angew. Chem. Int. Ed.*, 1 in *J. Am. Chem. Soc.*, 1 in *Chem. Sci.*, 2 in *Chem. Commun.*, 2 in *Chem. Eur. J.*, 2 in *Adv. Synth. Catal.*, 1 in *Polym. Chem.*, 5 in *Organometallics*, 4 in *Dalton Trans.*, 1 in *Langmuir* and 8 in other journals, 18 oral communications, 28 posters. h-index = 13 for 480 citations et average 16.0 citations per article (April 2019).

## Peer-reviewed journal publications

- 32-"Direct Access to  $\text{IMes}^{\text{F}}$  and  $\text{IMes}^{\text{F}_2}$  by Electrophilic Fluorination of Abnormal N-Heterocyclic Carbenes" A. A. Grineva, O. A. Filippov, S. E. Nefedov, N. Lugan, V. César, D. A. Valyaev, *Organometallics* **2019**, DOI: 10.1021/acs.organomet.9b00151.
- 31-"Phosphine-NHC Manganese Hydrogenation Catalyst Exhibiting a Non-Classical Metal-Ligand Cooperative  $\text{H}_2$  Activation Mode", R. Buhaibeh, O. A. Filippov, A. Bruneau-Voisine, J. Willot, C. Duhayon, D. A. Valyaev, N. Lugan, Y. Canac, J.-B. Sortais, *Angew. Chem. Int. Ed.* **2019** DOI: 10.1002/anie.201901169.
- 30-"Palladium(II) pincer complexes of a C,C,C-NHC, diphosphonium bis(ylide) ligand" R. Taakili, C. Lepetit, C. Duhayon, D. A. Valyaev, N. Lugan, Y. Canac, *Dalton Trans.* **2019**, 48, 1709-1721.

- 29-"Manganese phosphinocarbodithioate for RAFT polymerization with sunlight-induced chain end post-treatment" I. Kulai, A. Karpus, L. Soroka, D. A. Valyaev, V. Bourdon, E. Manoury, R. Poli, M. Destarac, S. Mazières, *Polym. Chem.* **2019**, *10*, 267-277.
- 28-"Unveiling the redox-active character of imidazolin-2-thiones derived from amino-substituted N-Heterocyclic Carbenes" M. Ruamps, S. Bastin, L. Rechinat, A. Sournia-Saquet, D. A. Valyaev, J.-M. Mouesca, N. Lugan, V. Maurel, V. César, *Chem. Commun.* **2018**, *54*, 7653-7656.
- 27-"Manganese catalyzed reductive amination of aldehydes using hydrogen as reductant" D. Wei, A. Bruneau-Voisine, D. A. Valyaev, N. Lugan, J.-B. Sortais, *Chem. Commun.* **2018**, *54*, 4302-4305.
- 26-"Oxidative coupling of anionic abnormal N-Heterocyclic carbenes: an efficient access to Janus-type 4,4'-bis(2*H*-imidazol-2-ylidenes)" A. A. Grineva, D. A. Valyaev, V. César, O. A. Filippov, V. N. Khrustalev, S. E. Nefedov, N. Lugan, *Angew. Chem. Int. Ed.* **2018**, *57*, 7986-7991, Frontispiece cover. Included into the list of significant achievements of INC du CNRS in 2018 [http://www.cnrs.fr/inc/communication/direct\\_labos/lugan2.htm](http://www.cnrs.fr/inc/communication/direct_labos/lugan2.htm).
- 25-"Hydrogenation of carbonyl derivatives catalysed by manganese complexes bearing bidentate pyridinyl-phosphine ligands" D. Wei, A. Bruneau-Voisine, T. Chauvin, V. Dorcet, T. Roisnel, D. A. Valyaev, N. Lugan, J.-B. Sortais, *Adv. Synth. Catal.* **2018**, *360*, 676-681.
- 24-"Dual reactivity pattern of Mn(I) carbyne complexes Cp(CO)<sub>2</sub>Mn<sup>+</sup>≡C-R (R = Ar, Alk) vs. dpmm: subtle balance between double intramolecular nucleophilic addition and nucleophilic addition followed by migratory CO insertion" D. A. Valyaev, K. I. Utegenov, V. V. Krivykh, J. Willot, N. A. Ustynyuk, N. Lugan, *J. Organomet. Chem.* **2018**, *867*, 353-358.
- 23-"Manganese-mediated synthesis of a NHC core non-symmetric pincer ligand and evaluation of its coordination properties" D. A. Valyaev, J. Willot, L. P. Mangin, D. Zargarian, N. Lugan, *Dalton. Trans.* **2017**, *46*, 10193-10196.
- 22-"Half-sandwich manganese complexes bearing Cp tethered N-heterocyclic carbene ligands: synthesis and mechanistic insights into the catalytic ketone hydrosilylation" D. A. Valyaev, D. Wei, S. Elangovan, M. Cavailles, V. Dorcet, J.-B. Sortais, C. Darcel, N. Lugan, *Organometallics* **2016**, *35*, 4090-4098.
- 21-"Post-coordination backbone functionalization of an imidazol-2-ylidene and its application to synthesize heteropolymetallic complexes incorporating the ambidentate IMe<sup>CO<sub>2</sub>-</sup> ligand" D. A. Valyaev, M. A. Uvarova, A. A. Grineva, V. César, S. N. Nefedov, N. Lugan, *Dalton Trans.* **2016**, *45*, 11953-11957.
- 20-"Catalytic scanning probe nanolithography (cSPL): control of the AFM parameters in order to achieve a sub-100 nm spatially resolved epoxidation of alkenes grafted on a surface" V. Mesquita, J. Botton, D. A. Valyaev, C. François, L. Patrone, S. T. Balaban, M. Abel, J.-L. Parrain, O. Chuzel, S. Clair, *Langmuir* **2016**, *32*, 4034-4042.

- 19- "Manganese organometallic compounds in homogeneous catalysis: past, present, and prospects" D. A. Valyaev, G. Lavigne, N. Lugan, *Coord. Chem. Rev.* **2016**, 308, 191-235.
- 18- "Umpolung of methylenephosphonium ions in their manganese half-sandwich complexes and application to the synthesis of chiral phosphorus-containing ligand scaffolds" D. A. Valyaev, O. A. Filippov, N. Lugan, G. Lavigne, N. A. Ustynyuk, *Angew. Chem. Int. Ed.* **2015**, 54, 6315-6319. Included into the list of significant achievements of INC du CNRS in 2015 [http://www.cnrs.fr/inc/communication/direct\\_labos/lugan.htm](http://www.cnrs.fr/inc/communication/direct_labos/lugan.htm).
- 17- "Hydrosilylation of aldehydes and ketones catalyzed by half-sandwich Mn(I) N-heterocyclic carbene complexes" J. Zheng, S. Elongovan, D. A. Valyaev, R. Brousses, V. César, J.-B. Sortais, C. Darcel, N. Lugan, G. Lavigne, *Adv. Synth. Catal.* **2014**, 356, 1093-1097.
- 16- "A direct, modular and efficient construction of the P-C-P structural motif via coupling of manganese carbyne complexes with phosphines" D. A. Valyaev, S. Bastin, K.I. Utegenov, N. Lugan, G. Lavigne, N. A. Ustynyuk, *Chem. Eur. J.* **2014**, 20, 2175-2178.
- 15- "Grafting a homogeneous transition metal catalyst onto a silicon AFM probe: a promising strategy for chemically constructive nanolithography" D. A. Valyaev, S. Clair, L. Patrone, M. Abel, L. Porte, O. Chuzel, J.-L. Parrain, *Chem. Sci.* **2013**, 4, 2815-2821. "Hot article", see: <http://blogs.rsc.org/sc/2013/06/10/homogeneous-catalysis-for-nanoscale-surface-designs/>. Highlighted in RSC Chemistry World and chemie.de Information Services, see: <http://www.rsc.org/chemistryworld/2013/06/nanoscale-surface-design-homogeneous-catalysis-epoxidation> and <http://www.chemeurope.com/en/news/143508/nano-tattoos-for-bespoke-surface-design.html>. Included into the list of significant achievements of INC du CNRS in 2013 [http://www.cnrs.fr/inc/communication/direct\\_labos/parrain.htm](http://www.cnrs.fr/inc/communication/direct_labos/parrain.htm)
- 14- "On the incidence of non-covalent intramolecular interligand interactions on the conformation of carbene complexes: a case study" N. Lugan, I. Fernández, R. Brousses, D. A. Valyaev, G. Lavigne, N. A. Ustynyuk, *Dalton Trans.* **2013**, 42, 898-901. "Hot article", see: <http://blogs.rsc.org/dt/2012/12/07/unexpected-interactions-for-piano-stool-carbene-complexes/>
- 13- "Do  $\nu(\text{CO})$  stretching frequencies in metal carbonyl complexes unequivocally correlate with the intrinsic electron-donicity of ancillary ligands?" D. A. Valyaev, R. Brousses, N. Lugan, I. Fernández, M. A. Sierra, *Chem. Eur. J.* **2011**, 17, 6602-6605.
- 12- "Synthesis of  $\eta^1$ - $\alpha$ -phosphinocarbene complexes of manganese and mechanistic insight into their base-induced transformations" D. A. Valyaev, N. Lugan, G. Lavigne, N. A. Ustynyuk, *Organometallics* **2011**, 30, 2318-2332.
- 11- "Protonation of zwitter-ionic manganese and rhenium phosphoniostyryl complexes ( $\eta^5\text{-C}_5\text{H}_5$ )(CO) $_2$ M $^-$ -C( $^+\text{PR}_3$ )=C(H)Ph: experimental and DFT study" V. V. Krivikh, D. A. Valyaev, K. I. Utegenov, A. M. Mazhuga, E. S. Taits, O. V. Semeikin, P. V. Petrovskii, I. A. Godovikov, I. V. Glukhov, N. A. Ustynyuk, *Eur. J. Inorg. Chem.* **2011**, 201-211.

- 10- "Generation of  $\alpha$ -phosphinocarbene complexes and their evolution: new light on relevant isomerization pathways" D. A. Valyaev, N. Lugan, G. Lavigne, N. A. Ustynyuk, *Organometallics* **2008**, *27*, 5180-5183.
- 9- "Proton reduction catalysis by manganese vinylidene and allenylidene complexes" D. A. Valyaev, M. G. Peterleitner, O. V. Semeikin, K. I. Utegenov, N. A. Ustynyuk, A. Sournia-Saquet, N. Lugan, G. Lavigne, *J. Organomet. Chem.* **2007**, *692*, 3207-3211.
- 8- "Redox induced reactions of transition metal  $\pi$ - and  $\sigma,\pi$ -complexes" N. A. Ustynyuk, O. V. Gusev, L. N. Novikova, M. G. Peterleitner, L. I. Denisovich, T. A. Peganova, O. V. Semeikin, D. A. Valyaev, *J. Solid. State Electrochem.* **2007**, *11*, 1621-1634.
- 7- "Intermolecular hydrogen bonding between neutral transition metal hydrides  $(\eta\text{-C}_5\text{H}_5)\text{M}(\text{CO})_3\text{H}$  (M = Mo, W) and bases" N. V. Belkova, E. I. Gutsul, O. A. Filippov, V. A. Levina, D. A. Valyaev, L. M. Epstein, A. Lledos, E. S. Shubina, *J. Am. Chem. Soc.* **2006**, *128*, 3486-3487.
- 6- "Redox induced reactions of transition metal vinylidene and related complexes" D. A. Valyaev, O. V. Semeikin, N. A. Ustynyuk, *Coord. Chem. Rev.* **2004**, *248*, 1679-1692.
- 5- "Oxidative dehydrodimerization of rhenium vinylidene complex  $(\eta^5\text{-C}_5\text{H}_5)(\text{CO})_2\text{Re}=\text{C}=\text{C}(\text{H})\text{Ph}$ : two competitive routes of coupling of  $\sigma$ -phenylethynyl intermediate  $[(\eta^5\text{-C}_5\text{H}_5)(\text{CO})_2\text{Re}-\text{C}\equiv\text{CPh}]^*$ . X-ray structures of rhenium mononuclear  $(\eta^5\text{-C}_5\text{H}_5)(\text{CO})_2\text{Re}=\text{C}=\text{C}(\text{H})\text{Ph}$  and binuclear  $[(\eta^5\text{-C}_5\text{H}_5)(\text{CO})_2\text{Re}]_2(\mu_2\text{-C}=\text{C}(\text{Ph})\text{C}\equiv\text{CPh})$  vinylidene compounds" D. A. Valyaev, O. V. Semeikin, M. G. Peterleitner, Yu. A. Borisov, V. N. Khrustalev, A. M. Mazhuga, E. V. Kremer, N. A. Ustynyuk, *J. Organomet. Chem.* **2004**, *689*, 3837-3846.
- 4- "Oxidative activation of the manganese bis-vinylidene complexes  $[(\eta^5\text{-C}_5\text{R}_5)(\text{CO})_2\text{Mn}=\text{C}=\text{CPh}]_2$  (R = H, Me) towards addition of nucleophiles" D. A. Valyaev, M. G. Peterleitner, L. I. Leont'eva, L. N. Novikova, O. V. Semeikin, V. N. Khrustalev, M. Yu. Antipin, N. A. Ustynyuk, B. W. Skelton, A. H. White, *Organometallics* **2003**, *22*, 5491-5497.
- 3- "Study of redox-induced reactions of vinylidene and bis-vinylidene complexes of manganese" M. G. Peterleitner, D. A. Valyaev, L. N. Novikova, O. V. Semeikin, N. A. Ustynyuk, *Russ. J. Electrochem.* **2003**, *39*, 1270-1277.
- 2- "Oxidative dehydrodimerization of manganese vinylidene complexes  $(\eta^5\text{-C}_5\text{R}_5)(\text{CO})(\text{L})\text{Mn}=\text{C}=\text{C}(\text{H})\text{Ph}$  (R = Me, L = CO; R = H, L = PPh<sub>3</sub>)" L. N. Novikova, M. G. Peterleitner, K. A. Sevumyan, O. V. Semeikin, D. A. Valyaev, N. A. Ustynyuk, *Appl. Organometal. Chem.* **2002**, *16*, 530-536.
- 1- "Oxidative dehydrodimerization of manganese phenylvinylidene complex  $(\eta^5\text{-C}_5\text{H}_5)(\text{CO})_2\text{Mn}=\text{C}=\text{C}(\text{H})\text{Ph}$ . X-Ray structure of phenyl(trityl)vinylidene complex  $(\eta^5\text{-C}_5\text{H}_5)(\text{CO})_2\text{Mn}=\text{C}=\text{C}(\text{CPh}_3)\text{Ph}$ " L. N. Novikova, M. G. Peterleitner, K. A. Sevumyan, O. V. Semeikin, D. A. Valyaev, N. A. Ustynyuk, V. N. Khrustalev, L. N. Kuleshova, M. Yu. Antipin, *J. Organomet. Chem.* **2001**, *631*, 47-53.