

Professor Irina Beletskaya

A Tribute



Irina Beletskaya was born in Leningrad (St-Petersburg) on 10 March 1933. After graduation from the Department of Chemistry of Lomonosov Moscow State University (MSU), she started her brilliant lifelong career at the Department. The onset of her academic carrier was swift and spectacular. By 1963 she reached the D.Sci. degree and soon after became a professor in the department. In less than a decade she obtained first the Candidate of Chemistry (analogous to Ph.D) degree (1958), and then the Doctor of Chemistry degree (1963). Besides intensive research, Beletskaya was always engaged in teaching, and since 1971 served as a professor of chemistry in the department giving lecture courses on general organic chemistry and special postgraduate courses on organometallic chemistry and transition metal catalysis.

Her initial research efforts were directed to the study of reaction mechanisms. What Hughes and Ingold did for nucleophilic substitution, Beletskaya (together with Prof. O. Reutov) did for electrophilic reactions at saturated carbon. She was the first to thoroughly investigate the mechanisms of reactions of organometallic compounds, revealing the regularities of S_E pathways in a set of articles and a monograph. In this period she also elaborated one of the earliest CH-acidity scales based on correlation with electrochemical data. These interests led her to an investigation of carbanion reactivity, with particular emphasis on the reactivity and structure of ion pairs. Later the mechanistic studies involved the investigation of the mechanisms of nucleophilic aromatic and vinylic substitution, including recent work devoted to special mechanisms of substitution reactions involving organometallic supernucleophiles.

Beletskaya was among the first to pay attention to the application of rare earth elements in organic chemistry, which is now a thriving field. The synthesis of novel organolanthanide

complexes was developed including Grignard-like organoytterbiums and similar compounds, which turned out to be useful reagents in organic synthesis. Other lanthanide complexes were shown to take part in various highly effective catalytic processes, e.g. hydrosilation, hydrogenation or oligomerization of olefins.

In the 70s Beletskaya, again among the first, realized the huge potential of a new field,- the application of transition metal catalysts in organic synthesis. She initiated the studies of palladium and nickel-catalyzed reactions, and developed a number of convenient protocols for C-C and C-heteroatom bond forming methods. Industrially important methods were thereby developed for the alkoxy-carbonylation of aryl and benzyl halides.

The studies of catalytic activity of various palladium complexes and the regularities governing catalyst deactivation brought forward an unusual idea of ligand-free (or phosphine-free) catalysis. The catalysts lacking strongly bonded ligands showed much higher activity in C-C bond forming reactions involving organoboron or organotin compounds. Further studies revealed a key role of water as solvent for palladium catalyzed reactions. All these findings put together afforded a general approach of aqueous phosphine-free catalysis. Huge catalytic efficiency, very mild conditions, simplicity of experimental setup characterized the processes realized within this fruitful methodology.

Well in advance of the burst of global interest in environmentally benign (*green*) chemistry, Beletskaya discovered a series of transition-metal catalyzed reactions in aqueous media, including unusual systems such as microemulsions or other high-capacity solubilizing media. A thorough study of aqueous phosphine-free catalysis helped to reveal yet another essential feature – the involvement of catalyst nanoparticles, which not only allowed the development of new catalytic systems (for example, a new series of palladacycles involving cheap CN-ligands), but also explained the catalysis by super-low amounts of phosphine-free palladium catalyst (now sometimes nicknamed as *homeopathic* catalysis).

Amazingly, in the last decade, in spite of harsh economic problems and huge cuts of support for science, the activity of Beletskaya in research progresses at an increasing pace. Her current interests are as broad as ever, including organometallic chemistry, catalysis, supramolecular chemistry, nanochemistry, synthetic methodology *etc.* Besides experimental research Beletskaya is very interested in methodology. There appeared and continue to appear, a vast series of highly acclaimed critical reviews and book chapters on various aspects of palladium and other transition metal catalyzed reactions, including the Heck reaction, C-C and C-heteroatom cross-coupling, addition to triple bond, carbonylation and carbonylative cyclizations, water in organometallic chemistry, and dendrimers.

In 1974 Beletskaya was elected a corresponding member of the Academy of Science of USSR, and in 1992 became a full member (an academician) of the Russian Academy of Science. Since 1989 Beletskaya has been head of the Organoelement Chemistry laboratory at the Department of Chemistry of MSU.

Professor Beletskaya is an emeritus academician of the Bashkir National Academy of Science, an emeritus professor of St-Petersburg State University, and Cordoba University

(Argentina). She has won the Mendeleev, Lomonosov, Nesmeyanov and Demidov Prizes for creativity and achievements in chemistry. Abroad she also won the Kapitza Award Fellowship (UK), and Women in the Engineering Science award (Sweden).

Irina Beletskaya served for many years as an editor-in-chief of the Russian Journal of Organic Chemistry. She is or has been a member of the editorial boards of a number of leading journals including The Bulletin of Russian Academy of Science (Izvestiya RAN, Mendellev Communications, The Proceedings of Russian Academy of Science (Vestnik RAN), Organometallics, Chemistry – A European Journal, and the Journal of Organometallic Chemistry.

For many years Beletskaya also participated in the activities of the International Union of Pure and Applied Chemistry (IUPAC) serving in late 80s first as a secretary, then a vice-president, and in 1991-1993 as a president of the Division of Organic Chemistry. Until 2001 she was working on the IUPAC Committee on chemical weapons destruction technologies (CWDT).

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Selected Papers

1. I. D. Titanyuk, D. V. Vorob'eva, S. N. Osipov, I. P. Beletskaya, 1-Trifluoromethyl-1-diethoxyphosphoryl carbene: A new synthon for the preparation of CF₃-containing hydroxy and amino phosphonic acid derivatives, *Synlett* **2006**, 1355.
2. P. K. Sazonov, G. A. Artamkina, K. A. Lyssenko, I. P. Beletskaya, A new mechanism of nucleophilic vinylic substitution and unexpected products in the reaction of chlorotrifluoroethylene with [Re(CO)₅]Na and [CpFe(CO)₂]K, *J. Organomet. Chem.* **2006**, 691, 2346.
3. D. A. Malyshev, N. M. Scott, N. Marion, E. D. Stevens, V. P. Ananikov, I. P. Beletskaya, S. P. Nolan, Homogeneous nickel catalysts for the selective transfer of a single arylthio group in the catalytic hydrothiolation of alkynes, *Organometallics* **2006**, 25, 4462.
4. N. V. Lukashev, G. V. Latyshev, P. A. Donez, G. A. Skryabin, I. P. Beletskaya, 6-Chloro- and 6-bromo-substituted steroids in the Suzuki-Miyaura cross-coupling reaction. A convenient route to potential aromatase inhibitors, *Synthesis* **2006**, 533.
5. O. V. Gusev, T. A. Peganova, A. M. Kalsin, N. V. Vologdin, P. V. Petrovskii, K. A. Lyssenko, A. V. Tsvetkov, I. P. Beletskaya, Palladium complexes with metallocene-bridged bidentate diphosphine ligands: Synthesis, structure, and catalytic activity in amination and cross-coupling reactions, *Organometallics* **2006**, 25, 2750.

6. A. D. Averin, O. A. Ulanovskaya, A. A. Borisenko, M. V. Serebryakova, I. P. Beletskaya, Synthesis of macrocycles containing two pyridine and two polyamine moieties via Pd-catalyzed amination, *Tetrahedron Lett.* **2006**, *47*, 2691.
7. I. P. Beletskaya, A. G. Bessmertnykh, A. D. Averin, F. Denat, R. Guilard, Palladium-catalysed amination of 1,8- and 1,5-dichloroanthracenes and 1,8- and 1,5-dichloroanthraquinones, *Eur. J. Org. Chem.* **2005**, 281.
8. I. P. Beletskaya, A. G. Bessmertnykh, A. D. Averin, F. Denat, R. Guilard, Palladium-catalyzed arylation of linear and cyclic polyamines, *Eur. J. Org. Chem.* **2005**, 261.
9. A. D. Averin, O. A. Ulanovskaya, I. A. Fedotenko, A. A. Borisenko, M. V. Serebryakova, I. P. Beletskaya, Palladium-catalyzed amination of 3,5-dihalopyridines - A convenient route to new polyazamacrocycles, *Helv. Chim. Acta* **2005**, *88*, 1983.
10. A. D. Averin, E. R. Ranyuk, N. V. Lukashev, I. P. Beletskaya, Synthesis of nitrogen- and oxygen-containing macrocycles - Derivatives of lithocholic acid, *Chem. Eur. J.* **2005**, *11*, 7030.
11. F. Alonso, I. P. Beletskaya, M. Yus, Non-conventional methodologies for transition-metal catalysed carbon-carbon coupling: A critical overview. Part 1: The Heck reaction, *Tetrahedron* **2005**, *61*, 11771.
12. O. S. Finikova, A. V. Cheprakov, I. P. Beletskaya, P. J. Carroll, S. A. Vinogradov, Novel Versatile Synthesis of Substituted Tetrabenzoporphyrins, *J. Org. Chem.* **2004**, *69*, 522.
13. I. P. Beletskaya, A. V. Cheprakov, Copper in cross-coupling reactions: The post-Ullmann chemistry, *Coord. Chem. Rev.* **2004**, *248*, 2337.
14. I. P. Beletskaya, A. V. Cheprakov, Palladacycles in catalysis - A critical survey, *J. Organomet. Chem.* **2004**, *689*, 4055.
15. F. Alonso, I. P. Beletskaya, M. Yus, Transition-metal-catalyzed addition of heteroatom-hydrogen bonds to alkynes, *Chem. Rev.* **2004**, *104*, 3079.
16. A. G. Sergeev, G. A. Artamkina, I. P. Beletskaya, Variation of xanthene-based bidentate ligands in the palladium-catalyzed arylation of ureas, *Tetrahedron Lett.* **2003**, *44*, 4719.
17. N. S. Goulioukina, T. M. Dolgina, G. N. Bondarenko, I. P. Beletskaya, M. M. Ilyin, V. A. Davankov, A. Pfaltz, Highly enantioselective hydrogenation of α -unsaturated phosphonates with iridium-phosphinooxazoline complex: Synthesis of a phosphorus analogue of naproxen, *Tetrahedron Asymm.* **2003**, *14*, 1397.
18. I. P. Beletskaya, G. V. Latyshev, A. V. Tsvetkov, N. V. Lukashev, The nickel-catalyzed Sonogashira-Hagihara reaction, *Tetrahedron Lett.* **2003**, *44*, 5011.
19. V. P. Ananikov, M. A. Kabeshov, I. P. Beletskaya, G. G. Aleksandrov, I. L. Eremenko, Mechanistic study of palladium catalyzed S-S and Se-Se bonds addition to alkynes, *J. Organomet. Chem.* **2003**, *687*, 451.
20. V. P. Ananikov, I. P. Beletskaya, G. G. Aleksandrov, I. L. Eremenko, Mechanistic investigation and new catalyst design in palladium- and platinum-catalyzed Se-Se bond addition to alkynes, *Organometallics* **2003**, *22*, 1414.

21. M. O. Shulyupin, M. A. Kazankova, I. P. Beletskaya, Catalytic hydrophosphination of styrenes, *Org. Lett.* **2002**, *4*, 761.
22. A. Y. Lebedev, V. V. Izmer, D. N. Kazyul'kin, I. P. Beletskaya, A. Z. Voskoboynikov, Palladium-catalyzed stereocontrolled vinylation of azoles and phenothiazine, *Org. Lett.* **2002**, *4*, 623.
23. A. N. Kashin, A. V. Mitin, I. P. Beletskaya, R. Wife, Palladium-catalyzed arylation of sulfonyl CH-acids, *Tetrahedron Lett.* **2002**, *43*, 2539.
24. I. P. Beletskaya, M. A. Kazankova, Catalytic methods for building up phosphorus-carbon bond, *Russ. J. Org. Chem.* **2002**, *38*, 1391.
25. F. Alonso, I. P. Beletskaya, M. Yus, Metal-mediated reductive hydrodehalogenation of organic halides, *Chem. Rev.* **2002**, *102*, 4009.
26. A. Z. Voskoboynikov, A. K. Shestakova, I. P. Beletskaya, 1-octene hydrosilylation catalyzed by lanthanide and yttrium hydrides and hydrocarbyls: A mechanistic study and the role of catalyst association, *Organometallics* **2001**, *20*, 2794.
27. L. A. Tjurina, V. V. Smirnov, G. B. Barkovskii, E. N. Nikolaev, S. E. Esipov, I. P. Beletskaya, Cluster Grignard reagents, *Organometallics* **2001**, *20*, 2449.
28. M. A. Kazankova, I. V. Efimova, A. N. Kochetkov, V. V. Afanas'ev, I. P. Beletskaya, P. H. Dixneuf, New approach to vinylphosphines based on Pd- and Ni-catalyzed diphenylphosphine addition to alkynes, *Synlett* **2001**, 497.
29. N. S. Goulioukina, T. M. Dolgina, I. P. Beletskaya, J. C. Henry, D. Lavergne, V. Ratovelomanana-Vidal, J. P. Genet, A practical synthetic approach to chiral aryl substituted ethylphosphonates, *Tetrahedron Asymmetry* **2001**, *12*, 319.
30. O. Finikova, A. Cheprakov, I. Beletskaya, S. Vinogradov, An expedient synthesis of substituted tetraaryltetrabenzoporphyrins, *Chem. Commun.* **2001**, 261.
31. I. P. Beletskaya, A. N. Kashin, N. B. Karlstedt, A. V. Mitin, A. V. Cheprakov, G. M. Kazankov, NC-palladacycles as highly effective cheap precursors for the phosphine-free Heck reactions, *J. Organomet. Chem.* **2001**, *622*, 89.
32. G. A. Artamkina, A. G. Sergeev, I. P. Beletskaya, Palladium-catalyzed reaction of aryl halides with ureas, *Tetrahedron Lett.* **2001**, *42*, 4381.
33. I. P. Beletskaya, A. V. Chuchurjukin, H. P. Dijkstra, G. P. M. van Klink, G. van Koten, Conjugated G(0) metallo-dendrimers, functionalized with tridentate 'pincer'-type ligands, *Tetrahedron Letters* **2000**, *41*, 1081.
34. I. P. Beletskaya, A. V. Chuchurjukin, H. P. Dijkstra, G. P. M. Van Klink, G. Van Koten, Conjugated G0 metallo-dendrimers, functionalized with tridentate 'pincer'-type ligands, *Tetrahedron Lett.* **2000**, *41*, 1081.
35. I. P. Beletskaya, A. V. Chuchurjukin, H. P. Dijkstra, G. P. M. Van Klink, G. Van Koten, Acetylene-bridged P,C,P'-ligands and corresponding cyclopalladated compounds, *Tetrahedron Lett.* **2000**, *41*, 1075.
36. I. P. Beletskaya, A. V. Cheprakov, Heck reaction as a sharpening stone of palladium catalysis, *Chem. Rev.* **2000**, *100*, 3009.

37. M. A. Kazankova, I. G. Trostyanskaya, S. V. Lutsenko, I. P. Beletskaya, Nickel- and palladium-catalyzed cross-coupling as a route to 1- and 2- alkoxy- or dialkylaminovinylphosphonates, *Tetrahedron Lett.* **1999**, *40*, 569.
38. I. P. Beletskaya, A. G. Bessmertnykh, R. Guillard, Halo-substituted aminobenzenes prepared by Pd-catalyzed amination, *Synlett* **1999**, 1459.
39. I. P. Beletskaya, A. G. Bessmertnykh, R. Guillard, Palladium-catalyzed amination of aryl dibromides with secondary amines: Synthetic and mechanistic aspects, *Tetrahedron Lett.* **1999**, *40*, 6393.
40. I. Beletskaya, C. Möberg, Element-Element Addition to Alkynes Catalyzed by the Group 10 Metals, *Chem. Rev.* **1999**, *99*, 3435.
41. I. P. Beletskaya, D. V. Davydov, M. Moreno-Mañas, Pd- and Cu-catalyzed selective arylation of benzotriazole, *Tetrahedron Lett.* **1998**, *39*, 5617.
42. A. Z. Voskoboynikov, I. N. Parshina, A. K. Shestakova, K. P. Butin, I. P. Beletskaya, L. G. Kuz'mina, J. A. K. Howard, Reactivity of lanthanide and yttrium hydrides and hydrocarbyls toward organosilicon hydrides and related compounds, *Organometallics* **1997**, *16*, 4041.
43. A. Z. Voskoboynikov, A. Y. Agarkov, E. A. Chernyshev, I. P. Beletskaya, A. V. Churakov, L. G. Kuz'mina, Synthesis and X-ray crystal structures of *rac*- and *meso*-2,2-propylidene-bis(1-indenyl) zirconium dichlorides, *J. Organomet. Chem.* **1997**, *530*, 75.
44. A. G. Bessmertnykh, K. A. Blinov, Y. K. Grishin, N. A. Donskaya, E. V. Tveritina, N. M. Yur'eva, I. P. Beletskaya, Synthesis of mono-, di-, and trisilyl-substituted alkenes via the hydrosilylation of methylenecyclopropanes catalyzed by Rh(I) complexes, *J. Org. Chem.* **1997**, *62*, 6069.
45. I. P. Beletskaya, A. G. Bessmertnykh, R. Guillard, Palladium-catalyzed synthesis of aryl-substituted polyamine compounds from aryl halides, *Tetrahedron Lett.* **1997**, *38*, 2287.
46. I. P. Beletskaya, Palladium catalyzed C-C and C-heteroatom bond formation reactions, *Pure Appl. Chem.* **1997**, *69*, 471.
47. I. Beletskaya, A. Pelter, Hydroborations catalysed by transition metal complexes, *Tetrahedron* **1997**, *53*, 4957.
48. N. A. Bumagin, L. I. Sukhomlinova, E. V. Luzikova, T. P. Tolstaya, I. P. Beletskaya, Catalytic coupling of terminal acetylenes with iodoarenes and diaryliodonium salts in water, *Tetrahedron Lett.* **1996**, *37*, 897.
49. I. P. Beletskaya, A. Z. Voskoboynikov, E. B. Chuklanova, N. I. Kirillova, A. K. Shestakova, I. N. Parshina, A. I. Gusev, G. K. I. Magomedov, Bimetallic lanthanide complexes with lanthanide-transition metal bonds. Molecular structure of $(C_4H_8O)(C_5H_5)_2Lu-Ru(CO)_2(C_5H_5)$. The use of ^{139}La NMR spectroscopy, *J. Am. Chem. Soc.* **1993**, *115*, 3156.
50. N. A. Bumagin, A. B. Ponomaryov, I. P. Beletskaya, A convenient synthesis of substituted propargyl alcohols and terminal acetylenes, *Synthesis* **1984**, *NO. 9*, 728.
51. I. P. Beletskaya, A. V. Cheprakov, Metal Complexes as Catalysts of C-C Bond Formation by Cross-coupling Reactions, in *Comprehensive Coordination Chemistry*, vol. 9 (Ed. M. Ward), Elsevier, Oxford, **2003**.

52. I. P. Beletskaya, A. V. Cheprakov, Aqueous Palladium Catalysis, in *Handbook of Organopalladium Chemistry* (ed. E.I.Negishi), vol. 2, Wiley Int., N.Y., **2002**, p. 2957.
53. I. P. Beletskaya, A. V. Cheprakov, Aqueous organometallic catalysis, In: *Aqueous organic chemistry* (Ed. P.Grieco), Chapman & Hall, London, **1998**