

Finally published on: *J. Catal.* **2019**, *380*, 391-395

Rebuttal to: Polemic against conclusions drawn in “Palladium/iodide catalyzed oxidative carbonylation of aniline to diphenylurea: Effect of ppm amounts of iron salts” (*J. Catal.* **369 (2019) 257-266)**

Fabio Ragaini,* Francesco Ferretti,* Claudia Gatti^a and Doaa R. Ramadan

Dipartimento di Chimica, Università degli Studi di Milano, via C. Golgi 19, 20133 Milano (Italy)

^a Present address: *Stephenson Institute for Renewable Energy, Department of Chemistry, University of Liverpool, Liverpool (UK)*

Email addresses: fabio.ragaini@unimi.it, francesco.ferretti@unimi.it

Abstract

In a recent paper on this Journal (*J. Catal.* **369** (2019) 257-266), we reported on the effect of ppm amounts of iron compounds on the palladium/iodide (and even palladium/chloride) catalytic system for the oxidative carbonylation of aniline to diphenylurea. In a "Polemic" against our work, Gabriele and coworkers argued against some of the conclusions we had drawn and even against our experimental practice. Here, we reply in detail to this polemic. Some of the content of the latter is due to some misunderstanding, whereas some assertions are untenable and in contrast with experimental data.

Keywords: oxidative carbonylation – aromatic amine – diphenylurea – palladium – iodide – iron chloride – dimethoxyethane – carbon monoxide

1. Discussion

The "Polemic" by Gabriele and coworkers to our paper [1] contains some misunderstanding and some untenable assertions. We are surprised by the harsh criticism by Gabriele and coworkers since in our paper we refrained from criticizing earlier works, avoiding entering a discussion on Gabriele's works, but only stuck to the new experimental findings.

In our paper, we did not say that the previous experimental results are incorrect. Indeed, Gabriele's results were reproducible once the reaction was performed directly in a stainless steel autoclave. We do not have a Hastelloy autoclave to reproduce results obtained in such a kind of apparatus, but we have no reason to say that the experimental results reported by others are incorrect and we did not say that. We also never stated that oxidation of palladium(0) species by I_2/I^- is not occurring. There

is enough experimental evidence, for example in a work by Yamamoto we cited [2], to make this point undisputable. What we clearly said in the paper is that this is only one of the roles of iodide/iodine and that another role, etching of steel autoclaves, contributes more to the final outcome of the reaction. Concerning the palladium reoxidation, what we wrote in our paper is that: "Direct oxidation of palladium(0) complexes by oxygen is possible, but is generally too slow to avoid precipitation of metallic palladium under carbonylation conditions. Indeed a co-catalyst, which acts as an oxidation catalyst for palladium, must be present and the I₂+KI system is able to play this role by oxidizing even metallic palladium and being quickly reoxidized by dioxygen [and we cited the reference mentioned by Gabriele]." To us, and we hope to most of the readers, it is clear that we are stating that the "I₂+KI" is the "promoter" for the oxidation of palladium(0) by dioxygen. The reaction between palladium(0) and dioxygen is slow because both palladium(0) and (II) complexes are singlet state molecules, whereas dioxygen has a triplet state. This is what also applies to most reactions involving O₂. However, the reaction with dioxygen is much faster in the case of heavy atoms like iodine because for these elements an enhanced spin-orbit coupling occurs (named "heavy atom effect") which lowers the energy of the spin-forbidden transition state. Thus, the full paragraph 3 of the "Polemic" is due to a misunderstanding. What we evidenced in our work is that iron can also play the role of a "promoter" in the palladium reoxidation. This is not surprising, because, for reasons different from those for which iodide is effective, oxidation of Fe(II) to Fe(III) by dioxygen is also very fast. The surprising finding is that ppm amounts of iron are sufficient to promote the reoxidation. A similar effect by large amounts of iron salt would have come to no surprise.

In order to clear another possible source of misunderstanding, we want to stress that all of the conclusions we draw in our paper on the relevance of iron in promoting the reoxidation of palladium and thus accelerating the reaction rate are valid exclusively for the oxidative carbonylation reaction of amines to ureas. Gabriele and coworkers employed the PdI₂+KI system to catalyze a number of other more complex reactions affording different N-heterocycles. For some reviews see [3-5]. For most of these reactions, it is likely that palladium reoxidation would be fast compared to at least some other steps of the reaction. Moreover, interaction of other functional groups in the organic substrates and intermediates to palladium will alter the speciation of palladium with respect to that obtained during the synthesis of ureas. Thus, even if small amounts of iron may still be present, we have no indication that these would play a role in the outcome of these reactions and the direct oxidation of zerovalent palladium intermediates by I₂ may indeed be the only or at least the main reaction involved in the regeneration of the catalyst. We never claimed a relevant role of iron in all reactions involving the use of Pd compounds + KI or I₂ and dioxygen.

Coming back to the presence of iron in solution, it should be stressed that performing catalytic reactions directly in a stainless steel autoclave should be accompanied by many periodic and cross tests. It has been known in the industry for decades that the use of noble metal compounds in contact with stainless steel eventually results in the deposition of the noble metals on the walls of the autoclave and the dissolution of less noble metal metals in solution. This is what can be expected by the simple examination of the redox potentials of the metals contained in any kind of steel and even Hastelloy. The phenomenon is known to cause the autoclaves to become "catalytically active" themselves, leading to irreproducible results. This is hardly written in papers or patents for obvious reasons, but is well established. In the system here investigated, as well as under the conditions employed by Gabriele and others, I₂ is also formed, which is very aggressive with respect to any metal or alloy. Part of the formed iodine can react with palladium(0) but when one considers that there is a ppm concentration of palladium in the system, whereas there is an enormously larger amount of more easily oxidizable metals on the autoclave walls, it immediately emerges that it is extremely

unlikely that corrosion of the latter is not occurring. Gabriele asserts that we did not provide enough evidence that iron is etched from the walls and even distorts some of our statements (we said that the "quantitative" measure of the formed iron is affected by an error due to incomplete mineralization of the aromatic compounds even under the harsher conditions reported in the literature, not that we could not detect iron in solution). However, we believe that it would rather be an extraordinary observation to find that no other metals apart from palladium are present in solution after a reaction performed directly in a stainless steel autoclave and under oxidative conditions.

Gabriele and coworkers requested us to use XPS to identify the oxidation state of iron at the end of the reaction. However, XPS is a solid state/high vacuum technique that cannot be employed to identify trace (ppm) amounts of metals. It works on small absolute amounts of the investigated element, but concentrated in a small volume. As far as we are aware, no analytical technique is available that may give an answer to this question. Moreover, simply discharging the CO/air pressure from the autoclave may alter the speciation of the metal compounds present, a problem well known to those used to study the reaction mechanism of reactions occurring under pressure. We do not think it is necessary to comment further on this.

The point is not whether iron or other metals from the autoclave walls are present in solution or not: they are surely all present. Moreover, iron is a ubiquitous element and at least ppb amounts of it are present in most laboratory reagents. Saying that we should have observed "no iron" in the control experiments does not correspond to any realistic experimental result. The point is whether the presence of other metals is relevant to the catalytic reaction or not. In Table 1 of our paper [1], we only mentioned a few comparative experiments to make the point clear, but actually we tried for months to reproduce Gabriele's results by working in different types of glass liners (completely open or having a glass-wool filled cap that allows gases to exchange) and also employing aliphatic amines, but we always failed. Since gas diffusion may be a problem in some settings, we finally resorted to having one of our autoclaves lined with Teflon by a specialized company and it was only after a further failure that we tested the reaction directly in the stainless steel autoclave and immediately got much better results. The results in Table 1 should alone be sufficient to unequivocally clarify that the walls of the autoclave have a role in the reaction.

Another general point to be clarified is the aim/relevance of our work. Our "aim" is to develop a catalytic system that may be better suited to be applied on an industrial scale than present ones, none of which is applied. We never declared that we succeeded in doing so in this work. However, we clarified which is the starting point and this is a "relevant" observation that deserves to be communicated to the scientific community. Any industry wishing to apply a chemical technology cannot prevent from having information on the active catalytic system, or the reaction may become irreproducible upon scale-up.

Gabriele insists very much on our presumed failure to compare our results with those reported in two of his previous works where the reaction was performed respectively in supercritical CO₂ [6] and an ionic liquid (1-butyl-3-methylimidazolium tetrafluoroborate)[7]. We would have preferred to avoid commenting these works, but we cannot avoid doing so now.

A comment that applies to both systems is that the reactions were always performed in stainless steel reactors, so the same problem of iron (and other metals) leaching is present even in these cases. Additionally, the following more specific comments should be made:

- 1) Concerning the reactions in supercritical CO₂, the authors found that the reactions are actually slower than those conducted in the neat amine as solvent for all aliphatic amines and proceeds

at comparable rates with respect to those run in neat amine for all aromatic amines that are liquid at room temperature, with the exception of aniline (the reason for which it should constitute an exception was not discussed). Even if a high TON was reached with this latter substrate, a very long reaction time (72 h) was required and the turnover frequency was 604/h (with respect to produced diphenylurea), compared to a 1780/h value obtained by us. For safety reasons we have problems in leaving reactions under pressure unattended for prolonged periods of time and we could not test the use of very high catalytic ratios, but this does not mean that our system deactivates after having consumed 5000 equivalents of aniline. Use of the neat amine has advantages and disadvantages. It is clearly beneficial from a kinetic point of view because of the higher concentration of at least one reactant, but it is not obvious that it may be convenient during the workup, especially when the final urea is a solid, as for diphenylurea.

- 2) Concerning the ionic liquid system, one should first note that 1-butyl-3-methylimidazolium tetrafluoroborate has such a high cost compared to a standard solvent, that it is highly questionable whether it will ever be applicable to a large scale industrial process. Moreover, the catalytic ratio is only 100:1 aniline/Pd in the cited work, compared to 1000:1 in the work we used as a reference [8] and up to or 5000:1 in ours. Catalyst deactivation is far from negligible, despite what the authors claim (yield in diphenylurea drops from 94 to 75 at the 6th reuse, that is after just 600 turnovers, less than 300 if referred to the formation of diphenylurea), which makes this system much less active than that employing traditional solvents, also considering that a longer reaction time was employed. Moreover, recovery of the produced urea required a series of extractions with CH₂Cl₂ and diethyl ether (3 mL of CH₂Cl₂ and 30 ml of diethyl ether were employed in the work-up of 2.2 mL of ionic liquid to recover 110 mg of diphenylurea) and cooling twice the solution at 0 °C for 15 h, which completely cancel out any "green" benefit in using a solvent with no vapor pressure for the reaction.

Taking into account what said above, we think that going back to the use of standard solvents is still a good option in view of a development strategy.

Concerning the problem of the presence of Fe(CO)₅ in steel tanks, there is no need to provide any experimental evidence for it as it is a well-known problem, which has been widely described in the literature. Just to cite a few references, an average Fe(CO)₅ contamination of 869 ppb (v/v) has been reported for CO stored in steel tanks, compared to 0.622 ppb when the same gas was stored in aluminum alloy tanks [9]. However, the Fe(CO)₅ amount is also known to vary as a function of storing time and temperature, so that higher and fluctuating values have also been reported [10]. The problem has been well known in the industry before. A patent to Eastman Kodak entitled "Removal of iron pentacarbonyl from gaseous streams containing carbon monoxide" [11] clearly shows that this problem was seriously considered. Our CO provider do not longer use steel tanks for this gas and we cannot make any further experiment to directly measure the contained Fe(CO)₅ amount. However, about ten years ago, when CO steel tanks were still employed, we performed a palladium/phenanthroline catalyzed carbonylation reaction of nitrobenzene [12] in the presence of an equimolar amount of aniline, that is under more basic conditions than usual, and with H₃PO₄ as a cocatalyst. The reaction was run in an autoclave of the same dimensions of that employed in this study, but working in a glass liner having a glass-wool filled cap that allows CO to enter the liner, but prevents solvent vapors to exit. A CO pressure of 60 bar was applied, which is of the same order of magnitude of that applied under most of the oxidative carbonylation reactions reported in the literature. A red precipitate was formed at the end of the reaction, that was found, by single crystal

X-ray diffraction, to be $[\text{Fe}(\text{Phen})_3][\text{HPO}_4]$ [13]. The amount of precipitated iron, $3.9 \cdot 10^{-2}$ mmol, corresponds to 20 times the palladium we employed in our work on the oxidative carbonylation of aniline. The origin of the formed iron could only be $\text{Fe}(\text{CO})_5$ in the CO gas and the precipitated complex clearly underestimate its total amount. Thus, plenty of iron with respect to what needed to promote the oxidative carbonylation reaction (the Fe/Pd mol ratio varies in the range 1-100 in our work) is available when CO from steel tanks is employed. We would like to stress that we did not ignore this fact and tested the effect of adding increasing amounts of $\text{Fe}(\text{CO})_5$ to the catalytic system. However, no measurable effect was found for the reductive carbonylation reaction of nitroarenes, further confirming that iron plays a role in allowing palladium oxidation by dioxygen, a problem that is not present when the oxidant is a nitroarene.

The presence of iron as a contaminant can explain several results previously reported in the literature. Gabriele and coworkers declare that their reactions could be reproduced in a Hastelloy autoclave and cite a work by Chaudhari and coworkers in support [14]. First of all, it should be clear that when speaking of catalytic reactions, "reproducible" does not mean that the same products are formed, but that exactly the same reaction rate is observed. A complete reproducibility between different laboratories is very rarely achievable when reactions run under pressure in an autoclave are performed because the shape of the autoclave itself and the kind/rate of stirring and heating can have a strong influence on the reaction. That said, the cited work describes a reaction run in methanol as solvent and affording a mixture of carbamate and urea, so that the results cannot be directly compared with those here discussed or those obtained by Gabriele. Moreover, a closer examination of the data reported in that paper leads support to our idea that iron from gas tanks can play an important role. Indeed the rate of the reaction run employing $\text{PdI}_2 + \text{NaI}$ as catalyst was only twice that of the reaction run employing $[\text{PdPy}_2\text{Cl}_2]$ in the absence of any iodide (entries 7 and 8 in Table 1 of the cited paper). The latter catalyst should show no activity at all if oxidation by $\text{I}_2 + \text{HI}$ were the only way of reactivating palladium(0) at the end of each catalytic cycle, since chloride is surely not transformed into chlorine under the reaction conditions. On the other hand, the results are perfectly explained by our hypotheses that iron is present and plays an active role.

Gabriele also casts doubts on our procedure of adding PdI_2 to the catalytic reaction as its aniline solution, employed to avoid large errors in weighing small amounts of catalyst (even less than 1 mg). He says: "from our experience, PdI_2 is insoluble in the absence of halides or other solubilizing ligands (aniline is a too weak ligand to ensure complete solubilization), so the real amount of PdI_2 present in solution can be unpredictable if it is added practically in suspension." We do not know which experience Gabriele and coworkers have in trying to solubilize PdI_2 in aniline, but we obviously considered the problem and worked properly. The solubilization of PdI_2 in aniline is not simply a dissolution process, but is a depolymerization reaction (PdI_2 is a polymer with iodide anions doubly bridging palladium ions) affording $[\text{PdI}_2(\text{PhNH}_2)_2]$ (which is a known, albeit scarcely characterized compound [15]. The corresponding chloride and bromide analogues have been reported many times). Whereas dissolution processes are usually fast, the depolymerization is a slow process, whose rate also depends on the average length of the polymeric chains. Thus, dissolution may proceed at different rates depending on the exact conditions under which PdI_2 was prepared. In our experience, when working at the highest 5000:1 $\text{PhNH}_2/\text{PdI}_2$ ratio, the dissolution of PdI_2 occurred even at RT to give a homogeneous solution. The process can take many hours under magnetic stirring, but can be speeded-up by sonication in an ultrasound cleaning bath. At the lowest 1000:1 $\text{PhNH}_2/\text{PdI}_2$ ratio, the dissolution of palladium was indeed not complete at RT, but heating the suspension at around 70-75 °C afforded a clear orange solution. The obtained solution is stable for around one hour after having been cooled to RT and only after such a time it slowly starts to become opalescent. What we always

did when working at this catalytic ratio was to heat the Schlenk flask (under dinitrogen) containing the PhNH₂/PdI₂ suspension until it had become a solution, cooled it and withdrawn the solution at RT before reprecipitation started. We did not specify in the experimental section that we had to heat to get a solution because it seemed to us that heating to favor dissolution is such a common procedure in the laboratory not to need a special note. Moreover, even at the highest palladium concentrations we employed, reprecipitation after cooling afforded a yellow product and not the original black PdI₂. Chaudhari also reported dissolution of PdI₂ in hot aniline + benzene to give yellow [PdI₂(PhNH₂)₂] in a paper on oxidative carbonylation of aniline [16] that has been cited by Gabriele [8].

Concerning our presumed failure to consider adsorption of iodine on Teflon as a reason for our inability to reproduce previous results working in a Teflon-lined autoclave, we can note two things. The first is that such an adsorption, if relevant, would have caused irreproducible reactions and we would have realized that a problem existed. The second, even more conclusive, is that no such adsorption takes place. We have reproduced the "adsorption" of iodine on Teflon as described in the paper cited by Gabriele [17] and can prove that, at least in the absence of a microwave treatment, no adsorption of iodine on either a Teflon strip or a Teflon-coated stirring bar occurs. The observed coloring is only due to a physical deposition of I₂ on the Teflon surface upon evaporation of the solvent. The interested reader can find a more detailed description of the experiments we did and the pictures of the obtained results in the Supplementary Material to this letter. We are not aware of any other paper in which adsorption of iodine on Teflon has been reported.

Concerning "isolated" or "HPLC" yields, it is clear that at an industrial level the products would not be separated by column chromatography or by the solvent-consuming and energy-intensive procedure reported in ref [7]. Doing that in a work like ours does not make much sense.

We regret that Gabriele at least partly misinterpreted our sentence on the intermediate formation of isocyanates. We did not want to say that isocyanates are not intermediates in the formation of ureas and we think this should be clear from what we wrote. We are fully convinced this is indeed the case and wrote it even in several research papers and reviews [18, 19]. Our warning was only related to the statement that observing the formation of isocyanates by GC is a sufficient proof for their presence in solution. At least for aromatic isocyanates, this is surely not the case. This sentence had been introduced to justify why we observed phenyl isocyanate in the GC-MS spectrum of a reaction mixture, but not when we performed other analytical measurements, and why we did not include it among the reaction products. It was not intended as a criticism to previous papers.

Concerning the byproducts we observed, the statement that they were not formed under the conditions previously employed by Gabriele is meaningless. Nowhere in previous papers (both by Gabriele and by others, with the notable exception of ref. [20]) it is said that a detailed investigation of the byproducts of the reaction had been undertaken and very few reactions are free from byproducts. Clearly methyl- and 2-methoxyethyl-carbamates will not be formed if a solvent different from dimethoxyethane is employed, but a statement such as "no byproducts were formed in our process" should sound odd to any chemist. The selectivity of the reaction is far from 100 % in many cases and some byproducts must be present. It is possible that the presence of iron indirectly plays a role in their formation, but iron is present under most, if not all, of the previously investigated conditions.

Gabriele also accuses us not to provide any mechanistic evidence for the role of iron in the catalysis system and to only provide a speculative statement on the involvement of dinuclear Pd-Fe complexes. Unfortunately, this is all that can be said. Identifying the true active species under catalytic conditions is a difficult task even for reactions running in a flask and becomes extremely difficult for reactions

under pressure. This is also the reason why no information is available on the active species even for the system that is claimed to work with just PdI₂+KI or K₂PdI₄ as catalyst. The only mechanistic studies available on palladium-catalyzed oxidative carbonylation of amines [2, 21, 22] were all conducted employing phosphines as ligands, which clearly alter the speciation of the metal in solution. A number of mononuclear and polynuclear palladium species with carbonyl groups and halide ligands are known [23] and it not obvious at all which of them are involved in the catalytic cycle. The proposal that an active role may be played by a palladium-iron species with halide bridges originates from the observation that the concentration of all the three components is very low under the conditions of at least some of the reactions and it would be difficult to justify from a kinetic point of view the high synergistic effect observed if the components were not bound together. We plan to try to study the mechanism of this reaction, but that will surely take years and a complete and undisputable picture is impossible with the current experimental and spectroscopical techniques. By the way, the observation that palladium sponge can be oxidized by iodine, present in high concentration [24], is not at all a proof that the same reaction occurs under much more dilute conditions and that, in case it occurs, it is kinetically relevant to the catalytic reaction.

Concerning "iodide" toxicity, we admit that there was a typing mistake: we meant "iodine", using this term to indicate the element and thus including not only I₂, but also iodinated organic compounds. Halogenated compounds are always formed when halogens contact organic compounds and organic iodides are toxic [25] and difficult to remove. The toxicity of iron compounds is a more complex topic because we assume relatively large amounts of iron with food every day. It cannot be discussed here. In any case, the use of iodide as promoter with steel autoclaves generates a solution that contains both iodine and iron, so removing one of the two can only be positive.

2. Conclusions

In conclusion, we think we have shown that all the comments by Gabriele et al. either are a misunderstanding or are not confirmed by data. We hope our explanations have been exhaustive.

Acknowledgements

This work was supported by the Italian Ministero dell'Università e della Ricerca (MiUR) (PRIN 20154X9ATP). F.F. thanks the Università degli Studi di Milano for a postdoctoral fellowship.

References.

- [1] F. Ferretti, E. Barraco, C. Gatti, D.R. Ramadan, F. Ragaini, *J. Catal.*, 369 (2019) 257-266. doi: 10.1016/j.jcat.2018.11.010
- [2] K. Hiwatari, Y. Kayaki, K. Okita, T. Ukai, I. Shimizu, A. Yamamoto, *Bull. Chem. Soc. Jpn.*, 77 (2004) 2237-2250.
- [3] B. Gabriele, G. Salerno, M. Costa, G.P. Chiusoli, *Curr. Org. Chem.*, 8 (2004) 919-946.
- [4] B. Gabriele, G. Salerno, M. Costa, *Top. Organomet. Chem.*, 18 (2006) 239-272.
- [5] B. Gabriele, R. Mancuso, G. Salerno, *Eur. J. Org. Chem.*, (2012) 6825-6839. doi: 10.1002/ejoc.201200794

- [6] N. Della Ca, P. Bottarelli, A. Dibenedetto, M. Aresta, B. Gabriele, G. Salerno, M. Costa, *J. Catal.*, 282 (2011) 120-127. doi: 10.1016/j.jcat.2011.06.003
- [7] R. Mancuso, D.S. Raut, N. Della Ca, F. Fini, C. Carfagna, B. Gabriele, *Chemosuschem*, 8 (2015) 2204-2211. doi: 10.1002/cssc.201500343
- [8] B. Gabriele, G. Salerno, R. Mancuso, M. Costa, *J. Org. Chem.*, 69 (2004) 4741-4750.
- [9] C. Wyse, J. Vininski, T. Watanabe, *Solid State Technol.*, 45 (2002) 125-129.
- [10] R.K. Tepe, D. Vassallo, T. Jacksier, R.M. Barnes, *Spectrochim. Acta Part B*, 54 (1999) 1861-1868. doi: 10.1016/s0584-8547(99)00135-4
- [11] T.J. Devon, T. Longview, US Pat. US4608239 (1986), to Eastman Kodak Company (Rochester, NY)
- [12] F. Ragaini, M. Gasperini, S. Cenini, *Adv. Synth. Catal.*, 346 (2004) 63-71.
- [13] F. Ferretti, F. Ragaini, P. Macchi, Unpublishes results.
- [14] S. Kanagasabapathy, S.P. Gupte, R.V. Chaudhari, *Ind. Eng. Chem. Res.*, 33 (1994) 1-6.
- [15] M.A.J. Jungbauer, C. Curran, *Spectrochim. Acta*, 21 (1965) 141-148. doi: 10.1016/0371-1951(65)80020-0
- [16] S.A.R. Mulla, S.P. Gupte, R.V. Chaudhari, *J. Mol. Catal.*, 67 (1991) L7-L10. doi: 10.1016/0304-5102(91)80038-5
- [17] A. Mouradzadegun, M.R. Ganjali, F. Abadast, F. Rahimi, *Monatsh. Chem.*, 149 (2018) 27-32. doi: 10.1007/s00706-017-2061-2
- [18] F. Ragaini, M. Gasperini, S. Cenini, L. Arnera, A. Caselli, P. Macchi, N. Casati, *Chem. Eur. J.*, 15 (2009) 8064-8077.
- [19] F. Ragaini, *Dalton Trans.*, (2009) 6251-6266. doi: 10.1039/b902425p
- [20] A. Krogul, G. Litwinienko, *J. Mol. Catal. A: Chem.*, 407 (2015) 204-211. doi: 10.1016/j.molcata.2015.06.027
- [21] P. Giannoccaro, *J. Organomet. Chem.*, 336 (1987) 271-278.
- [22] P. Giannoccaro, A. Dibenedetto, M. Gargano, E. Quaranta, M. Aresta, *Organometallics*, 27 (2008) 967-975.
- [23] T.A. Stromnova, I.I. Moiseev, *Russ. Chem. Rev.*, 67 (1998) 485-514.
- [24] B. Gabriele, M. Costa, G. Salerno, G.P. Chiusoli, *J. Chem. Soc., Perkin Trans. 1*, (1994) 83-87. doi: 10.1039/p19940000083
- [25] J.W. DePierre, Mammalian toxicity of organic compounds of bromine and iodine, in: *Handbook of Environmental Chemistry*, Springer, 2003, pp. 205-251.