Transition Metal Catalysis for a Sustainable and Prosperous World

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A vast number of items of our need including foods, textile materials for clothing, building materials, fuels, and so on are organic compounds. Until recently, these items have been mostly generated biologically by nature. With time, however, an increasing number of them have been ably supplemented and substituted with "man-made" materials prepared by "organic synthesis". It seems safe to predict that, with steady increase in population, the role of organic synthesis will become increasingly significant in the 21st century and beyond. It is then critically important that organic synthesis be preformed in "green and sustainable" manners. To this end, organic synthesis must be performed (i) in high **y**ields (**Y**), (ii) **e**fficiently (**E**), (iii) **s**electively (**S**), (iv) **e**conomically (**E**), and (v) **s**afely (**S**), namely in **Y(ES)**^{2} manner.

Contrary to a surprisingly popular notion that "organic synthesis without the use of non-organic elements, such as metals and non-metallic heteroatoms, would be greener than those involving their use," this author firmly believes that **the greenness of organic synthesis must be evaluated in a more wholesome or overall manner with consideration of the above-mentioned Y(ES)^2 factors**. If we do so, we will be led to the following guidelines: In addition to just ten or so "organic elements", i.e., H, C, N, O, P, S, F, Cl, Br, I, etc., **consider** all 60 or so "good and usable" metal elements including 20 or so main group metals, 23 *d*-block transition metals, and 14 or so rare-earth metals. They must be used mostly as components of reagents and intermediates. It goes without saying that in those cases where the final organic products do not contain such elements, as in the great majority of cases, their use as catalysts must be actively sought, especially when they are expensive.

It should be noted that, as early as 1912, the vast but predominantly stoichiometric chemistry of organomagnesium compounds extensively developed by V. Grignard as well as hydrogenation of alkenes and others catalyzed by *d*-block transition metals, mostly Ni, developed by P. Sabatier, were recognized with Nobel Prizes given in the area of organometallic chemistry most certainly for the first time. As versatile as the overall Grignard chemistry is, its use for the synthesis of R^1-R^2 from R^1MgX^1 and R^2X^2 via cross-coupling had, until recently, been severely limited without the use of catalysts containing transition metals.

Today, we are blessed with the Pd- or Ni-catalyzed cross-coupling reactions of R^1M, where M is Mg, Zn, B, Al, In, Si, Sn, Cu, Zr, etc. with a wide variety of R^2X.(1) In a large number of cases, these reactions indeed proceed in $Y(ES)^2$ manners. Although further studies are needed, the overall scope of Pd-catalyzed cross-coupling may well surpass eventually that of the entire Grignard reactions.

The highly catalytic nature of Pd complexes is especially noteworthy. Under the Negishi coupling conditions, Pd-catalyst turnover numbers exceeding 10^6 may be readily and routinely observable with the use of bidentate ligands.(2)

This author is inclined to predict that many more *d*-block transition metal-catalyzed green organic synthetic methods will be and will have to be discovered and developed for a sustainable 21st century and beyond.

References

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