Critical Information Summary (CIS) for XiMoPac Users

General Notes:

Mo- and W-based metathesis catalysts **are very sensitive to oxygen and moisture** when they are handled in pure, isolated form or used in solution (use of the unformulated catalyst would require a glovebox). However, **XiMoPacs** (organometallic reagents/catalysts (eg. metathesis catalysts)formulated in paraffin pellets) are stable enough to be handled, weighed or even stored under air for up to eight hours. This new formulation allows the reactions to be accomplished using ordinary Schlenk techniques (air-free technique; https://en.wikipedia.org/wiki/Air-free_technique).

Nevertheless it is important to note that **once a XiMoPac pellet is dissolved,** the active catalyst is liberated from the protecting matrix; **the metathesis complex becomes** just as **sensitive** to oxygen and moisture as it was without the paraffin. Therefore the solvents and reactants as well as the reaction environment have to be kept oxygen and moisture free. **This is absolutely essential for a successful experiment; therefore all manipulation with the solvents, substrates and reagents (once they are pretreated for the reaction) has to be accomplished under inert atmosphere. To fulfill these requirements, the below practice should be observed:**

a) The equipment used in the experiments, especially the glassware, has to be kept in an oven at 120-140 °C for at least 4 hours in order to remove all moisture adsorbed on their surfaces and has to be cooled down under inert atmosphere.
b) Solvents, reagents and the substrates have to be free from **water**, organic **hydroperoxides**, **acidic protons**, **alcohols**, **aldehydes** and **dissolved oxygen**. Sonication and inert gas purge, distillation under inert atmosphere and storage, or percolation through activated molecular sieves or alumina can be applied.
c) To transfer substrates, solvents or stock solutions properly, Schlenk technique is needed.
d) Recommended solvents: toluene, dichloromethane, acetonitrile (water and oxygen free!)
e) Formulated catalyst dissolves in toluene at ambient temperature. However, in certain cases gentle heating to 30-40 °C is required; the required temperature is dependent on the amount of solvent and polarity of the media. When XiMoPacs are applied as neat pellets, the reaction vessel has to be heated to 65 °C to melt the paraffin matrix. *Please note that at elevated temperature and high catalyst loading, migratory isomerization of double bonds can happen.*

Storage of Catalysts:

Unopened catalyst packages (sachets) should be kept in a fridge at 4 °C or below. To prevent condensation of moisture onto the surface of pellets (when packages are taken out of the fridge), they should be allowed to warm to ambient temperature prior to opening.

Reactions step-by-step (a simplified procedure):

In general, reactions are performed in dry Schlenk-tubes/2-neck round bottom flask attached to a vacuum-argon manifold, or at least to an inert gas cylinder equipped with a gas drying unit.

i. Under continuous Ar/N_2-atmosphere, into a pre-dried Schlenk-tube, a piece of XiMoPac pellet is placed before the appropriately pretreated substrate (neat or in stock solution) is added.

ii. The vessel is closed with a silicon oil filled bubbler (or a pre-dried glass stopper, if no gaseous product can form or vacuum is applied) and the reaction is gently heated to the reaction temperature for a given time. *Please note that paraffin has to melt or dissolve to release the active catalyst.*

iii. If the reaction mixture turned immediately green or greenish after dissolution of the catalyst, this signifies either the solvent or the substrate applied is contaminated and the catalyst has decomposed.

iv. At the end, a wet solvent such as acetonitrile or methanol is used to quench the reaction.

Work-up:

The work-up procedure may vary depending on the substrate. When the polarity of the product significantly differs from the paraffin, the separation is usually less problematic. However, when non-polar product is generated, the removal of paraffin can be troublesome. To overcome this problem a simple procedure was elaborated in which the paraffin is precipitated with acetonitrile followed by the filtration of the obtained slurry through a pad of SiO_2.

More detailed description of possible pretreatments, reaction set-ups, and typical metathesis conditions can be found at: www.aspirasci.com/metathesis.