Technology Offer

Air-stable binary Ni(0)–olefin (pre)catalyst

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A family of 16-electron binary Ni(0)-stilbene complexes Ni(^{R}stb)$_3$ as a new class of air-stable Ni(0) (pre)catalysts was developed.

Background

The use of Ni(0) as catalyst in organic synthesis has expanded over the past decade as a sustainable alternative to more noble metals such as palladium.
Ni(0) catalysts are used for instance in industrial world-scale processes like SHOP (Shell Higher Olefin Process), which enables the oligomerization of ethylene to obtain higher molecular weight α-olefins and in the isomerization of 2-methyl-3-butenenitrile (2M3BM) to 3-pentenenitrile (3PN) in the production of Nylon.
Currently, the most frequently employed source of Ni(0) is the precatalyst Ni(COD)$_2$ which is mixed with other ligands, such as phosphines, amines or N-heterocyclic carbenes, to replace cyclooctadiene forming the active catalyst. However, Ni(COD)$_2$ suffers from great instability and fast decomposition when exposed to air, requiring handling under inert atmosphere using gloveboxes or Schlenk techniques. Moreover Ni(COD)$_2$ is temperature sensitive and will eventually decompose if not stored at low temperature (<20^{o}C). Consequently, the development of a simple, scalable and modular Ni(0) source which is stable to air and room temperature and retains the reactivity demonstrated by Ni(COD)$_2$ is highly desirable.

Technology

Here is introduced a family of 16-electron binary Ni(0)-stilbene complexes Ni(^{R}stb)$_3$ (with R describing the substitution pattern of the aryl group in the stilbene ligand, Fig. 1) as a new class of Ni(0) precatalysts that overcome the limitations described above. In term of stability and catalytic activity, Ni($^{4\text{-}tBu}$stb)$_3$ was identified as superior to the other members of the family and it proved to be stable at room temperature and at open air for approximately 1 month.

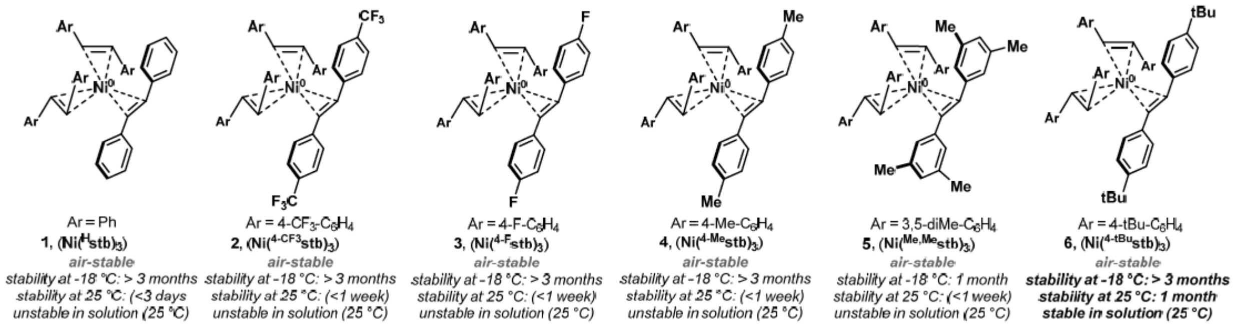

Fig. 1: Overview Ni(0)-stilbene catalyst family

The Ni(0)-stilbene complexes can be synthesized via a simple protocol that starts from cheap and available Ni(acac)$_2$ and AlEt$_3$ as a reducing agent in the presence of substituted stilbene (Fig. 2).

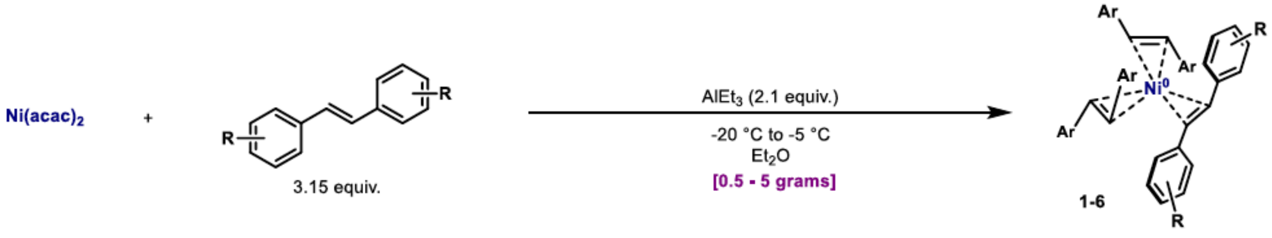

Fig.2: Ni(0)-stilbene catalysts synthesis process

Ni($^{4\text{-}tBu}$stb)$_3$ in particular was obtained in multi gram quantities (100 g) and in high yield .

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The performance of these complexes in catalysis is exemplified by the success of Ni($^{4\text{-CF3}}$stb)$_3$ in catalyzing *>15 relevant transformations*, including Suzuki, Heck and Negishi cross-couplings, previously restricted to the use of Ni(COD)$_2$.
The more robust catalyst Ni($^{4\text{-tBu}}$stb)$_3$ was demonstrated to excel in industrially relevant settings, thus providing an air and temperature stable alternative to the currently available Ni(0) catalysts. For instance the isomerization of 2M3BM to 3PN mentioned earlier, which is crucial in the efficient synthesis of adiponitrile from butadiene, affords comparable level of reactivity towards the product with respect to the reaction catalyzed by Ni(COD)$_2$. Similarly, the use of Ni($^{4\text{-tBu}}$stb)$_3$ in the SHOP process, also mentioned earlier, successfully promotes the formation of a mixture of □-olefins in high efficiency and without pre-catalyst isolation. The Buchwald-Hartwig amination reaction, used in the industrial preparation of numerous pharmaceuticals, proved to give yields comparable to those given by the Ni(COD)$_2$-catalyzed reaction. Similarly, the alkyl-alkyl cross coupling developed by Kambe between alkyl bromides and alkyl Grignard reagents, the conversion of vinyl triflates to vinyl halides developed by Reisman and the amide activation protocol developed by Garg were all carried out successfully with Ni($^{4\text{-tBu}}$stb)$_3$.

Summary

The more robust of the 16-electron binary Ni(0)-stilbene family, Ni($^{4\text{-tBu}}$stb)$_3$:

- Is stable at room temperature and can be stored opened to air in the bench for long periods of time (ca. 1 month);
- Has high stability in solution with various solvents;
- Is catalytically competent in organic transformations and industrial relevant transformations typically catalyzed by Ni(COD)$_2$ pre-catalysts;
- Can be prepared in multi-gram quantities with high yields.

Ni($^{4\text{-tBu}}$stb)$_3$ catalyst is available for R&D purposes via STREM (Catalog Number 28-0070), other catalyst family members will be made available soon.

(Field)Exclusive licenses for large scale applications (>1 kg catalyst per costumer per year) are still available.

Literature

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Lukas Nattmann, Josep Cornella: "Second Generation of Air-stable Ni(0)-stilbene Binary Complexes: Identification of a Superior Ni(0) Source for Catalysis" *Organometallics* asaps, (2020), doi: 10.1021/acs.organomet.0c00485

Patent Information

EP priority patent application filed in July 2019.
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