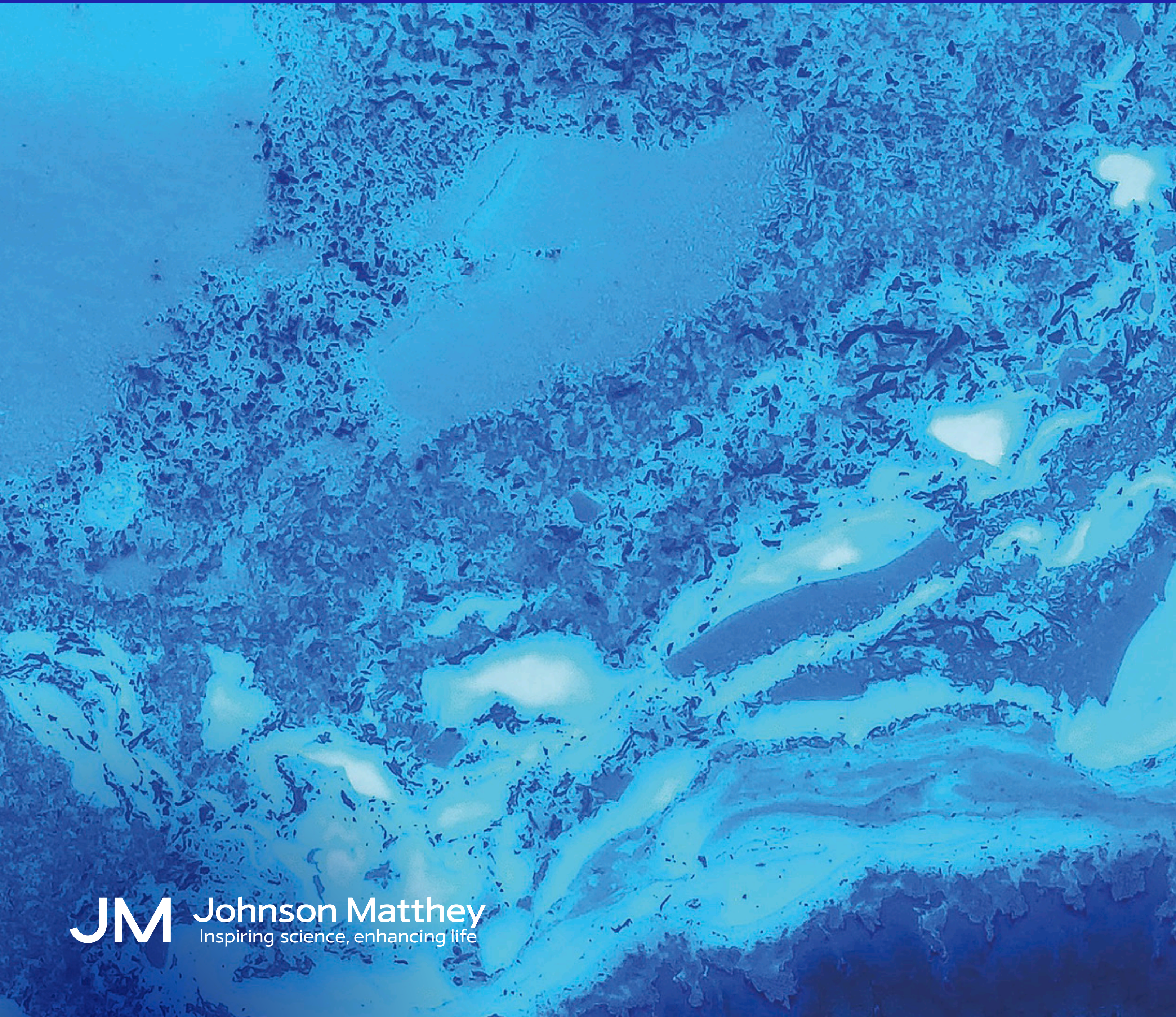
Technical Brief

Nickel complexes for cross-coupling



Johnson Matthey
Inspiring science, enhancing life

Leveraging novel chemistries to enhance the cross-coupling toolbox

In recent years, the advancement of base metal catalysis, particularly nickel, in various industrial applications has received significant attention in scientific literature.[1] A major benefit of homogeneous nickel catalysis is that it enables the use of novel chemistries and substrates in synthetic applications that can't be achieved with stoichiometric reagents or other catalytic technologies. For example, nickel catalysis uniquely unlocks photoredox, energy transfer, and electrochemical methodologies to further enhance the synthetic toolbox available to both industrial and academic chemists.

In cross-coupling applications, homogeneous nickel-phosphine or nickel-bipyridyl catalyst systems have been shown to activate an orthogonal array of electrophilic substrates for coupling when compared to copper or palladium-based catalyst systems. Johnson Matthey (JM) is now offering a selection of catalysts and precursors to support these developing applications of nickel homogeneous catalysis.

In situ catalyst precursors

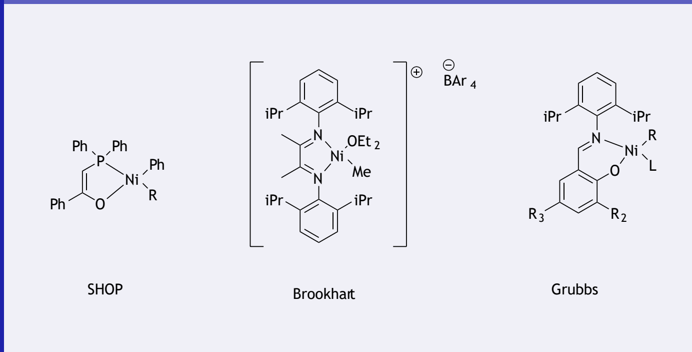
$Ni(COD)_2$ (Ni-129)

$Ni(COD)_2$ is a precursor for *in situ* catalyst generation that has been used in a wide variety of applications since its introduction in 1960. Due to its versatile solubility properties and high ligand lability, $Ni(COD)_2$ has seen extensive use in the polymer industry as both a catalyst precursor and co-catalyst.[2]

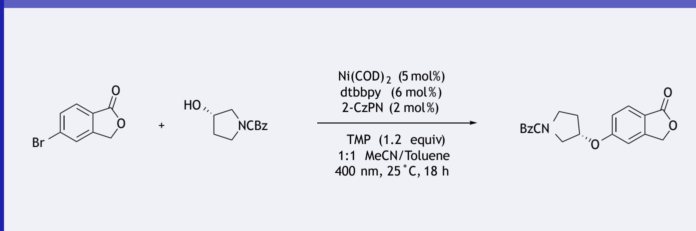
More recently, $Ni(COD)_2$ has been shown to be an effective catalyst precursor for a variety of novel applications:

- Catellani reaction[3]
- Kumada sp^3-sp^3 couplings of isotopically labelled nucleophiles[4]
- Atroposelective C-H alkylation of benzimidazoles[5]
- Energy transfer catalysis for sp^2-sp^3 bond construction with novel TADF materials[6]
- Catalytic degradation of BPA epoxy resins[7]
- Deoxygenative functionalisation of phenol derivatives[8]

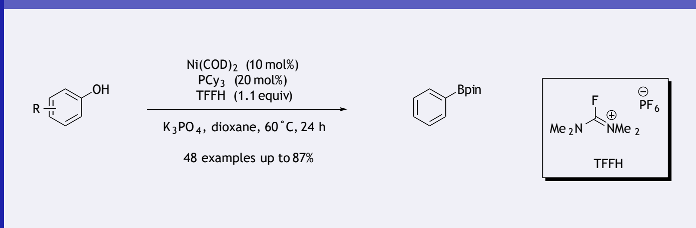
Ethylene oligimerization catalysts using $Ni(COD)_2$ as a pre-cursor and/or co-catalyst



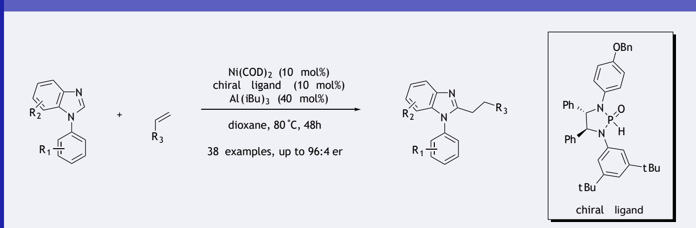
a) Photoredox/Ni-catalysed C - O coupling



b) Ni-catalysed deoxygenative borylation



c) Atroposelective alkylation of benzimidazole derivatives



Selected recent catalytic transformations using $Ni(COD)_2$ as the catalyst pre-cursor.

In situ catalyst precursors

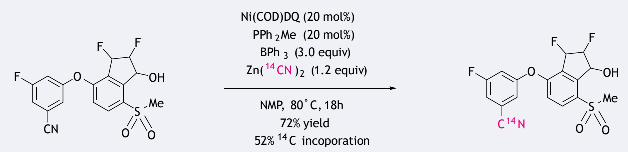
Ni(COD)(DQ) (Ni-131)

While $Ni(COD)_2$ is a versatile option, there are challenges in its use in industrial processes due to its air sensitivity. The development of a general, air-stable Ni(0) precursor has been highly sought after in recent years. Ni(COD)(DQ) is an air and shelf-stable precursor for *in situ* catalyst generation introduced by the Engle lab in collaboration with an industrial partner.[9]

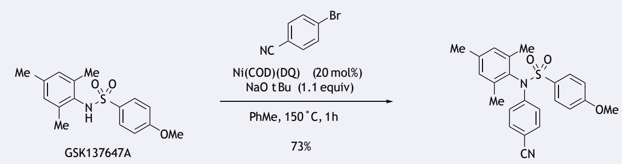
Since its introduction to the chemical industry, Ni-131 has seen various applications as a catalyst precursor:

- Carbon isotope exchange of aryl nitriles[10]
- Preparation of polythiophene materials[11]
- Cross-coupling of sulfonamides with aryl bromides[12]

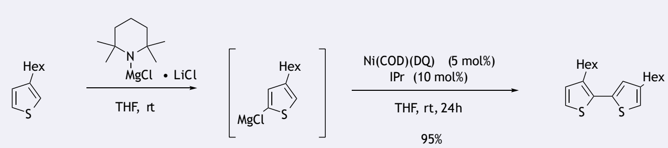
a) Ni-catalysed isotope exchange of aryl nitriles



b) Ni-catalysed cross-coupling of aryl sulfonamides



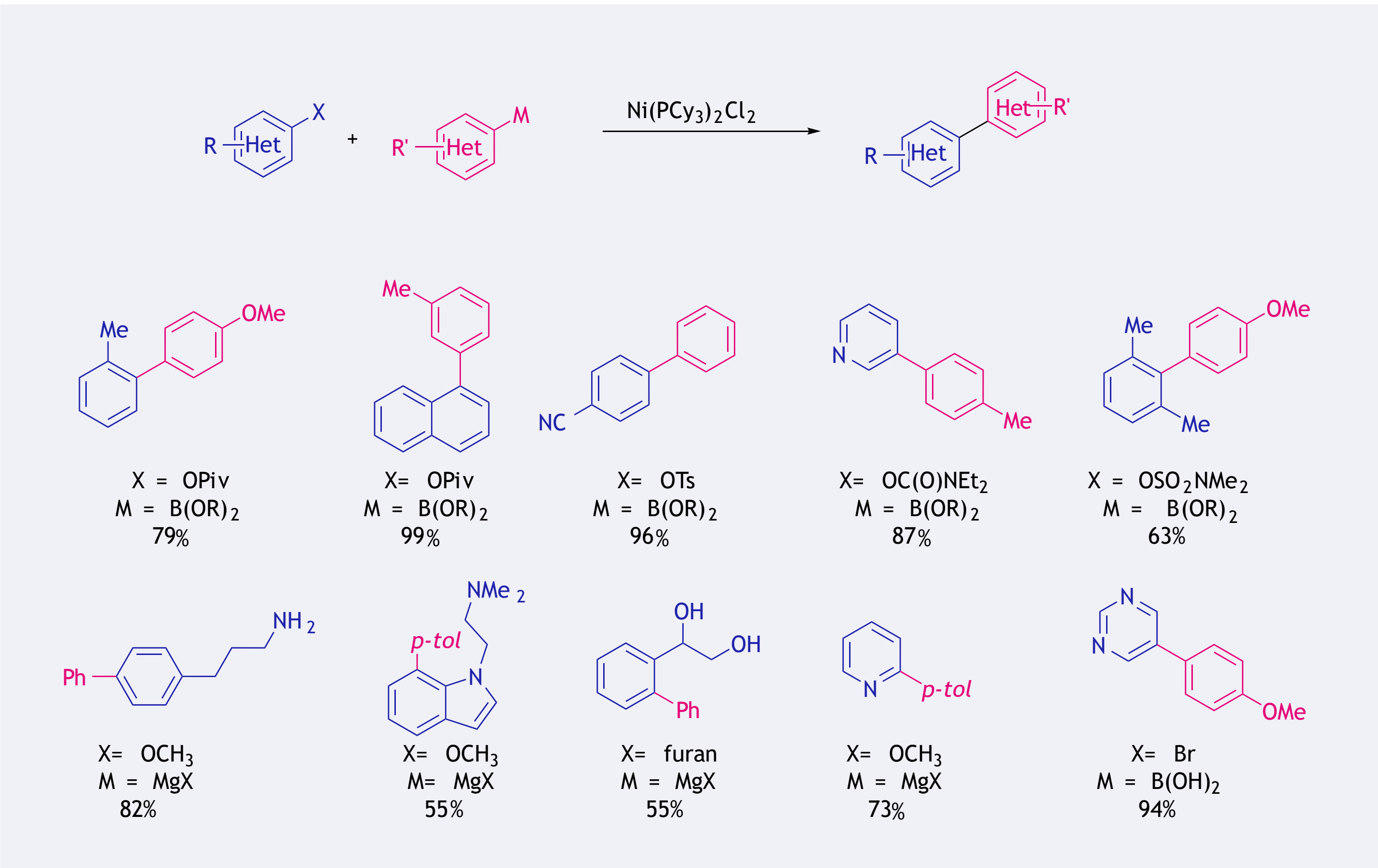
c) Ni-catalysed Kumada-type CTP to prepare polythiphene semi-conductors



Selected applications

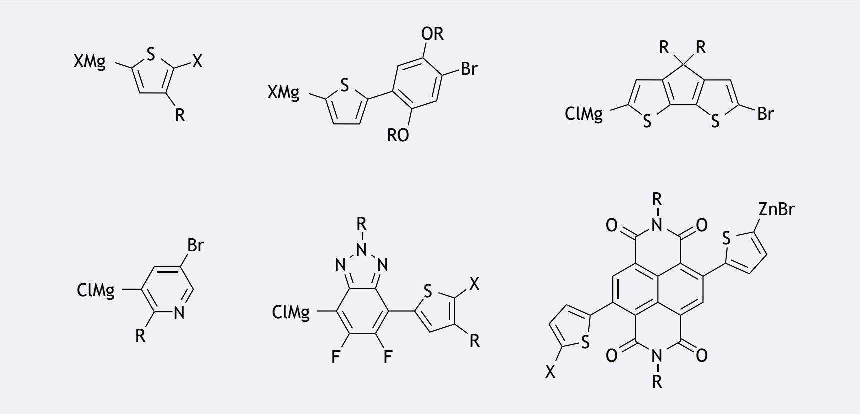
Pre-formed air-stable nickel(II) complexes

Air-stable nickel(II) complexes have also gained significant attention for a variety of novel catalysis applications such as photoredox, cross-electrophile, and electrochemical coupling reactions. In addition, nickel phosphine complexes have expanded the scope of viable electrophilic coupling partners within cross-coupling methodologies due to the inherent reactivity and selectivity differences between nickel and palladium organometallic complexes. Over the past two decades $NiCl_2(PCy_3)_2$ (Ni-114) has proven to be an effective catalyst for cross-couplings utilising aryl pivalates, tosylates, carbamates, ethers, amides, and other non-traditional electrophiles.[13]



Representative cross-coupling applications and electrophile scope for $Ni(PCy_3)Cl_2$

Within the performance materials industry, Ni(dppe)Cl_2 (Ni-103) and Ni(dppp)Cl_2 (Ni-126) are privileged catalyst systems for preparing poly-3-hexylthiophene semiconductive polymers via a catalyst-transfer polymerisation (CTP) chain growth mechanism. The resulting polymers can be produced with excellent control over the polymer molecular weights, high regioregularities and narrow dispersity.[14]



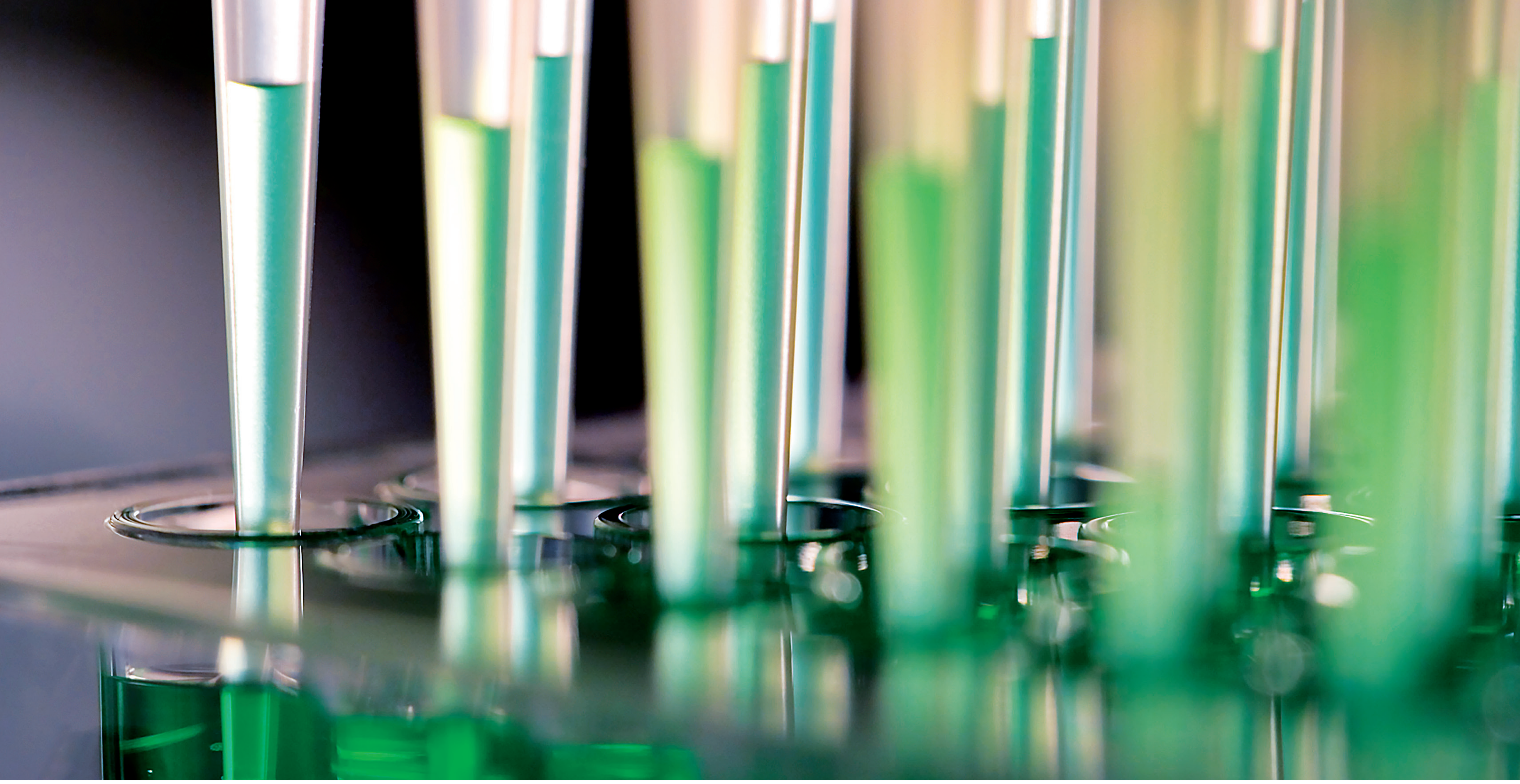
Representative substrates for Ni-catalysed catalyst transfer-polycondensation (CTP) using Ni(dppe)Cl_2 and Ni(dppp)Cl_2

Advancements and looking ahead

While Ni homogeneous catalysts possess a bright future for industrial applications, several challenges associated with base metal catalysis still need to be overcome. Many of the methodologies described above require high catalyst loadings or require expensive specialty ligands/additives. From a sustainability perspective, nickel does not have a well-established global refining loop like platinum group metals and the regulatory implications for the use of nickel catalysts in human health applications are not fully understood. Despite these challenges, base metal catalysis will continue to grow and play an important role in the future of the life science and fine chemical industries.

Catalogue ID	Nickel complex	Mol Wt	% Metal	CAS Number
Ni-103	**$NiCl_2$(dppe)**	528.02	11.12	14647-23-5
Ni-107	**$NiCl_2$(dppf)**	683.98	8.58	67292-34-6
Ni-114	**$NiCl_2(PCy_3)_2$**	690.46	8.5	19999-87-2
Ni-126	**$NiCl_2$(dppp)**	542.05	10.83	15629-92-2
Ni-127	**$NiCl_2$(dcypf)**	708.18	8.29	917511-89-8
Ni-128	**$NiCl_2(PPh_3)_2$**	654.17	8.97	14264-16-5
Ni-129	**$Ni(COD)_2$**	275.06	21.34	1295-35-8
Ni-131	**Ni(COD)(DQ)**	301.48	17.73	40759-64-6

Ni complexes available from JM



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