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Nucleophilic Carbenes and their Applications in Modern Complex Catalysis

by Anthony J. Arduengo
and Thomas Bannenberg

Chiral Diphosphine Ligands – Steps to Commercialization

by Hans-Ulrich Blaser, Marc Thommen,
Martin Studer, Heinz Steiner,
Felix Spindler and Benoit Pugin

Boronate Esters for
Suzuki Coupling
Ionic Liquids

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BIOGRAPHICAL SKETCHES

Anthony J. Arduengo III, was born in Tampa, Florida, in 1952. He studied chemistry at the Georgia Institute of Technology, receiving his B.S. in 1974 and Ph.D. in 1976. After beginning his career with DuPont, he moved to the University of Illinois – Urbana as a member of the Organic Faculty. From 1984 to 1998, he worked as a member of the research staff at DuPont, advancing to Research Leader/Research Fellow. Professor Arduengo currently holds the Saxon Chair in Organic Chemistry at the University of Alabama – Tuscaloosa and is adjunct professor of chemistry at the Technische Universität Braunschweig, Germany. His research interests include unusual bonding arrangements, main group element chemistry, and various aspects of applied chemistry.

Thomas Bannenberg was born in Berlin, Germany, in 1969. After he studied chemistry at the Freie Universität (FU) Berlin, he received his "Diplom" in Chemistry in 1998. In connection with the appointment of Professor F. E. Hahn to the "Lehrstuhl für Anorganische Chemie" at the Westfälischen Wilhelms-Universität (WWU) Münster he moved with his Ph.D. adviser Dr. Matthias Tamm from Berlin to Münster, receiving his Ph.D. in July 2001. He is currently a visiting Research Scientist in the research group of Professor Arduengo and since December 2001 he is a Feodor-Lynen Fellow of the German Humboldt Foundation.

The Solvias Team:

Back row (left to right): Heinz Steiner, Martin Studer, Robert Häusel, Bernd Geiser, Frederic Naud, Orazio Tagliente, Martin Kesselgruber

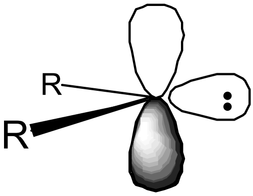
Front row (left to right): Benoit Pugin, Marc Thommen, Felix Spindler, Gianpietro Melone, Heidi Landert, Hans Meier, Romano Grande. Small picture: Hans-Urich Blaser (in Australia when the group picture was taken)

Nucleophilic Carbenes and their Applications in Modern Complex Catalysis

Anthony J. Arduengo and Thomas Bannenberg

Introduction

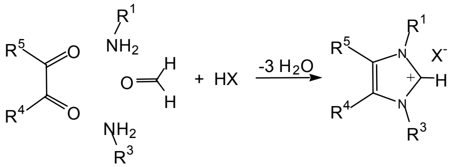
Soon after we reported the first X-ray structure of a stable imidazol-2-ylidene in 1991[1] a renaissance of the rich chemistry of these nucleophilic carbenes began and continues to flourish. Access to the easily-handled, "bottle-able" imidazol-2-ylidene class of carbenes (often referred to as "Arduengo Carbenes")[2] has greatly facilitated their study. Within the last decade numerous variations of the basic imidazol-2-ylidene structure have appeared and have found application in modern catalysis as carbene-metal complexes .[3]



The electronic structure of the carbene center of an imidazol-2-ylidene can be simplified to a strongly bent singlet carbene model ($^1A_1$) in which the carbene carbon is approximately sp^2 hybridized. The two substituents and a lone pair of electrons occupy the three sp^2-hydrid orbitals and a formally vacant p-orbital remains at carbon. The lone pair of electrons on carbon behaves chemically similar to the lone pair of electrons on phosphorous in phosphines. Guided by this simple analogy, organometallic chemists have successfully replaced the ubiquitous phosphine ligand with the imidazol-2-ylidene ligand in a large number of organometallic complexes. However, the real strength and versatility of the new imidazolylidene ligand rests not in its similarity with phosphines, but rather in how it differs from the more conventional phoshines and in the new structural and electronic features it can introduce. In this latter respect imidazol-2-ylidenes have their own special features to offer over phosphines. The coordinating lone pair of electrons in an imidazol-2-ylidene is "harder" and more basic than a phosphine lone pair. The formally vacant p-orbital at the carbene center has the potential to function as a weak π-acceptor, but has different directional character than P-X σ^*-bonds (or d-orbitals) on a phosphine. The planar imidazol-2-ylidenes also present a steric profile that is greatly different from that of phosphines.

The Beginning of a Renaissance

Our entry at the DuPont company into the field of imidazol-2-ylidene and stable carbene chemistry is an interesting story of industrial chemistry and fundamental research that has been described elsewhere.[4] Our activity now continues at The University of Alabama. The one-pot synthesis of imidazolium salts from simple starting materials is a key development in driving this chemistry (scheme 1).[5] In addition to the important imidazole based ligands, catalysts and synthetic intermediates that are made more economically available via this route, the imidazolium salts themselves are interesting as ionic liquids with widespread applications[6].



Scheme 1. Synthesis of Imidazolium salts from α,β-diketones, amines, and an aldehyde.

The initial isolation of a crystalline sample of 1,3-diadmantylimidazol-2-ylidene was the beginning point for much of the modern chemistry of stable imidazol-2-ylidenes. This compound holds a special meaning for us. A one to ten-billion scale model of this first stable crystalline carbene stands in a pasture on the Arduengo ranch just North of Tuscaloosa, Alabama. The model is about 15 feet high and over 10 yards long (Figure 1) and offers a unique perspective on these interesting structures.

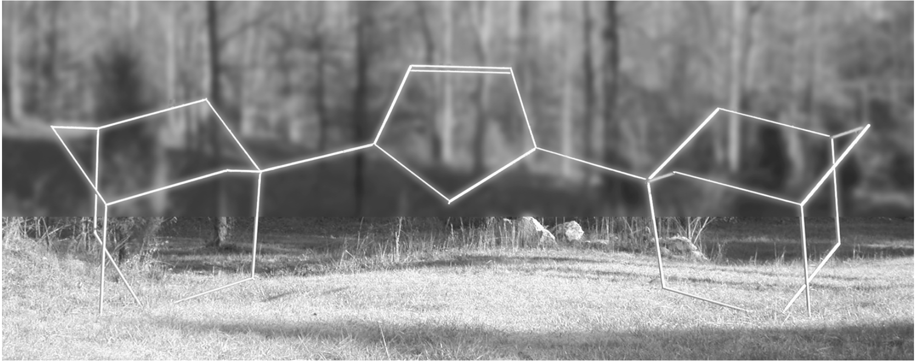
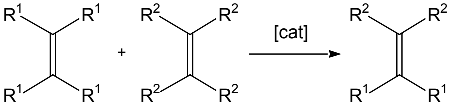


Figure 1. Picture of 1:10^{10} scale model of 1,3-diadamantylimidazol-2-ylidene.

Imidazol-2-ylidenes and their application in homogenous catalysis

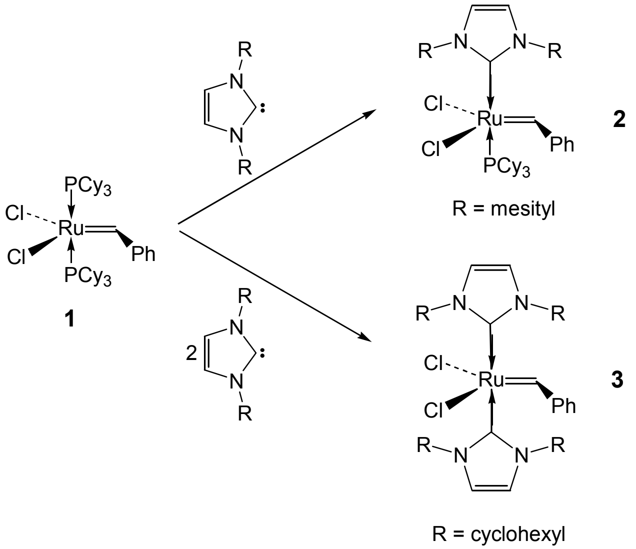
Imidazol-2-ylidenes are increasingly important as ligands for transition metal centered catalysts. Imidazol-2-ylidenes have found practical applications in olefin chemistry for metathesis,[7] hydrogenation, hydroformylation,[8] and hydroamination.[9] However, in contrast to phosphine based transition metal catalysts, the imidazolylidene based catalysts exhibit longer life-times in catalytic cycles. It has been suggested that this longer life-time may be due to better retention of the imidazolyidene ligands over their phosphine analogs on the metal center.[10] Furthermore imidazolylidene complexes generally possess better stability against air and moisture than their phosphine analogs.

Olefin Metathesis

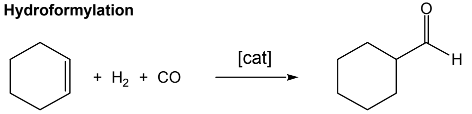


In recent years there has been tremendous progress in the cross-coupling reactions of olefins. Professor Robert Grubbs and his group have pioneered much of the work that now sets the standard in this field.[11,12] Ruthenium(II) complexes like the *Grubbs-catalyst* [$(Cy_3P)_2RuCl_2(=CHPh)$] (Cy = cyclohexyl)

1[11a] (Scheme 2) have found widespread application in organic synthesis and polymer chemistry. These phosphine based catalysts exhibit a high catalytic activity and stability, and are widely tolerant of substituents and functional groups. In 1998, Herrmann *et al.* reported a bis(imidazolylidene)ruthenium complex $[(Cy_2ImC:)_2RuCl_2(=CHPh)]$ ($Cy_2ImC:$ = 1,3-bis(cyclohexyl)imidazol-2-yliden) **3**[13] that showed a substantially higher catalytic activity than the original Grubbs catalyst. Shortly thereafter, Grubbs and coworkers developed a mono(imidazolylidene) complex $[(Cy_3P)(Mes_2ImC:)RuCl_2(=CHPh)]$ (Mes = Mesityl) **2** with still superior activity.[14] Since then other research groups worldwide have produced numerous nucleophilic carbene-bearing ruthenium complexes[15] that show interesting and useful catalytic activity.[16]



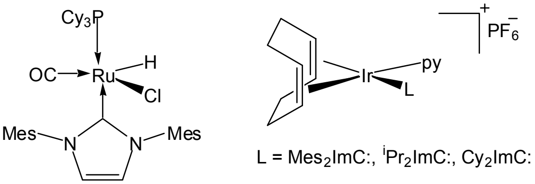
Scheme 2. Modifications of the traditional *Grubbs-catalyst* **1** that employ imidazolylidenes.



A catalytic reaction practiced on a particularly large scale commercially is the hydroformylation reaction, or "oxosynthesis." In these processes Rhodium(I)-phosphine complexes like $[RhH(CO)(PPh_3)_3]$ are employed as catalysts to accomplish the addition of carbon monoxide and hydrogen to olefins. With terminal olefins the ratio of internal to terminal addition (branched or linear product) is minimized through the addition of an excess of phosphine (up to 1:1000).[17] This also minimizes the decomposition of the catalysts and deposition of a metallic mirror. Superior catalysts are observed with imidazolylidene based complexes in place of phosphine based catalysts. Rhodium(I)-imidazolylidene complexes like $[(ImC:)RhCl(\eta^4\text{-}1,5\text{-cod})]$ (ImC: = Imidazol-2-yliden; cod = cyclooctadien), $[(ImC:)RhCl(PPh_3)_2]$ or $[(ImC:)_2RhCl(PPh_3)]$ are markedly more stable so that an excess of ligand in the reaction mixture can be avoided. In the case of mixed rhodium(I)-

imidazolylidene/phosphine complexes both a longer life-time and higher activity can be achieved over conventional rhodium phosphine catalysts.[18]

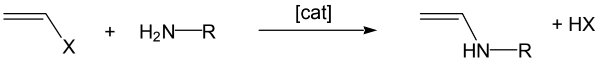
Efficient hydrogenation catalysts have been developed for alkenes and alkynes from 5-coordinate metal hydride complexes of the type $[HMCl(CO)L_2]$ (M = Ru, Os; L = $P^{i}Pr_3$, $P^{t}Bu_3$, $P^{t}Bu_2Me$).[19] Recently, it was shown that the catalytic activity of these complexes can be improved through the use of sterically demanding phosphines $[HRuCl(CO)(P^{i}Pr_3)_2]$.[20] Based on this observation, Nolan *et al.* showed that the ruthenium(II)-hydrido/imidazolylidene complex **4,**[21a] as well as the novel iridium(I)-imidazolylidene complex [(ImC:)Ir(py)(cod)] (py = pyridine) **5**[21b] (Figure 2) offer superior catalytic properties and higher thermal stabilities.



4 **5**

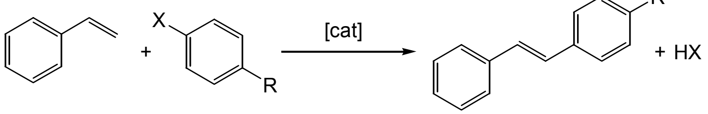
Figure 2. Ruthenium(II) imidazolylidene complex **4** and Iridium(I)-imidazolylidene complex **5**.

Amination

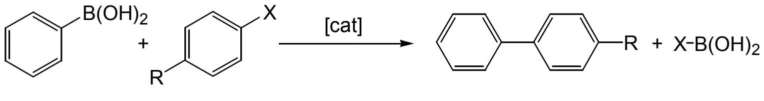


Enamines and enamides are important building blocks in the production of agricultural, pharmaceutical, and other fine chemicals. Successful copper(I)- and palladium(II)-complexes have been developed as catalysts for the coupling of vinyl- and aryl-halides with NH-functionalized compounds.[22] Based again upon their nucleophilic imidazolylidenes, DuPont developed an *in situ* generated nickel(0)-catalyst that possesses a high activity in these amination reactions.[23] The probable catalyst in this system is a mononuclear nickel(0)-complex derived from 1,3-diadamantylimidazol-2-ylidene $[(Ad_2ImC:)Ni(olefin)]$.

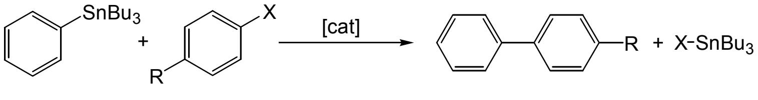
Mizoroki-Heck Reaction



Suzuki-Miyanara Reaction

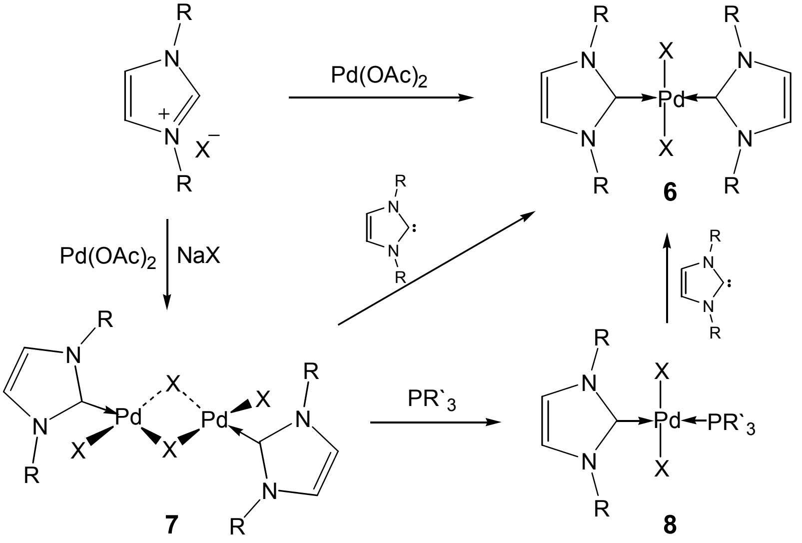


Stille-Coupling



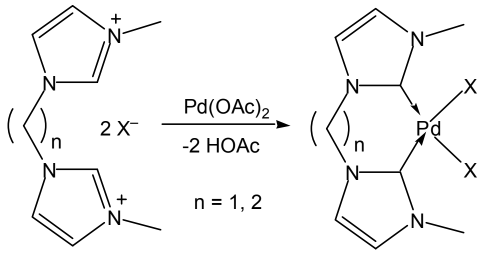
In various coupling reactions like the *Mizoroki-Heck* reaction,[24] the *Suzuki-Miyanara* reaction[25] or the *Stille-coupling*[26] palladium(II)-complexes of imidazolylidenes have been employed very successfully as catalysts. A convenient entry into this class of catalysts is found in the reaction of a metal complex bearing a mildly basic ligand (and leaving group) like acetate with an imidazolium salt. Under these conditions imidazolylidenes can be generated *in situ* under conditions where they are able to complex further with a metal center (Scheme 3). The by-product (acetic acid) can be easily separated if it is not tolerated in the catalyst cycle. With this approach numerous mononuclear complexes of the type $[(\text{ImC:})_2\text{PdX}_2]$ (ImC: = Imidazol-2-yliden; X = halide) **6**[27] and binuclear complexes like $[(\text{ImC:})\text{PdX}(\mu\text{-X}_2)(\text{ImC:})\text{PdX}]$ **7**[28] have been prepared. These complexes also serve as intermediates for other catalysts. Thus, phosphines reacted with complex **7** to afford the phosphine/imidazolylidene complex $[(\text{ImC:})\text{PdX}_2(\text{PR`}_3)]$ **8**.[29]

The good σ-donor properties of imidazolylidenes account for the superior thermal stability of these palladium complexes that enable higher yields and use of less reactive chlorarenes in reactions like Heck-olefinations.[30] Reduced Pd(0) species exhibit greater stability with imidazolylidene ligands yet are able to function as reactive intermediates in catalytic cycles. The reaction of **8** with additional imidazolylidene to form **6** demonstrates experimentally the strong σ-donor properties of imidazolylidenes over phosphines.



Scheme 3. Synthesis and reactivity of imidazolylidene palladium(II) complexes **6**-**8**.

A structural principle often applied in organometallic chemistry is the construction of polydentate chelates . As shown in Scheme 4 imidazolylidenes that are bridged with alkyl chains will function as chelating ligands in complexes of the type $[(\text{ImC:})\text{-}(\text{CH}_2)_n\text{-}(\text{ImC:})\text{PdX}_2]$ **10**.[31]

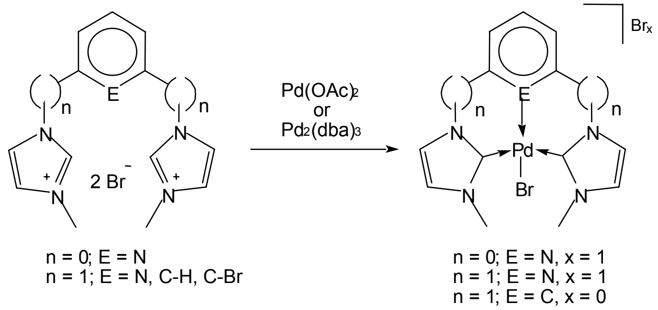


9 **10**

Scheme 4. Synthesis of bidentate Imidazolylidene palladium(II) complexes **10**.

However, palladium complexes like **10** appear to be less effective for couplings with chloroarenes because they decompose at temperatures above 70 °C in solution.[32]

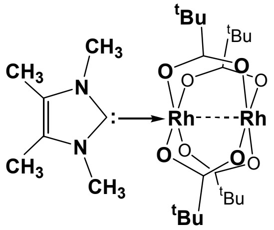
In two recent publications Crabtree and coworkers[33] described the synthesis of the imidazolylidene-pincer-ligand **11**[34] and its complexation with palladium. (Scheme 5). These chelated palladium complexes (**12**) are thermally very robust and show a high reactivity with chloroarenes in Heck-olefinations.



11 **12**

Scheme 5. Complexation of Imidazolylidene-Pincer-Ligand **11** with palladium.

Rhodium(II) complexes have often been used as catalysts to control the decomposition of diazocompounds in reactions like the cyclopropanation of olefins. A carbene-rhodium intermediate has never been directly observed in these reactions, but it has been postulated. The imidazolylidene-rhodium complex **13** was recently prepared and structurally characterized.[35] Complex **13** was also shown to be an effective promoter for cyclopropanations of olefins with α-diazoketones.[35]



13

Conclusion

Since the rebirth of interest in imidazolylidenes and their transition metal complexes, these interesting carbenes have become important tools for the design and construction of a new generation of organometallic catalysts. In only a few short years new and very effective catalysts for hydrogenations, hydrocarbonylations, aminations, olefin metathesis, and assorted coupling reactions have appeared. Accomplishments in this area are expected to continue into the future. The synthesis of new imidazolylidene-based ligands and the increasing understanding of the electronic and structural properties of these carbenes offer to extend further their utility as implementers for modern catalyst design. These new tools await the further creative applications and innovations that will surely follow.

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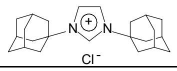
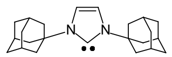
IMIDAZOLIUM PRODUCTS REFERENCED IN ARTICLE 1

NITROGEN

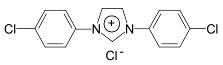
07-0322 1,3-Bis(1-adamantyl)imidazolium chloride
NEW→
250mg



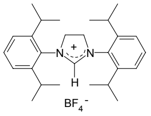
07-0324 1,3-Bis(1-adamantyl)imidazol-2-ylidene
NEW→
250mg



07-0490 1,3-Bis(4-chlorophenyl)imidazolium chloride
NEW→
250mg



07-0587 1,3-Bis(2,6-di-i-propylphenyl)-4,5-dihydroimidazolium tetrafluoroborate, min. 95%
NEW→
1g
5g

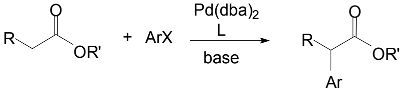


Technical Notes:

1. Ligand used in the palladium-catalyzed coupling of aryl chlorides with amines at room temperature.
2. Ligand used in the palladium-catalyzed arylation of ketones and esters.

$$\text{ArCl} + \text{NHRR'} \xrightarrow[\text{NaO-}t\text{-Bu, DME; RT-100}^{\circ}\text{C}]{\text{Pd(dba)}_2\text{, 0.02-2 mol\%; Ligand 1, 0.08-2 mol\%}} \text{Ar-NRR'} \quad (71\% \text{ - quant.})$$

Ref. (1)

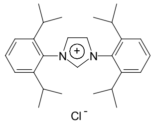


R=H, Me, NR_2, N=CHAr, $NCPh_2$
R'=*t*-Bu, Et, Me

References:
1. *Organic Letters*, **2000**, *2(10)*, 1423.

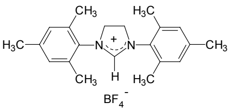
07-0590 1,3-Bis(2,6-di-i-propylphenyl)imidazolium chloride, min. 95%
500mg
2g

Technical Note:
1. See 07-0299 Catalog 19 page 329.



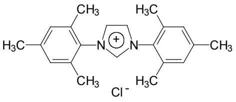
07-0302 1,3-Bis(2,4,6-trimethylphenyl)-4,5-dihydroimidazolium tetrafluoroborate
1g
5g

Technical Note:
1. See 44-7770 Catalog 19 page 375.

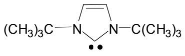


07-0299 1,3-Bis(2,4,6-trimethylphenyl)imidazolium chloride, min. 95%
1g
5g

Technical Note:
1. See Catalog 19 page 329.



07-0333 1,3-Di-t-butylimidazol-2-ylidene
NEW→
250mg



PRODUCTS REFERENCED IN ARTICLE 1

PALLADIUM

46-0252 Bis(tri-t-butylphosphine)palladium (0), 98%

250mg

1g

Technical Note:

1. Introduced as an air-stable palladium catalyst to effect Negishi cross-coupling of aryl and vinyl chlorides.

$$R{-}ZnCl + R'{-}Cl \xrightarrow{Pd[P(t\text{-}Bu)_3]_2} R{-}R'$$

R=aryl, alkyl R'=aryl, heteroaryl, vinyl

Reference:

1. *J. Am. Chem. Soc.*, **2001**, *123*, 2719.

46-1780 Palladium (II) acetate, min. 98%

1g

5g

Technical Note:

1. See Catalog 19 page 338.

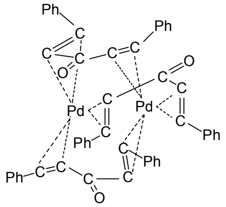
46-3000 Tris(dibenzylideneacetone)dipalladium (0)

1g

5g

Technical Note:

1. See Catalog 19 page 340.



46-3010 Tris(dibenzylideneacetone)dipalladium (0) chloroform adduct

500mg

2g

Technical Note:

1. See 46-3000 Catalog 19 page 340.

PHOSPHORUS

15-5810 Tri-t-butylphosphine, 99%

1g

5g

Technical Note:

1. See Catalog 19 page 357.

15-5811 Tri-t-butylphosphine, 99% (10 wt% in hexane)

10g

50g

Technical Note:

1. See 15-5810 Catalog 19 page 357.

15-5812 Tri-t-butylphosphine, 99% (10 wt% in hexane) (Sure/Seal™ bottle)

50g

Technical Note:

1. See 15-5810 Catalog 19 page 357.

15-6000 Tri-t-butylphosphonium tetrafluoroborate, 99%

NEW→

1g

5g

Technical Note:

1. Air-stable, non-pyrophoric precursor of the Tri-t-butylphosphine ligand which is used in a variety of catalytic processes. See 15-5810 Catalog 19 page 357.

15-6950 Tri-i-propylphosphine, 98%

1g

5g

25g

15-6952 Tri-i-propylphosphine, 98% (Sure/Seal™ bottle)

25g

15-6954 Tri-i-propylphosphine, 98% (10 wt% in hexane)

10g

50g

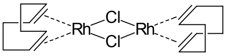
250g

PRODUCTS REFERENCED IN ARTICLE 1 (cont.)

RHODIUM

45-0380 Chloro(1,5-cyclooctadiene)rhodium (I) dimer, 98%

250mg
1g
5g



Technical Note:
1. See Catalog 19 page 364.

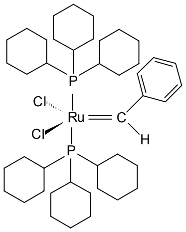
45-0900 Hydridocarbonyltris(triphenylphosphine)rhodium (I), 98%

1g
5g

RUTHENIUM

44-0065 Bis(tricyclohexylphosphine)benzylidine ruthenium (IV) dichloride GRUBBS'S CATALYST

1g
5g
25g

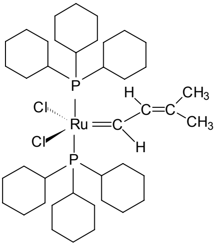


Note:
Sold for research purposes only. Use of the catalyst for purposes other than research must be licensed by the California Inst. of Technology.

Technical Note:
1. See Catalog 19 page 368.

44-0070 Bis(tricyclohexylphosphine)-3-methyl-2-butenylidene ruthenium (IV) dichloride

1g
5g



Note:
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Technical Note:
1. See Catalog 19 page 369.

44-0075 Bis(tricyclopentylphosphine)benzylidine ruthenium (IV) dichloride

250mg
1g

Note:
Sold for research purposes only. Use of the catalyst for purposes other than research must be licensed by the California Inst. of Technology.

Technical Note:
1. See 44-0065 Catalog 19 page 368.

44-0080 Bis(tricyclopentylphosphine)-3-methyl-2-butenylidene ruthenium (IV) dichloride

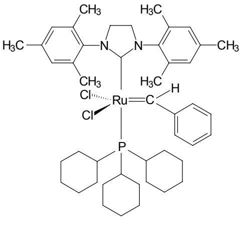
1g
5g

Note:
Sold for research purposes only. Use of the catalyst for purposes other than research must be licensed by the California Inst. of Technology. Sold in collaboration with Materia, Inc.

Technical Note:
1. See Catalog 19 page 370.

44-7770 Tricyclohexylphosphine[1,3-bis(2,4,6-trimethylphenyl)-4,5-dihydroimidazol-2-ylidene][benzylidine]ruthenium (IV) dichloride

500mg
2g



Note:
Sold for research purposes only. Use of the catalyst for purposes other than research must be licensed by the California Inst. of Technology.

Technical Note:
1. See Catalog 19 page 375.

Chiral Diphosphine Ligands – Steps to Commercialization

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Introduction and Scope

In a very recent review [1], we aimed at describing all enantioselective catalytic processes that have been and/or still are used for the commercial manufacture of enantioenriched intermediates. Information was also collected on pilot and bench scale processes not yet used in commercial production. In hindsight, this review appears to be especially well timed since with the awarding of the Nobel Prize 2001 to W.S. Knowles, R. Noyori and K.B. Sharpless, the area of enantioselective catalysis using chiral complexes eventually gained long deserved attention. From the point of view of the industrial chemist, it was especially gratifying that the development of a technical process for L-dopa was the basis for the award to W.S. Knowles, a very rare event indeed!

In the present article we would like to focus on a set of key prerequisites to develop commercial enantioselective catalytic processes. Assuming that the retrosynthetic evaluations for a chosen target molecule led to a competitive route involving one or more enantioselective transformations, the development chemist faces a demanding challenge: Which ligands shall/can be chosen? The answer is not straight forward since it involves screening and optimizing catalyst performance, and consideration of important economical aspects such as available options for sourcing the chiral ligand. Commercial applications require ligands produced reliably on a multi-kilogram scale with guaranteed quality, reasonable lead times, and at competitive prices. Other considerations are Intellectual Property (IP) payments required for the use of a proprietary ligand.

This article is aimed at the development chemist facing the above tasks and gives a review of the present situation for chiral diphosphine ligands. In order to do this we will first discuss current chemical pathways to produce enantioenriched intermediates that use enantioselective catalysis, and then discuss the criteria that make a chiral ligand successful. Then we will present the strategy used by Solvias to assist the development chemist in finding the optimal ligands for his or her specific enantioselective process.

Conclusions of Recent Review [1]

- Chiral molecules such as pharmaceuticals or agrochemicals usually have complex, multifunctional structures and are produced via multi-step syntheses. Compared to basic chemicals, they are relatively small volume but high value products with restricted product lifetimes which are traditionally produced in multipurpose batch equipment. The time available to develop their production process is often very short since "time to market" highly affects the profitability of the product.

- Four general approaches for producing enantiopure (ee >99%) or enantioenriched compounds economically have evolved: i) *Separation of enantiomers* via classical resolution or chiral HPLC using simulated moving bed technology; ii) the *chiral pool* approach, i.e., the use of chiral building blocks originating from natural products; iii) *enzymatic and microbial transformations* and iv) *enantioselective syntheses* especially *enantioselective catalysis* since the typically expensive chiral auxiliaries can be used in catalytic amounts.
- Most applications of enantioselective catalysis have been reported for the production of pharmaceuticals, vitamins, agrochemicals, flavors and fragrances, and chiral building blocks without dedicated use.

Enantioselective Catalysis

- Over the years, three types of enantioslective catalysts have proven to be synthetically useful: i) *homogeneous metal complexes* with chiral ligands; ii) *heterogeneous metallic catalyst*, modified with chiral auxiliaries and iii) chiral soluble *organic bases or acids*.
- Homogeneous metal complexes with chiral ligands are the most versatile catalysts. Preferred ligands are bidentate, i.e., they have chiral backbones with two coordinating heteroatoms . For noble metals, especially Rh, Pd, Ru and Ir, the coordinating atoms are usually tertiary substituted P or N atoms. For the early transition metals such as Ti, B or Zn, ligands with O or N are preferred. A very good review can be found in the recent monograph *Comprehensive Asymmetric Catalysis* edited by Jacobsen, Yamamoto and Pfaltz [2].
- Despite the dramatic progress in the scientific domain, relatively few enantioselective catalytic reactions are used on an industrial scale today due to some special challenges and problems [3]. From a technical point of view, the following are important: i) Catalyst performance, i.e., *enantioselectivity* expressed as enantiomeric excess (ee, %); *catalyst productivity*, given as turnover number (ton = mol product / mol catalyst) or as substrate/catalyst ratio (s/c), and *catalyst activity* given as average turnover frequency (tof (h^{-1}) = mol product / mol catalyst / reaction time). ii) Development time, especially for a new chemical entity in the pharmaceutical or agrochemical industry. iii) Availability and cost of the chiral ligand and/or catalyst for large scale applications.

What Makes a Successful Chiral Ligand?

As pointed out above, metal complexes bearing chiral ligands arguably constitute the most versatile catalysts for enantioselective transformations. Indeed, an impressively large number of chiral ligands are reported in the literature that produce high enantioselectivity in a variety of catalytic reactions [4]. However, if one takes a closer look at which ligands are really used by the synthetic organic chemist in academia, and even more so in industry, a very different picture emerges. As a matter of fact, only very few chiral catalytic systems are used on a regular basis for the synthesis of target molecules. Most of them contain defined classes of ligands. Eric Jacobsen [5] has coined the term "privileged ligands" for ligands in such classes. We have listed those with possibly the greatest potential for synthetic applications in *Fig. 1*.

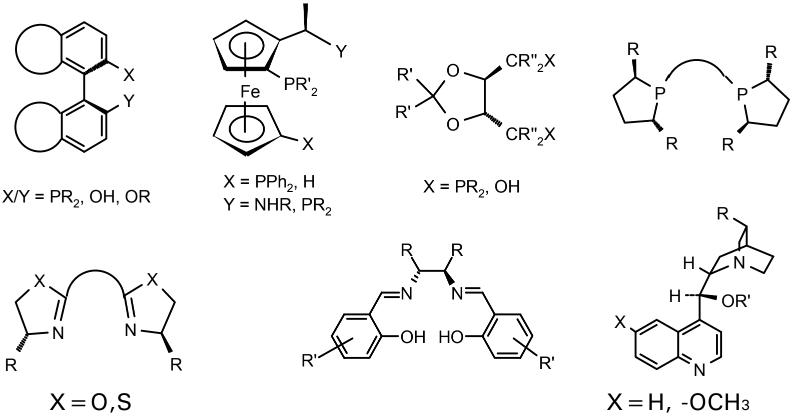


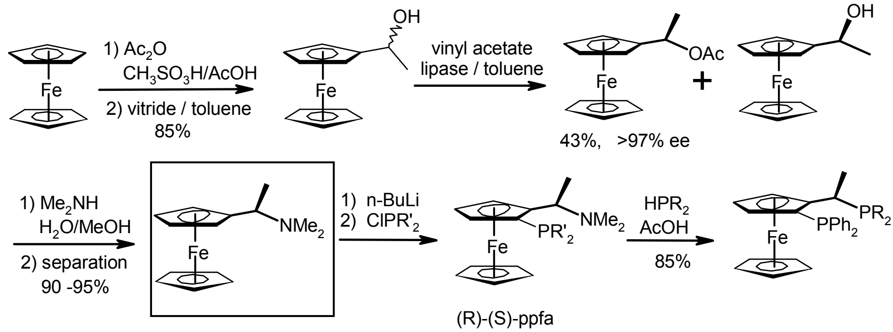
Fig. 1. Structure of families of privileged chiral ligands and auxiliaries

The following factors should be considered for a chiral ligand to be successfully applied in a catalytic process. [3a]

Scope, Limitations, Specificity and Functional Group Tolerance

The usefulness of a ligand can be limited if it is extremely air and/or moisture sensitive. In addition, catalysts are often substrate specific and ligands need to be "tailored" for each individual substrate, since small changes in the substrate can strongly affect the catalyst performance. This ligand tuning is best achieved with modular ligand types (cf. *Scheme 1*) such as the Biphep or the Josiphos [6] families which allow easy variation of the substituents at a late stage of the ligand synthesis.

Scheme 1. Example of the modular Josiphos ligand family



late stage common intermediate
only two steps needed to tune the ligand

With complex substrates, good chemoselectivity of a catalyst demands tolerance towards functional groups. Needless to say, ligands with a proven, well-defined wide scope, low substrate specificity, and good functional group tolerance have a much better chance of being applied to organic synthesis than ligands that are less characterized. It is also an important advantage for the ligand to exhibit a high stability towards ambient conditions – air-sensitivity being a disadvantage for commercial use.

Catalyst Performance

Many researchers overemphasize the fact that a high enantioselectivity is the most important factor for a catalyst system to be considered successful. Catalyst *productivity* (given as turnover number (ton) or as substrate/catalyst ratio (s/c) and catalyst *activity* (turnover frequency, tof, h^{-1}) are also very important criteria for an economical large scale application [3a].

Ligand Synthesis and Availability

For homogeneous catalysts, both (chiral) ligands and metal precursors can be expensive. Ligands often have unusual structures and most are prepared via multi-step syntheses. Particularly for (chiral) phosphines, considerable know how in organic synthesis and the handling of phosphorous derivatives is required. In the past, the ligand synthesis has often been part of the whole multi-step process development required for a given target, but, more and more, collaborations among external manufacturers and technology-providing companies are becoming popular. The full range of collaborations from pure ligand toll manufacturing to development of the catalytic enantioselective transformations on a production scale is imaginable. Obviously, the chances of a ligand to be used for a synthetic application increases with its ready availability.

Patent Protection and Licensing

As a rule, new ligands will be patented both by academic groups and, of course, also by companies. For commercial applications, a royalty-bearing license will usually be needed by the manufacturer to produce a target molecule using a patent-protected ligand. On the one hand, patent protection and income from royalties are strong motivators to design and make new ligands. On the other hand, a patented ligand is less likely to be used by industrial process chemists if the owner of the patent has a restrictive licensing policy. The supply terms and quality standards set by the ligand producer and/or ligand owner also trigger the choice for a ligand system.

Marketing of Chiral Ligands

Considering today's information explosion, it is not surprising that the synthetic chemist has a hard time keeping up with the progress of catalytic methodology. It is not enough to simply report the synthesis of a new ligand in a communication together with a set of "high ee" results for model reactions. Scope and limitations need to be investigated and described to shed light on both its scientific and commercial usefulness. Up to a few years ago, only a small number of ligands and chiral auxiliaries were available in the amounts needed to encourage commercial applications. Recently, the situation has improved significantly and commercial quantities (with necessary licenses) can be obtained today for a variety of ligands.

A Commercialization Example: The Solvias Strategy

Solvias has much experience in developing industrially feasible enantioselective catalytic processes and designing and synthesizing chiral ligands. Solvias' objective is to be a leading producer and provider of chiral diphosphines and related ligands as well as their metal complexes to serve the Life Sciences and Fine Chemical Industries. Solvias' strategy includes a partnership with Strem Chemicals to distribute products to the R&D community.

The Solvias business strategy can be summarized as follows:

> *Solvias ligands and catalysts are designed and produced to be used in the customers' vessels and plants. Solvias assists only as much as desired by the customer during the various stages of the development. This assistance is based on 20 years of experience in commercial scale enantioselective catalytic hydrogenation. Solvias' involvement can vary from ligand supply, to screening, to scale up, to pilot and finally chemical production.*

The chemist who intends to employ chiral ligands for a given transformation has a hierarchy of criteria to consider at various stages of the development process:

Stage of development	**Activities**	**Sourcing aspects**	**Milestones**	**Performance criteria**
1 early phases of development	*screening*	*availability in screening amounts (ca. 100mg)*	*chemical feasibility*	*selectivity*
2 bench scale phase, demonstration of technical feasibility	*optimization, scale up, catalyst handling quality risk analysis*	*catalyst supply <1kg typically, Quality, lead times*	*technical feasibility*	*selectivity* *activity* *productivity* *recycling* *metal removal*
3 pilot and production process	*process adaptation of / to infrastructure*	*>kg quantities of ligand and metal precursor,* *lead times, quality, refining of metal*	*verification of production process*	*selectivity* *activity* *productivity* *recycling/refining* *metal removal*

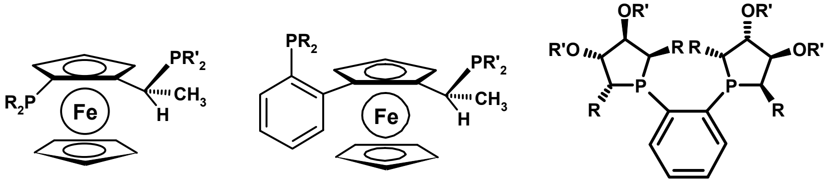
If viable candidates yield products with good ee's and reasonable activity in the first phase, then additional criteria (cf. **2** and later **3**) can be applied to make a choice between the candidates to achieve optimum catalytic performance.

Early Phase: Selection of the Right Ligand

In order to find the right ligand and catalyst, the development chemist will rely on his or her intuition, as well as personal experience and the literature. However, since many enantioselective catalysts are quite substrate-specific, analogies can prove to be fairly unreliable. For this reason ligand screening is still necessary. Screening is most efficient when the scope and limitations of as many ligands as possible are known. In addition, the ligand must be available to the development chemist via commercial sources otherwise it will take too much time for the experiment to be done.

To assist the development chemist in this early phase, Solvias has developed a **Ligand Kit** with a wide variety of proven chiral ligands. The first version of this kit is available from Strem with 10 sterically and electronically varied **Josiphos** [6] ligands. New members of the **Walphos** [6] and **Rophos** [7] ligand families are also planned (see *Fig. 2*). Solvias is developing commercially feasible synthetic routes to these important ligand families and is carrying out an extensive profiling of new kit members to get a clear picture on scope and limitations.

In addition, the **kit is equipped with the first version of a CD-ROM** serving as a tool for the selection of suitable ligands based on known commercial applications (pilot scale or larger). The information on the CD ROM is not restricted to Solvias-owned ligands. It contains information on all ligands that are available in research quantities. It is updated every half year. It contains a substructure search tool ("find your ligand") that allows the development chemist to assess quickly his or her target based on known processes. This reduces the screening time and increases the "hit" possibility. For convenience, this tool can also be accessed via the internet at www.solvias.com/ligands. Solvias will alert subscribed users when new ligands/catalysts become available or new catalytic technologies using Solvias ligands/catalysts emerge. Updates of the database will be announced as well.



Josiphos
(10 different R/R' combinations)

Walphos
(planned for 2002)

Rophos
(planned for 2002)

Fig. 2. Structures of the present and planned ligands of the Solvias Ligand Kit

Bench Scale, Pilot and Production Phases: Ligands on a Gram to Multi-kilogram Scale

For bench scale and pilot phase of process development, multi-gram to multi-hundred gram quantities of the ligands are needed. Until very recently there were limited supplies of ligands. Therefore, the synthesis of the ligand was part of the process development, for example, as described for metolachlor [8] or levoprotiline [9]. This has been a key disadvantage for developers of synthetic routes who employ a homogeneous enantioselective catalytic step. To lower the activation barrier for the development chemist to pursue such a route, Solvias offers a service to develop a commercial synthesis program for new ligands. Ligands in the Solvias ligand kit are readily available in developmental quantities from Solvias or Strem.

At Solvias, larger quantities of ligands are manufactured on request. Solvias' strategy of building modular ligands is also advantageous because the late stage intermediate for most of Solvias' ligands is common, allowing delivery of >1kg amounts within 2-4 months. Solvias has various quantities of important intermediates in stock. For the **Walphos** series, the commercial synthesis relies on a similar modular concept.

Licensing for Target Molecule Production

In this phase, aspects such as costs, delivery, and licensing terms and conditions must be discussed. Due to the fact that Solvias is a technology provider without in-house capabilities to perform commercial production of the target molecule (apart from kilo laboratory synthesis), the use of Solvias' ligands or technology by the customers (or subcontractor of the customers' choice) in their own vessels and plants is the desired strategy. If requested, the Solvias expertise to render the process ready for production and/or to perform trouble shooting in this phase is available. Not having to support such a tremendous production infrastructure allows Solvias to license its technology at attractive conditions.

Solvias Ligand Contest

Solvias has established a contest to generate new applications and new reactions with Solvias Ligands and to improve performance in hydrogenations and other reactions. These ideas can be submitted to either Dr. Hans-Ulrich Blaser or Dr. Michael E. Strem as a manuscript, preprint or communication. The jury consisting of Prof. A. Togni (ETH Zürich), Prof. A. Pfalz (University of Basel), Prof. M. Beller (University of Rostock) and Dr. Hans-Ulrich Blaser (Solvias) will review the contributions and the winner will be awarded a prize and invited for a lecture at the annual Solvias Science Day, all expenses paid. This years Solvias Science Day will be on the 20th September 2002.

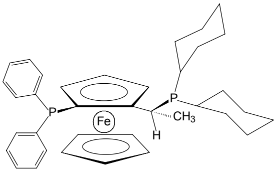
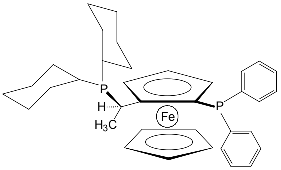
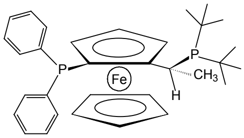
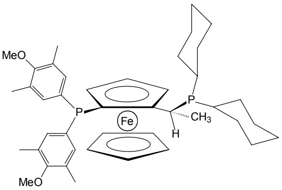
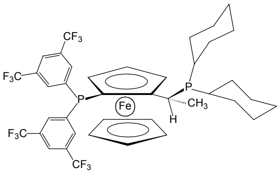
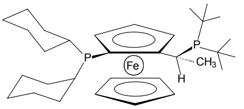
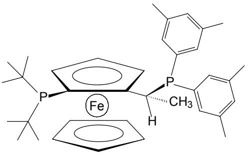
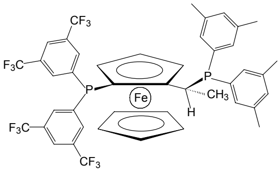
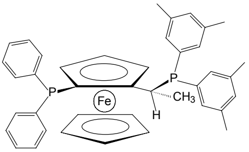
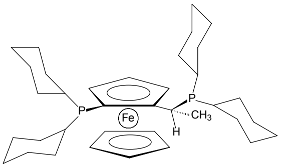
For terms and further details please consult www.solvias.com/ligands.

References:

[1] H.U. Blaser, F. Spindler, M. Studer, Appl. Catal. A: General 221 (2001) 119.
[2] Comprehensive Asymmetric Catalysis, E.N. Jacobsen, H. Yamamoto, A. Pfaltz (eds.), Springer, Berlin,1999.
[3] a) R.A. Sheldon, Chirotechnology, Marcel Decker Inc, New York, 1993.
b) H.U. Blaser, B. Pugin, F. Spindler in Applied Homogeneous Catalysis by Organometallic Complexes, B. Cornils, W.A. Herrmann (eds.), Verlag Chemie, Weinheim, 1996, p. 992.
[4] H. Brunner, W. Zettlmeier, Handbook of Enantioselective Catalysis, VCH, Weinheim, 1993.
[5] E.N. Jacobsen, Acc. Chem. Res. 33 (2000) 421, ref. 8.
[6] The Solvias Josiphos and Walphos ligands are patent protected and a license is needed for their commercial application. Solvias has the exclusive right to grant licenses to third parties and will do so with certain exceptions of pre-existing rights.
[7] The Rophos ligands are patent protected (owner: BASF) and a license is needed for their commercial application. Solvias has the exclusive right to grant licenses to third parties and will do so with certain exceptions of pre-existing rights.
[8] H.U. Blaser, H.P. Buser, K. Coers, R. Hanreich, H.P. Jalett, E. Jelsch, B. Pugin, H.D. Schneider, F. Spindler, A. Wegmann, Chimia 53 (1999) 275.
[9] H.U. Blaser, R. Gamboni, G. Rihs, G. Sedelmeier, E. Schaub, E. Schmidt, B. Schmitz, F. Spindler, Hj. Wetter in K.G. Gadamasetti (ed.), Process Chemistry in the Pharmaceutical Industry, Marcel Dekker Inc, New York, 1999, p. 189.

PRODUCTS REFERENCED IN ARTICLE 2

SOLVIAS LIGAND KIT

Solvias Ligand Kit: featuring the Josiphos family of ligands for asymmetric hydrogenation and other catalytic applications **Catalog #96-3650** **Components include:**		Cat. #26-1210  200mg
Cat. #26-1209  100mg	Cat. #26-1200  200mg	Cat. #26-1150  100mg
Cat. #26-0960  100mg	Cat. #26-0975  100mg	Cat. #26-0970  100mg
Cat. #26-0965  100mg	Cat.#26-1255  200mg	Cat.#26-1000  200mg

The Solvias Ligand Kit includes:

- CD-ROM with technical application notes, practical examples and a substructure search tool
- Variety of substituents for steric and electronic tuning
- For more information visit www.strem.com or www.solvias.com/ligands

Ligand components are also available on an individual basis, along with other Josiphos Ligands not in the kit. See (page 21-22).

Sold in collaboration with Solvias for research purposes only. Solvias' commercial strategy is for the customer to use these ligands in the customers' own vessels and plants. Several attractive intellectual property models are available. Commercial quantities are available from Solvias and require a license.

PRODUCTS REFERENCED IN ARTICLE 2 (cont.)

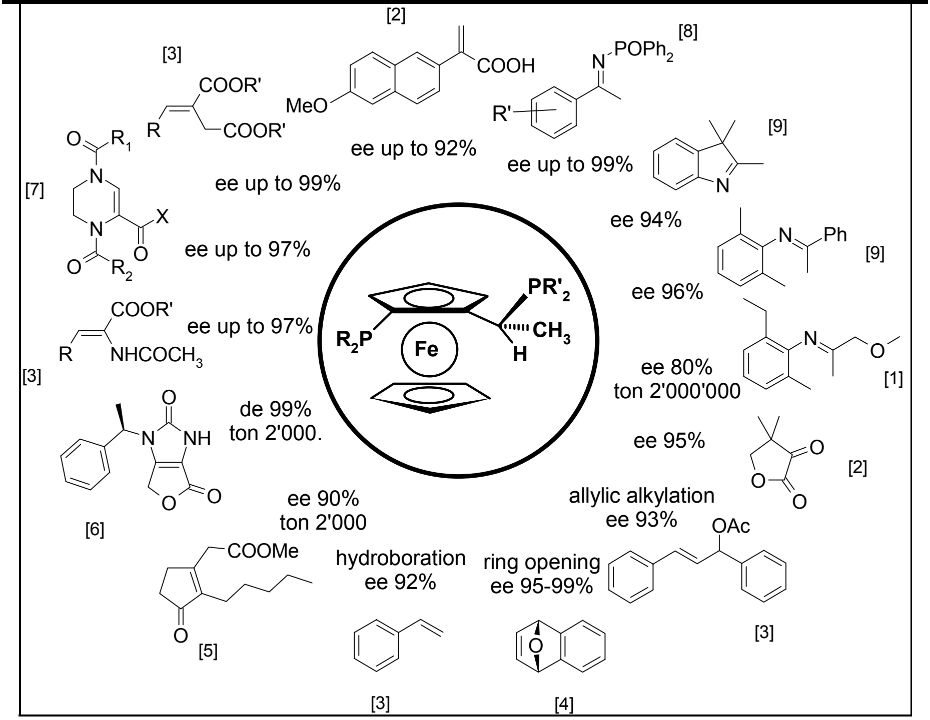
Available Josiphos Ligands	**Technical Note: See 26-1210 Catalog 19 page 320.**	
96-3650 NEW→	Solivas Ligand Kit	1 kit
26-0960 NEW→	(R)-(-)-1-[(S)-2-(Di(3,5-bis-trifluoromethylphenyl)phosphino)ferrocenyl]ethyldicyclohexylphosphine, min. 97%	100mg 500mg
26-0965 NEW→	(R)-(-)-1-[(S)-2-(Di(3,5-bis-trifluoromethylphenyl)phosphino)ferrocenyl]ethyldi(3,5-dimethylphenyl)phosphine, min. 97%	100mg 500mg
26-0970 NEW→	(R)-(-)-1-[(S)-2-(Di-t-butylphosphino)ferrocenyl]ethyldi(3,5-dimethylphenyl) phosphine, min. 97%	100mg
26-0975 NEW→	(R)-(-)-1-[(S)-2-(Dicyclohexylphosphino)ferrocenyl]ethyldi-t-butylphosphine, min. 97%	100mg
26-1000	(R)-(-)-1-[(S)-2-(Dicyclohexylphosphino)ferrocenyl]ethyldicyclohexylphosphine, min. 97%	100mg 500mg
26-1001	(S)-(+)-1-[(R)-2-(Dicyclohexylphosphino)ferrocenyl]ethyldicyclohexylphosphine, min. 97%	100mg 500mg
26-1230	(R)-(-)-1-[(S)-2-(Dicyclohexylphosphino)ferrocenyl]ethyldiphenylphosphine, min. 97%	100mg 500mg
26-1101	(S)-(+)-1-[(R)-2-(Dicyclohexylphosphino)ferrocenyl]ethyldiphenylphosphine, min. 97%	100mg 500mg
26-1150 NEW→	(R)-(-)-1-[(S)-2-(Di(3,5-dimethyl-4-methoxyphenyl)phosphino)ferrocenyl]ethyldicyclohexylphosphine, min. 97%	100mg 500mg
26-1200	(R)-(-)-1-[(S)-2-(Diphenylphosphino)ferrocenyl]ethyldi-t-butylphosphine, min. 97%	100mg 500mg
26-1201	(S)-(+)-1-[(R)-2-(Diphenylphosphino)ferrocenyl]ethyldi-t-butylphosphine, min. 97%	100mg 500mg
26-1209 NEW→	(R)-(+)-1-[(R)-2-(Diphenylphosphino)ferrocenyl]ethyldicyclohexylphosphine, min. 97% (R)-(R)-JOSIPHOS	100mg
26-1210	(R)-(-)-1-[(S)-2-Diphenylphosphino)ferrocenyl]ethyldicyclohexylphosphine, min. 97% (R)-(S)-JOSIPHOS	100mg 500mg

Structures for *NEW* Solvias Josiphos Ligands
see page 20.

PRODUCTS REFERENCED IN ARTICLE 2 (cont.)

Available Josiphos Ligands (cont.)	Technical Note: See 26-1210 Catalog 19 page 320.
26-1211	(S)-(+)-1-[(R)-2-Diphenylphosphino)ferrocenyl]ethyldicyclohexylphosphine, min. 97% (S)-(R)-JOSIPHOS 100mg 500mg
26-1255 NEW→	(R)-(-)-1-[(S)-2-Diphenylphosphino)ferrocenyl]ethyldi(3,5-dimethylphenyl) phosphine, min. 97% 100mg 500mg
	Structures for *NEW* Solvias Josiphos Ligands see page 20.

Starburst diagram of various enantioselective reactions that the Josiphos Ligands help catalyze.



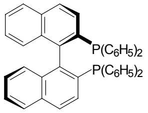
References:
1. *Chimia* 53, **1999**, 275.
2. *Solvias AG*, unpublished.
3. *J. Am. Chem. Soc.*, 116, **1994**, 4062.
4. *Org. Lett.* 2, **2000**, 1677 and *J. Am. Chem. Soc.*, 122, **2000**, 5650.
5. *Angew. Chem. Int. Ed.*, 39, **2000**, 1992.
6. *Chimia* 51, **1997**, 300.
7. *EP 744401*, **1995**.
8. *Adv. Synth. Catal.* 343, **2000**, 68.
9. *J. Organomet. Chem.* 621, **2001**, 34.

Ligand Families

BINAP

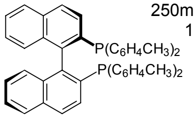
15-0433 rac-BINAP
1g
5g
25g

15-0150 (R)-BINAP
250mg
1g
5g



15-0151 (S)-BINAP
250mg
1g
5g

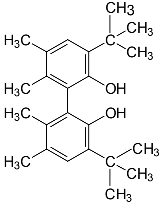
15-0152 (R)-Tol-BINAP
250mg
1g



15-0153 (S)-Tol-BINAP
250mg
1g

BIPHEN

08-2045 rac-BIPHEN H_2
5g
25g

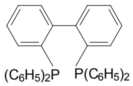


08-2046 (R)-BIPHEN H_2
100mg
500mg
2g

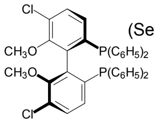
08-2047 (S)-BIPHEN H_2
(See 08-2046 for sizes)

BIPHEP

15-0145
250mg
1g



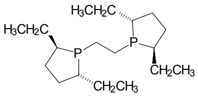
15-1055 NEW→ (R)-Cl-MeO-BIPHEP
(See page 28 for sizes)



15-1056 NEW→ (S)-Cl-MeO-BIPHEP
(See page 29 for sizes)

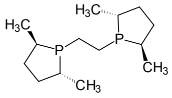
BPE

15-0101 (R,R)-Et-BPE
100mg
500mg
2g



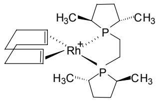
15-0102 (S,S)-Et-BPE
(See 15-0101 for sizes)

15-0104 (R,R)-Me-BPE
(See 15-0101 for sizes)



15-0105 (S,S)-Me-BPE
(See 15-0101 for sizes)

45-0170 (S,S)-Me-BPE-Rh
100mg
500mg
2g

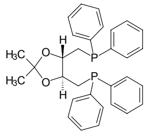


45-0171 (R,R)-Me-BPE-Rh
(See 45-0170 for sizes)

DIOP

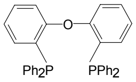
15-2970 (R,R)-DIOP
250mg
1g

15-2960 (S,S)-DIOP
250mg
1g



DPEphos

15-0380
5g
25g



DPEN

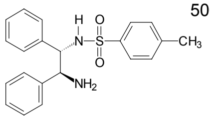
07-0474 (R,R)-DPEN
100mg
500mg

07-0475 (S,S)-DPEN
(See 07-0474 for sizes)

Ligand Families (cont.)

DPEN (cont.)

07-2370 (S,S)-TsDPEN

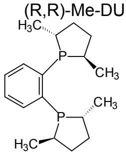


500mg
2g

07-2371 (R,R)-TsDPEN
(See 07-2370 for sizes)

DUPHOS

15-0096 (R,R)-Me-DUPHOS



100mg
500mg
2g

15-0092 (S,S)-Me-DUPHOS
(See 15-0096 for sizes)

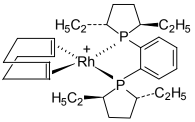
15-0097 (R,R)-Et-DUPHOS
(See 15-0096 for sizes)

15-0098 (S,S)-Et-DUPHOS
(See 15-0096 for sizes)

15-0410 (R,R)-i-Pr-DUPHOS
(See 15-0096 for sizes)

15-0411 (S,S)-i-Pr-DUPHOS
(See 15-0096 for sizes)

45-0150 (R,R)-Et-DUPHOS-Rh



100mg
500mg
2g

45-0151 (S,S)-Et-DUPHOS-Rh
(See 45-0150 for sizes)

45-0148 (R,R)-Et-DUPHOS-Rh
(See 45-0150 for sizes)

45-0149 (S,S)-Et-DUPHOS-Rh
(See 45-0150 for sizes)

45-0158 (R,R)-Me-DUPHOS-Rh
(See 45-0150 for sizes)

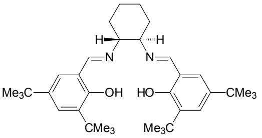
45-0159 (S,S)-Me-DUPHOS-Rh
(See 45-0150 for sizes)

45-0160 (R,R)-Me-DUPHOS-Rh
(See 45-0150 for sizes)

45-0161 (S,S)-Me-DUPHOS-Rh
(See 45-0150 for sizes)

JACOBSEN

07-0316 (R,R)-Jacobsen Ligand

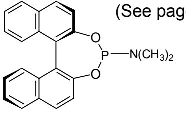


1g
5g

07-0317 (S,S)-Jacobsen Ligand
(See 07-0316 for sizes)

MONOPHOS

15-1232 (R)-MONOPHOS
NEW→

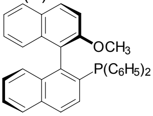


(See page 29 for sizes)

15-1233 (S)-MONOPHOS
NEW→
(See page 29 for sizes)

MOP

15-1775 (R)-MOP

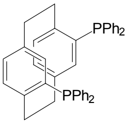


100mg
500mg

15-1776 (S)-MOP
(See 15-1775 for sizes)

PHANEPHOS

15-0426 (S)-PHANEPHOS

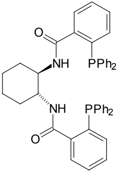


100mg
500mg

15-0425 (R)-PHANEPHOS
(See 15-0426 for sizes)

TROST

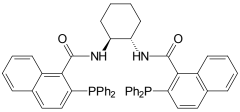
15-0960 (R)-TROST LIGAND



100mg
500mg
2g

15-0961 (S)-TROST LIGAND
(See 15-0960 for sizes)

15-0964 (S)-TROST LIGAND (NAPHTHYL

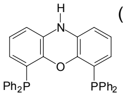


100mg
500mg
2g

15-0963 (R)-TROST LIGAND (NAPHTHYL)
(See 15-0964 for sizes)

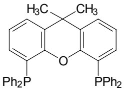
XANTPHOS

15-0437 NIXANTPHOS
NEW→



(See page 28 for sizes)

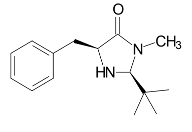
15-1242 XANTPHOS



1g
5g

NITROGEN

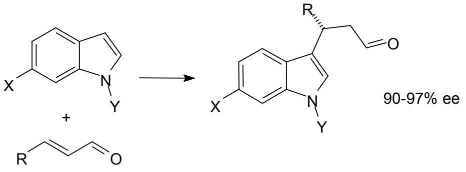
07-0206 (2S,5S)-(-)-5-Benzyl-2-(t-butyl)-3-methylimidazolidin-4-one, 97% MacMillan OrganoCatalysts™



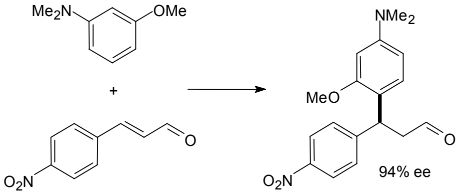
Note: Sold in collaboration with Materia, Inc. for research purposes only. Use for purposes other than research must be licensed from Materia, Inc.

500mg
2g

Technical Notes:
1. Catalyst for asymmetric indole additions.
2. Catalyst for asymmetric Friedel-Crafts alkylations.
3. Catalyst for Michael, Mukaiyama Michael, and vinylogous Michael additions.

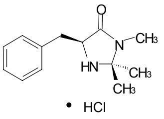


X = H, Cl Y = H, Me, Bn R = Me, Pr, CH_2OBz, i-Pr, Ph



*works for a variety of benzene derivatives

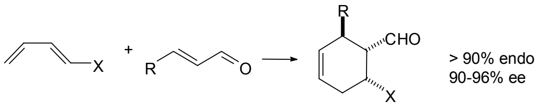
07-0208 (S)-(-)-5-Benzyl-2,2,3-trimethylimidazolidin-4-one, hydrochloride salt, 97% MacMillan OrganoCatalysts™

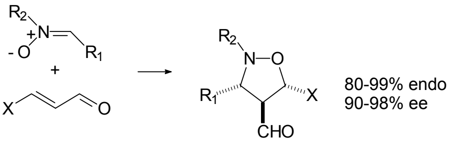


Note: Sold in collaboration with Materia, Inc. for research purposes only. Use for purposes other than research must be licensed from Materia, Inc.

500mg
2g

Technical Notes:
1. Catalyst for asymmetric Diels Alder reactions.
2. Catalyst for asymmetric 1,3-dipolar additions.
3. Catalyst for asymmetric pyrrole alkylations.



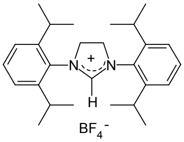


References:
1. *J. Am. Chem. Soc.*, **2000**, *122*, 4243.
2. *J. Am. Chem. Soc.*, **2000**, *122*, 9874.
3. *J. Am. Chem. Soc.*, **2001**, *123*, 4370.

New Products Introduced Since Catalog 19 – Metal Catalysts for Organic Synthesis

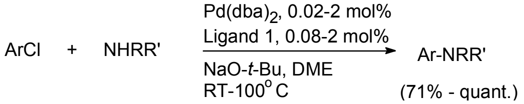
NITROGEN (cont.)

07-0587	1,3-Bis(2,6-di-i-propylphenyl)-4,5-dihydroimidazolium tetrafluoroborate, min. 95%	1g 5g



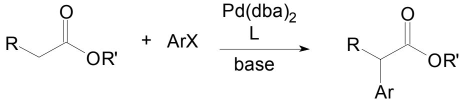
Technical Notes:

1. Ligand used in the palladium-catalyzed coupling of aryl chlorides with amines at room temperature.
2. Ligand used in the palladium-catalyzed arylation of ketones and esters.



$$\mathrm{ArCl} + \mathrm{NHRR'} \xrightarrow[\text{NaO-}t\text{-Bu, DME; RT-100}^{\circ}\text{C}]{\text{Pd(dba)}_2\text{, 0.02-2 mol\%; Ligand 1, 0.08-2 mol\%}} \underset{(71\%\text{ - quant.})}{\mathrm{Ar\text{-}NRR'}}$$

Ref. (1)



R=H, Me, NR $_2$, N=CHAr, NCPh$_2$
R'=t-Bu, Et, Me

References:

1. *Organic Letters*, **2000**, *2(10)*, 1423.

Catalog “Blue Pages” & Metal Catalysts for Organic Synthesis Brochure

The “Blue Pages” printed in the catalog are periodically updated with *new* products and current references between catalogs. They are printed for distribution at Conferences and Trade Shows as a separate brochure.

Please contact us if you would like a copy or download a pdf file from our website www.strem.com/code/mcos0202.pdf.

New Products Introduced Since Catalog 19 – Metal Catalysts for Organic Synthesis

PALLADIUM

46-0210 Bis(dibenzylideneacetone)palladium (0)

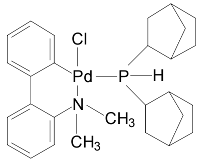
250mg
1g
5g

Technical Note:

1. See 46-3000 Catalog 19 page 340.

46-0270 Chloro(di-2-norbornylphosphino)(2'-dimethylamino-1,1'-biphenyl-2-yl)palladium (II), 97% min.

250mg
1g

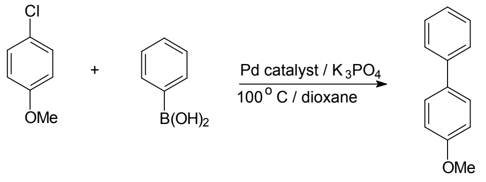


Note:

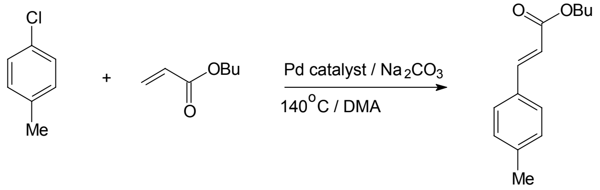
Sold in collaboration with Solvias for research purposes only.

Technical Note:

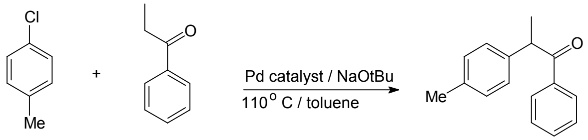
1. A new, air and moisture-stable, palladium catalyst useful in a broad scope of C-C and C-N coupling reactions. The highly-active catalyst can tolerate substrates containing a wide variety of functional groups such as alkyls, alkoxides, ketones, aldehydes, esters, amines, trifluoromethyl and nitro groups.



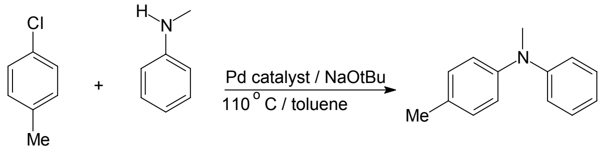
GC yield: 95%



GC yield: 97%



GC yield: 97%
Isolated yield: 80%



GC yield: 96%
Isolated yield: 85%

Reference:

1. *Solvias A.-G.*, EP1132361.

New Products Introduced Since Catalog 19 – Metal Catalysts for Organic Synthesis

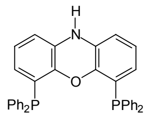
PHOSPHORUS

96-5500 Biaryl Ligand Kit for Aromatic Carbon-Heteroatom and Suzuki Coupling

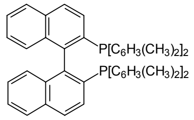
Kit contains: 1kit

15-1043	racemic-2-(Di-t-butylphosphino)-1,1'-binaphthyl, 98%	250mg
15-1045	2-(Di-t-butylphosphino)biphenyl, 99%	500mg
15-1048	2-Di-t-butylphosphino-2'-(N,N-dimethylamino)biphenyl,98%	500mg
15-1140	2-(Dicyclohexylphosphino)biphenyl, 98%	500mg
15-1145	2-Dicyclohexylphosphino-2'-(N,N-dimethylamino)biphenyl, 98%	500mg
15-1148	2-(Dicyclohexylphosphino)-2'-methylbiphenyl, 99%	500mg
15-1745	2-(Diphenylphosphino)-2'-(N,N-dimethylamino)biphenyl, 98%	500mg

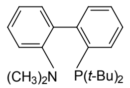
15-0437 4,6-Bis(diphenylphosphino)phenoxazine, min. 98%
NIXANTPHOS
500mg
2g



15-0475 racemic-2,2'-Bis[di(3,5-xylyl)phosphino]-1,1'-binaphthyl, 98% rac-xylyl-BINAP
500mg
2g



15-1048 2-Di-t-butylphosphino-2'-(N,N-dimethylamino)biphenyl, 98%
500mg
2g



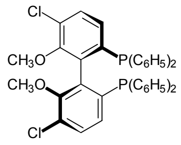
Technical Note:

1. Useful as ligands for the Pd-catalyzed intramolecular formation of carbon-oxygen bonds.

Reference:

1. *J. Am. Chem. Soc.*, **2001**, *123*, 12202.

15-1055 (R)-(+)-5,5'-Dichloro-6,6'-dimethoxy-2,2'-bis(diphenylphosphino)-1,1'-biphenyl, min. 95%
(R)-Cl-MeO-BIPHEP
250mg
1g

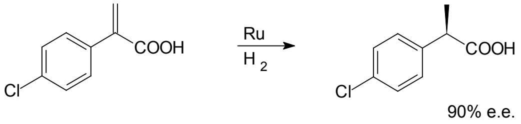


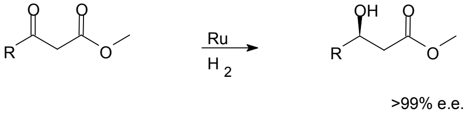
Note:

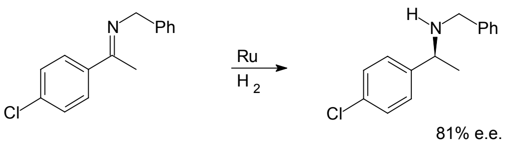
Sold in collaboration with Bayer. The product and its uses fall within the scope of US-patents 5,710,339 and 5,801,261 and is sold with the right to use such product for research only.

Technical Note:

1. Ligand used in the ruthenium catalyzed, enantioselective hydrogenation of alkenes, carbonyls, and imines.







Reference:

1. US Patents 5,710,339 and 5,801,261.

New Products Introduced Since Catalog 19 – Metal Catalysts for Organic Synthesis

PHOSPHORUS (cont.)

15-1056 (S)-(-)-5,5'-Dichloro-6,6'-dimethoxy-2,2'-bis(diphenylphosphino)-1,1'-biphenyl, min. 95% (S)-Cl-MeO-BIPHEP

250mg
1g

Note:

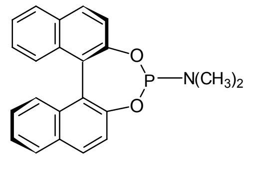
Sold in collaboration with Bayer. The product and its uses fall within the scope of US-patents 5,710,339 and 5,801,261 and is sold with the right to use such product for research only.

Technical Note:

1. See 15-1055 page 28.

15-1232 (R)-(-)-[4-N,N-Dimethylamino]dinaphtho[2,1-d:1',2'-f] [1,3,2]dioxaphosphepin, min. 98%
(R)- MONOPHOS

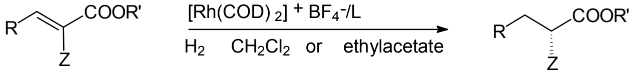
1g
5g



Note: Sold in collaboration with DSM for research purposes only. Patent WO 02 04466.

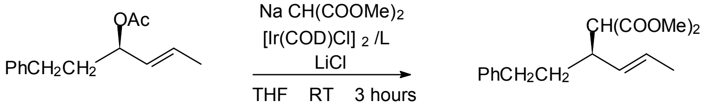
Technical Notes:

1. Ligand used in the enantioselective, rhodium-catalyzed hydrogenation of substituted olefins, such as N-acetyldihydroamino acids, enamides, and unsaturated acids.
2. Ligand used in the enantioselective, iridium-catalyzed allylic substitution of allyl acetates containing only a single substituent in the 1 or 3 position.



Tech. Note (1)
Ref. (1)

R = H, Ph R' = H, CH_3 Z = $NHCOCH_3$, CH_2COOH > 97% ee



Tech. Note (2)
Ref. (2)

93% ee

References:

1. *J. Am. Chem. Soc.*, **2000**, *122*, 11539.
2. *J.C.S. Chem. Comm*, **1999**, 741.

15-1233 (S)-(+)-[4-N,N-Dimethylamino]dinaphtho[2,1-d:1',2'-f] [1,3,2]dioxaphosphepin, min. 98% (S)-MONOPHOS

1g
5g

Note: Sold in collaboration with DSM for research purposes only. Patent WO 02 04466.

Technical Note:

1. See 15-1232 page 29.

15-6000 Tri-t-butylphosphonium tetrafluoroborate, 99%

1g
5g

Technical Note:

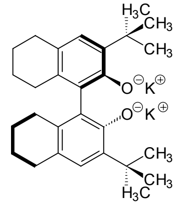
1. Air-stable, non-pyrophoric precursor of the Tri-t-butylphosphine ligand which is used in a variety of catalytic processes. See 15-5810 Catalog 19 page 357.

POTASSIUM

19-1600 (R)-(-)-5,5',6,6',7,7',8,8'-Octahydro-3,3'-di-t-butyl-1,1'-bi-2-naphthol, dipotassium salt

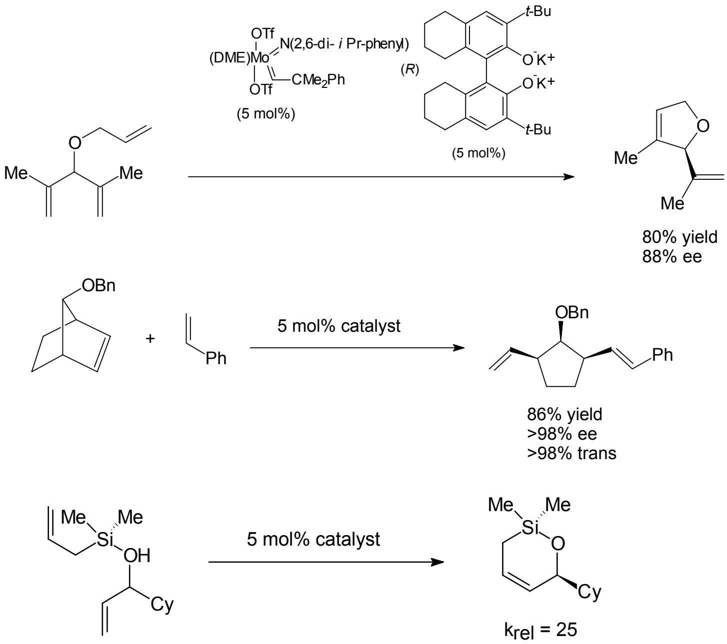
100mg

500mg



Technical Note:

1. Ligand used in combination with 42-1210 (See Catalog 19 page 324) for asymmetric ring closing and ring opening metathesis.



Reference:

1. *Angew. Chem. Int. Ed.*, **2001**, *40(8)*, 1452.

19-1601 (S)-(+)-5,5',6,6',7,7',8,8'-Octahydro-3,3'-di-t-butyl-1,1'-bi-2-naphthol, dipotassium salt

100mg

500mg

Technical Note:

1. See 19-1600 page 30.

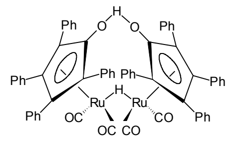
New Products Introduced Since Catalog 19 – Metal Catalysts for Organic Synthesis

RUTHENIUM

44-0780 1-Hydroxytetraphenylcyclopentadienyl(tetraphenyl-2,4-cyclopentadien-1-one)-μ-hydrotetracarbonyldiruthenium (II), 98% SHVO'S CATALYST

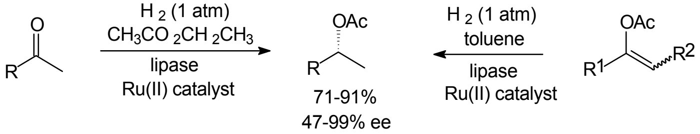
500mg

2g

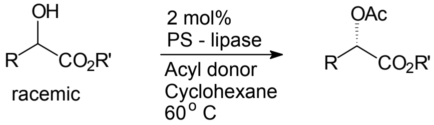


Technical Notes:

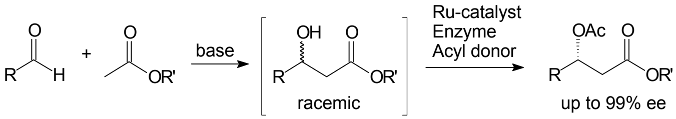
1. In conjugation with lipase, ruthenium catalyst used in the asymmetric transformation of ketones and enol acetates into chiral acetates.
2. Dynamic kinetic resolution resulting from the ruthenium catalyzed racemization of enzymatically-resolved substrates.
3. Ruthenium catalyst used in the aerobic oxidation of alcohols to ketones utilizing various quinones as hydrogen acceptors.



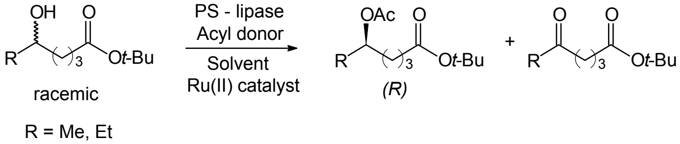
Tech. Note (1)
Ref. (1)



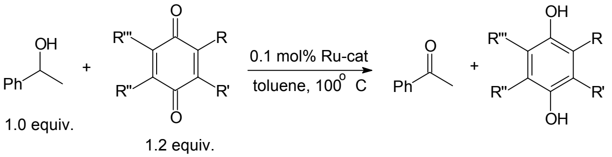
Tech. Note (2)
Ref. (2)



Tech. Note (2)
Ref. (3)



Tech. Note (2)
Ref. (4)



Tech. Note (3)
Ref. (5)

References:

1. *Org. Lett.*, **2000**, *2*, 2487.
2. *Org. Lett.*, **2000**, *2*, 1037.
3. *Org. Lett.*, **2001**, *3*, 1209.
4. *J. Org. Chem.*, **2002**, *67*, 1261.
5. *J. Org. Chem.*, **2002**, *67*, 1657.

New Products Introduced Since Catalog 19 – Ligands

CARBON

06-1296 1,2,3,4,5-Pentaphenyl-1,3-cyclopentadiene, 99%
1g
5g

New Products Introduced Since Catalog 19 – Phosphorus Compounds

PHOSPHORUS

15-0088 Bis(3,5-dimethylphenyl)phosphine, 99%
500mg
2g

15-0540 t-Butyldicyclohexylphosphine, 98%
500mg
2g

15-1010 Di-t-butylcyclohexylphosphine, 98%
500mg
2g

15-5990 Tri-n-butylphosphonium tetrafluoroborate, 99%
1g
5g

Technical Note:
1. Air-stable, non-pyrophoric precursor of 15-5800 Tri-n-butylphosphine.

15-6000 Tri-t-butylphosphonium tetrafluoroborate, 99%
1g
5g

Technical Note:
1. See page 11.

15-6355 Triethylphosphonium tetrafluoroborate, 99%
1g
5g

Technical Note:
1. Air-stable, non-pyrophoric precursor of 15-6300 Triethylphosphine.

15-6655 Tri-n-octylphosphine, min. 97% TOP
25g
100g
500g

15-6661 Trioctylphosphine oxide, 99% TOPO
25g
100g

15-7901 Tris(hydroxymethyl)phosphine, min. 95%
1g
5g

15-8021 Tris(trimethylsilyl)phosphine, min. 98% (10 wt% in hexane)
10g
50g

New Products Introduced Since Catalog 19 - MOCVD & CVD Precursors

ERBIUM

68-6900 Erbium (III) hexafluoroacetylacetonate hydrate (99.9%-Er) (REO)
1g
5g

HAFNIUM

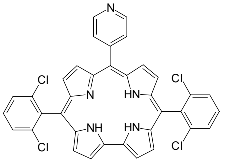
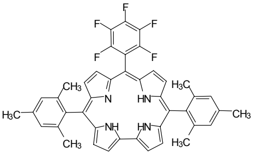
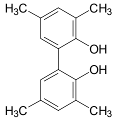
72-0700 Bis(cyclopentadienyl)dimethylhafnium, min. 97%
500mg
2g

RUTHENIUM

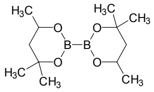
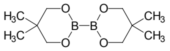
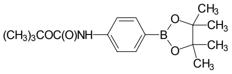
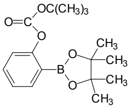
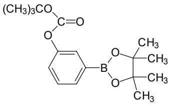
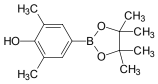
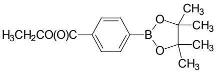
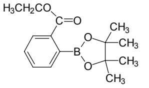
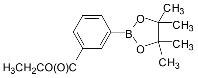
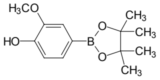
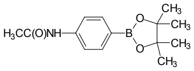
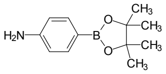
44-0040 Bis(ethylcyclopentadienyl)ruthenium (II), 98%
500mg
2g

Technical Note:
1. Liquid, ruthenium CVD precursor.

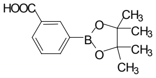
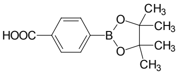
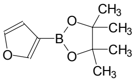
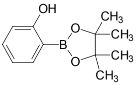
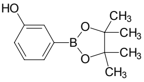
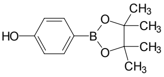
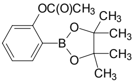
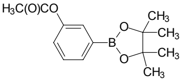
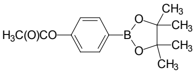
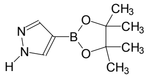
New Products Introduced Since Catalog 19 – Other New Products

BORON			
05-5000	Trityl(tetrapentafluorophenyl)borate, min. 98%	1g 5g	
CERIUM			
58-9000	Tris(1,2,3,4-tetramethyl-2,4-cyclopentadienyl)cerium (III) (99.9%-Ce) (REO)	1g 5g	
ERBIUM			
68-8740	Tris(methylcyclopentadienyl)erbium (99.9%-Er) (REO)	1g 5g	
HAFNIUM			
72-7700	Tetrabenzylhafnium	500mg 2g	
NITROGEN			
07-0250	5,15-Bis(2,6-dichlorophenyl)-10-(4-pyridyl)corrole	25mg	
07-0308	5,15-Bis(2,4,6-trimethylphenyl)-10-(pentafluorophenyl) corrole	25mg	
OXYGEN			
08-2043	3,3',5,5'-Tetramethyl-2,2'-biphenol, 99%	500mg 2g	
RUTHENIUM			
44-0145	Chloro(pentamethylcyclopentadienyl)ruthenium (II) tetramer	500mg 2g	
44-7000	Tetrakis(dimethylsulfoxide)dichlororuthenium (II), 98%	1g 5g	
ZIRCONIUM			
40-1650	Tetrabenzylzirconium, min. 95%	1g 5g	
SAFETY GLASSES			
96-0003	Safety Glasses, purple	1pr 5pr	
96-0004	Safety Glasses, white	1pr 5pr	

NEW BORONATE ESTERS for Suzuki Coupling

05-0020	Bis(hexyleneglycolato) diboron, 99% 1g 5g	
05-0025	Bis(neopentylglycolato) diboron, min. 97% 1g 5g	
05-0360	t-Butyl-N-[4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl) phenyl]carbamate, min. 97% 1g 5g	
05-0370	t-Butyl-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl) phenyl carbonate, min. 97% 1g 5g	
05-0380	t-Butyl-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl) phenyl carbonate, min. 97% 1g 5g	
05-0760	2,6-Dimethyl-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl) phenol, min. 97% 1g 5g	
05-0765	Ethyl-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl) benzoate, min. 97% 1g 5g	
05-0770	Ethyl-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl) benzoate, min. 97% 1g 5g	
05-0775	Ethyl-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl) benzoate, min. 97% 1g 5g	
05-0950	2-Methoxy-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl) phenol, min. 97% 1g 5g	
05-1032	4-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)acetanilide, min. 97% 1g 5g	
05-1034	4-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl) aniline, min. 97% 1g 5g	

NEW BORONATE ESTERS for Suzuki Coupling

05-1036	3-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)benzoic acid, min. 97% 1g 5g	
05-1037	4-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)benzoic acid, min. 97% 1g 5g	
05-1039	3-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)furan, min. 97% 1g 5g	
05-1042	2-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)phenol, min. 97% 1g 5g	
05-1043	3-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)phenol, min. 97% 1g 5g	
05-1044	4-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)phenol, min. 97% 1g 5g	
05-1045	2-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl acetate, min. 97% 1g 5g	
05-1046	3-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl acetate, min. 97% 1g 5g	
05-1047	4-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl acetate, min. 97% 1g 5g	
05-1048	4-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)-1H-pyrazole, min. 97% 1g 5g	

NEW Microencapsulated & Supported Catalysts

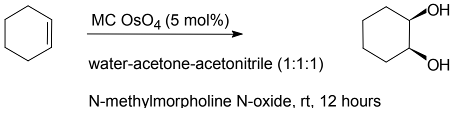
OSMIUM

76-2956 Osmium (VIII) oxide, Microencapsulated in a Styrene Polymer (~10% OsO_4)

1g

Technical Note:

1. Microencapsulated Osmium (VIII) oxide, in combination with a suitable co-oxidant, is a useful catalyst for the asymmetric dihydroxylation of olefins to yield chiral diols. The encapsulated OsO_4 is easily separated from the reaction mixture and is reusable. Furthermore, encapsulation suppresses the volatilization of hazardous osmium tetroxide.



Reference:

1. *J. Org. Chem.*, **1998**, *63*, 6094.

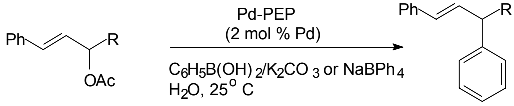
PALLADIUM

46-0101 Allylpalladium chloride dimer, supported on poly(ethylene glycol) polystyrene graft copolymer beads [~6% $(C_3H_5PdCl)_2$]

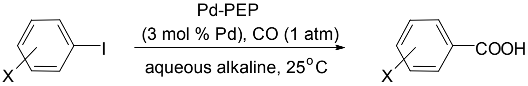
250mg

Technical Note:

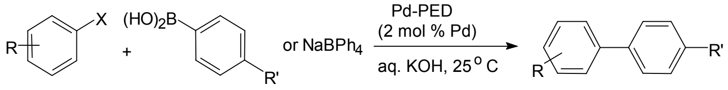
1. Resin supported Allylpalladium chloride dimer is a highly active catalyst useful in allylic substitution reactions, hydrocarbonylation of aryl halides, and cross-coupling of aryl halides and allylacetates with aryl boron reagents. The supported complex can easily be separated from the reaction mixture, and is reusable.



Ref. (1)



Ref. (2)



Ref. (1)

References:

1. *J. Org. Chem.*, **1999**, *64*, 3384.
2. *J. Org. Chem.*, **1999**, *64*, 6921.

NEW Microencapsulated & Supported Catalysts (cont.)

SCANDIUM

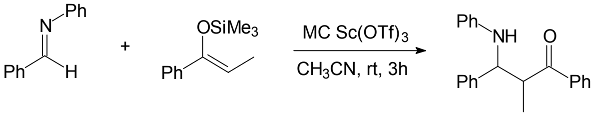
21-2004 Scandium (III) trifluoromethanesulfonate (Scandium triflate) Microencapsulated in a Styrene Polymer [~13% $Sc(SO_3CF_3)_3$]

500mg

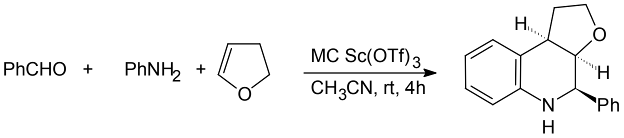
Technical Note:

1. Microencapsulated Scandium triflate is a useful Lewis acid catalyst which can be applied to various synthetic procedures such as the aldol, Michael, alkylation, Friedel-Crafts acylation, Mannich and Strecher type reactions. The encapsulated $Sc(SO_3CF_3)_3$ has a higher activity than the free monomer, can easily be separated from the reaction mixture, and is reusable.

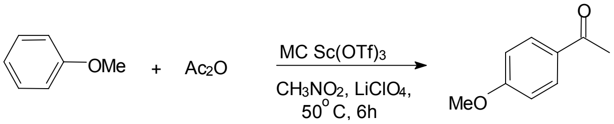
Imino Aldol Reaction (Flow System)



Quinoline Synthesis (Flow System)



Friedel-Crafts Acylation (Batch System)



References:

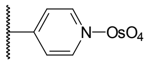
1. *J. Am. Chem. Soc.*, **1998**, *120*, 2985.
2. *Eur. J. Org. Chem.*, **1999**, 15.

NEW FibreCat™ Products

OSMIUM

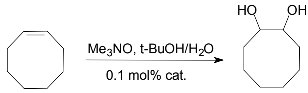
76-2970 Tetraoxopyridineosmium (VIII) (~7.5% Os) polymer-bound FibreCat™

5g



Technical Note:

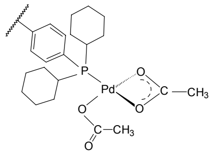
1. Polymer-bound osmium tetroxide, in combination with a suitable co-oxidant, is a useful catalyst for the hydroxylation of olefins. The osmium tetroxide is bonded to the polymer support through a pyridine pendant, effectively eliminating the hazards associated with its volatility and toxicity in the free state, while still maintaining its activity as a catalyst.



PALLADIUM

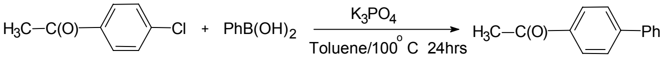
46-1500 Di(acetato)dicyclohexylphenylphosphinepalladium (II) (~5% Pd) polymer-bound FibreCat™

5g



Technical Note:

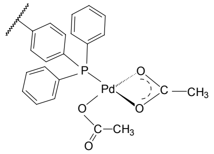
1. Similar to 46-1550, but more useful in the coupling of less reactive aryl chlorides with boronic acids.



> 90%

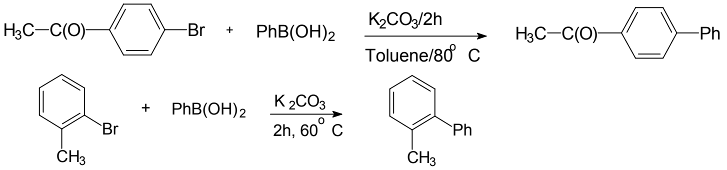
46-1550 Bis(acetato)triphenylphosphinepalladium (II) (~5% Pd) polymer-bound FibreCat™

5g



Technical Note:

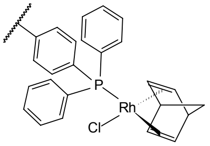
1. Versatile polymer-bound catalyst used in the Suzuki coupling of aryl bromides and iodides with boronic acids. The polymer-bound catalyst is generally more selective than the free homogeneous catalyst, and palladium leaching is very low.



RHODIUM

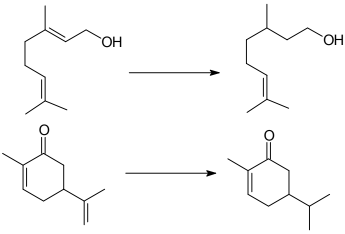
45-1700 Chloronorbornadienetriphenylphosphinerhodium (I) (~5% Rh) polymer-bound FibreCat™

5g

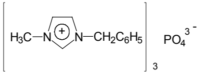
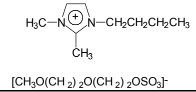
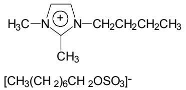
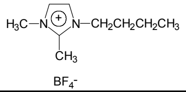
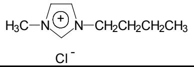
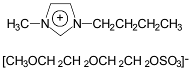
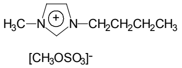
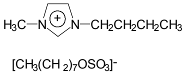
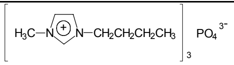
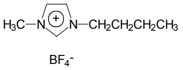
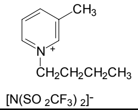
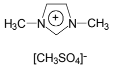
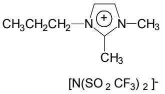
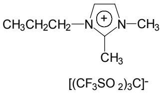
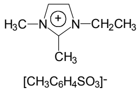


Technical Note:

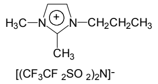
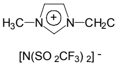
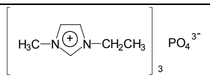
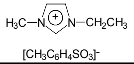
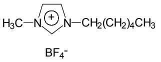
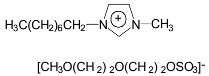
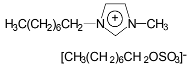
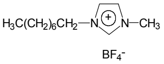
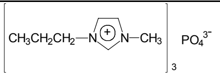
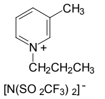
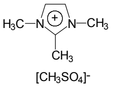
1. Versatile polymer-bound catalyst used for the selective hydrogenation of polyolefins. The supported rhodium catalyst exhibits similar selectivity to its homogeneous counterpart. In most cases, rhodium leaching is negligible.



NEW Ionic Liquids

07-0090	1-Benzyl-3-methylimidazolium phosphate, 99% 5g	
07-0050	1-Butyl-2,3-dimethylimidazolium diethyleneglycolmonomethylethersulfate, 98% [BDiMIM] [MDEGSO$_4$] 5g	
07-0060	1-Butyl-2,3-dimethylimidazolium octylsulfate, 98% [BDiMIM] [OcSO$_4$] 5g	
07-0075	1-Butyl-2,3-dimethylimidazolium tetrafluoroborate, 98% [BDiMIM] [BF$_4$] 5g	
07-0100	1-Butyl-3-methylimidazolium chloride, 98% [BMIM]Cl 5g	
07-0110	1-Butyl-3-methylimidazolium diethyleneglycolmonomethylethersulfate, 98% [BMIM] [MDEGSO$_4$] 5g	
07-0140	1-Butyl-3-methylimidazolium methylsulfate, 98% [BMIM] [MeSO$_4$] 5g	
07-0150	1-Butyl-3-methylimidazolium octylsulfate, 98% [BMIM] [OcSO$_4$] 5g	
07-0160	1-Butyl-3-methylimidazolium phosphate, 99% [BMIM] [PO$_4$] 5g	
07-0170	1-Butyl-3-methylimidazolium tetrafluoroborate, 98% [BMIM] [BF$_4$] 5g	
07-0180	N-Butyl-3-methylpyridinium bis(trifluoromethylsulfonyl) imide [BMPIm] 5g "Product protected by U.S. Patent 5,827,602 assigned to Covalent Associates, Inc."	
07-0455	1,3-Dimethylimidazolium methylsulfate, 98% [DiMIM] [MeSO$_4$] 5g	
07-0465	1,2-Dimethyl-3-propylimidazolium bis(trifluoromethylsulfonyl) imide [DMPIIm] 5g "Product protected by U.S. Patent 5,827,602 assigned to Covalent Associates, Inc."	
07-0470	1,2-Dimethyl-3-propylimidazolium tris(trifluoromethylsulfonyl) methide [DMPIMe] 2g "Product protected by U.S. Patent 5,827,602 assigned to Covalent Associates, Inc."	
07-0535	1-Ethyl-2,3-dimethylimidazolium tosylate, 98% [EDiMIM] [TOS] 5g	

NEW Ionic Liquids (cont.)

07-0578	1-Ethyl-3-methylimidazolium bis(pentafluoroethylsulfonyl)imide [EMIBeti] 2g "Product protected by U.S. Patent 5,827,602 assigned to Covalent Associates, Inc."	
07-0579	1-Ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide [EMIIm] 5g "Product protected by U.S. Patent 5,827,602 assigned to Covalent Associates, Inc."	
07-0584	1-Ethyl-3-methylimidazolium phosphate, 99% [EMIM] [PO_4] 5g	
07-0588	1-Ethyl-3-methylimidazolium tosylate, 98% [EMIM] [TOS] 5g	
07-0968	1-Hexyl-3-methylimidazolium tetrafluoroborate, 98% [HMIM] [BF_4] 5g	
07-1230	1-Methyl-3-octylimidazolium diethyleneglycolmonomethylether-sulfate, 98% [OMIM] [$MDEGSO_4$] 5g	
07-1256	1-Methyl-3-octylimidazolium octylsulfate, 98% [OMIM] [$OcSO_4$] 5g	
07-1264	1-Methyl-3-octylimidazolium tetrafluoroborate, 98% [OMIM] [BF_4] 5g	
07-1725	1-Methyl-3-propylimidazolium phosphate, 99% 5g	
07-1775	N-Propyl-3-methylpyridinium bis(trifluoromethylsulfonyl)imide [PMPIm] 5g "Product protected by U.S. Patent 5,827,602 assigned to Covalent Associates, Inc."	
07-2660	1,2,3-Trimethylimidazolium methylsulfate, 98% [TriMIM] [$MeSO_4$] 5g	

NEW Ionic Liquid Kits

96-6500	**IONIC LIQUID KIT 1: Hydrophobic (water-immiscible) Kit** Contains the following:	
07-0180	N-Butyl-3-methylpyridinium bis(trifluoromethylsulfonyl)imide [BMPIm]	5g
07-0465	1,2-Dimethyl-3-propylimidazolium bis(trifluoromethylsulfonyl)imide [DMPIIm]	5g
07-0470	1,2-Dimethyl-3-propylimidazolium tris(trifluoromethylsulfonyl)methide [DMPIMe]	2g
07-0578	1-Ethyl-3-methylimidazolium bis(pentafluoroethylsulfonyl)imide [EMIBeti]	2g
07-0579	1-Ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide [EMIIm]	5g
07-1775	N-Propyl-3-methylpyridinium bis(trifluoromethylsulfonyl)imide [PMPIm]	5g

The items contained in this kit are hydrophobic (water-immiscible) ionic liquids and are more thermally and hydrolytically stable than their PF_6 counterparts.

Note:

Ionic Liquid Kit 1 products protected by U.S. Patent 5,827,602 assigned to Covalent Associates, Inc.

96-6510	**IONIC LIQUID KIT 2: BMIM Kit** Contains the following:	
07-0100	1-Butyl-3-methylimidazolium chloride, 98% [BMIM]Cl	5g
07-0110	1-Butyl-3-methylimidazolium diethyleneglycolmonomethylethersulfate, 98% [BMIM] [$MDEGSO_4$]	5g
07-0140	1-Butyl-3-methylimidazolium methylsulfate, 98% [BMIM] [$MeSO_4$]	5g
07-0150	1-Butyl-3-methylimidazolium octylsulfate, 98% [BMIM] [$OcSO_4$]	5g
07-0160	1-Butyl-3-methylimidazolium phosphate, 99% [BMIM] [PO_4]	5g
07-0170	1-Butyl-3-methylimidazolium tetrafluoroborate, 98% [BMIM] [BF_4]	5g

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