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Phosphonium Ionic Liquids

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1 - Ionic Liquids: A Brief History

The term "ionic liquids" is usually used to describe ionic salts with melting points less than ~100 ºC. Many of the most interesting systems actually have melting points around or below room temperature. The story of ionic liquids has been described elsewhere by some of the key workers in the field, both from a scientific[1a] and personal[2] perspective, but is worth reviewing briefly here. The first report of a room temperature molten salt was made by Walden in 1914, who noted the physical properties of ethylammonium nitrate (mp: 12-14ºC) formed by the reaction of ethylamine with concentrated nitric acid.[3] The next half century saw sporadic reports of ionic liquids as media for electrochemical studies and, less commonly, as solvents for organic reactions.[1a] Much of this work involved eutectic mixtures of chloroaluminate-based salts such as $AlCl_3$–NaCl and pyridinium hydrochloride.[4] Ionic liquids didn't reach a more general audience until seminal research efforts by the groups of Osteryoung[5] and Wilkes[2,6] in the 1970s, and Hussey[7] and Seddon[8] in the 1980s. This period also saw the first use of ionic liquids as reaction media for organic synthesis,[9] and, in 1990, for biphasic catalysis.[10] In the early 1990s, a report by Wilkes and co-workers describing the first air and moisture stable imidazolium salts, based on tetrafluoroborate, $[BF_4]^-$, and hexafluorophosphate, $[PF_6]^-$,[11] fueled further interest in the field. This interest has seen explosive growth during the past decade.[12] Reflecting this, the number of papers published on ionic liquids has grown from approximately 40 per year in the early 1990s to multiple hundreds per year today.[12]

2 - Phosphonium Ionic Liquids

Compared to their quaternary nitrogen-based analogues, specific accounts of ionic liquids containing phosphonium cations are quite rare.[1] While ionic liquids containing nitrogen-based cations have undergone extensive investigation in a myriad of applications over the last several years, studies involving quaternary phosphonium systems are much rarer. Cytec Industries has a great deal of experience in the manufacture of quaternary phosphonium salts that translates naturally to the manufacture of phosphonium ionic liquids. Over the past several years our research program has developed a diverse range of new products by pairing tetraalkylphosphonium cations with various anions (Figure 1) to produce the CYPHOS® IL range of phosphonium ionic liquids.

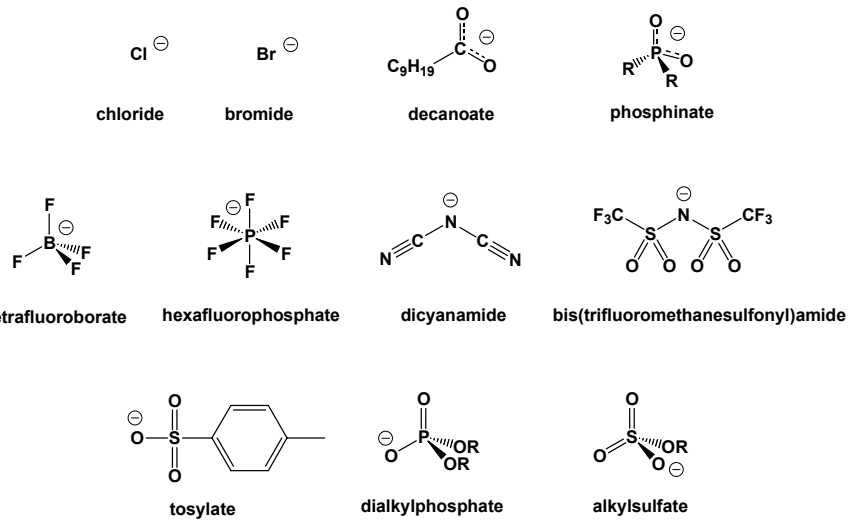


Figure 1: Examples of anions that can be paired with tetraalkylphosphonium cations to produce ionic liquids.

3 - Synthesis of Phosphonium Ionic Liquids

3.1 – Alkylphosphine Precursors

Tertiary phosphines, [PR_3], can be prepared *via* free radical addition of phosphine gas, [PH_3],[13] to alpha olefins,[14] often in the presence of a suitable promoter such as DuPont's Vazo® series.[15] While the pK_as for tertiary phosphines are typically lower than the corresponding amines, their larger radii and more polarizable lone pair make them more nucleophilic. Hence the kinetics of salt formation are, in general, much faster than for amines.[16,17]

Typical phosphonium cations have the general formula $[R'PR_3]^+$, in which three of the alkyl groups are identical while the fourth is different (Eq. 1). This arises from the usual synthetic route (Eq. 1, from homologous tertiary phosphines) but does not have to be the case. Primary and secondary alkylphosphines (RPH_2, R_2PH) are also available and can be converted to asymmetric tertiary phosphines (RR'_2P or $R_2R'P$) through free radical addition to olefins.[14] The resulting phosphonium cations have generic formulas of $[RR'_2R''P]^+$ and $[R_2R'R''P]^+$.

3.2 – Phosphonium Halides

Phosphonium salts, especially halides, have been available commercially for many years. Asymmetrical tetraalkylphosphonium halides, $[R'PR_3^+]X^-$, are typically prepared by nucleophilic (S_N2) addition of tertiary phosphines, [PR_3], to haloalkanes, [R'X (X = Cl, Br, I)] (Eq.

1),[18] although other methods have been reported.[19] These have historically had use as biocides[20] and phase transfer catalysts.[21] Though innumerable phosphonium cations can be imagined as constituents of phosphonium ionic liquids, we have utilized the trihexyl(tetradecyl) phosphonium cation, $[(C_6H_{13})_3P(C_{14}H_{29})]^+$, in much of our work. This is for reasons of cost and convenience, and because we have found it works well in many cases.

$$PR_3 + R'X \longrightarrow [R'PR_3]^+X^- \qquad (1)$$

Burgeoning interest in ionic liquids prompted us to closely examine our own range of phosphonium salts in order to target their potential as ionic liquids. In fact, we discovered several ionic compounds that were liquid at or near room temperature. Trihexyl(tetradecyl)phosphonium chloride, long a commercial product, has subsequently seen new life as a starting material for the synthesis of numerous phosphonium ionic liquids by anion exchange reactions.[22]

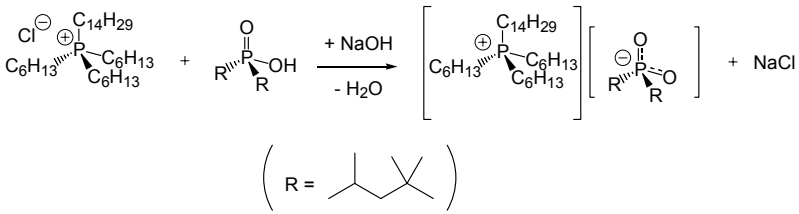
3.3 - Metathesis Routes to Phosphonium Ionic Liquids

Phosphonium halides can be converted by metathesis methods to other anions such as phosphinate, carboxylate, tetrafluoroborate, hexafluorophosphate, *etc.* (Figure 1).[22] These conversions generally fall into two categories (Eq. 2-3), and ionic liquids containing the anions shown in Figure 1 can be synthesized by one or the other of these routes depending on the starting materials chosen.

$$[R'PR_3]^+X^- + MA \longrightarrow [R'PR_3]^+A^- + MX \qquad (2)$$

$$[R'PR_3]^+X^- + HA + MOH \longrightarrow [R'PR_3]^+A^- + MX + H_2O \qquad (3)$$

(R, R' = alkyl; X = halogen; M = alkali metal; A = anion)



(4)

In addition to being novel ionic liquids, phosphonium phosphinates couple Cytec's existing expertise in phosphonium salt and phosphinic acid manufacturing. A notable example is derived from bis(2,4,4-trimethylpentyl)phosphinic acid (CYANEX® 272 Extractant) as shown in

Eq. 4. This is a well-known and popular solvent for the extraction of cobalt from nickel in both sulfate and chloride media,[23] and is currently used to produce more than half of the western world's cobalt.[24] Ionic liquids containing the bis(2,4,4-trimethylpentyl)phosphinate anion are thus of interest not only for the usual reasons, but particularly for solvent extraction applications.

3.4 - Halide Free Routes to Phosphonium Ionic Liquids

As indicated above, many phosphonium ionic liquids are prepared by quaternization of tertiary phosphines to form chlorides, with subsequent anion exchange if other anions are required.[1] The materials thus prepared inevitably contain residual chloride ions, which may adversely affect metal catalysts[1,25] and/or contaminate reaction products. This is true, for example, of phosphonium ionic liquids used in the production of halogen-free epoxy resins[26] and polycarbonates.[27] In addition, anion exchange processes are typically wasteful and expensive, often involving the use of environmentally hazardous molecular solvents. Factors such as these increase the final cost of ionic liquids produced industrially, and effectively limit their application range. For these reasons and others, chloride free routes to phosphonium salts are desirable.[28]

Halogen free systems can be produced by direct reaction of tertiary phosphines with alkylating agents such as benzenesulfonate, alkyltosylates (some examples of which have been described previously[36]), trialkylphosphates, and dialkylsulfates (see Eq. 5-7).

$$SO_2(OR)_2 + PR'_3 \longrightarrow [RPR'_3]^+[SO_3(OR)]^- \quad (5)$$

$$O{=}P(OR)_3 + PR'_3 \longrightarrow [RPR'_3]^+[PO_2(OR)_2]^- \quad (6)$$

$$O{=}PR(OR)_2 + PR'_3 \longrightarrow [RPR'_3]^+[PRO_2(OR)]^- \quad (7)$$

4 - Properties of Phosphonium Ionic Liquids

One major difference between phosphonium and ammonium salts is their stability with respect to degradation under various conditions.[36,29] For example, although both can decompose by internal displacement at higher temperatures (Eq. 8), phosphonium salts are generally more thermally stable than ammonium salts in this respect.[29]

$$[R_4E]^+X^- \xrightarrow{\Delta} R_3E + R\text{-}X \quad (E = N, P) \quad (8)$$

Unlike their ammonium counterparts, which can undergo facile Hoffmann or β-elimination in the presence of base,[30] phosphonium salts decompose to yield a tertiary phosphine oxide and alkane under alkaline conditions (Eq. 9).[31] Alternatively, depending on the nature of R and R', stable phosphoranes can be formed (Eq. 10) such as well known Wittig reagents. While the decomposition of phosphonium salts by these pathways may occur even at room temperature in some cases, contrasting examples are known where tetraalkylphosphonium halides

can be combined with concentrated sodium hydroxide well above room temperature without any degradation[29] (*e.g.* $[(C_{16}H_{33})P(C_4H_9)]Br$[32]).

$$[R_3P\text{-}CH_2\text{-}R']^+ + OH^- \longrightarrow R_3P{=}O + CH_3\text{-}R' \quad (9)$$

$$[R_3P\text{-}CH_2\text{-}R']^+ + OH^- \longrightarrow R3P{=}CHR' + H_2O \quad (10)$$

While the decomposition point of neat phosphonium ionic liquids on heating varies somewhat depending on the anion, thermogravimetric analyses (TGA) indicate dynamic thermal stability in excess of 300 ºC for many species. However, we note that dynamic thermal stabilities normally reported for ionic liquids are typically much higher than static thermal stabilities. Thus, most ionic liquids are not stable for extended periods of time at, or even well below, the "onset of decomposition" temperature typically measured by TGA. Figure 2 shows TGA data for trihexyl(tetradecyl)phosphonium tetrafluoroborate, which exhibits a profile typical of most phosphonium salts. This enhanced thermal stability relative to quaternary nitrogen based salts is an important factor when, for example, reaction products must be removed from an ionic liquid by high temperature distillation.

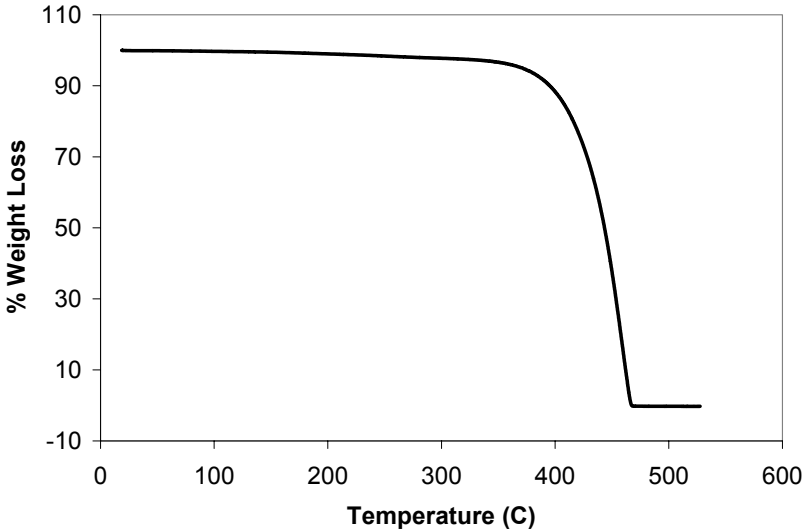


Figure 2: Stability with respect to temperature, as demonstrated by thermogravimetric analysis (TGA), for trihexyl(tetradecyl)phosphonium tetrafluoroborate, $[(C_6H_{13})_3P(C_{14}H_{29})][BF_4]$.

Viscosity is a particularly important characteristic for solvents being considered in industrial applications. Phosphonium based ionic liquids tend to have viscosities somewhat higher than their ammonium counterparts, especially at or near room temperature. However, on heating from ambient to typical industrial reaction temperatures (*e.g.* 70-100 ºC), their viscosities generally decrease to < 1 P. (For comparison,

the viscosity of olive oil is approximately 0.9 P). This is shown for trihexyl(tetradecyl)phosphonium chloride in Figure 4. Ionic liquid viscosities are also very sensitive to solutes,[33] and the addition of reactants and/or catalysts can be expected to further reduce viscosity. For example, mixing trihexyl(tetradecyl)phosphonium chloride with 1% (w/w) of hexane, water, or toluene decreases viscosity at all temperatures (Figure 3).

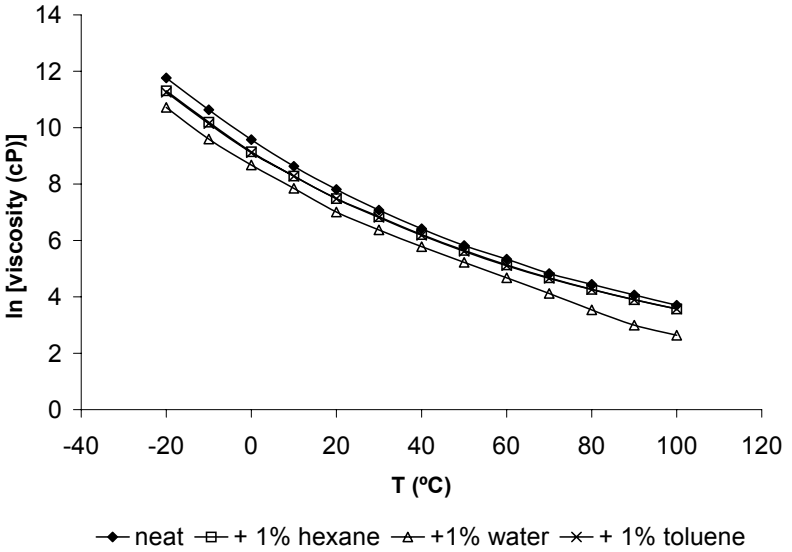


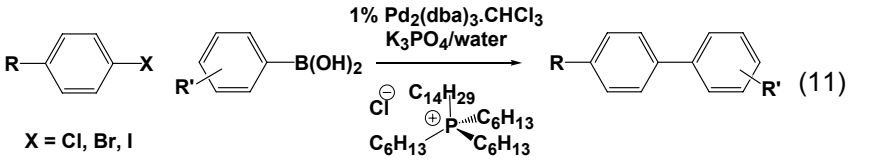
Figure 3: Viscosity with respect to temperature for trihexyl(tetradecyl)phosphonium chloride, $[(C_6H_{13})_3P(C_{14}H_{29})]Cl$, neat and with 1% (w/w) of impurities.

An important difference between imidazolium and phosphonium salts is the acidic protons present in the former. Relative to phosphonium cations, imidazolium cations are not entirely inert and can interact with solutes either through hydrogen bonding interactions or through the aromatic nature of the ring system.[34] Tetraalkylphosphonium salts do not have such acidic protons or aromatic rings, and consequently there is less potential for interaction with solutes.

5 – Uses of Phosphonium Ionic Liquids

Specific accounts of phosphonium ionic liquids in the journal literature are relatively rare. Two areas of exception are liquid crystalline applications (particularly the work of Weiss *et al.*)[35] and catalysis. Three accounts of catalysis in phosphonium ionic liquids have been reported: 1) tetraalkylphosphonium tosylates as solvents for hydroformylation;[36] 2) tetraalkylphosphonium halides as solvents for palladium catalyzed Heck

reactions;[37] and 3) trihexyl(tetradecyl)phosphonium chloride as a solvent for palladium mediated Suzuki cross-coupling reactions (Eq. 11).[38]



(11)

This last application demonstrates a particularly elegant use of three phase behaviour exhibited by mixtures of trihexyl(tetradecyl) phosphonium chloride, hexane, and water (Figure 3a). Although hexane and the ionic liquid are miscible in this case, three phases develop when water is added. Eq. 1 takes good advantage of this feature (Figure 3b), with product separation being easily accomplished by washing the reaction mixture with hexane and water to form a three layer system. The palladium catalyst remains fully dissolved in the central phosphonium ionic liquid layer, which can be recycled and reused. The product collects in the hexane layer and can be removed by decantation in virtually quantitative yield, while the by-products collect in the water layer and can be drained and discarded. Several cycles with no loss in yield or activity have been demonstrated using this work-up procedure. The same three phase behaviour is also observed for trihexyl(tetradecyl)phosphonium bis(2,4,4-trimethylpentyl)phosphinate.

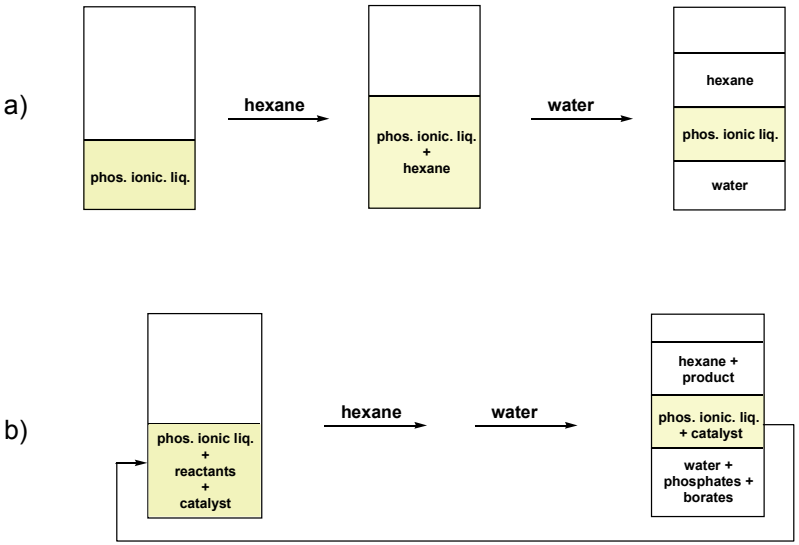


Figure 3: Three phase behavior for phosphonium halides and phosphinates.

Contrasting the dearth in the journal literature, the use of phosphonium ionic liquids for various applications is covered in numerous patents. For example, several uses of ionic liquids for nuclear fuel reprocessing are protected in patents (assigned to British Nuclear Fuels Plc) which make no distinction based on composition.[39] Similarly, the use of any ionic liquids in inks for marker pens and ink jet printers has been claimed,[40] as has the use of any ionic liquid for removal of scale (typically $BaSO_4$ and $CaSO_4$, but also paraffin, wax, and sludge) from wellbores in oilfield applications.[41]

Although several other applications-related patents relevant to phosphonium ionic liquids have been filed in recent years, the work of Institute Français du Petrole (IFP) is of particular note. IFP have commercialized the use of certain ionic liquids as solvents for catalysis for the dimerization, codimerization, and oligomerization of olefins using transition metal catalysts (part of the Dimersol and Diafsol processes).[42] Ionic liquids containing an alkylaluminum dihalide with a quaternary ammonium or phosphonium halide wherein the alkyl chains are less than 12 carbon atoms long, and which are liquid below 80 ºC, are covered.

Of particular interest for Friedel-Crafts chemistry applications, ionic liquids comprised of mixtures of R_nMX_{3-n} (R = C_1-C_6; M = Al, Ga; X = halide; n = 0, 1, 2) and ammonium, imidazolium, pyridinium, or phosphonium halides, and the use of these in alkylation reactions have also been claimed.[43]

6 - Conclusions

While the exact path for future development of ionic liquids is currently unclear, the potential for the field as a whole seems enormous. We believe that successful commercialization of technologies utilizing these new materials will be a key driver for their continued development and integration into the chemical industry. Large-scale, industrial manufacture of the ionic liquids themselves is clearly a necessary precursor for this process. Here we have described a small part of our continuing efforts in this area.

Equally important, however, is getting samples of production quality ionic liquids into the hands of capable researchers in both academia and industry. Ionic liquids based on quaternary nitrogen cations such as imidazolium and pyridinium have been extensively investigated in this regard. By comparison, phosphonium ionic liquids have previously received scant attention. Judging by patent activity, however, there is significant interest in phosphonium ionic liquids for industrial use. We believe that phosphonium salts offer a good alternative to ammonium salts for many applications. While neither family is “better” than the other, each will undoubtedly offer advantages and disadvantages for any particular function. This being the case, we anticipate that phosphonium ionic liquids will take their place alongside molecular solvents, imidazolium ionic liquids, and other modern materials in the toolboxes of chemists, chemical engineers, process developers, and inventors.

7 - Acknowledgements

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Products Referenced in the Article

Ionic Liquid Kit 3 :
CYPHOSIL Phosphonium Salt Kit

1 kit

96-6520

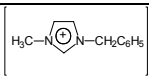
Contains a 10g unit of each of the eight items listed below.

Also available in the following sizes for individual sale.

15-6370	Trihexyl(tetradecyl)phosphonium bis(trifluoromethane-sulfonyl)amide CYPHOSIL 109	10g 50g
15-6374	Trihexyl(tetradecyl)phosphonium bis(2,4,4-trimethyl-pentyl)phosphinate CYPHOSIL 104	10g 50g
15-6378	Trihexyl(tetradecyl)phosphonium bromide CYPHOSIL 102	10g 50g
15-6382	Trihexyl(tetradecyl)phosphonium chloride CYPHOSIL 101	10g 50g
15-6386	Trihexyl(tetradecyl)phosphonium decanoate CYPHOSIL 103	10g 50g
15-6390	Trihexyl(tetradecyl)phosphonium dicyanamide CYPHOSIL 105	10g 50g
15-6394	Trihexyl(tetradecyl)phosphonium hexafluorophosphate CYPHOSIL 110	10g 50g
15-6398	Trihexyl(tetradecyl)phosphonium tetrafluoroborate CYPHOSIL 111	10g 50g

Ionic Liquids and Kits

Purchased individually or in kits



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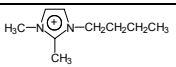
5g



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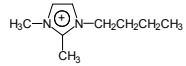

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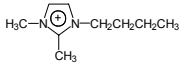

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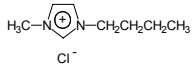

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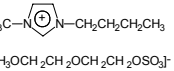

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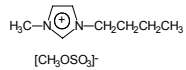

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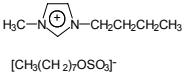

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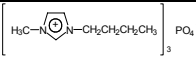

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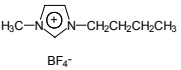

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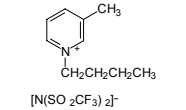

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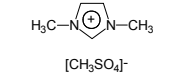

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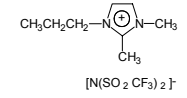

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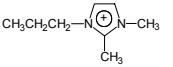

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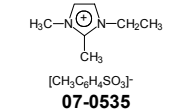

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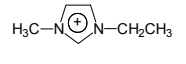

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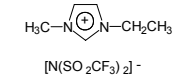

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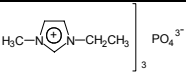

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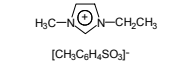

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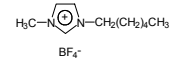

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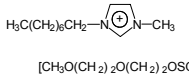

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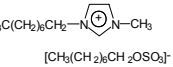

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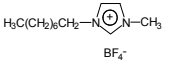

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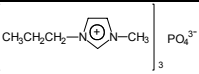

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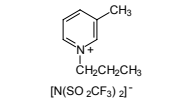

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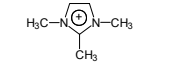


07-2660
5g

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

NEW CATALYST and LIGAND KITS		
96-6650	Degussa Heterogeneous Catalyst Kit Contains a 10g unit of each of the 12 items listed below. Weight is quantity contained.	1 kit
Also available in the following sizes for individual sale.		
46-1700	Palladium, 5% on activated carbon, eggshell, oxidic (50% wetted powder) Degussa E3	10g 50g
46-1703	Palladium, 5% on activated carbon, eggshell, reduced (50% wetted powder) Degussa E5	10g 50g
46-1706	Palladium, 10% on activated carbon, Pearlman (50% wetted powder) Degussa E4	10g 50g
46-1709	Palladium, 5% on activated carbon, uniform, oxidic (50% wetted powder) Degussa E1	10g 50g
46-1712	Palladium, 5% on activated carbon, uniform, oxidic (50% wetted powder) Degussa E2	10g 50g
78-1500	Platinum, 5% on activated carbon, bismuth doped (50% wetted powder) Degussa F3	10g 50g
78-1503	Platinum, 5% on activated carbon, eggshell, reduced (50% wetted powder) Degussa F2	10g 50g
78-1506	Platinum, 3% on activated carbon, sulfided (50% wetted powder) Degussa F5	10g 50g
78-1509	Platinum, 5% on activated carbon, uniform, reduced (50% wetted powder) Degussa F1	10g 50g
78-1512	Platinum, 1% on activated carbon, vanadium doped (50% wetted powder) Degussa F4	10g 50g
45-1863	Rhodium, 5% on activated carbon (50% wetted powder) Degussa G1	10g 50g
44-4059	Ruthenium, 5% on activated carbon (50% wetted powder) Degussa H1	10g 50g
Visit www.strem.com/code/degussakit.html for Recommendations Guide.		

Distributed by STREM

degussa. Catalysts & Initiators

Catalyst	5% Pd/C, uni, ox	5% Pd/C, uni, ox	5% Pd/C, egg, ox	10% Pd/C, Pearlman	5% Pd/C, egg, red	5% Pt/C, uni, red	5% Pt/C, egg, red	5% Pt/C, Bi doped	1% Pt/C, V doped	3% Pt/C, sulfided	5% Ru/C	5% Rh/C
Strem #	46-1709	46-1712	46-1700	46-1706	46-1703	78-1509	78-1503	78-1500	78-1512	78-1506	44-4059	45-1863
Application Degussa #	E1	E2	E3	E4	E5	F1	F2	F3	F4	F5	H1	G1
Hydrogenation of C=C double bonds	○	●	●	●	●							
Hydrogenation of CN bonds	○	●	●	○	○	○	○					●
Reduction of the C=O group			○		○	○					●	●
Hydrogenation of Nitro Groups	○	○	●	●	●	○	○		●	○		
Hydrogenolysis Reactions	●	○	●	●	●							
Reductive Alkylation and Amination	○	○	○	○						●		
Hydrogenation of (Hetero) Aromatic Rings	○	○	○	○	○	○	○				●	●
Oxidations (Alcohols and Sugars)						●	○	●				
CC Coupling reactions	○	●	○	●	○							

*uni = uniform Precious Metal (PM) distribution; egg = egg-shell PM distribution; ox = oxidized PM; red = reduced PM

○ recommended
● preferred

Note: Please refer to the different reaction classes in the Recommendations Guide for more detailed information regarding selectivity, activity and reaction conditions.
This sample kit is designed as an entry point to find a suitable catalyst. Please contact one of our technical specialists for further recommendations.
Most often the catalyst performance can be improved significantly by tailoring the catalyst to your requirements.

The recommendations given above are believed to be accurate at the time of publication, but Degussa makes no warranty with respect thereto, including but not limited to any results to be obtained or the infringement of any proprietary right.

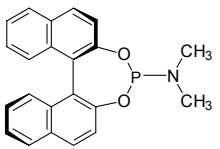
NEW CATALYST and LIGAND KITS (cont.)

DSM MonoPhos™ Ligand Kit

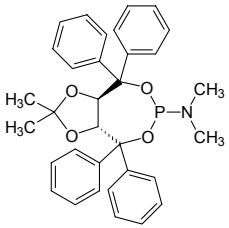
1 kit

Sold in collaboration with DSM for research purposes only.

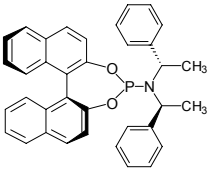
96-5650 – Contains the following:



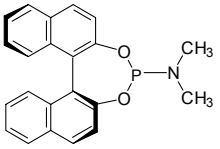
15-1232 1g



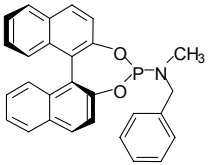
15-1505 100mg



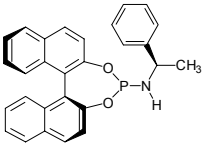
15-1521 100mg



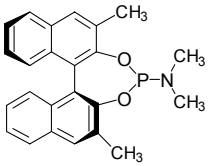
15-1233 1g



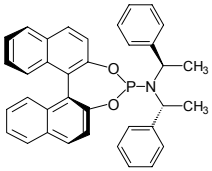
15-1510 100mg



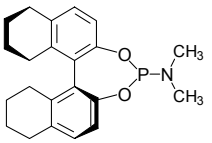
15-1525 100mg



15-1255 100mg



15-1520 100mg



15-3495 100mg

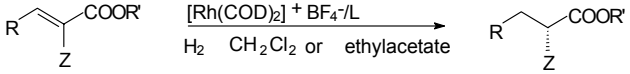
Patent WO 02 04466.

Also available in the following sizes for individual sale.

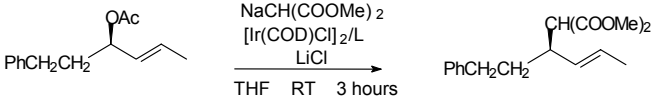
15-1232	(R)-(-)-(3,5-Dioxa-4-phospha-cyclohepta[2,1-a;3,4-a'] dinaphthalen-4-yl)dimethylamine, min. 98% (R)-MONOPHOS	1g 5g

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.



R = H, Ph R' = H, CH_3 Z = $NHCOCH_3$, CH_2COOH > 97% ee **Tech. Note (1)**
Ref. (1)



93% ee **Tech. Note (2)**
Ref. (2)

References:

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

DSM MonoPhos™ Ligand Kit (cont.)

Sold in collaboration with DSM for research purposes only.

15-1233	(S)-(+)-(3,5-Dioxa-4-phospha-cycloheptа[2,1-a;3,4-a'] dinaphthalen-4-yl)dimethylamine, min. 98% (S)-MONOPHOS	1g 5g

Technical Note:

1. See 15-1232 page 16.

15-1255	(S)-(+)-(2,6-Dimethyl-3,5-dioxa-4-phospha-cyclohepta [2,1-a;3,4-a']dinaphthalen-4-yl)dimethylamine, min. 98%	100mg 500mg

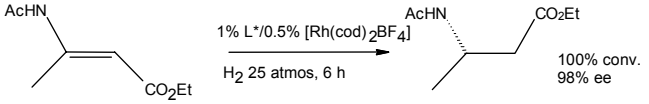
Technical Note:

1. See 15-3495 page 18.

15-1505	(3aR,8aR)-(-)-(2,2-Dimethyl-4,4,8,8-tetraphenyl-tetrahydro- [1,3]dioxolo[4,5-e][1,3,2]dioxaphosphepin-6-yl)dimethylamine, min. 98%	100mg 500mg
15-1510	(S)-(+)-(3,5-Dioxa-4-phospha-cycloheptа[2,1-a;3,4-a'] dinaphthalen-4-yl)benzyl(methyl)amine, 99%	100mg 500mg

Technical Note:

1. A ligand in the rhodium-catalyzed enantioselective hydrogenation of (E)-N-acylated dehydro-β-aminoacid esters. For (Z) isomer, use 15-1525 page 18.



Reference:

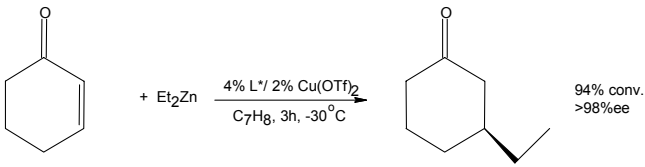
1. *J. Am. Chem. Soc.*, **2002**, *124*, 14552.

15-1520	(S)-(+)-(3,5-Dioxa-4-phospha-cycloheptа[2,1-a;3,4-a'] dinaphthalen-4-yl)bis[(1R)-1-phenylethyl]amine, dichloromethane adduct, 99%	100mg 500mg

Technical Notes:

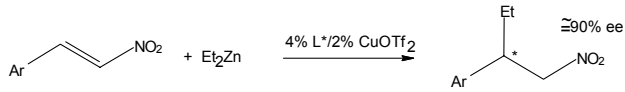
1. A ligand for asymmetric conjugate addition of dialkyl zinc reagents to activated olefins.

   (a) Catalytic stereocontrol of conjugate addition of dialkyl zinc reagents to enones.



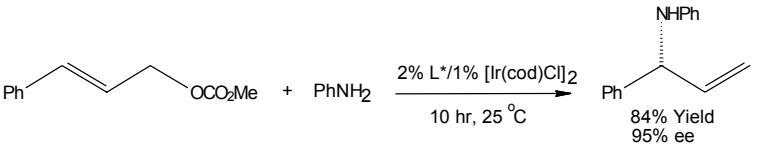
Ref. (1)

   (b) Enantioselective addition to nitroalkenes, cinnamyl halides.



Ref. (2)

2. Iridium catalyzed enantioselective addition of amines to achiral allylic esters to produce enantiomerically enriched allylic amines.



Ref. (3)

References:

1. *Angew. Chem. Int. Ed.*, **1997**, *36*, 2620.
2. *Tetrahedron*, **2002**, *58*, 5773.
3. *J. Am. Chem. Soc.*, **2002**, *124*, 15164.

DSM's MonoPhos™ Ligand Kit (cont.)

Sold in collaboration with DSM for research purposes only.

15-1521	(S)-(+)-(3,5-Dioxa-4-phospha-cyclohepta[2,1-a;3,4-a'] dinaphthalen-4-yl)bis[(1S)-1-phenylethyl]amine, min. 95%	100mg 500mg

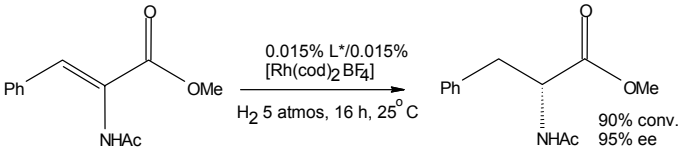
Technical Note:
1. See 15-1520 page 17.

15-1525	(S)-(+)-(3,5-Dioxa-4-phospha-cyclohepta[2,1-a;3,4-a'] dinaphthalen-4-yl)[(1R)-1-phenylethyl]amine, min. 95%	100mg 500mg

Technical Note:
1. See 15-1510 page 17.

15-3495	(S)-(+)-(8,9,10,11,12,13,14,15-Octahydro-3,5-dioxa-4-phospha- cyclohepta[2,1-a;3,4-a']dinaphthalen-4-yl) dimethylamine, 99%	100mg 500mg

Technical Note:
1. A ligand for enantioselective hydrogenation of prochiral functional olefins



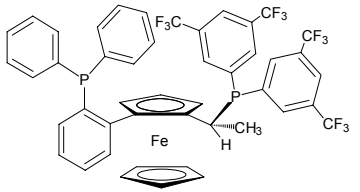
Reference:
1. *Adv. Synth. Catal.*, **2003**, *345*, 308.

NEW CATALYST and LIGAND KITS (cont.)

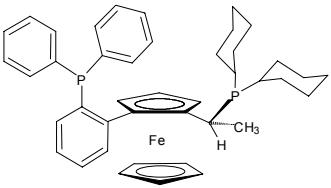
Solvias Walphos Ligand Kit

Sold in collaboration with Solvias for research purposes only. 1 kit

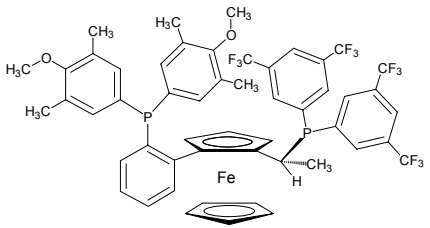
96-3651 Contains a 100mg unit of each of the items listed below.



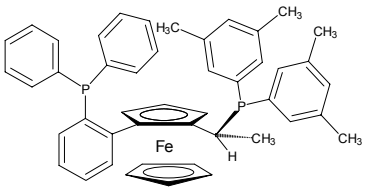
26-1300



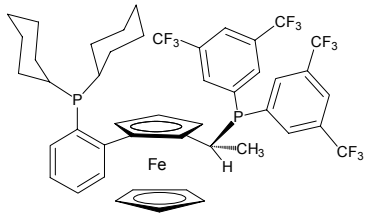
26-1310



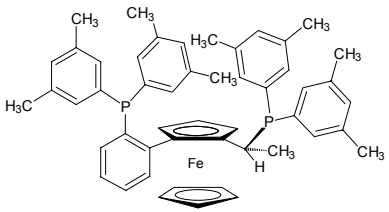
26-1130



26-1320



26-1120



26-1555

Ligands are air-stable.
Also available in the following sizes for individual sale.

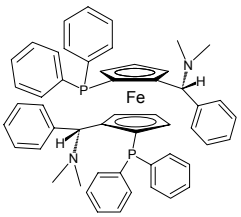
26-1300	(R)-(-)-1-[(R)-2-(2'-Diphenylphosphinophenyl) ferrocenyl]ethyldi(bis-3,5-trifluoromethylphenyl) phosphine, min. 97%	100mg 500mg
26-1310	(R)-(-)-1-[(R)-2-(2'-Diphenylphosphinophenyl) ferrocenyl]ethyldicyclohexylphosphine, min. 97%	100mg 500mg
26-1130	(R)-(+)-1-[(R)-2-(2'-Di(3,5-dimethyl-4-methoxyphenyl) phosphinophenyl)ferrocenyl]ethyldi(bis-3,5-trifluoromethylphenyl)phosphine, min. 97%	100mg 500mg
26-1320	(R)-(+)-1-[(R)-2-(2'-Diphenylphosphinophenyl) ferrocenyl]ethyldi(3,5-xylyl)phosphine, min. 97%	100mg 500mg
26-1120	(R)-(+)-1-[(R)-2-(2'-Dicyclohexylphosphinophenyl) ferrocenyl]ethyldi(bis-3,5-trifluoromethylphenyl) phosphine, min. 97%	100mg 500mg
26-1555	(R)-(+)-1-[(R)-2-(2'-Di(3,5-xylyl)phosphinophenyl) ferrocenyl]ethyldi(3,5-xylyl)phosphine, min. 97%	100mg 500mg

NEW CATALYST and LIGAND KITS (cont.)

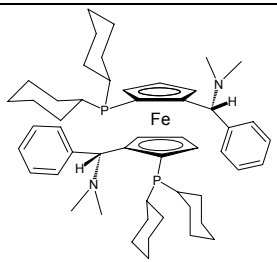
Solvias Mandyphos™ Ligand Kit

Sold in collaboration with Solvias for research purposes only. 1 kit

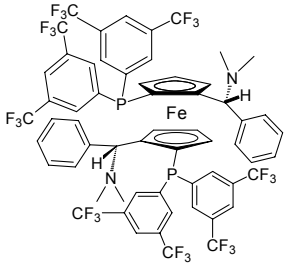
96-3652 Contains a 100mg unit of each of the items listed below.



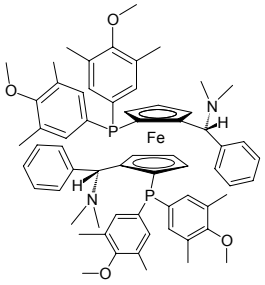
26-0252



26-0240



26-0244



26-0248

Ligands are air-stable.
Also available in the following sizes for individual sale.

26-0252	(S,S)-(-)-2,2'-Bis[(R)-(N,N-dimethylamino)(phenyl) methyl]-1,1'-bis(diphenylphosphino)ferrocene, min. 97%	100mg 500mg
26-0240	(S,S)-(+)-2,2'-Bis[(R)-(N,N-dimethylamino)(phenyl) methyl]-1,1'-bis(dicyclohexylphosphino)ferrocene, min. 97%	100mg 500mg
26-0244	(S,S)-(-)-2,2'-Bis[(R)-(N,N-dimethylamino)(phenyl) methyl]-1,1'-di[bis(3,5-trifluoromethylphenyl)phosphino] ferrocene, min. 97%	100mg 500mg
26-0248	(S,S)-(-)-2,2'-Bis[(R)-(N,N-dimethylamino)(phenyl) methyl]-1,1'-di[bis(3,5-dimethyl-4-methoxyphenyl) phosphino]ferrocene, min. 97%	100mg 500mg

NEW CATALYST and LIGAND KITS (cont.)

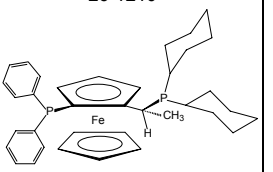
Solvias Josiphos Ligand Kit: featuring the Josiphos family of ligands for asymmetric hydrogenation and other catalytic applications.

Sold in collaboration with Solvias for research purposes only.

96-3650

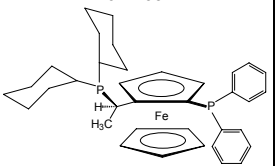
Components include:

26-1210



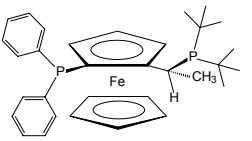
200mg

26-1209



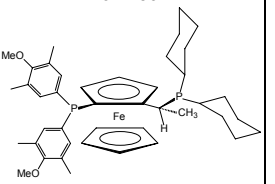
100mg

26-1200



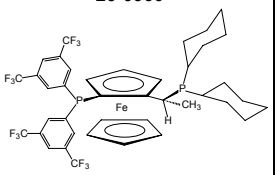
200mg

26-1150



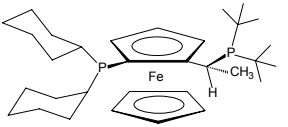
100mg

26-0960



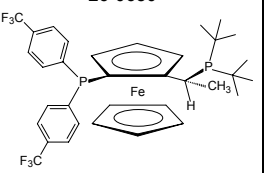
100mg

26-0975



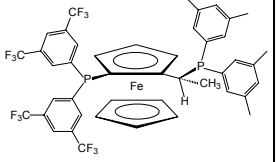
100mg

26-0650



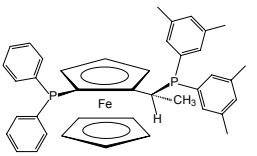
100mg

26-0965



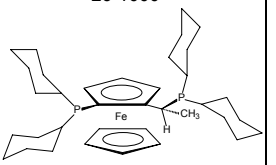
100mg

26-1255



200mg

26-1000



200mg

Ligands are air-stable.
Also available in the following sizes for individual sale.

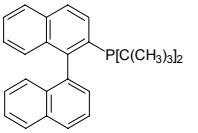
26-0650	(R)-(-)-1-[(S)-2-(Bis(4-trifluoromethylphenyl)phosphino) ferrocenyl]ethyl-di-t-butylphosphine, min. 97%	100mg 500mg
26-0960	(R)-(-)-1-[(S)-2-(Di(3,5-bis-trifluoromethylphenyl)phosphino) ferrocenyl]ethyldicyclohexylphosphine, min. 97%	100mg 500mg
26-0965	(R)-(-)-1-[(S)-2-(Di(3,5-bis-trifluoromethylphenyl)phosphino) ferrocenyl]ethyldi(3,5-dimethylphenyl)phosphine, min. 97%	100mg 500mg
26-0975	(R)-(-)-1-[(S)-2-(Dicyclohexylphosphino)ferrocenyl]ethyldi-t-butylphosphine, min. 97%	100mg
26-1000	(R)-(-)-1-[(S)-2-(Dicyclohexylphosphino)ferrocenyl]ethyldi-cyclohexylphosphine, min. 97%	100mg 500mg
26-1150	(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
26-1209	(R)-(+)-1-[(R)-2-(Diphenylphosphino)ferrocenyl] ethyldicyclohexylphosphine, min. 97% (R)-(R)-JOSIPHOS	100mg
26-1210	(R)-(-)-1-[(S)-2-Diphenylphosphino)ferrocenyl]ethyldicyclo-hexylphosphine, min. 97% (R)-(S)-JOSIPHOS	100mg 500mg
26-1255	(R)-(-)-1-[(S)-2-Diphenylphosphino)ferrocenyl]ethyldi(3,5-dimethylphenyl)phosphine, min. 97%	100mg 500mg

Buchwald Biaryl Phosphine Ligand Kit

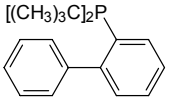
for Aromatic Carbon-Heteroatom Formation and Suzuki Coupling

96-5500 1 kit

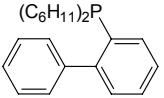
Contains the smallest unit of the nine items listed below.



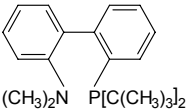
15-1043



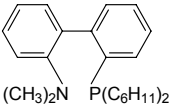
15-1045



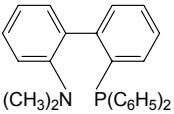
15-1140



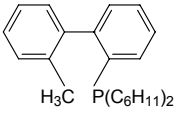
15-1048



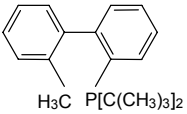
15-1145



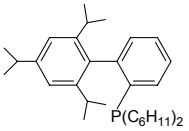
15-1745



15-1148



15-1049



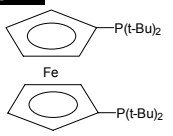
15-1149

Also available in the following sizes for individual sale.

15-1043	racemic-2-(Di-t-butylphosphino)-1,1'-binaphthyl, 98%	250mg 1g
15-1045	2-(Di-t-butylphosphino)biphenyl, 99%	500mg 2g 10g 50g
15-1140	2-(Dicyclohexylphosphino)biphenyl, 98%	500mg 2g 10g 50g
15-1048	Di-t-butylphosphino-2'-(N,N-dimethylamino)biphenyl, 98%	500mg 2g
15-1145	2-(Dicyclohexylphosphino)-2'-(N,N-dimethylamino) biphenyl, 98%	500mg 2g 10g 50g
15-1745	2-(Diphenylphosphino)-2'-(N,N-dimethylamino) biphenyl, 98%	500mg 2g
15-1148	2-(Dicyclohexylphosphino)-2'-methylbiphenyl, min. 98%	500mg 2g
15-1049	2-(Di-t-butylphosphino)-2'-methylbiphenyl, 99% Technical Note: See page 26.	500mg 2g 10g 50g
15-1149	2-(Dicyclohexylphosphino)-2',4',6'-tri-i-propyl-1,1'-biphenyl, min. 98% X-PHOS Technical Note: See page 27.	500mg 2g

New Products Introduced Since Chemiker XIX
Metal Catalysts for Organic Synthesis

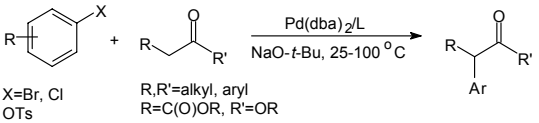
IRON



26-0150

1,1'-Bis(di-t-butylphosphino)ferrocene, 500mg
min. 98% 2g

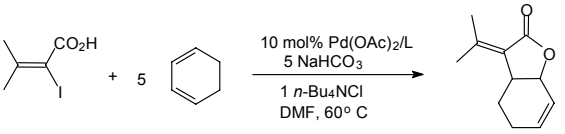
Technical Notes:
1. Ligand used in the palladium-catalyzed α-arylation of ketones.
2. Ligand used in the palladium-catalyzed heteroannulation of 1,3-dienes to form α-alkylidene-γ-butyrolactones.



X=Br, Cl
OTs

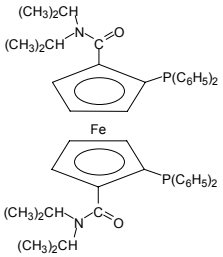
R,R'=alkyl, aryl
R=C(O)OR, R'=OR

Tech. Note (1)
Ref. (1)



Tech. Note (2)
Ref. (2)

References:
1. *J. Am. Chem. Soc.*, **1999**, *121*, 1473.
2. *J. Org. Chem.*, **2000**, *65*, 1525.

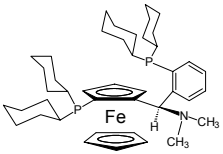


26-0255

(R)-(+)-1,1'-Bis(diphenylphosphino)-2,2'-bis(N,N-di-i-propylamido)ferrocene 100mg 500mg
(R)-CTH-JAFAPhos

Note:
Sold in collaboration with Synetix for research purposes only. US Patent Application No US Patent 5 856 540 and patents arising therefrom.

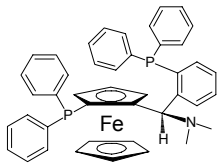
Technical Note:
1. Versatile catalyst used in asymmetric hydrogenation, allylic alkylations, grignard cross coupling and aldol reactions.



26-0955

(S)-(+)-[(R)-2-Dicyclohexylphosphino-ferrocenyl](N,N-dimethylamino)(2-dicyclohexylphosphinophenyl)methane, min. 97% 100mg 500mg

Note:
Sold in collaboration with Solvias for research purposes only.



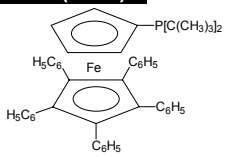
26-1155

(S)-(+)-[(R)-2-Diphenylphosphino-ferrocenyl](N,N-dimethylamino)(2-diphenylphosphinophenyl)methane, min. 97% TANIAPHOS 100mg 500mg

Note:
Sold in collaboration with Solvias for research purposes only.

New Products Introduced Since Chemiker XIX (cont.)
Metal Catalysts for Organic Synthesis (cont.)

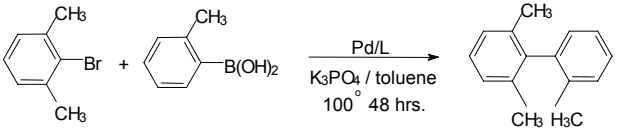
IRON (cont.)



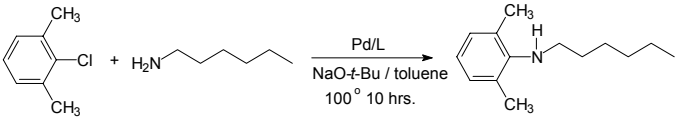
26-3575

1,2,3,4,5-Pentaphenyl-1'-(di-t-butylphosphino)ferrocene, 95% — 100mg, 500mg
CTC-Q-PHOS

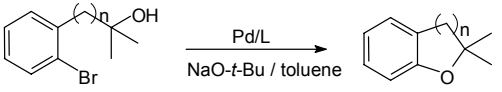
Note:
Sold in collaboration with Synetix for research purposes only.
Technical Note:
1. Ligand used in the preparation of highly active palladium catalysts for C-C, C-N and C-O bond formation.



87%



97%

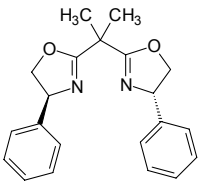


n = 1,2

93% (n=2) RT 10 mins.
97% (n=1) RT 15 hrs.

Reference:
1. *J. Org. Chem.*, **2002**, *67*, 5553.

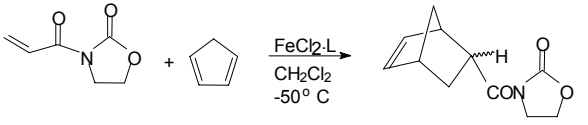
NITROGEN



07-0275

(-)-2,2-Bis[(4S)-4-phenyl-2-oxazolin-2-yl]propane, 98% — 250mg, 1g

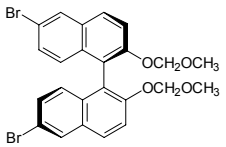
Technical Note:
1. Ligand used for enantioselective Diels-Alder addition.



93:7 enantioselectivity
99:1 endo/exo

Reference:
1. *J. Am. Chem. Soc.*, **1991**, *113*, 728.

OXYGEN



08-0620

(R)-(+)-6,6'-Dibromo-2,2'-bis(methoxymethoxy)-1,1'-binaphthyl — 250mg, 1g, 5g

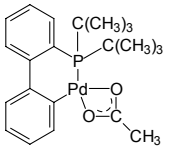
Technical Note:
1. Starting material for the preparation of a variety of 6,6' and 3,3'-substituted BINOLS.

08-0621

(S)-(-)-6,6'-Dibromo-2,2'-bis(methoxymethoxy)-1,1'-binaphthyl — 250mg, 1g, 5g

Technical Note:
1. See 08-0620 page 24.

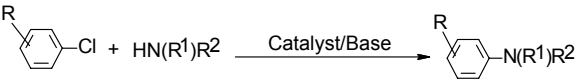
PALLADIUM

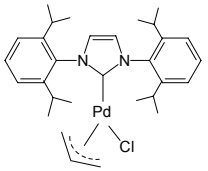


46-0025

Acetato(2'-di-t-butylphosphino-1,1'-biphenyl-2-yl)palladium (II), min. 98% — 250mg, 1g

Technical Note:
1. Air and thermally stable, one component precatalyst for the amination of aryl halides.

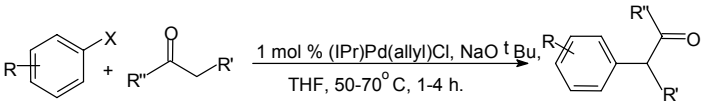




46-0040

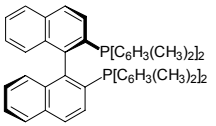
Allylchloro[1,3-bis(2,6-di-i-propylphenyl) imidazol-2-ylidene]palladium (II), 97% — 250mg, 1g

Technical Note:
1. Air and moisture stable catalyst useful in the arylation of amines and ketones in a variety of cross-coupling reactions.



References: X=Br, OTf, Cl
1. *Org. Lett.*, **2002**, *4*, 4053-4056.
2. *Organometallics*, **2002**, *21*, 5470-5472.

PHOSPHORUS



15-0476

(R)-(+)-2,2'-Bis[di(3,5-xylyl)phosphino]-1,1'-binaphthyl, 98% (R)-3,5-xylyl-BINAP — 100mg, 500mg

Technical Note:
1. See 15-0150 Catalog 19 page 345.

15-0477

(S)-(-)-2,2'-Bis[di(3,5-xylyl)phosphino]-1,1'-binaphthyl, 98% (S)-3,5-xylyl-BINAP — 100mg, 500mg

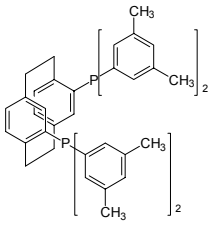
Technical Note:
1. See 15-0150 Catalog 19 page 345.

15-0730

(R)-(-)-4,12-Bis(di(3,5-xylyl)phosphino)-[2.2]-paracyclophane, min. 95% CTH-(R)-3,5-xylyl-PHANEPHOS — 100mg, 500mg

Note:
Sold in collaboration with Synetix for research purposes only.

Technical Note:
1. See 15-0426 Catalog 19 page 347.



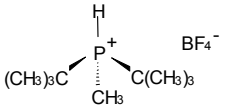
15-0731

(S)-(+)-4,12-Bis(di(3,5-xylyl)phosphino)-[2.2]-paracyclophane, min. 93% CTH-(S)-3,5-xylyl-PHANEPHOS — 100mg, 500mg

Note:
Sold in collaboration with Synetix for research purposes only.

Technical Note:
1. See 15-0426 Catalog 19 page 347.

PHOSPHORUS (cont.)



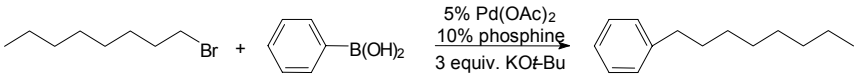
15-1023

Di-t-butylmethylphosphonium tetrafluoroborate, 99% — 1g, 5g

Note: See page 32 for list of other phosphonium salts available.

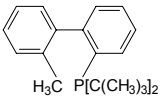
Technical Note:

1. Air and moisture-stable phosphonium salt used in the palladium-catalyzed Suzuki coupling reaction under mild conditions. The phosphonium salt, and the free phosphine ligand, were essentially interchangable. Both furnished nearly identical yields of desired product.



Reference:

1. *J. Am. Chem. Soc.*, **2002**, *124*, 13662.



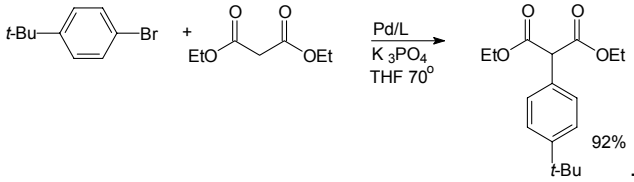
15-1049

2-(Di-t-butylphosphino)-2'-methylbiphenyl, 99% — 500mg, 2g, 10g, 50g

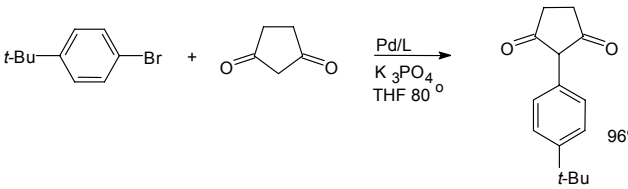
Note: See page 22 for other Buchwald Biaryl Phosphine Ligands available.

Technical Notes:

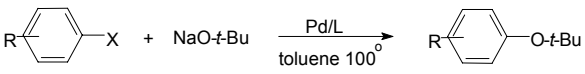
1. Ligand used in the palladium-catalyzed arylations of malonate esters and 1,3-diketones.
2. Ligand used in the palladium-catalyzed formation of t-butyl ethers from unactivated aryl halides.
3. Ligand used in the palladium-catalyzed α-arylations of nitroalkanes.



Tech. Note (1)
Ref. (1)

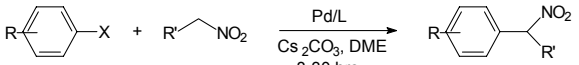


Tech. Note (1)
Ref. (1)



X = Cl, Br

Tech. Note (2)
Ref. (2)



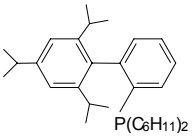
X = Cl, Br

Tech. Note (3)
Ref. (3)

References:

1. *J. Am. Chem. Soc.*, **2000**, *122*, 1360.
2. *J. Org. Chem.*, **2001**, 66, 2498.
3. *J. Org. Chem.*, **2002**, 67, 106.

PHOSPHORUS (cont.)

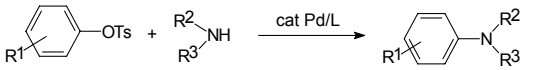


15-1149

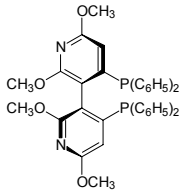
2-Dicyclohexylphosphino-2',4',6'-tri-i-propyl-1,1'-biphenyl, min. 98% X-PHOS — 500mg, 2g

Note: See page 22 for other Buchwald Biaryl Phosphine Ligands available.

Technical Note:
1. Exceptional ligand for the Pd-catalyzed amination of aryl halides and sulfonates. Air-stable and easily handled.



Reference:
1. *J. Am. Chem. Soc.*, *In press*.

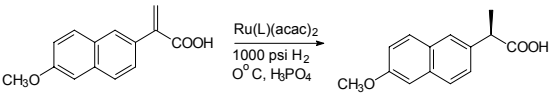


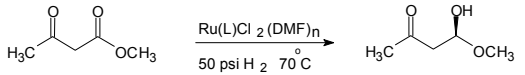
15-5200

(R)-(+)-2,2',6,6'-Tetramethoxy-4,4'-bis(diphenylphosphino)-3,3'-bipyridine, min. 95% CTH-(R)-P-PHOS — 100mg, 500mg

Note:
Sold in collaboration with Synetix for research purposes only.

Technical Note:
1. New class of highly effective chiral dipyridylphosphine ligands used in the asymmetric hydrogenation of 2-arylacylic acids and β-ketoesters.





Reference:
1. *J. Am. Chem. Soc.*, **2000**, *122(46)*, 11513.

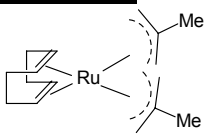
(S)-(-)-2,2',6,6'-Tetramethoxy-4,4'-bis(diphenylphosphino)-3,3'-bipyridine, min. 95% CTH-(S)-P-PHOS — 100mg, 500mg

15-5201

Note:
Sold in collaboration with Synetix for research purposes only.

Technical Note:
1. See 15-5200 page 27.

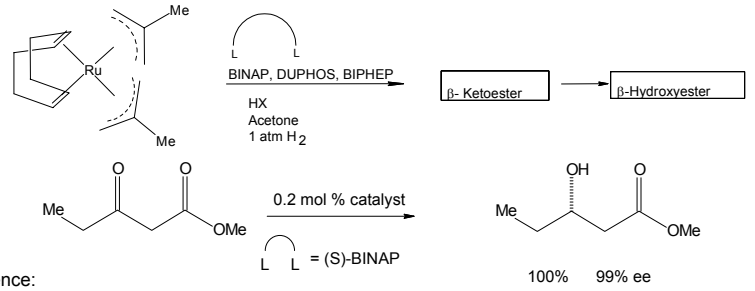
RUTHENIUM



44-0046

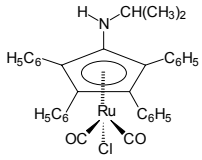
Bis(2-methylallyl)(1,5-cyclooctadiene) ruthenium (II), min. 97% — 250mg, 1g

Technical Note:
1. Convenient precatalyst for Ru-catalyzed asymmetric hydrogenations (L_2RuBr_2 prepared *in situ*).



Reference:
1. *Tetrahedron Lett.*, **1995**, *36*, 4801.

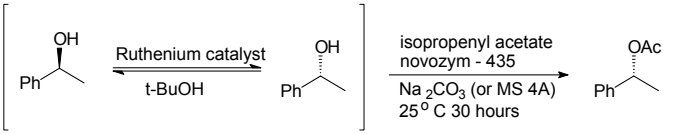
RUTHENIUM (cont.)



44-0123

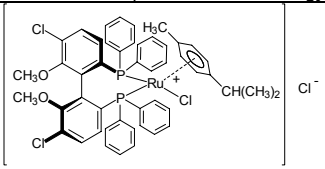
Chlorodicarbonyl[1-(i-propylamino)-2,3,4,5-tetraphenylcylcopentadienyl]ruthenium (II), min. 95% — 500mg, 2g

Technical Note:
1. Metal catalyst used in conjunction with enzymes for enantioselective transformations via dynamic kinetic resolution.



97%
>99.5% ee

Reference:
1. *Current Opinion in Biotechnology*, **2002**, *13*, 578.

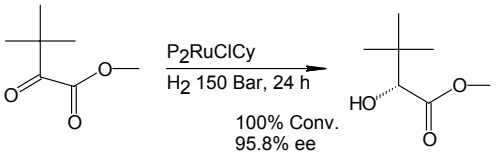


44-0121

Chloro[(R)-(+)-5,5'-dichloro-6,6'-dimethoxy-2,2'-bis(diphenylphosphino)-1,1'-biphenyl] (p-cymene)ruthenium (II) chloride CH_2Cl_2 adduct — 250mg, 1g

Note:
Sold in collaboration with Bayer for research purposes only. 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 Notes:
1. Catalyst for asymmetric hydrogenation of α and β-keto esters.
2. Catalyst for asymmetric hydrogenation of α,β unsaturated acids.[2]



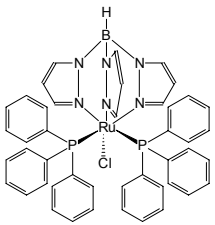
Tech. Note (1)
Ref. (1)

References:
1. EP1160237 (2001).
2. US5801261 (1998).

44-0122

Chloro[(S)-(-)-5,5'-dichloro-6,6'-dimethoxy-2,2'-bis(diphenylphosphino)-1,1'-biphenyl] (p-cymene)ruthenium (II) chloride CH_2Cl_2 adduct — 250mg, 1g

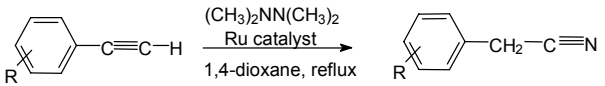
Technical Note:
1. See 44-0121 page 28.



44-0124

Chloro[hydrotris(pyrazol-1-yl)borato]bis(triphenylphosphine)ruthenium (II) ethanol adduct — 250mg, 1g

Technical Note:
1. Catalyst used with hydrazines for the transformation of terminal alkynes to nitriles.



Reference:
1. *Organometallics*, **2002**, *21(19)*, 3845.

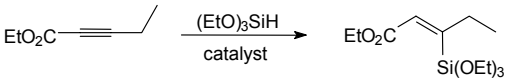
New Products Introduced Since Chemiker XIX (cont.)
Metal Catalysts for Organic Synthesis (cont.)

RUTHENIUM (cont.)

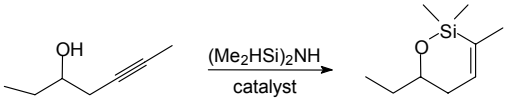
44-7880 — Tris(acetonitrile)pentamethylcyclopentadienyl-ruthenium (I) hexafluorophosphate, min. 98% — 250mg, 1g

Technical Note:

1. Useful catalyst for the hydrosilylation of internal and terminal alkynes. The reaction has also been extended to intramolecular hydrosilylation.



yield 99%
major/minor product 5:1 **Ref. (1)**

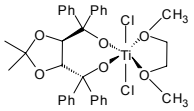


yield 79% **Ref. (2)**

References:

1. *J. Am. Chem. Soc.*, **2001**, *123*, 12726.
2. *J. Am. Chem. Soc.*, **2003**, *125*, 30.

TITANIUM

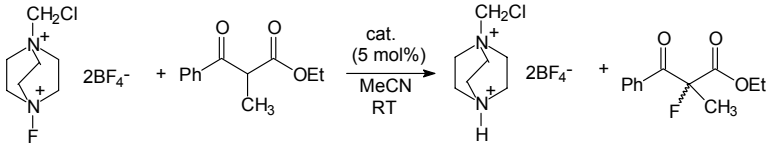


22-0780

(4R,5R)-(-)-2,2-Dimethyl-α,α,α',α'-tetraphenyl-1,3-dioxolane-4,5-dimethanolato[1,2-bis(dimethoxy)ethane]titanium (IV) dichloride acetonitrile adduct — 250mg, 1g

Technical Notes:

1. Catalyst used in the enantioselective fluorination of β-ketoesters.
1. Versatile catalyst used in the enantioselective 1,2 and 1,4 additions to carbonyl compounds, transfer of allyl groups to aldehydes, cycloadditions and others. See reference (2).



Tech. Note (1)
Ref. (1)

References:

1. *Angew. Chem. Int. Ed.*, **2000**, *39*, 4359.
1. *Angew. Chem. Int. Ed.*, **2001**, *40*, 92-138.

OTHER NEW PRODUCTS

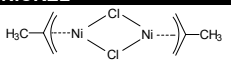
BORON

05-1295 — Triphenylboron, ammonia complex, min. 98% — 1g, 5g

GADOLINIUM

64-3700 — Gadolinium (III) i-propoxide (99.9%-Gd) (REO) — 1g, 5g

NICKEL



28-0900

Methallylnickel chloride dimer — 250mg, 1g

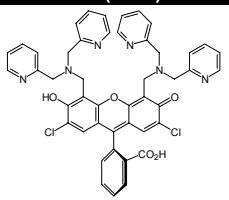
NITROGEN

07-0270 — trans-N,N'-Dimethyl-1,2-cyclohexanediamine, 98% — 500mg, 2g

References:

1. *J. Am. Chem. Soc.*, **2002**, *124*, 7421.
1. *J. Am. Chem. Soc.*, **2002**, *124*, 11684

NITROGEN (cont.)

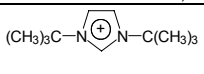


07-0314

9-(2-Carboxyphenyl)-2,7-dichloro-4,5-bis[di(2-pyridyl)aminomethyl]-6-hydroxy-3-xanthanone
ZINPYR-1 — 10mg

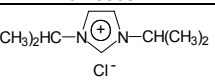
Technical Note:
1. ZINPYR-1 is a new lipophilic, zinc-sensitive, fluorescent dye able to penetrate cell membranes. Excitation and emission wavelengths are in the visible range (lambda>500nm). This property is a clear advantage over other dyes requiring high energy, tissue damaging UV radiation.

References:
1. *J. Am. Chem. Soc.*, **2003**, *125(7)*, 1778.
1. *J. Am. Chem. Soc.*, **2001**, *123(32)*, 7831.



07-0368

1,3-Di-t-butylimidazolium chloride — 250mg



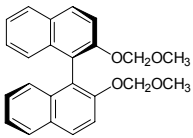
07-0485

1,3-Di-i-propylimidazolium chloride — 1g, 5g

OXYGEN

08-0160 — (R)-(-)-1,1'-Bi-2-naphthol bis(trifluoromethanesulfonate), 98% — 250mg, 1g, 5g

08-0161 — (S)-(+)-1,1'-Bi-2-naphthol bis(trifluoromethanesulfonate), 98% — 250mg, 1g, 5g



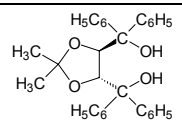
08-0170

(R)-(+)-2,2'-Bis(methoxymethoxy)-1,1'-binaphthyl — 250mg, 1g, 5g

Technical Note:
1. Starting material for the preparation of a variety of 3,3'-substituted binaphthols.

08-0171 — (S)-(-)-2,2'-Bis(methoxymethoxy)-1,1'-binaphthyl — 250mg, 1g, 5g

Technical Note:
1. See 08-0170 page 30.



08-2008

(4R,5R)-(-)-2,2-Dimethyl-α,α,α',α'-tetraphenyl-1,3-dioxolane-4,5-dimethanol (R,R)-TADDOL — 500mg, 2g

POTASSIUM

19-1500 — Potassium allyltrifluoroborate, 99% — 250mg, 1g

Technical Note:
1. Versatile reagent used in Lewis acid catalyzed, high yield synthesis of homoallylic alcohols from aldehydes.

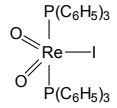
Reference:
1. *Synthesis*, **2000**, 990.

44-1750 — Potassium perruthenate — 1g, 5g

New Products Introduced Since Chemiker XIX (cont.)

OTHER NEW PRODUCTS (cont.)

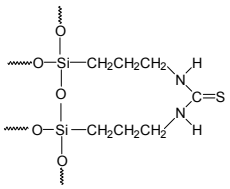
RHENIUM



75-2345

Iododioxobis(triphenylphosphine)rhenium (V), 98% — 1g, 5g

SILICON



14-1870

Deloxan® THP II Macroporous, Thiourea-Functionalized Polysiloxane (Metal Absorbing Resin) — 50g, 250g

Deloxan® THP II is a Registered trade mark of Degussa AG.

Technical Note:

1. Deloxan® THP II is a metal absorbing resin with a high affinity for precious and heavy metals, especially Ru, Rh, Pd, Pt, Au, Cu(I), Cd, Hg and Pb. The resin can absorb very low concentrations of metal ions from either aqueous or organic solutions, even in the presence of complexing agents such as phosphines, amines and nitriles. The particle size and morphology allow for easy handling and filtration.

Reference:

1. *Extraction and Ion Exchange*, **1991**, *9(2)*, 289.

14-7750 — Triethylsilane, 99% — 25g, 100g

14-7850 — Triethylsilylacetylene, min. 97% — 5g, 25g

SILVER

47-1700 — Silver perrhenate, 99% (99.995+%-Re) — 1g, 5g

STRONTIUM

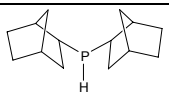
38-2100 — Strontium nitrate, 99+% (ACS) — 25g, 250g, 1kg

YTTRIUM

39-2980 — Yttrium (III) phosphate hydrate (99.99%-Y) (REO) — 5g, 25g

PHOSPHORUS LIGANDS and COMPOUNDS

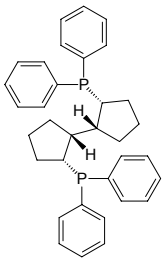
15-0800 — Cyclohexyldichlorophosphine, 98% — 1g, 5g



15-1460

Di-2-norbornylphosphine, min. 98% (mixture of endo and exo isomers) — 1g, 5g

15-1461 — Di-2-norbornylphosphine, min. 98% (mixture of endo and exo isomers) (10 wt% in hexane) — 10g, 50g



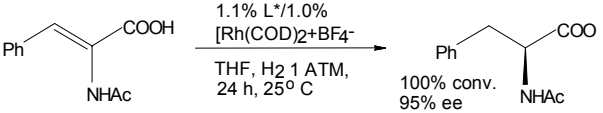
15-1742

(1R,1'R,2R,2'R)-(-)-2,2'-Diphenylphosphino-1,1'-bicyclopentyl, 99% (R,R)-BICP — 100mg, 500mg

Note: Sold in collaboration with DSM for research purposes only.

Technical Notes:

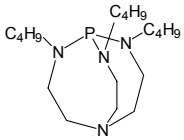
1. Ligand used in the enantioselective, rhodium-catalyzed hydrogenation of α-(acylamino)-acrylic acids.
1. Ligand used with ruthenium catalysts for enantioselective hydrogenation of aromatic ketones. (Ref. 1)

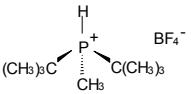
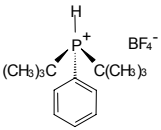
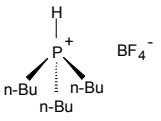
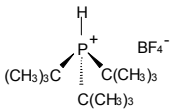
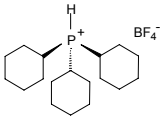
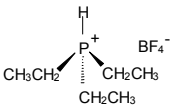
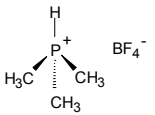


References:

1. *J. Org. Chem.*, **1999**, *64*, 2127.
2. *J. Am. Chem. Soc.*, **1997**, *119*, 1799.

New Products Introduced Since Chemiker XIX (cont.)
PHOSPHORUS LIGANDS and COMPOUNDS (cont.)

15-1743	(1S,1'S,2S,2'S)-(+)-2,2'-Diphenylphosphino-1,1'-bicyclopentyl, 99% (S,S)-BICP Note: 1. See 15-1742 page 31.	100mg 500mg
15-1800	Di-i-propylchlorophosphine, min. 98%	1g 5g
15-1815	Di-o-tolylchlorophosphine, min. 98%	1g 5g
 15-6020	2,8,9-Tri-i-butyl-2,5,8,9-tetraaza-1-phosphabicyclo[3.3.3]undecane, 97%	250mg 1g 5g
15-7940	Tris(4-methoxy-3,5-dimethylphenyl) phosphine, min. 98%	1g 5g

Air-stable, Non-pyrophoric Phosphine Ligand Precursors	 15-1023	 15-1028	 15-5990
 15-6000	 15-6160	 15-6355	 15-6560

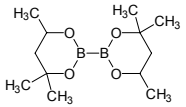
Technical Note:
1. Non-pyrophoric, air-stable derivative suitable as a replacement for the neat phosphine in a variety of stoichiometric and catalytic processes.

Reference:
1. *Organic Letters*, **2001**, *3*, 4295.

15-1023	Di-t-butylmethylphosphonium tetrafluoroborate, 99% Technical Note: See page 26.	1g 5g
15-1028	Di-t-butylphenylphosphonium tetrafluoroborate, 97%	1g 5g
15-5990	Tri-n-butylphosphonium tetrafuoroborate, 99%	1g 5g
15-6000	Tri-t-butylphosphonium tetrafluoroborate, 99%	1g 5g
15-6160	Tricyclohexylphosphonium tetrafluoroborate, 99%	1g 5g
15-6355	Triethylphosphonium tetrafluoroborate, 99%	1g 5g
15-6560	Trimethylphosphonium tetrafluoroborate, 99%	1g 5g

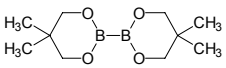
Boronate Esters for Suzuki Coupling

05-0020



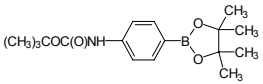
1g 5g

05-0025



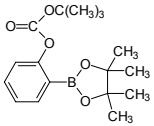
1g 5g

05-0360



1g 5g

05-0370



1g 5g

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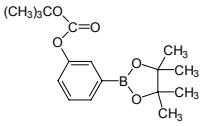
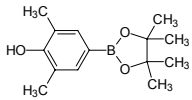


1g 5g

05-0760



1g 5g

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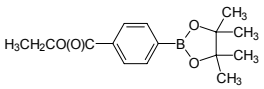

1g 5g

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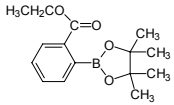

1g 5g

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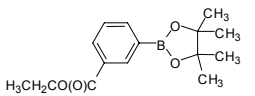

1g 5g

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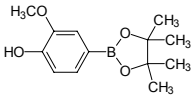

1g 5g

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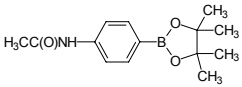

1g 5g

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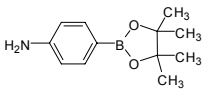

1g 5g

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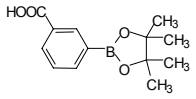

1g 5g

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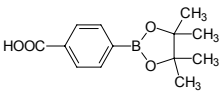
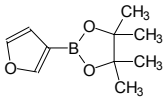


1g 5g

05-1039



1g 5g

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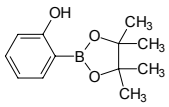

1g 5g

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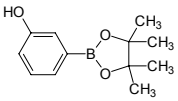

1g 5g

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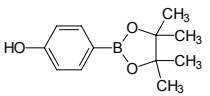
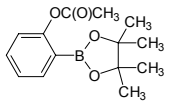


1g 5g

05-1045



1g 5g

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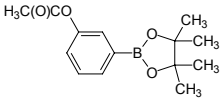

1g 5g

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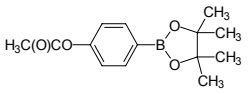
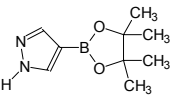


1g 5g

05-1048



1g 5g