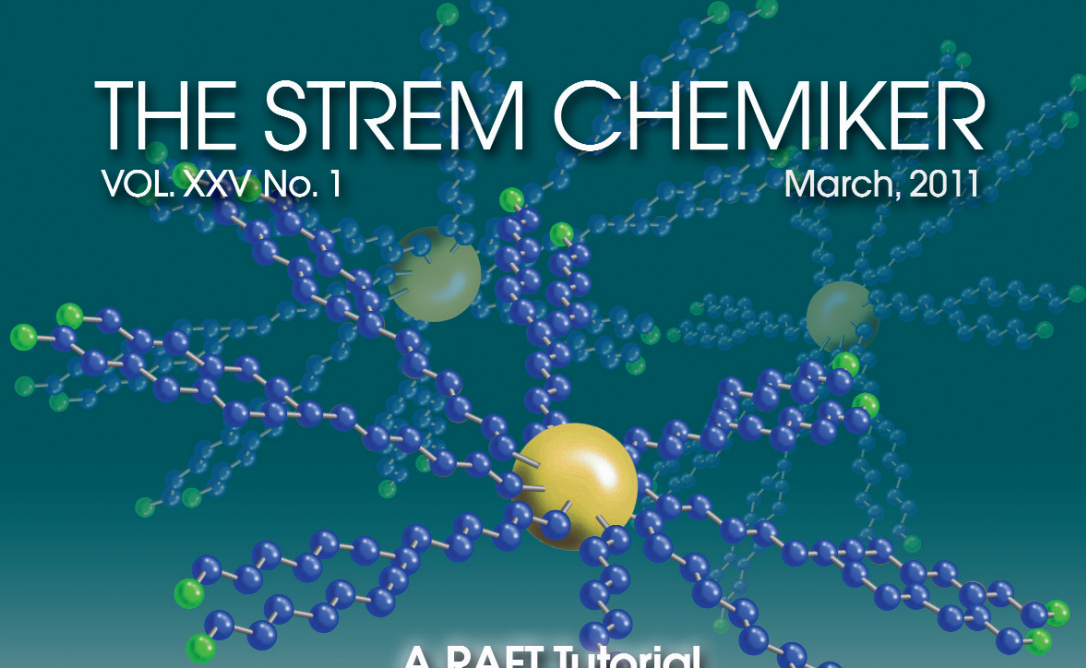
THE STREM CHEMIKER

VOL. XXV No. 1 March, 2011

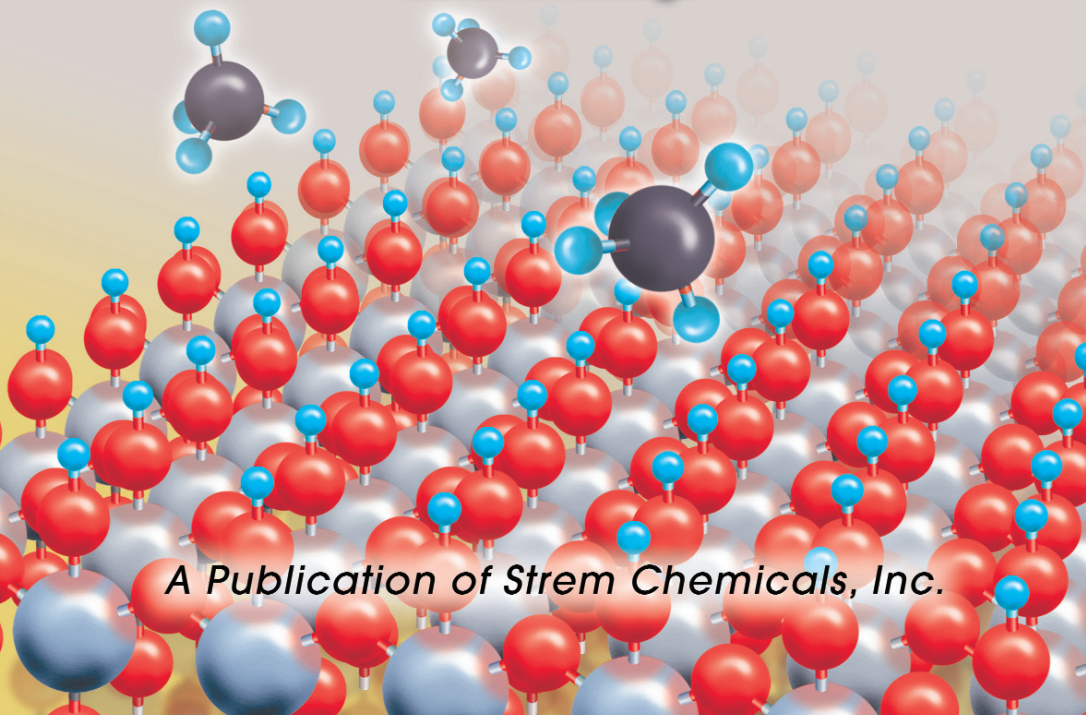


A RAFT Tutorial

Graeme Moad, Ezio Rizzardo and San H. Thang

Hybrid Organic-Inorganic Films Grown Using Molecular Layer Deposition

Steven M. George



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The Strem Chemiker
Vol. XXV, No. 1
March, 2011

www.strem.com

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Biographical Sketches

Graeme Moad obtained his Ph.D. in 1977 from the Adelaide University. After postdoctoral research at Pennsylvania State University, he joined CSIRO in 1979 where he is currently a chief research scientist. Dr. Moad has contributed to >130 journal papers and >32 patent families and is coauthor of "The Chemistry of Radical Polymerization".

Ezio Rizzardo received his Ph.D. from the University of Sydney and joined CSIRO in 1976 after postdoctoral research at Rice University, RIMAC, and the Australian National University. His CSIRO research has focussed on developing methods for controlling free radical polymerization. Ezio is a CSIRO Fellow and a Fellow of the Royal Society.

San Thang received his Ph.D. from Griffith University in 1987. He is a Senior Principal Research Scientist at CSIRO where his research focuses on the interface between biology and polymer chemistry. San has made many contributions in polymer science and significantly, he is a co-inventor of the RAFT process.

Prof. Steven M. George is Professor in the Dept. of Chemistry and Biochemistry and Dept. of Chemical and Biological Engineering at the University of Colorado at Boulder. Dr. George's research interests are in the areas of surface chemistry, thin film growth and nanostructure engineering. He is currently directing a research effort focusing on atomic layer deposition (ALD) and molecular layer deposition (MLD). This ALD & MLD research is examining new surface chemistry, measuring thin film growth rates, characterizing the properties of films and developing new reactors for ALD & MLD. Dr. George teaches a one-day short course on ALD for the AVS. He is also on the Board of Directors of the AVS (2010-2012). Dr. George has received a number of awards including an NSF Presidential Young Investigator Award (1988-1993), an Alfred P. Sloan Foundation Fellowship (1988) and an NSF Creativity Award (2002-2004). He is a Fellow of the American Vacuum Society (2000) and a Fellow of the American Physical Society (1997). Dr. George received his B.S. in Chemistry from Yale University (1977) and his Ph.D. in Chemistry from the University of California at Berkeley (1983).

A RAFT Tutorial

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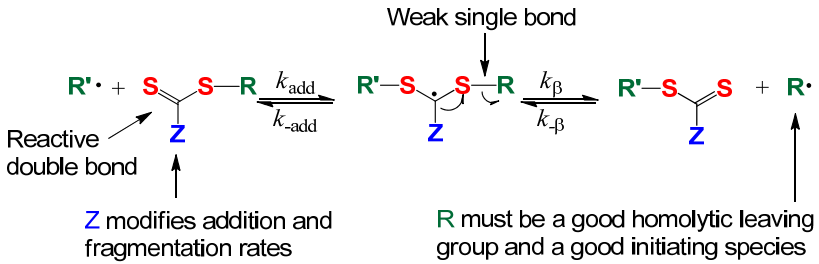
Introduction

RAFT is an acronym for Reversible Addition Fragmentation chain Transfer. It is a reversible deactivation radical polymerization (RDRP)[1] and arguably the most versatile method for providing living characteristics to radical polymerization.[2-10] The historical development of RAFT polymerization at CSIRO has been outlined.[3,5]

RAFT polymerization provides the ability to control polymerization of most monomers polymerizable by radical polymerization. These include (meth)acrylates, (meth) acryl-amides, acrylonitrile, styrenes, dienes and vinyl monomers. It is tolerant of unprotected functionality in monomer and solvent (*e.g.* OH, NR_2, COOH, $CONR_2$, SO_3H). The process is compatible with a wide rage of reaction conditions (*e.g.* bulk, organic or aqueous solution, emulsion, miniemulsion, suspension). It is simple to implement and inexpensive in relation to competitive RDRP.

A mechanism for RAFT process is shown in Scheme 1. In an ideal living polymerization, all chains are initiated at the beginning of the process, grow at a similar rate and survive the polymerization (there is no irreversible chain transfer or termination). If initiation is rapid with respect to propagation the molecular weight distribution is very narrow and chains can be extended by the provision of further monomer. In a radical polymerization all chains cannot be simultaneously active. In RAFT polymerization, the majority of living chains are maintained in a dormant form. A rapid equilibrium between active (propagating radicals) and dormant chains (macroRAFT agents) ensures that all chains grow at a similar rate. Under these conditions, molecular weights can increase linearly with conversion and molecular weight distributions can be very narrow. The product of polymerization will comprise overwhelmingly dormant chains. It is a macroRAFT agent.

Scheme 1. Mechanism for reversible addition-fragmentation chain transfer (RAFT)



The reactions associated with RAFT equilibria (Scheme 1) are in addition to those that occur during conventional radical polymerization (*i.e.* initiation, propagation and termination). The RAFT agent is a transfer agent and does not suppress termination. Retention of the thiocarbonylthio groups in the polymeric product is responsible for the living character of RAFT polymerization. RAFT polymerization can be used in the synthesis of well-defined homo-, gradient, diblock, triblock and star polymers and more complex architectures including microgels and polymer brushes. Many applications have been reported and are described in recent reviews.[10-13]

It is important to select the RAFT agent (ZC(=S)SR) according to the monomers being polymerized and reaction conditions. The effectiveness of RAFT agents is determined by the substituents R and Z and guidelines for selection have been proposed (Figure 1).[3,9] Dithioester and trithiocarbonate RAFT agents are appropriate for the polymerization of more activated monomers (MAMs) such as methyl methacrylate (MMA), methacrylic acid (MAA), hydroxypropyl methacrylamide (HPMAM), methyl acrylate (MA), acrylic acid (AA), acrylamide (AM), acrylonitrile (AN) and styrene (St). Xanthates and dialkyl dithiocarbamates are suited to the polymerization of less activated monomers (LAMs) such as vinyl acetate (VAc), *N*-vinylpyrrolidone (NVP) and *N*-vinylcarbazole (NVC). Recently, we reported 4-pyridinyl-*N*-methyldithiocarbamate derivatives that can be switched to allow control both MAMs and LAMs.[14,15]

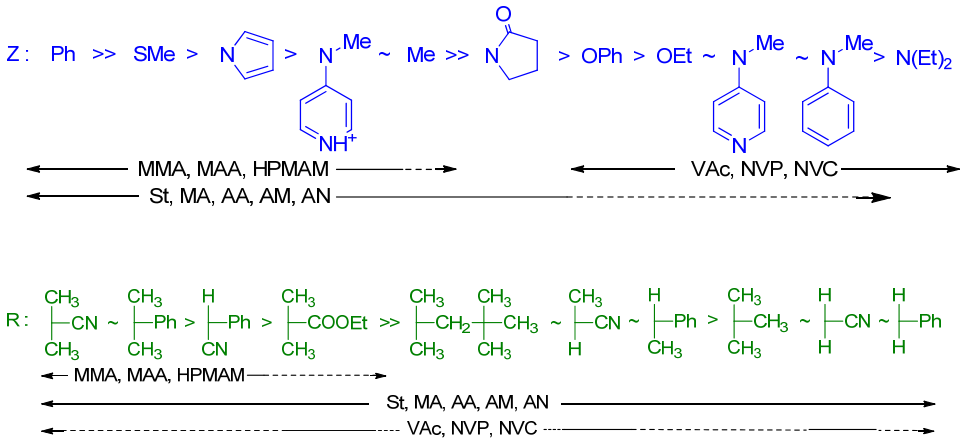
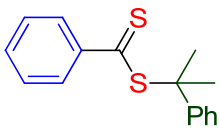


Figure 1. Guidelines for selection of RAFT agents (Z-C(=S)S-R) for various polymerizations.[3,16] For 'Z', addition rates and transfer constants decrease and fragmentation rates increase from left to right. For 'R', fragmentation rates decrease from left to right. A dashed line indicates limited control (e.g., retardation, high dispersity likely).

RAFT Polymerization of 'More-Activated' Monomers (MAMs)

Aromatic dithioesters (Z=aryl, e.g., **1**, **2**) are amongst the most active RAFT agents and have general utility in the polymerization of MAMs.[3,4] However, the latter RAFT agents may give retardation particularly when used in high concentrations and are more sensitive to hydrolysis and decomposition induced by Lewis acids.[17,18] Trithiocarbonates (Z=S-alkyl, e.g., **3**-**6**) and also provide good control over polymerization of MAMs and have greater hydrolytic stability than the dithioesters. Z is preferably based on a thiol with low volatility.



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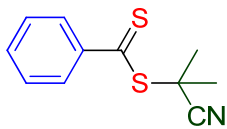

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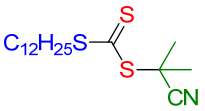

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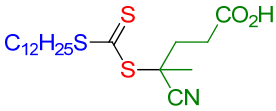

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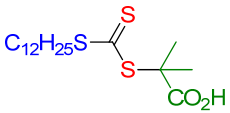

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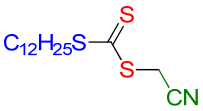

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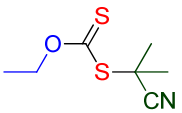
The choice of R is also important for good control. R must efficiently reinitiate polymerization and must be a good homolytic leaving group with respect to the propagating radical.[19] R· must also be efficient in reinitiating polymerization. The choice of 'R' is critical in the case of methacrylates. In some of the most effective RAFT agents R is cumyl (e.g.,) or tertiary cyanoalkyl (e.g., **2**-**4**). RAFT agents such as **5** and **6** are not suitable. A wider range of RAFT agents are suitable for controlling the polymerization of monosubstituted MAMs such as styrene, acrylates or acrylamides. The above mentioned RAFT agents (**1**-**4**) can be used and those where R is tertiary carboxylic acid (e.g**., 5**) or cyanomethyl (e.g., **6**) are also good choices for R for of these monomers.

RAFT Polymerization of 'Less-Activated Monomers' (LAMs)

Dithioesters and trithiocarbonates inhibit polymerization of LAMs. The less active RAFT agents with Z=NR'$_2$ (dithiocarbamates), Z=OR' (xanthates) where R' = alkyl or aryl offer good control over the polymerization of LAMs.



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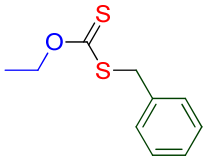

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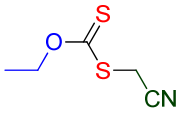

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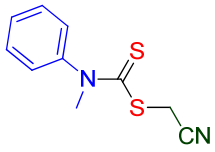

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The choice of R group is also critical because most monomers in the class have a high propagation rate constant. In polymerization of VAc inhibition periods due to slow reinitiation are observed for RAFT agents such as **7** and **8** where R is benzyl or tertiary cyanoalkyl respectively. Some preferred RAFT agents are **9** and **10** where R is cyanomethyl.

Switchable RAFT agents

We recently reported on a new class of stimuli-responsive RAFT agents that can be "switched" to offer good control over polymerization of both MAMs and LAMs and thus a more convenient route to polyMAM-*block*-polyLAM with narrow molecular weight distributions.[14,15] This approach has been demonstrated with the use of 4-pyridinyl-*N*-methyldithiocarbamate derivatives (e.g., **11**-**14**) to prepare PMMA-*block*-PVAc[15] and PMA-*block*-PNVC[15] and PSt-*block*-PVAc.[14] The RAFT agents **11**-**14** provide effective control over polymerization of LAMs and, when protonated as **11-H$^+$**-**14-H$^+$**, also provide excellent control over the polymerization of MAMs.

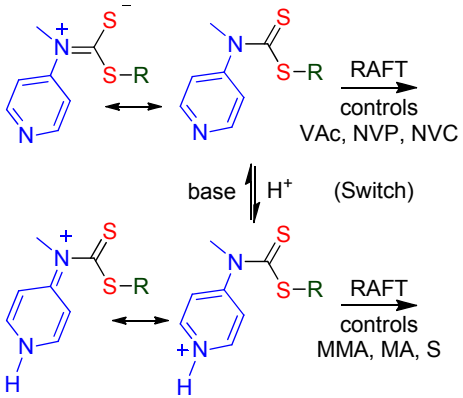
Scheme 2. Switchable RAFT Agents.

11 R= CH_2CN

12 R= $CH(CH_3)CO_2CH_3$

13 R= $C(CH_3)_2CN$

14 R= $C(CH_3)(CN)CH_2C(CH_3)_2OCH_3$



$11\text{-}H^+$ R= CH_2CN

$12\text{-}H^+$ R= $CH(CH_3)CO_2CH_3$

$13\text{-}H^+$ R= $C(CH_3)_2CN$

$14\text{-}H^+$ R= $C(CH_3)(CN)CH_2C(CH_3)_2OCH_3$

Reaction Conditions

The reaction conditions used for RAFT polymerization are those used for conventional radical polymerization. However, for optimal control of the RAFT process, it is important to pay attention to such factors as initiator concentration and selection.[3] RAFT polymerization is usually carried out with conventional radical initiators. In principle, any source of radicals can be used but most often thermal initiators (*e.g.*, azobis(isobutyronitrile), potassium persulfate) are used. Styrene polymerization may be initiated thermally between 100-120 °C.

The initiator concentration and rate of radical generation in RAFT polymerization should be chosen to provide a balance between an acceptable rate of polymerization and an acceptable level of dead chains (radical-radical termination). One useful guideline is to choose conditions such that the target molecular weight is ~10% of that which would have been obtained in the absence of RAFT agent. The initiator concentration will usually be at least 5-fold less than the RAFT agent concentration. A common misconception is that it is necessary to use very low rates of polymerization in order to achieve narrow molecular weight distributions. Sometimes, using a high rate of polymerization and a correspondingly short reaction time can provide excellent results However, it is very important not to use prolonged reaction times when retention of the RAFT functionality is important. Once the monomer is fully converted, continued radical generation may still lead to formation of dead chains by termination and consequent loss of the thiocarbonylthio end group. Addition of initiator to a RAFT synthesized polymer is one recognized method for thiocarbonylthio end group removal.[20]

The molecular weight of the polymer formed can usually be estimated knowing the concentration of the monomer consumed and the initial RAFT agent concentration ([T]) using the relationship (1). Positive deviations from equation (1) indicate incomplete usage of RAFT agent. Negative deviations indicate that other sources of polymer chains are significant. These include the initiator-derived chains.[21]

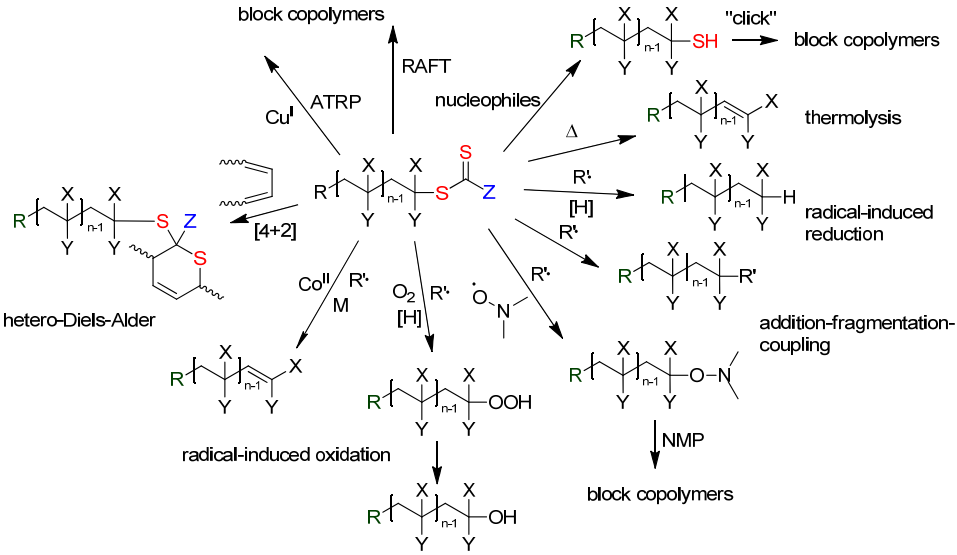
$$\overline{M}_n(\text{calc}) \sim \frac{[\text{M}]_o - [\text{M}]_t}{[\text{T}]_o} m_{\text{M}} \qquad (1)$$

The RAFT process is compatible with a wide range of reaction media including all common organic solvents, protic solvents such as alcohols and water and less conventional solvents such as ionic liquids and supercritical carbon dioxide. It is important that RAFT agent should be selected for solubility in the reaction medium. In polar media and in the presence of Lewis acids RAFT agents can show hydrolytic sensitivity.[18] We have found that this order roughly correlates with RAFT agent activity (dithiobenzoates > trithiocarbonates ~ aliphatic dithioesters).

Although some RAFT polymerization can be carried out in air, for optimal control they should be carried out in degassed media under an inert atmosphere.[3]

End Group Removal/Transformation

The reactions of the thiocarbonylthio-group are well known from small molecule chemistry and much of this knowledge has been shown applicable to transforming the thiocarbonylthio-groups present in RAFT-synthesized polymers. Many of the methods used for thiocarbonylthio-group removal are summarized in Scheme 3.[22] Note that some of these processes are specific to certain types of RAFT agent or to certain polymers. One of the best way of completely replacing the thiocarbonylthio functionality with hydrogen is by radical induced reduction in the presence of a hypophosphite.[23]



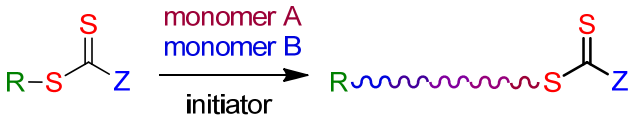
Scheme 3. Processes for RAFT End-group Transformation (**R'·** = radical, **[H]** = H atom donor, **M** = monomer, **Co^{II}** = square planar cobalt complex). Adapted from ref. 22.

Copolymerization

In radical copolymerization, the monomers are typically consumed at different rates dictated by the steric and electronic properties of the reactants. Consequently, both the monomer feed and copolymer composition will drift with conversion. Thus conventional copolymers are generally not homogeneous in composition at the molecular level. In RAFT polymerization processes, where all chains grow throughout the polymerization, the compositional drift is captured within the chain structure (Scheme 4). Therefore,

essentially all chains will have similar composition. The copolymers are called gradient or tapered copolymers. Reactivity ratios are generally unaffected by the RAFT process. However, for very low conversions when molecular weights are low, copolymer composition may be different from that seen in conventional copolymerization depending on the specificity shown by the initiating species 'R'. A wide variety of gradient copolymers have been synthesized by RAFT copolymerization. One application is the synthesis of dispersants for polymer-clay nanocomposites.[24,25]

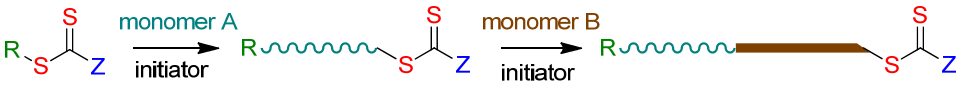
Scheme 4. Gradient copolymer synthesis



Block Copolymerization

The synthesis of AB diblock copolymers (and ABA, ABC, etc.) can be accomplished by sequential of monomer as shown in Scheme 5.[26,27]

Scheme 5. AB diblock copolymer synthesis

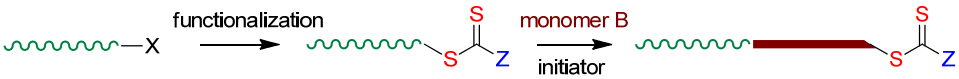


Of considerable interest has been the ability to make hydrophilic-hydrophobic or double hydrophilic block copolymers where the hydrophilic block is composed of unprotected polar monomers such as AA or DMAEMA.

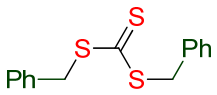
The order of constructing the blocks is important.[19,26] In RAFT polymerization the propagating radical for the first formed block must be a good homolytic leaving group with respect to that of the second block. This requires, for example, in the synthesis of a methacrylate-acrylate or methacrylate-styrene blocks, the methacrylate block should be prepared first [19,26,28,29]. The propagating radicals sited on a styrene or acrylate unit are very poor leaving groups with respect to methacrylate propagating radicals. The use of feed addition protocols, where the monomer concentration is kept low with respect to the RAFT agent concentration, can alleviate this requirement.[7,30].

Block copolymers based on polymers formed by other mechanisms can be by forming a macroRAFT agent from a precursor polymer by end group transformation Scheme 6. This methodology has been used to prepare PEO-*block*-PS from commercially available hydroxy end-functional PEO.[26,31,32]

Scheme 6. A-B diblock synthesis from end-functional polymers via RAFT process



Use of a bis-RAFT agent allows the direct synthesis of triblock copolymers in a 'one-pot' reaction. The RAFT agent functionalities may be connected through the 'Z' or 'R' groups to give ABA (Scheme 7) or BAB (Scheme 8) block copolymers respectively. Symmetrical trithiocarbonates such as **15** and **16** can be considered to be in the class of 'Z connected' bis-RAFT agents (n=0 in Scheme 7).



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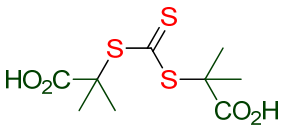

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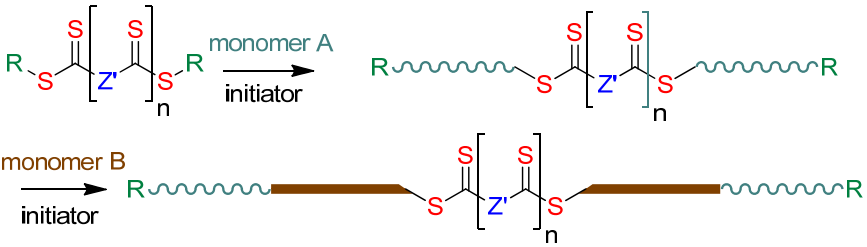
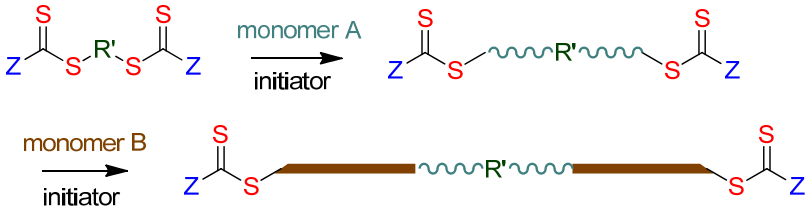
Scheme 7. ABA triblock synthesis from symmetrical trithiocarbonates (n=0) or 'Z-connected' bis-RAFT agents (n=1).



Scheme 8. BAB triblock synthesis from 'R-connected' bis-RAFT agents.



With 'Z-connected' RAFT agents the thiocarbonylthio functionality is retained in the centre of the block. A potential disadvantage is that reactions that cleave the thiocarbonylthio groups (*e.g.* hydrolysis, thermolysis) also destroy the block structure. With 'R-connected' RAFT agents the thiocarbonylthio functionality remains on the periphery of the block. Because the thiocarbonylthio groups are end groups, they can be cleaved without destroying the structure.

Typical Experimental Procedures

Solvents were of analytical reagent grade and were distilled before use. Monomers (BA, MMA) were filtered through neutral alumina (70-230 mesh), fractionally distilled under reduced pressure, and redistilled under reduced pressure immediately before use. Initiators azobisisobutyronitrile and 1,1'-azobis(cyclohexanenitrile (VAZO-64® and VAZO-88® respectively from DuPont) were purified by crystallization from chloroform/methanol.

Butyl Acrylate Polymerization [$NCCH_2$-PBA-SC(=S)$SC_{12}H_{25}$].[23]

A solution containing BA (6.0 mL), RAFT agent **6** (400 mg, 0.126 M), azobisisobutyronitrile (2.2 mg, 0.0013 M) and benzene (4.0 mL) was placed in an ampoule, degassed with three freeze-evacuate-thaw cycles, sealed and heated in a thermostatted bath at 60±1 °C for 5 h. Removal of the volatiles at ambient temperature under reduced pressure provided the polymer as a yellow gum (3.4 g, 63% conversion $\overline{M}_n$ 3080, $\overline{M}_w / \overline{M}_n$ 1.09). The ^{1}H NMR spectrum of the polymer showed signals associated with poly(butyl acrylate) and signals associated with the end group at 4.8 [-C**H**(COOBu)SC(S)S-] and 3.3 ppm [-SC(S)SC**H**$_2C_{11}H_{23}$].

Methyl Methacrylate Polymerization [$(CH_3)_2$C(CN)-PMMA-SC(=S)$SC_{12}H_{25}$].[23]

A solution of the RAFT agent **3** (685 mg, 0.198 M) and 1,1'-azobis(cyclohexanenitrile (10.5 mg, 0.0043 M) in MMA (7.0 mL) and benzene (3.0 mL) was placed in an ampoule, degassed with three freeze-evacuate-thaw cycles, sealed and heated at 90±1 ºC for 6 h. Removal of the volatiles under reduced pressure afforded the polymer as a yellow powder (5.3 g, 81% conversion) of $\overline{M}_n$ 3400, $\overline{M}_w / \overline{M}_n$ 1.18. The ^{1}H NMR spectrum of the polymer showed signals attributable to poly(methyl methacrylate) and the methylene hydrogens next to sulfur [associated with the end group -SC(S)SC**H**$_2C_{11}H_{23}$] at 3.2 ppm.

Conclusions

Reversible Addition Fragmentation chain Transfer (RAFT) has emerged as one of the most robust and versatile methods for controlling radical polymerization. It is applicable to the majority of monomers subject to radical polymerization.

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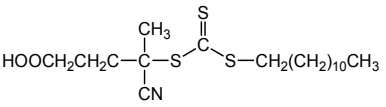

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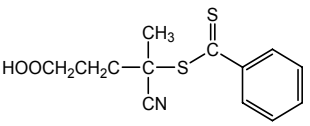

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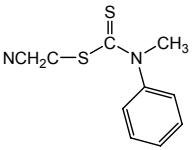

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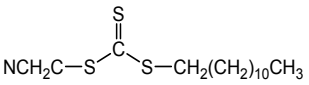

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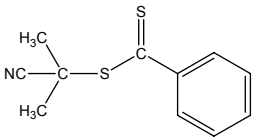

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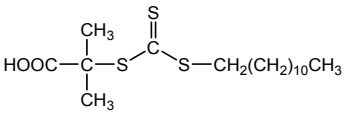

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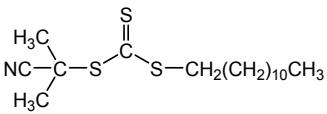

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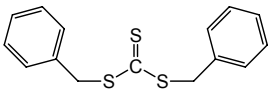

16-0617 500mg

16-0415	4-Cyano-4-(dodecylsulfanylthiocarbonyl)sulfanylpentanoic acid, min. 97% *[870196-80-8]*	500mg	See page 12
16-0422	4-Cyano-4-(thiobenzoylthio)pentanoic acid, min. 97% *[201611-92-9]*	500mg	
16-0423	2-Cyanomethyl-N-methyl-N-phenyldithiocarbamate, min. 97% *[76926-16-4]*	500mg	
16-0425	S-Cyanomethyl-S-dodecyltrithiocarbonate, min. 97% *[796045-97-1]*	500mg	
16-0430	2-Cyanoprop-2-yl -dithiobenzoate, min. 97% *[201611-85-0]*	500mg	
16-0460	2-Methyl-2-[(dodecylsulfanylthiocarbonyl)sulfanyl]propanoic acid, min. 97% *[461642-78-4]*	500mg	
16-0610	S-(2-Cyanoprop-2-yl)-S-dodecyltrithiocarbonate, min. 97% *[870196-83-1]*	500mg	
16-0617	S,S-Dibenzyltrithiocarbonate, min. 97% *[26504-29-0]*	500mg	

Note: Sold for research purposes only. Not for use in humans or animals.
Patents: WO98/01478, WO99/311444.

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16-0415 **4-Cyano-4-(dodecylsulfanylthiocarbonyl)sulfanyl-pentanoic acid, min. 97%** *[870196-80-8]* — 500mg, 2g, 10g
$C_{19}H_{33}NO_2S_3$; FW: 403.67; pale yellow solid; m.p. 59-62°
light sensitive

Technical Note:
1. A sulfur-based, chain-transfer agent providing a high degree of control for living radical polymerizations utilizing the RAFT (reversible addition-fragmentation chain-transfer polymerization) technique.

References:

1. *Macromolecular Symposia,* **2007**, *248*, 104.
2. *Polymer* 49 (**2008**) 1079-1131.

16-0425 **S-Cyanomethyl-S-dodecyltrithiocarbonate, min. 97%** *796045-97-1]* — 500mg, 2g, 10g
$C_{15}H_{27}NS_3$; FW: 317.58; yellow-orange solid; m.p. 30-33°
light sensitive, (store cold)

Technical Note:
1. See 16-0415 (page 12).

16-0423 NEW→ **2-Cyanomethyl-N-methyl-N-phenyldithiocarbamate, min. 97%** — 500mg, 2g, 10g
[76926-16-4]
$C_{10}H_{10}N_2S_2$; FW: 222.33; pale yellow xtl.
light sensitive, (store cold)

Technical Note:
1. See 16-0415 (page 12).

16-0430 NEW→ **2-Cyanoprop-2-yl-dithiobenzoate, min. 97%** *[201611-85-0]* — 500mg, 2g, 10g
$C_{11}H_{11}NS_2$; FW: 221.34; purple liq.
light sensitive, (store cold)

Technical Note:
1. See 16-0415 (page 12).

16-0610 NEW→ **S-(2-Cyanoprop-2-yl)-S-dodecyltrithiocarbonate, min. 97%** — 500mg, 2g, 10g
[870196-83-1]
$C_{17}H_{31}NS_3$; FW: 345.63; orange liq.
light sensitive, (store cold)

Technical Note:
1. See 16-0415 (page 12).

16-0422 NEW→ **4-Cyano-4-(thiobenzoylthio)pentanoic acid, min. 97%** — 500mg, 2g, 10g
[201611-92-9]
$C_{13}H_{13}NO_2S_2$; FW: 279.38; pink pwdr.
light sensitive, (store cold)

Technical Note:
1. See 16-0415 (page 12).

16-0617 NEW→ **S,S-Dibenzyltrithiocarbonate, min. 97%** *[26504-29-0]* — 500mg, 2g, 10g
$C_{15}H_{14}S_3$; FW: 290.47; dark yellow liq.
(store cold)

Technical Note:
1. See 16-0415 (page 12).

16-0460 NEW→ **2-Methyl-2-[(dodecylsulfanylthiocarbonyl)sulfanyl]propanoic acid, min. 97%** *[461642-78-4]* — 500mg, 2g, 10g
$C_{17}H_{32}O_2S_3$; FW: 364.63; pale yellow solid
light sensitive, (store cold)

Technical Note:
1. See 16-0415 (page 12).

Note: Sold for research purposes only. Not for use in humans or animals.
Patents: WO98/01478, WO99/311444. RAFT Agent Kit components. See (page 11).

Hybrid Organic-Inorganic Films Grown Using Molecular Layer Deposition

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Depts. of Chemistry and Chemical Engineering
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1. Introduction

There has been a dramatic growth in the field of atomic layer deposition (ALD) over the past 10 years [1]. Some of this ALD development has been driven by the needs of the semiconductor industry. Other developments have resulted from the application of ALD to non-semiconductor arenas. The atomic layer control and conformality of the ALD film thickness have proved useful for a diverse array of applications such as the fabrication of photonic bandgap materials [2] and gas diffusion barriers [3]. In addition to the new technological developments, there also has been an expansion of the types of films that can be grown using ALD-inspired processes. The introduction of organic precursors using molecular layer deposition (MLD) has greatly extended the compositional identity of the deposited film. MLD is distinguished from ALD because a molecular fragment can be added during one self-limiting sequential surface reaction [4]. An illustration of the sequential, self-limiting growth in MLD is displayed in Figure 1 [5].

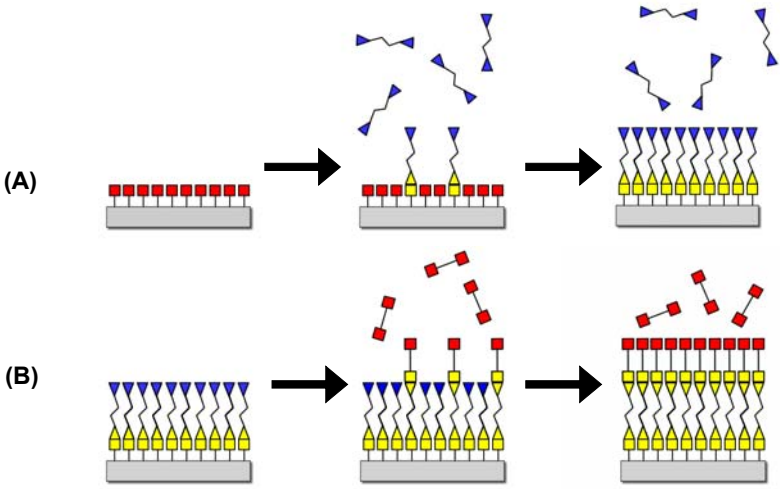

Figure 1 Schematic illustrating ideal sequential, self-limiting reactions for MLD growth using two homobifunctional reactants.

The original definition of MLD described the sequential, self-limiting chemistry used for the growth of an organic polymer. The first MLD system was based on condensation polymerization reactions and deposited a polyimide [6]. More recently, the MLD of a variety of organic polymers has been demonstrated including polyimide [7], polyamide [5, 8], polyurea [9], polyurethane [10], polythiourea [11] and polythiolene [12]. The organic precursors used for all-organic MLD can also be mixed with the inorganic ALD precursors to define new hybrid organic-inorganic materials [13, 14]. The expanded basis set introduced by these hybrid materials has greatly enlarged the possible materials that can be grown using ALD and MLD. The large quantity of organic precursors available from

organic chemistry leads to a huge variety of possibilities for hybrid organic-inorganic films using MLD.

Several hybrid organic-inorganic materials have been developed recently using MLD techniques [4, 13-20]. These systems have begun to define the wide range of materials that can be deposited using MLD. The possibility to mix and match organic and inorganic precursors and their relative fraction in the film will lead to a wide spectrum of film properties. In particular, the mechanical properties can be tuned by controlling the organic and inorganic proportions. This short report will first review several MLD systems that have been demonstrated to illustrate the current state-of-the-art. Some new systems will then be introduced to show the diversity of chemistries that can be employed to grow various hybrid organic-inorganic films. Lastly, speculations will be offered on the future prospects for the MLD of hybrid organic-inorganic materials.

2. Previously Demonstrated Hybrid Organic-Inorganic MLD Films

One of the first hybrid organic-inorganic materials grown using MLD was an "alucone" [21] based on the reaction between trimethylaluminum (TMA) and ethylene glycol (EG) [13]. The EG molecule, HO-CH_2-CH_2-OH, contains two hydroxyls groups and is very analogous to H_2O as a reactant in the well-studied Al_2O_3 ALD process [22, 23]. The difference is that a –CH_2-CH_2- molecular fragment is introduced into the hybrid organic-inorganic film. A schematic showing the growth of the alucone based on TMA and EG is displayed in Figure 2 [13].

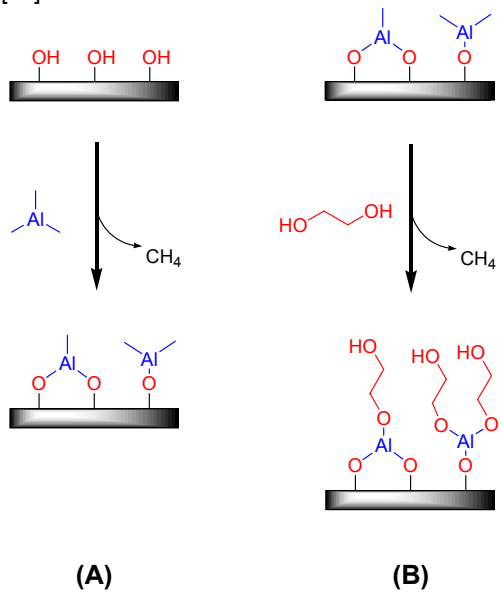

Figure 2 Schematic depicting two-step AB alucone MLD growth using trimethylaluminum (TMA) and ethylene glycol (EG). TMA is exposed to a hydroxylated surface and produces a surface covered with -$AlCH_3$ species. The subsequent EG exposure produces a surface covered with –OCH_2CH_2OH species.

In general, a two-step MLD reaction between a metal alkyl, such as TMA, and a diol, such as EG, can be written as follows [4, 13]:

(A) $SR'OH^* + MR_x \rightarrow SR'O\text{-}MR_{x-1}^* + RH$ (1)

(B) $SMR^* + HOR'OH \rightarrow SM\text{-}OR'OH^* + RH$ (2)

The asterisks indicate the surface species and S denotes the substrate with the reaction products from the previous reactions. In the A reaction, the reaction stops when all the SR'OH* species have completely reacted to produce $SR'O\text{-}MR_{x-1}^*$ species. In the B reaction, the reaction stops when all the SMR* species have completely reacted to produce SM-OR'OH* species. The sequential and self-limiting reactions of TMA and EG ideally yield a polymeric film described by (Al-(O-CH_2-CH_2-O-) linkages.

Previous studies have demonstrated that alucone MLD using TMA and EG is very efficient [13]. X-ray reflectivity (XRR) investigations showed that the MLD growth rate was linear versus the number of TMA/EG cycles. In addition, the MLD growth rate was temperature dependent and decreased from 4.0 Å per TMA/EG cycle at 85°C to 0.4 Å per TMA/EG cycle at 175°C [13]. Quartz crystal microbalance (QCM) measurements also revealed the linearity of alucone MLD growth versus TMA and EG exposures [13]. The QCM results also showed a large mass increase during the TMA exposures that subsequently decayed immediately after the TMA exposure. This mass transient was consistent with TMA diffusion into and out of the AB alucone MLD film [24]. The TMA diffusion also helped explain the temperature dependence of the MLD growth.

The surface reactions during MLD with TMA and EG displayed self-limiting behavior [13]. The AB alucone MLD films also displayed a contraction of ~22% over the first 3 days that the films were exposed to air. After this contraction, the films were extremely stable. The AB alucone films were extremely smooth and conformal when deposited on nanoparticles. Figure 3 shows the TEM image of a $BaTiO_3$ particle that was coated with 40 AB cycles of Al_2O_3 ALD and then 50 AB cycles of AB alucone MLD at 135°C [13]. The quality of the overlying MLD film is comparable with the underlying ALD film.

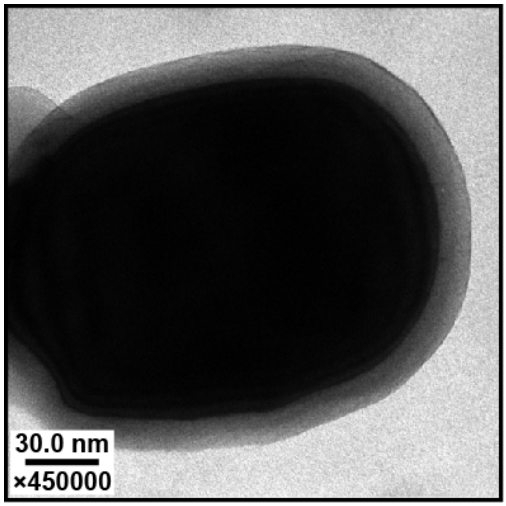

Figure 3 TEM image of a $BaTiO_3$ particle coated at 135 °C with 40 AB cycles of Al_2O_3 ALD and then 50 AB cycles of AB alucone MLD using TMA and EG.

EG is one of many organic diols that can be used together with TMA for alucone film growth. One difficulty with diols is that they are homobifunctional precursors and can react twice with the $AlCH_3$* surface species [4, 8]. These "double reactions" lead to a loss of reactive surface sites and could produce a decreasing growth per cycle during MLD. The problem of double reactions may be minimized using polyols to assure that a hydroxyl group will be available for the subsequent TMA exposure. This strategy will be discussed below for the MLD of the alucone based on TMA and glycerol.

Alternatively, a heterobifunctional precursor, such as ethanolamine, HO- CH_2-CH_2-NH_2 (EA) can be employed that shows preferential reactivity between its hydroxyl group and the $AlCH_3$* surface species [20]. This preference leaves an amine (-NH_2) group available for the subsequent surface reaction. Likewise, ring-opening reactions can be employed that will react and then express a new functional group when the ring is opened [4, 20]. The ring-opening reaction also has the advantage of containing the functional group in a hidden form. The hidden functionality leads to higher vapor pressures and shorter purge times compared with precursors that have the same exposed functionality.

One three-step ABC MLD process that can be accomplished without using homobifunctional precursors is based on: (1) TMA, a homomultifunctional inorganic precursor; (2) ethanolamine (EA), a heterobifunctional organic reactant and (3) maleic anhydride (MA) a ring-opening organic reactant [20]. The proposed surface reactions during the ABC growth are [20]:

(A) S-COOH* + $Al(CH_3)_3$ → S–COO-$Al(CH_3)_2$* + CH_4 (3)
(B) S–$AlCH_3$* + $HO(CH_2)_2$-NH_2 → S–Al–$O(CH_2)_2NH_2$* + CH_4 (4)
(C) S–NH_2* + $C_4H_2O_3$ (MA) → S–NH-C(O)CHCHCOOH* (5)

This surface reaction mechanism is illustrated in Figure 4 [20].

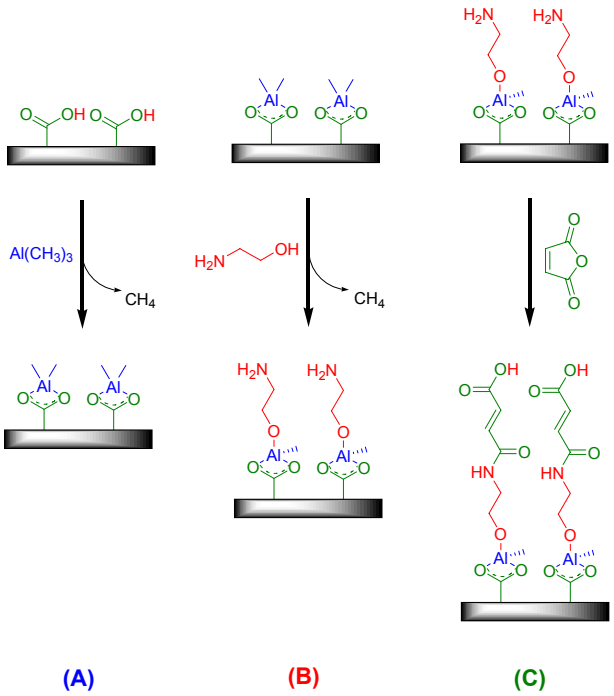

Figure 4 Schematic showing the three-step reaction sequence for ABC MLD growth using (A) trimethylaluminum (TMA), (B) ethanolamine (EA), and (C) maleic anhydride (MA).

In this ABC reaction sequence, TMA reacts with carboxylic groups in reaction A given by Eqn. 3 to form $AlCH_3$* species. Subsequently, the $AlCH_3$* species react preferentially with the hydroxyl end of the EA reactant to form Al-$OCH_2CH_2NH_2$* surface species in reaction B given by Eqn. 4. MA then reacts with amine-terminated surface functional groups to reform carboxylic groups through a ring-opening reaction in reaction C given by Eqn. 5. The three-step reaction sequence is repeated by exposure to TMA, EA and MA to grow the ABC MLD film.

A variety of studies have characterized the ABC MLD process [18, 20]. FTIR difference spectra were consistent with the reaction mechanism shown in Figure 4. The ABC MLD displayed linear growth as evidenced by the QCM measurements. However, large mass gains of ~2500 ng/cm^2 per ABC cycle were observed at 90°C [18]. This large mass gain may indicate the diffusion of a substantial quantity of TMA into the ABC MLD film. After the TMA exposure, there was also a subsequent mass loss that was consistent with the diffusion of TMA out of the ABC MLD film. The diffusion of TMA in and out of the ABC film was measured experimentally and then fit using a numerical model based on Fick's Law [18]. The importance of TMA diffusion into and out of the ABC film was verified by observing that the mass gain per cycle was dependent on the TMA purge time.

In addition to TMA, other inorganic ALD precursors can be matched with various organic precursors to define other classes of hybrid organic-inorganic materials. For example, diethylzinc (DEZ) can react with diols to produce "zincone" MLD films [17, 19]. Zincone MLD has been demonstrated using DEZ and EG [17, 19]. The growth and film characteristics of zincone MLD were similar to alucone MLD. Linear growth rates were observed for zincone MLD versus number of MLD cycles [19]. However, the growth rates were lower for higher growth temperatures and the EG precursor was observed to react twice almost exclusively at the highest growth temperatures [19].

3. New Hybrid Organic-Inorganic MLD Films

A. Use of Homotrifunctional Precursor to Promote Cross-linking

The AB alucone MLD system using TMA and EG displayed efficient reactions [13]. However, this MLD system suffered from double reactions because EG is a homobifunctional precursor. This MLD system also displayed some film contraction over the first several days after this film was exposed to air [13]. In addition, tensile strain measurements of MLD films grown using TMA and EG with a thickness of 100 nm had a low critical tensile strain of 0.69% [25]. This low critical tensile strain may result from the small amount of cross-linking in the MLD film. These problems with the TMA + EG MLD system led to the recent exploration of the TMA + glycerol system. Glycerol provides an additional hydroxyl group for reaction and should increase the cross-linking between the chains in the deposited film. The proposed reaction sequence TMA and glycerol (GL) is displayed in Figure 5 [26].

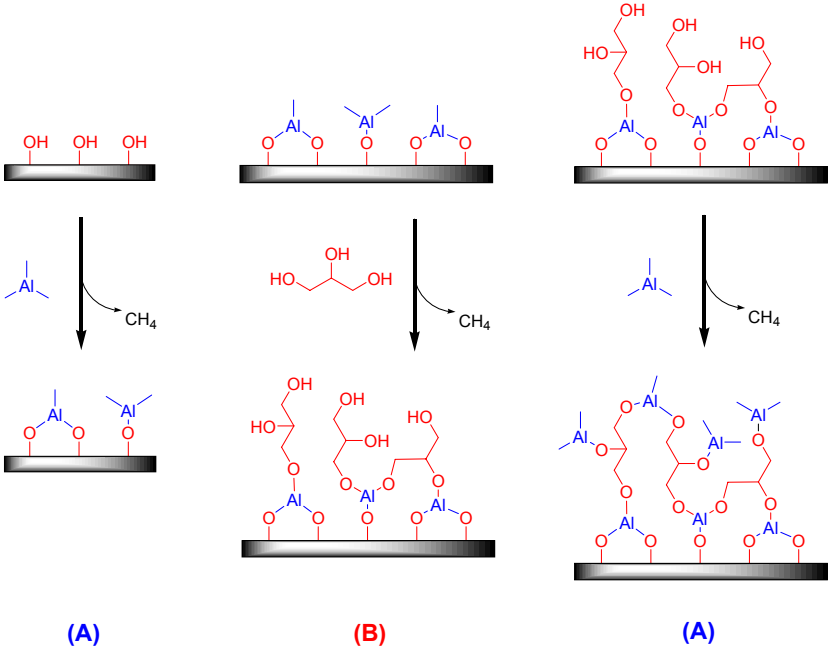

Figure 5 Schematic depicting two-step AB alucone MLD growth using trimethylaluminum (TMA) and glycerol (GL).

Studies of the surface species using Fourier transform infrared (FTIR) difference spectra after the TMA and GL exposures revealed that the surface reactions are efficient and proceed to near completion [26]. Figure 6 shows the FTIR difference spectra for Glycerol – TMA and TMA – Glycerol [26]. The spectra are displaced for clarity in presentation. The added surface species appear as positive absorbance features and the removed surface species appear as negative absorbance features. The FTIR spectra show the "flipping" of the O-H stretching vibrations at higher frequencies with each TMA and GL exposure. This flipping between positive absorbance for one reactant and then a mirror image negative absorbance for the second reactant is consistent with repetitive self-limiting reactions. There is also a flipping of the strong $AlCH_3$ deformation mode at lower frequencies that is consistent with the addition and subtraction of the $AlCH_3^*$ surface species.

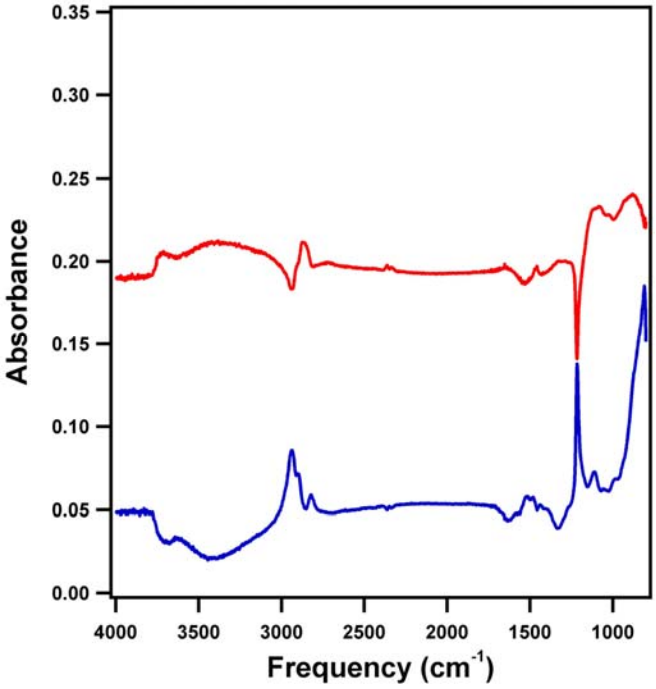

Figure 6 FTIR difference spectra after TMA and GL exposures during AB alucone MLD at 150 ºC. The FTIR difference spectra are referenced with respect to the previous reactant exposure.

The TMA + GL reaction can also be characterized using QCM studies. The QCM analysis revealed linear MLD growth with an average mass gain of 41.5 ng/cm^2/cycle at 150ºC. This mass gain of 41.5 ng/cm^2/cycle is equivalent to a growth rate of 2.5 Å/cycle. Figure 7 displays QCM results for two TMA + GL cycles at 150°C [26]. The QCM shows that a mass gain is observed during the TMA exposure. Likewise, a small mass loss is observed after the TMA exposure. This behavior suggests that some TMA may be diffusing out of the MLD film after the TMA exposure. A similar mass gain is observed during the GL exposure. The slight mass loss after the GL exposure may also indicate that some GL diffuses out of the MLD film.

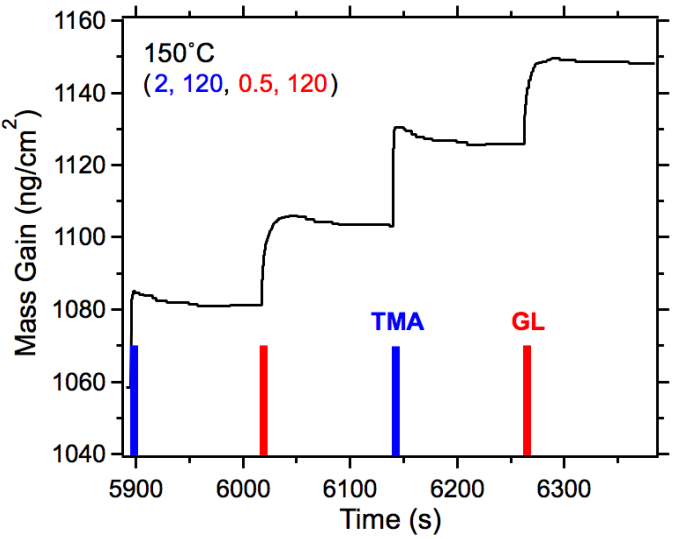

Figure 7 Mass gain from QCM measurements for two cycles of AB alucone MLD film growth with TMA and GL in the linear growth region at 150 ºC. The pulse sequence was TMA 2 s, N_2 purge 120 s, GL 0.5 s and N_2 purge 120 s.

The TMA + GL system also shows a growth rate that is much less dependent on temperature than the growth rate for TMA + EG [13]. XRR analysis was employed to study the film thickness after various numbers of MLD cycles at temperatures of 150, 170 and 190°C. These XRR results are shown in Figure 8 [26]. The film thicknesses are similar for all three temperatures and are consistent with a growth rate of 2.0-2.3 Å per cycle. The growth rate of 2.3 Å per cycle at 150°C is in reasonable agreement with the QCM measurement of 2.5 Å/cycle at 150°C under similar reaction conditions. These more constant growth rates versus temperature compared with TMA + EG suggests that TMA diffusion may be less of a factor because of the more extensive cross-linking between the growing chains.

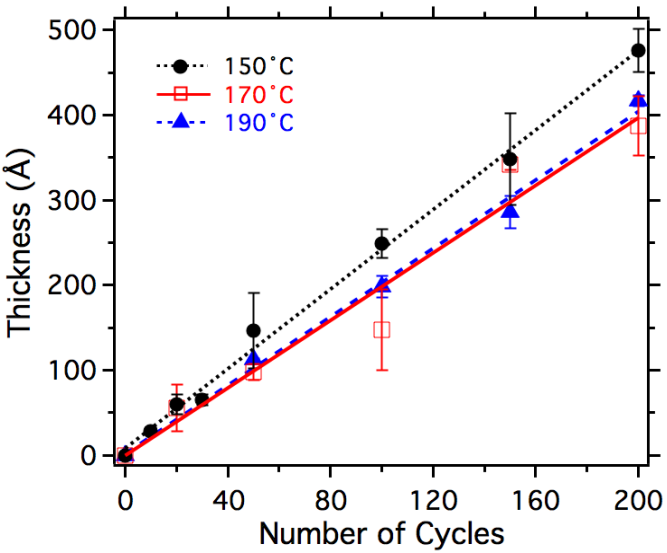

Figure 8 Thickness of AB alucone MLD films grown using TMA and GL measured using XRR analysis versus number of AB reaction cycles. Results are shown for growth temperatures of 150, 170 and 190 °C.

The XRR analysis of the TMA + GL MLD films indicated that the film thickness was nearly constant versus time after exposure to ambient [26]. The MLD films grown using TMA + GL were not observed to contract like the MLD films grown using TMA + EG [13]. This higher film stability may indicate that there is more cross-linking that increases the MLD film stability. Recent mechanical testing has also revealed that the MLD films grown using TMA + GL have a higher critical tensile strain for cracking than the MLD films grown using TMA + EG [26].

B. MLD of Hybrid Alumina-Siloxane Films Using an ABCD Process

Polydimethylsiloxane (PDMS) is one of the most important organic-inorganic polymers and contains $[\text{-Si}(\text{CH}_3)_2\text{-O}]_n$ chains. The strength and flexibility of the Si-O bonds and bond angles give PDMS desirable thermal and mechanical properties [27, 28]. PDMS MLD would be extremely useful for the growth of flexible and compliant thin films. However, initial attempts at PDMS MLD revealed that the growth rate became negligible after approximately 15 MLD cycles. These attempts were made using the sequential dosing of water with homobifunctional silane molecules such as bis(dimethylamino)dimethylsilane and 1,3-dichlorotetramethyldisiloxane or hetrobifunctional silane molecules such as dimethylmethoxychlorosilane (DMMCS). The lack of growth after approximately 15 MLD cycles was attributed to the competing desorption of cyclic siloxanes such as hexamethylcyclotrisiloxane (D3) or decamethylcyclopentasiloxane (D5) from the PDMS film [29, 30].

To prevent the desorption of cyclic siloxanes, a new approach was pursued where DMMCS and H_2O were used together with TMA in an ABCD process defined by $\text{TMA/H}_2\text{O/DMMCS/H}_2\text{O}$ [31]. A schematic of this reaction sequence is given in Figure 9 [31]. This reaction sequence introduces the $\text{-Si}(\text{CH}_3)_2\text{-O-}$ linkage into the growing film. The addition of TMA adds –Al-O- subunits into the growing chain and prevents the

competing desorption of cyclic siloxanes. The TMA can be introduced during every reaction cycle. The TMA can also be introduced less frequently to grow longer [-Si(CH_3)$_2$-O-]$_n$ chains before inserting the –Al-O- subunit.

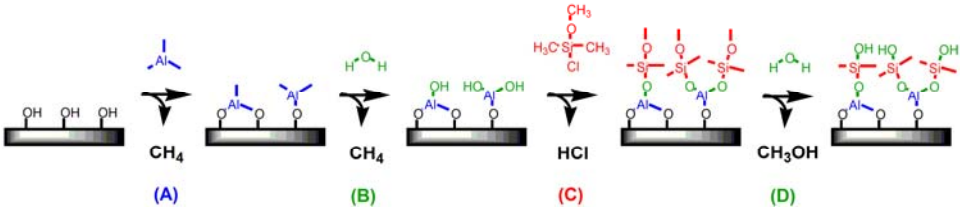

Figure 9 Schematic showing the four-step reaction sequence for ABCD MLD growth of an alumina-siloxane film using trimethylaluminum (TMA), H_2O, dimethylmethoxychlorosilane (DMMCS) and H_2O.

Initial work has explored the ABCD process to demonstrate the growth of alumina-siloxane hybrid organic-inorganic films [31]. QCM experiments revealed that the MLD growth was linear with a mass gain of ~21 ng/cm^2/cycle at 200°C. The film growth at 200°C was also examined using XRR analysis. The XRR measurements confirmed linear growth at 200°C with a growth rate of 0.9 Å/cycle [31]. Using the density of 2.3 g/cm^3 for the alumina-siloxane MLD films, the mass gain of ~21 ng/cm^2/cycle yields a growth rate of 0.9 Å/cycle. FTIR analysis of the surface reactions was also consistent with the reaction mechanism shown in Figure 9. However, a low atomic concentration of silicon in the MLD film measured by x-ray photoelectron spectroscopy indicated that the chlorosilane reaction with the hydroxylated surface was not very efficient.

8. Future Prospects for MLD of Hybrid Organic-Inorganic Films

The use of various organic and inorganic precursors offers a nearly limitless set of combinations for the MLD of hybrid organic-inorganic films. Many of these combinations can be used to fabricate films with specific functional properties. One example of a functional hybrid organic-inorganic film is an MLD film grown using TMA and triethylenediamine (TED). TMA is a Lewis acid and TED is a Lewis base. An exposure sequence of TMA and TED can be used to grow an MLD film with unreacted $AlCH_3$ species remaining in the film [32]. A schematic of this reaction sequence is given in Figure 10 [32]. These $AlCH_3$ species can react with H_2O and serve as a H_2O getter. The H_2O getters may be useful as interlayers in multilayer gas diffusion barrier films.

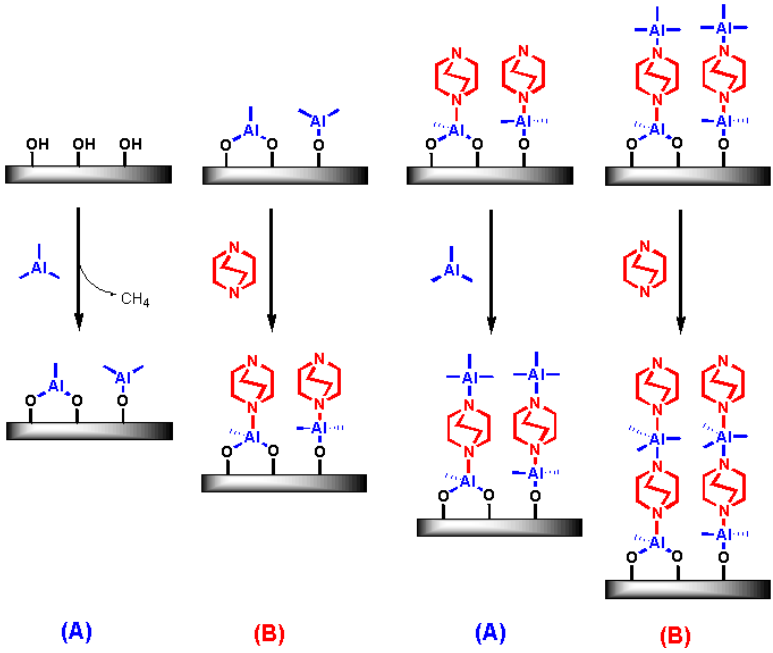

Figure 10 Schematic depicting the two-step reaction sequence for AB MLD growth of a Lewis acid-Lewis base film using trimethylaluminum (TMA) and triethylenediamine (TED).

Conductive hybrid organic-inorganic films may also be useful for flexible displays. ZnO ALD films are known to have a low resistivity of ~1 x 10^{-2} Ω cm [33]. ZnO ALD films are grown using diethylzinc (DEZ) and H_2O [34]. Hybrid organic-inorganic MLD films can be grown using DEZ and EG as mentioned earlier and are called "zincones" [17, 19]. Although the zincone MLD film based on DEZ and EG does not display any conductivity, recent results have shown that zincone films based on DEZ and hydroquinone (HQ) have displayed some conductivity when alloyed with ZnO ALD films [35]. The schematic showing the surface chemistry for zincone MLD using DEZ and HQ is given in Figure 11 [35]. If these conducting MLD alloy films display sufficient toughness because of their organic constituents, then they may be useful for flexible displays and may be candidates to replace indium tin oxide (ITO).

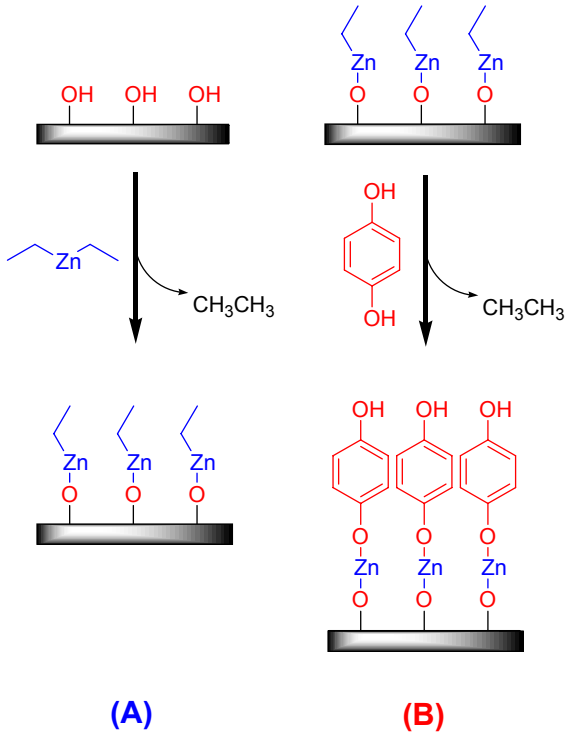

Figure 11 Schematic showing the two-step reaction sequence for AB zincone MLD growth using diethylzinc (DEZ) and hydroquinone (HQ).

The hybrid organic-inorganic MLD films have a low density that approaches the low densities of organic polymers. In contrast, inorganic ALD films have a much higher density. Mixtures of hybrid organic-inorganic MLD layers with ALD layers can be used to obtain films with a density that varies from the low density of the pure MLD film to the high density for the inorganic ALD film [36]. As an example, the density of hybrid Al_2O_3 ALD: AB Alucone MLD films are shown in Figure 12 [36]. Al_2O_3 ALD was grown using TMA and H_2O [22, 23]. AB Alucone MLD was grown using TMA and EG [13]. The density was varied by changing the relative number of ALD and MLD cycles during the alloy growth.

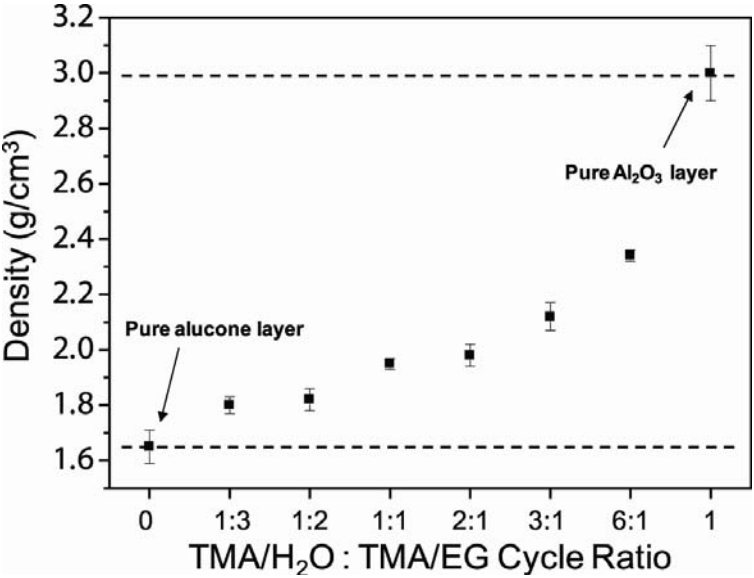

Figure 12 Density of alloys of Al_2O_3 and AB alucone using TMA and EG from XRR analysis. The alloys were prepared using different numbers of TMA/H_2O and TMA/EG cycles. For example, the 3:1 ratio sample was prepared using repetitive sequences of 3 cycles of TMA/H_2O and then 1 cycle of TMA/EG.

Figure 12 indicates that the density can be varied widely with changing organic-inorganic film composition. Other properties that are dependent on density will also change accordingly. For example, mechanical properties such as the elastic modulus and stiffness should be tunable [37]. Optical and electrical properties such as refractive index and dielectric constant should also vary with the composition of the alloy film [38]. In general, films with a variety of tunable properties should be possible by changing the ratio of ALD and MLD cycles used to grow the alloy film.

Most of the MLD systems reviewed in this chapter have been based on AB, ABC or ABCD processes using TMA. Other organometallic and organic precursors are also possible. As mentioned earlier, hybrid organic-inorganic films based on zinc are possible using DEZ [17, 19]. Other hybrid organic-inorganic systems based on zirconium and titanium are possible using $Zr(O\text{-}t\text{-}Bu)_4$ and $TiCl_4$, respectively [36, 39]. Many other organometallic precursors can also be used to define other hybrid organic-inorganic MLD polymers. For example, metal alkyls based on magnesium (Mg) and manganese (Mn) are available as $Mg(EtC_p)_2$ and $Mn(EtC_p)_2$. These metal alkyls are expected to react with diols or carboxylic acids to define new MLD systems [40, 41].

The possibilities for the MLD of hybrid organic-inorganic films are virtually unlimited given all the metals on the periodic table and organic compounds available from organic chemistry. The challenge over the next few years will be to determine the hybrid organic-inorganic films that may be grown easily and that may display useful properties. The tunable mechanical, optical, dielectric, conductive and chemical properties of the hybrid organic-inorganic films should be valuable for a wide range of applications.

Acknowledgements

This research was funded by the National Science Foundation (NSF), the Air Force Office of Scientific Research (AFOSR), the Defense Advanced Research Program Agency (DARPA) and DuPont Central Research and Development. The author also thanks B. Yoon, R.A. Hall, A.I. Abdulagatov, Y. Lee, and B.H. Lee. These members of his research group were responsible for the recent MLD and ALD results presented in this report.

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CVD/ALD Precursors Contained in 50ml Swagelok® Cylinder

98-4003 NEW→ HAZ	**Trimethylaluminum, min. 98%, 93-1360, contained in 50 ml Swagelok® cylinder for CVD/ALD** *[75-24-1]* $(CH_3)_3Al$; FW: 72.09; colorless liq.; m.p. 15.4°; b.p. 20°/8 mm; f.p. -1°F; d. 0.752 (20°) *moisture sensitive, pyrophoric*	25g
98-4021 NEW→ HAZ	**Tetrakis(dimethylamino)hafnium, 98+% (99.99+%-Hf, <0.2%-Zr) PURATREM, 72-8000, contained in 50 ml Swagelok® cylinder for CVD/ALD** *[19962-11-9]* $Hf(N(CH_3)_2)_4$; FW: 709.60; colorless to pale yellow xtl.; m.p. 38-41°; b.p. 85°/0.1mm *moisture sensitive, (store cold)*	25g
98-4048 NEW→ HAZ	**Tetrakis(ethylmethylamino)hafnium, 99% (99.99+%-Hf, <0.15% Zr) PURATREM, 72-7720, contained in 50 ml Swagelok® cylinder for CVD/ALD** *[352535-01-4]* $Hf[N(CH_3)(CH_2CH_3)]_4$; FW: 410.90 *moisture sensitive*	10g
98-4006 NEW→ HAZ	**Bis(ethylcyclopentadienyl)magnesium, min. 98%, 12-0510, contained in 50 ml Swagelok® cylinder for CVD/ALD** *[114460-02-5]* $(C_2H_5C_5H_4)_2Mg$; FW: 210.60; colorless to pale yellow liq. *air sensitive, moisture sensitive*	10g
98-4024 NEW→	**(Trimethyl)methylcyclopentadienylplatinum(IV), 99%, 78-1350, contained in 50 ml Swagelok® cylinder for CVD/ALD** *[94442-22-5]* $(CH_3)_3(CH_3C_5H_4)Pt$; FW: 319.32; off-white pwdr.; m.p. 30-31°; b.p. subl. 23°/0.053mm; d. 1.88 *air sensitive*	10g
98-4009 NEW→	**Bis(ethylcyclopentadienyl)ruthenium(II), 98% (99.9%-Ru), 44-0040, contained in 50 ml Swagelok® cylinder for CVD/ALD** *[32992-96-4]* $[(CH_3CH_2)C_5H_4]_2Ru$; FW: 287.37; pale yellow liq.; d. 1.3412.	10g
98-4036 NEW→ HAZ	**3-Aminopropyltriethoxysilane, 98%, 93-1402, contained in 50 ml Swagelok® cylinder for CVD/ALD** *[919-30-2]* $H_2N(CH_2)_3Si(OC_2H_5)_3$; FW: 221.38; colorless liq.; b.p. 217°; f.p. 220°F; d. 0.943 *moisture sensitive*	25g
98-4045 NEW→	**t-Butylimidotris(dimethylamido)tantalum(V), min. 98%, 73-0700, contained in 50 ml Swagelok® cylinder for CVD/ALD** *[69039-11-8]* $C_{10}H_{27}N_4Ta$; FW: 384.30; colorless solid *air sensitive, moisture sensitive*	25g
98-4043 NEW→ HAZ	**Tetrakis(diethylamino)titanium, 99%, 22-1050, contained in 50 ml Swagelok® cylinder for CVD/ALD** *[4419-47-0]* $Ti[N(C_2H_5)_2]_4$; FW: 336.40; yellow to orange liq.; b.p. 133°/1.2mm; f.p. -18°F; d. 0.938 *moisture sensitive*	10g

Note: High temperature Swagelok® cylinder assembly 96-1071 available at extra cost.

CVD/ALD Precursors Contained in 50ml Swagelok® Cylinder

98-4015 NEW→ HAZ	**Tetrakis(dimethylamino)titanium(IV), 99% TDMAT, 93-2240, contained in 50 ml Swagelok® cylinder for CVD/ALD** *[3275-24-9]* $Ti[N(CH_3)_2]_4$; FW: 224.20; yellow to orange liq.; b.p. 50°/0.5 mm; f.p. -22°F; d. 0.96 *moisture sensitive*	25g
98-4033 NEW→ HAZ	**Titanium(IV) chloride, 99.8+%, 22-1150, contained in 50 ml Swagelok® cylinder for CVD/ALD** *[7550-45-0]* $TiCl_4$; FW: 189.73; pale yellow liq.; m.p. -25°; b.p. 136°; d. 1.726 *moisture sensitive*	25g
98-4030 NEW→ HAZ	**Titanium(IV) i-propoxide, min. 98%, 93-2216, contained in 50 ml Swagelok® cylinder for CVD/ALD** *[546-68-9]* $Ti[OCH(CH_3)_2]_4$; FW: 284.25; colorless liq.; m.p. 20°; b.p. 58°/1mm; f.p. 81°F; d. 0.9550 *moisture sensitive*	25g
98-4018 NEW→	**Tris[N,N-bis(trimethylsilyl)amide]yttrium, min. 98% (99.9%-Y) (REO), 39-1500, contained in 50 ml Swagelok® cylinder for CVD/ALD** *[41836-28-6]* $\{[(CH_3)_3Si]_2N\}_3Y$; FW: 570.06; white to off-white pwdr.; m.p. 180-184°; b.p. subl. 105°/10^{-4}mm *air sensitive, moisture sensitive*	10g
98-4000 NEW→ HAZ	**Diethylzinc, min. 95%, 93-3030, contained in 50 ml Swagelok® cylinder for CVD/ALD** *[557-20-0]* $Zn(C_2H_5)_2$; FW: 123.49; colorless liq.; m.p. -28°; b.p. 124°; f.p. -1°F; d. 1.18 *moisture sensitive, pyrophoric*	25g
98-4039 NEW→ HAZ	**Tetrakis(ethylmethylamino)zirconium(IV) 99%, 40-1710, contained in 50 ml Swagelok® cylinder for CVD/ALD** *[175923-04-3]* $Zr[N(CH_3)(CH_2CH_3)]_4$; FW: 323.63; light yellow liq. *moisture sensitive*	10g
98-4012 NEW→ HAZ	**Tetrakis(dimethylamino)zirconium(IV), 99%, 40-4100, contained in 50 ml Swagelok® cylinder for CVD/ALD** *[19756-04-8]* $Zn[N(CH_3)_2]_4$; FW: 267.53; light yellow xtl.; m.p. 57-60°; b.p. 80°/.01mm *moisture sensitive, (store cold)*	25g

Note: High temperature Swagelok® cylinder assembly 96-1071 available at extra cost.

96-1071 High Temp Assembly

CADMIUM (Compounds)

48-0150 NEW→ HAZ
Cadmium arsenide (99.999%-Cd) PURATREM *[12006-15-4]* — 5g, 25g
Cd_3As_2; FW: 487.07; dark gray solid; d. 3.031

CARBON (Elemental forms)

06-0440 NEW→
Carbon nanotube array, multi-walled, on quartz (diameter= 100nm, length=30 microns) — 1pc
black microfibers; (diameter=100nm, length=30microns)

Technical Note:
1. Arrays grown on 10x10x1mm quartz substrate using a single source CVD process that yields vertically aligned MWNTs (< 1% catalyst impurity). Arrays are 30µm tall (± 3µm) and are composed of MWNTs 100nm in diameter (± 10nm). Arrays up to 150µm in height can be provided on request.

COPPER (Compounds)

29-0490 NEW→
Copper(I) iodide/cesium carbonate admixture [5.50 wt% CuI] — 5g, 25g
[7681-65-4]
CuI/Cs_2CO_3; off-white pwdr.

Note:
Weight-percent of components:
5.50 wt% copper(I) iodide
94.50 wt% cesium carbonate

Technical Note:
1. Copper catalyst/base admixture useful for screening reactions involving the N-arylation of nitrogen-containing heterocycles.

Reference:
1. *J. Org. Chem.*, **2007**, *72*, 8535.

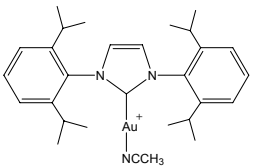
GOLD (Elemental forms)

79-0095 NEW→
Gold wire (99.99%) *[7440-57-5]* — 2cm, 10cm
1.4 mm dia.

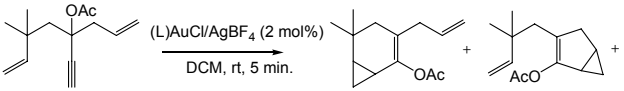
79-0085 NEW→
Gold wire (99.999%) *[7440-57-5]* — 2cm, 10cm
1.4mm dia. (~0.6g/2cm)

GOLD (Compounds)

79-0300 NEW→
1,3-Bis(2,6-di-i-propylphenyl) imidazol-2- ylidene(acetonitrile) gold(I) tetrafluoroborate, 95% — 100mg, 500mg
[896733-61-2]
$C_{29}H_{29}AuBF_4N_3$; FW: 713.41;
white solid
air sensitive
Note: US Patent 7,767,841



Technical Note:
1. Gold(I) catalyst for the cycloisomerization of 1,5-enynes bearing a propargylic acetate.



Tech. Note (1)
Ref. (1)

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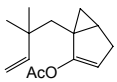
1. *Chem. Commun.*,**2005**, 2048.
2. US Patent 7,767,841.

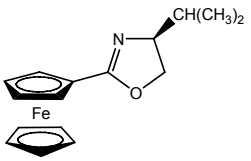


HAFNIUM (Compounds)

72-7720 NEW→ amp HAZ
Tetrakis(ethylmethylamino)hafnium, 99% (99.99+%-Hf, <0.15% Zr) PURATREM *[352535-01-4]* — 2g, 10g
$Hf[N(CH_3)(CH_2CH_3)]_4$; FW: 410.90; light yellow pwdr.
moisture sensitive

IRON (Compounds)

26-1490 NEW→
(S)-(-)-[4,5-Dihydro-4-(1-methylethyl)-2-oxazolyl]ferrocene, min. 98% — 1g, 5g
[162157-03-1]
$C_{16}H_{19}FeNO$; FW: 297.17;
orange pwdr.;
$[\alpha]_D$ -135° (c 1.0, Ethanol)



MAGNESIUM (Compounds)

12-1200 NEW→
Magnesium bis(trifluoromethylsulfonyl)imide, min. 97% — 1g, 5g
[133395-16-1]
$Mg[(CF_3SO_2)_2N]_2$; FW: 584.60; white pwdr.
moisture sensitive

NANOMATERIALS (Compounds)

79-2035 NEW→
Hexachlorododecakis[diphenyl(m-sulfontophenyl)phosphine] pentapentacontagold, dodecasodium salt (water soluble) Schmid Au_{55} Cluster *[115804-59-6]* — 10mg
$Na_{12}\{Au_{55}[P(C_6H_5)_2(C_6H_4SO_3)]_{12}Cl_6\}$; FW: 15417.85; black solid

14-6010 NEW→
Silica Nanosprings™ grown on aluminum foil substrate (3.5 x 8cm) — 1pc, 5pc
reddish white plate; S.A. 260m^2/g

14-6012 NEW→
Silica Nanosprings™ grown on fiber glass substrate (3.5 x 8cm) — 1pc, 5pc
reddish white plate; S.A. 260m^2/g.

14-6014 NEW→
Silica Nanosprings™ grown on glass slide substrate (2.5 x 7.5cm) — 1pc, 5pc
reddish white plate; S.A. 260m^2/g

14-6030 NEW→
Silica Nanosprings™ coated with titanium dioxide and grown on aluminum foil substrate (3.5 x 8cm) — 1pc, 5pc
white plate

14-6032 NEW→
Silica Nanosprings™ coated with titanium dioxide and grown on fiber glass substrate (3.5 x 8cm) — 1pc, 5pc
white plate

14-6034 NEW→
Silica Nanosprings™ coated with titanium dioxide and grown on glass slide substrate (2.5 x 7.5cm) — 1pc, 5pc
white plate

14-6050 NEW→
Silica Nanosprings™ coated with zinc oxide and grown on aluminum foil substrate (3.5 x 8cm) — 1pc, 5pc
white to beige plate

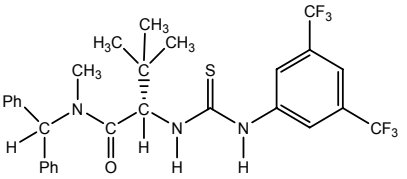
14-6052 NEW→
Silica Nanosprings™ coated with zinc oxide and grown on fiber glass substrate (3.5 x 8cm) — 1pc, 5pc
white to beige plate

14-6054 NEW→
Silica Nanosprings™ coated with zinc oxide and grown on glass slide substrate (2.5 x 7.5cm) — 1pc, 5pc
white to beige plate

Note: Silica Nanosprings™ sold under license from GoNano for research purposes only.
US 11-993,452 & PCT WO2007/002369A3.

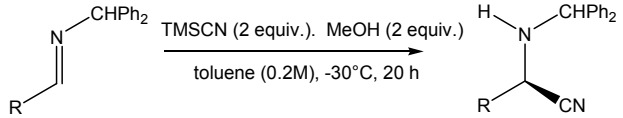
NITROGEN (Compounds)

07-0215 NEW→ **(2S)-(-)-2-{[[[3,5-Bis(tifluoro-methyl)phenyl]amino] thioxomethyl]amino}-N-(diphenylmethyl)-N,3,3-trimethylbutanamide, 95%** *[1186602-28-7]*
$C_{29}H_{29}F_6N_3OS$; FW: 581.62; white to gray solid;
$[\alpha]_D$ -57° (c 1.0, $CHCl_3$);
m.p. 193-198°
Note: US Patent Application 61/240,558.



50mg
250mg
1g

Technical Note:
1. Organocatalyst used for the asymmetric hydrocyanation of imines.



Ref. (1)

Reference:
1. *J. Am. Chem. Soc.,* **2009**, *131,* 15358.

PALLADIUM (Compounds)

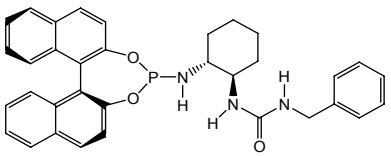
46-1810 NEW→ **Palladium(II) benzoate, 99%** *[3375-32-4]*
$Pd(C_7H_6O_2)_2$; FW: 348.65; light-brown pwdr.

250mg
1g

PHOSPHORUS (Compounds)

96-3740 NEW→ **UREAphos and METAMORPhos Ligand Kit for Asymmetric Hydrogenation**
See (page 51).

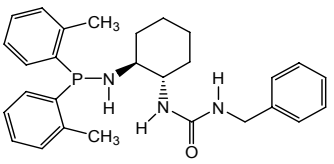
15-2208 NEW→ **1-Benzyl-3-{(1R,2R)-2-[(11bS)-dinaphtho[2,1-d:1',2'-f][1,3,2] dioxaphosphepin-4-ylamino] cyclohexyl}urea, min. 97%**
$C_{34}H_{32}N_3O_3P$; FW: 561.61; white pwdr.
moisture sensitive, (store cold)
Note: Sold under license from InCatT for research purposes only. WO2004/103559. UREAPhos and METAMORPhos Ligand Kit component . See (page 51).



50mg
250mg

Technical Note:
1. See 15-2200 (page 36).

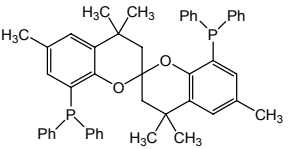
15-2210 NEW→ **1-Benzyl-3-[(1S,2S)-2-(di-o-tolyl-phosphinoamino)cyclohexyl] urea, min. 97%**
$C_{28}H_{34}N_3OP$; FW: 459.56; white pwdr.
moisture sensitive, (store cold)
Note: Sold under license from InCatT for research purposes only. WO2004/103559. UREAPhos and METAMORPhos Ligand Kit component. See (page 51).



50mg
250mg

Technical Note:
1. See 15-2200 (page 36).

15-5165 NEW→ **racemic-8,8'-Bis(diphenylphosphino)-3,3',4,4'-tetrahydro-4,4,4',4',6,6'-hexamethyl-2,2'-spirobi[2H-1-benzopyran], min. 95% SPANphos** *[556797-94-5]*
$C_{47}H_{46}O_2P_2$; FW: 704.81; white pwdr.



100mg
500mg

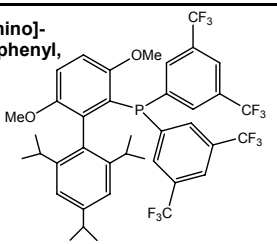
Technical Note:

1. A binucleating diphosphine ligand used as a trans-spanning ligand which rigidly links mutually trans coordination sites via phosphorous atoms separated by a large distance to form a cavity over the face of square planar mono and di-metallic complexes, e.g. in MCl_2(SPANphos) (M = Pd, Pt), $Rh_2(\mu\text{-}Cl)_2(CO)_2$(SPANphos), the latter useful in, for example, the homogeneous catalytic carbonylation of methanol to acetic acid.

References:

1. *Angew. Chem. Int. Ed.*, **2003**, *42*, 1284.
2. *Angew. Chem. Int. Ed.*, **2005**, *44*, 4385.

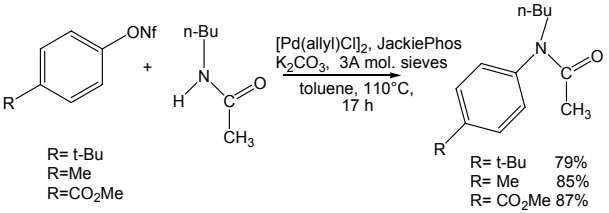
15-1157 NEW→ **2-[3,5-Bis(trifluoromethyl)phenylphosphino]-3,6-dimethoxy-2'-4'-6'-tri-i-propyl-1,1'-biphenyl, min. 98% JackiePhos** *[1160861-60-8]*
$C_{39}H_{37}F_{12}O_2P$; FW: 796.66;
white xtl.
Note: Buchwald Biaryl Phosphine Ligand Master Kit component. Buchwald Biaryl Phosphine Ligand Mini Kit 1 component. See (page 43).
Patents: US 6,395,916, US 6,307,087



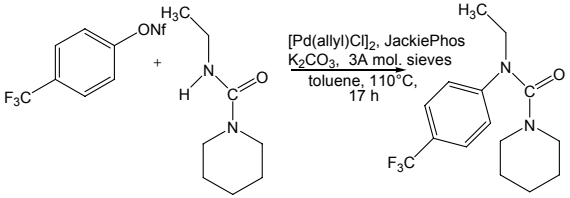
100mg
500mg
2g

Technical Notes:

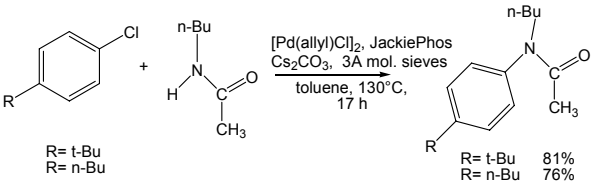
1. Ligand used in the Pd-catalyzed coupling of aryl nonaflates and triflates with secondary amides.
2. Ligand used in the Pd-catalyzed coupling of aryl nonaflates and triflates with secondary ureas, carbamates, and sulfonamides.
3. Ligand used in the Pd-catalyzed coupling of aryl chlorides with secondary amides, carbamates, and sulfonamides.



Tech. Note (1)
Ref. (1)



Tech. Note (2)
Ref. (1)

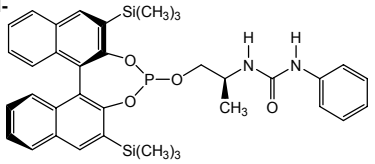


Tech. Note (3)
Ref. (1)

Reference:

1. *J. Am. Chem. Soc.*, **2009**, *131*, 16720.

15-2216 NEW→ **1-{2S)-1-[(11bR)-2,6-Bis(trimethylsilyl)dinaphtho[2,1-d:1',2'-f][1,3,2] dioxaphosphepin-4-yloxy] propan-2-yl}-3-phenylurea, min. 97%**

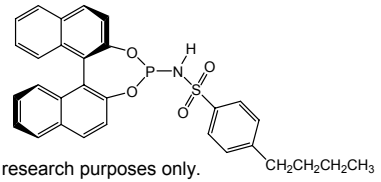


50mg
250mg

$C_{36}H_{41}N_2O_4PSi_2$; FW: 652.87; white pwdr.
moisture sensitive, (store cold)
Note: Sold under license from InCatT for research purposes only. WO2004/103559. UREAPhos and METAMORPhos Ligand Kit component. See (page 51).

Technical Note:
1. See 15-2200 (page 36).

15-2218 NEW→ **4-Butyl-N-[(11bR)-dinaphtho[2,1-d:1', 2'-f][1,3,2]dioxa-phosphepin-4-yl] benzenesulfonamide triethylamine adduct, min. 97%** *[1150592-91-8]*

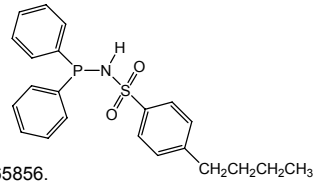


50mg
250mg

$C_{30}H_{26}NO_4PS\cdot(CH_3CH_2)_3N$; FW: 527.57 (628.76)
moisture sensitive, (store cold)
Note: Sold under license from InCatT for research purposes only. WO2009/065856. UREAPhos and METAMORPhos Ligand Kit component. See (page 51).

Technical Note:
1. See 15-2228 (page 37).

15-2220 NEW→ **4-Butyl-N-(diphenylphosphino) benzenesulfonamide, min. 97%** *[1025096-61-0]*

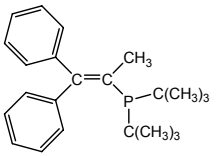


50mg
250mg

$C_{22}H_{26}NO_2PS$; FW: 397.47; white pwdr.
moisture sensitive, (store cold)
Note: Sold under license from InCatT for research purposes only. WO2009/065856. UREAPhos and METAMORPhos Ligand Kit component. See (page 51).

Technical Note:
1. See 15-2228 (page 37).

15-1065 NEW→ **Di-t-butyl(2,2-diphenyl-1-methylvinyl) phosphine vBRIDP** *[384842-25-5]*



250mg
1g
5g

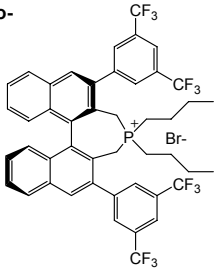
$C_{21}H_{31}P$; FW: 314.45; off-white pwdr.
air sensitive, (store cold)
Note: Manufactured under license of Takasago patent US6455720.

Technical Note:
1. See 15-1005 (Visit www.strem.com).

15-1457 NEW→

(11bR)-(+)-4,4-Dibutyl-2,6-bis[3,5-bis(trifluoromethyl)phenyl]-4,5-dihydro-3H-dinaphtho [2,1-c:1',2'-e]phosphepinium bromide, 99% R-MARUOKA CAT P-NB

$[C_{46}H_{38}F_{12}P]^+Br^-$; FW: 929.65; white xtl.;
$[\alpha]_D$ +29.8° (c 0.5, $CHCl_3$); m.p. 262-263°
Note: Maruoka Chiral Phase-Transfer Phosphonium Organocatalyst Kit component. See (page 46).



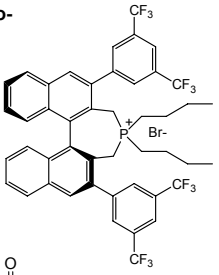
50mg
250mg

Technical Note:
1. See 15-1458 (page 34).

15-1458 NEW→

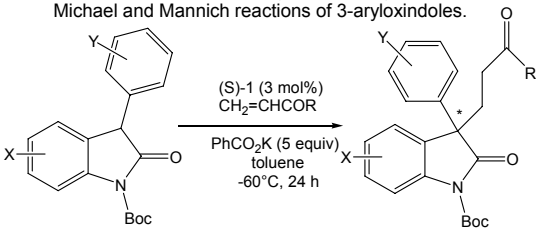
(11bS)-(-)-4,4-Dibutyl-2,6-bis[3,5-bis(trifluoromethyl)phenyl]-4,5-dihydro-3H-dinaphtho [2,1-c:1',2'-e]phosphepinium bromide, 99% S-Maruoka CAT P-NB *[1110813-90-5]*

$[C_{36}H_{3D}F_{12}P]^+Br^-$; FW: 929.65; white xt.;
m.p. 262-263°
Note: Maruoka Chiral Phase-Transfer Phosphonium Organocatalyst Kit component. See (page 46).

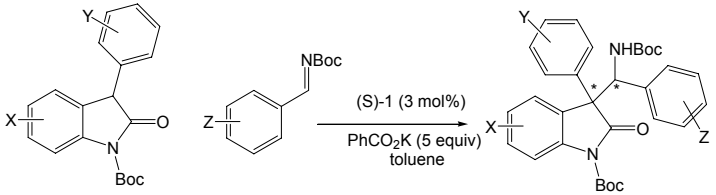


50mg
250mg

Technical Note:
1. Chiral, phase-transfer catalyst for the asymmetric Michael and Mannich reactions of 3-aryloxindoles.



Tech. Note (1)
Ref. (1)



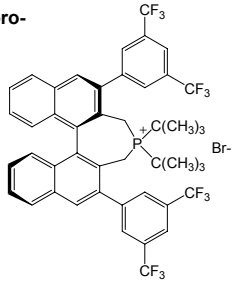
Tech. Note (1)
Ref. (1)

Reference:
1. *Angew. Chem. Int. Ed.*, **2009**, *48*, 4559.

15-1464 NEW→

(11bR)-(+)-4,4-Di-t-butyl-2,6-bis[3,5-bis(trifluoromethyl)phenyl]-4,5-dihydro-3H-dinaphtho [2,1-c:1',2'-e]phosphepinium bromide, 99% R-MARUOKA CAT P-TB

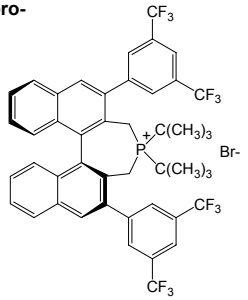
$[C_{46}H_{38}F_{12}P]^+Br^-$; FW: 929.65; white xtl.;
$[\alpha]_D$ -13.8° (C 0.5, $CHCl_3$); m.p. 202-204°
Note: Maruoka Chiral Phase-Transfer Phosphonium Organocatalyst Kit component. See (page 46).



50mg
250mg

Technical Note:
1. See 15-1458 (page 34).

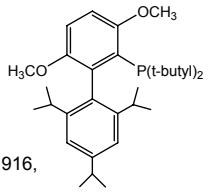
15-1465 NEW→ **(11bS)-(-)-4,4-Di-t-butyl-2,6-bis[3,5-bis(trifluoromethyl)phenyl]-4,5-dihydro-3H-dinaphtho[2,1-c:1',2'-e]phosphepinium bromide, 99% S-MARUOKA CAT P-TB** 50mg 250mg



$[C_{46}H_{38}F_{12}P]^+Br^-$; FW: 929.65; white xtl.;
$[\alpha]_D$ +14.3° (c 0.5, $CHCl_3$); m.p. 202-203°
Note: Maruoka Chiral Phase-Transfer Phosphonium Organocatalyst Kit component. See (page 46).

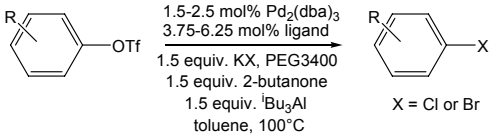
Technical Note:
1. See 15-1458 (page 34).

15-1164 NEW→ **2-(Di-t-butylphosphino)-3,6-dimethoxy-2'-4'-6'-tri-i-propyl-1,1'-biphenyl, min. 98% t-butylBrettPhos** 100mg 500mg

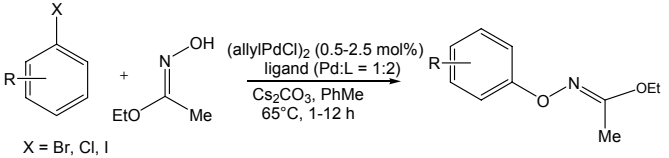


$C_{31}H_{50}O_2P$; FW: 485.35; white xtl.
Note: Buchwald Biaryl Phosphine Ligand Master Kit component.
Buchwald Biaryl Phosphine Ligand Mini Kit 1 component. See (page 43). Patents: US 6,395,916, US 6,307,087

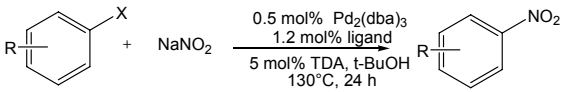
Technical Notes:
1. Ligand used in the Pd-catalyzed conversion of aryl and vinyl triflates to bromides and chlorides.
2. Ligand used in the Pd-catalyzed O-arylation of ethyl acetohydroximates.
3. Ligand used in the Pd-catalyzed conversion of aryl chlorides, triflates, and nonaflates to nitroaromatics.
4. Ligand used in the Pd-catalyzed cross-coupling of amides and aryl mesylates.



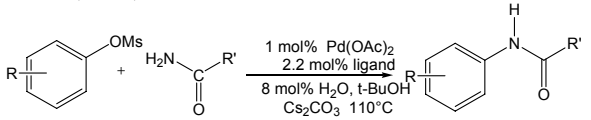
Tech. Note (1)
Ref. (1)



Tech. Note (2)
Ref. (2)



Tech. Note (3)
Ref. (3)

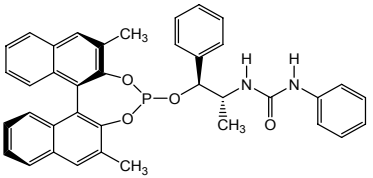


Tech. Note (4)
Ref. (4)

References:
1. *J. Am. Chem. Soc.*, **2010**, *132,* 14076.
2. *J. Am. Chem. Soc.*, **2010**, *132,* 9990.
3. *J. Am. Chem. Soc.*, **2009**, *131,* 12898.
4. *Org. Lett.*, **2010**, *12(10),* 2350.

15-2206 NEW→

1-{(1S,2R)-1-[(11bR)-2,6-Dimethyl-dinaphtho[2,1-d:1',2'-f][1,3,2]dioxa-phosphepin-4-yloxy]-1-phenyl-propan-2-yl}-3-phenylurea, min. 97%
$C_{38}H_{33}N_2O_4P$; FW: 612.65; white pwdr.
moisture sensitive, (store cold)
Note: Sold under license from InCatT for research purposes only.
WO2004/103559. UREAPhos and METAMORPhos Ligand Kit component. See (page 51).

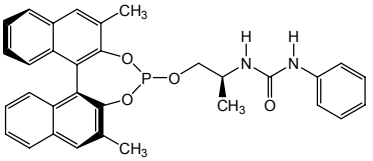


50mg
250mg

Technical Note:
1. See 15-2200 (page 36).

15-2204 NEW→

1-{(2S)-1-[(11bS)-2,6-Dimethyl-dinaphtho[2,1-d:1',2'-f] [1,3,2]dioxa-phosphepin-4-yloxy]propan-2-yl}-3-phenylurea, min. 97%
$C_{32}H_{29}N_2O_4P$; FW: 536.56; white pwdr.
moisture sensitive, (store cold)
Note: Sold under license from InCatT for research purposes only.
WO2004/103559. UREAPhos and METAMORPhos Ligand Kit component. See (page 51).

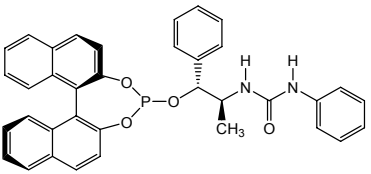


50mg
250mg

Technical Note:
1. See 15-2200 (page 36).

15-2202 NEW→

1-{(1R,2S)-1-[(11bR)-Dinaphtho[2,1-d:1',2'-f][1,3,2] dioxaphosphepin-4-yl-oxy]-1-phenylpropan-2-yl}-3-phenylurea, min. 97% *[1198080-55-5]*
$C_{36}H_{29}N_2O_4P$; FW: 584.60; white pwdr.
moisture sensitive, (store cold)
Note: Sold under license from InCatT for research purposes only.
WO2004/103559. UREAPhos and METAMORPhos Ligand Kit component . See (page 51).

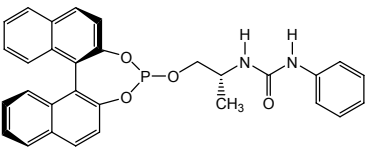


50mg
250mg

Technical Note:
1. See 15-2200 (page 36).

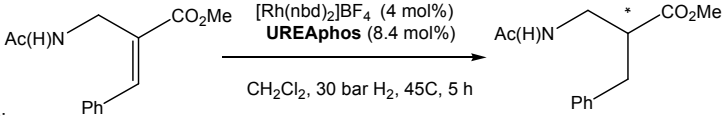
15-2200 NEW→

1-{(2R)-1-[(11bR)-Dinaphtho[2,1-d:1',2'-f][1,3,2]dioxaphosphepin-4-yloxy] propan-2-yl}-3-phenylurea, min. 97% UREAPhos *[1198080-53-3]*
$C_{30}H_{25}N_2O_4P$; FW: 508.50; white pwdr.
moisture sensitive, (store cold)
Note: Sold under license from InCatT for research purposes only.
WO2004/103559. UREAPhos and METAMORPhos Ligand Kit component. See (page 51).



50mg
250mg

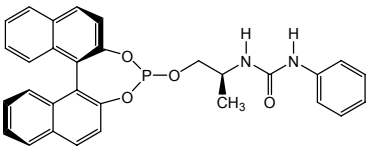
Technical Note:
1. The UREAphos ligands are a new class of ligands containing a urea group, which due to its self-complementary hydrogen bond character, enables the formation of bidentate ligands in a supramolecular fashion. This interesting feature makes this ligand class highly suitable for combinatorial approaches and high throughput experimentation.



84%, 96% ee

References:
1. *J. Chem. Soc. Chem. Comm.*, **2007**, 864.
2. WO2004103559A2.

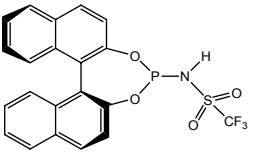
15-2201 NEW→ **1-{(2S)-1-[(11bR)-Dinaphtho[2,1-d:1',2'-f][1,3,2]dioxaphosphepin-4-yl-oxy]propan-2-yl}-3-phenylurea, min. 97%** 50mg 250mg



$C_{30}H_{25}N_2O_4P$; FW: 508.50; white pwdr.
moisture sensitive,
(store cold)
Note: Sold under license from InCatT for research purposes only. WO2004/103559, WO2009/065856. UREAPhos and METAMORPhos Ligand Kit component. See (page 51).

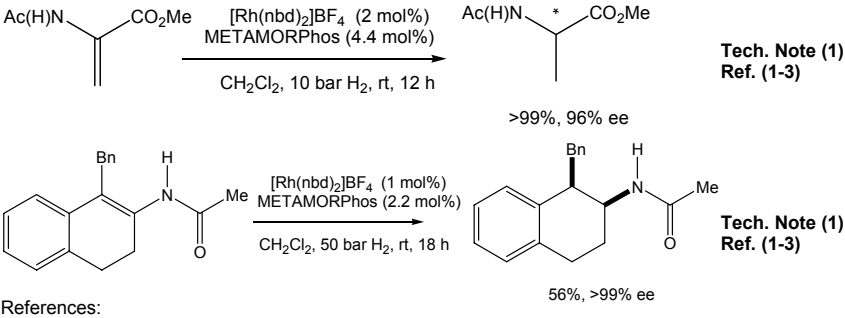
Technical Note:
1. See 15-2200 (page 36).

15-2228 NEW→ **N-[(11bS)-Dinaphtho[2,1-d:1',2'-f][1,3,2]dioxaphosphepin-4-yl]-1,1,1-trifluoro-methanesulfonamide triethylamine adduct, min. 97% METAMORPhos** 50mg 250mg



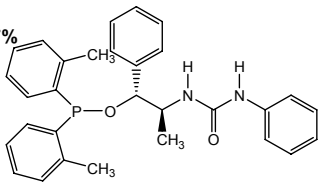
$C_{21}H_{28}F_3N_2O_4PS\cdot(C_2H_5)_3N$;
FW: 463.37(564.56)
moisture sensitive, (store cold)
Note: Sold under license from InCatT for research purposes only. WO2009/065856. UREAPhos and METAMORPhos Ligand Kit component. See (page 51).

Technical Note:
1. Chiral ligand for the rhodium-catalyzed asymmetric hydrogenation of α-β unsaturated substrates.



References:
1. *J. Am. Chem. Soc.,* **2009**, *131*, 6683.
2. *Angew. Chem. Int. Ed.,* **2008**, *47*, 3180.
3. Patent WO2009065856.

15-2214 NEW→ **1-[(1R,2S)-1-(Di-o-tolylphosphinooxy)-1-phenylpropan-2-yl]-3-phenylurea, min. 97%** 50mg 250mg



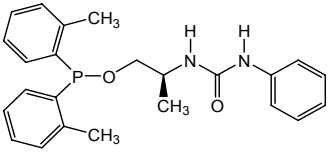
$C_{30}H_{31}N_2O_2P$;
FW: 482.55; white pwdr.
moisture sensitive, (store cold)
Note: Sold under license from InCatT for research purposes only. WO2004/103559. UREAPhos and METAMORPhos Ligand Kit component. See (page 51).

Technical Note:
1. See 15-2200 (page 36).

PHOSPHORUS (Compounds)

15-2212 NEW→

1-[(2S)-1-(Di-o-tolylphosphinooxy) propan-2-yl]-3-phenylurea, min. 97%
$C_{24}H_{27}N_{22}P$; FW: 406.46; white pwdr.
moisture sensitive, (store cold)
Note: Sold under license from InCatT for research purposes only. WO2004/103559. UREAPhos and METAMORPhos Ligand Kit component. See (page 51).

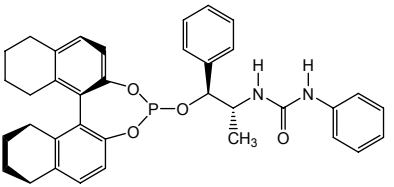


50mg
250mg

Technical Note:
1. See 15-2200 (page 36).

15-2224 NEW→

1-{(1S,2R)-1-[(11bR)-8,9,10,11,12, 13,14,15-Octahydro-dinaphtho[2,1-d: 1',2'-f][1,3,2]dioxaphosphepin-4-yl-oxy]-1-phenylpropan-2-yl}-3-phenylurea, min. 97%
$C_{36}H_{37}N_2O_4P$; FW: 592.86; white pwdr.
moisture sensitive, (store cold)
Note: Sold under license from InCatT for research purposes only. WO2004/103559. UREAPhos and METAMORPhos Ligand Kit component . See (page 51).

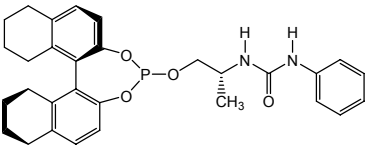


50mg
250mg

Technical Note:
1. See 15-2200 (page 36).

15-2222 NEW→

1-{(2R)-1-[(11bR)-8,9,10,11,12, 13,14,15-Octahydro-dinaphtho[2,1-d:1',2'-f][1,3,2]dioxaphosphepin-4-yloxy]propan-2-yl}-3-phenylurea, min. 97%
$C_{30}H_{33}N_2O_4P$; FW: 516.57; white pwdr.
moisture sensitive, (store cold)
Note: Sold under license from InCatT for research purposes only. WO2004/103559. UREAPhos and METAMORPhos Ligand Kit component. See (page 51).



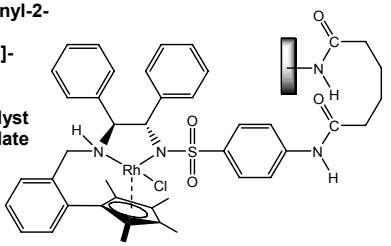
50mg
250mg

Technical Note:
1. See 15-2200 (page 36).

RHODIUM (Compounds)

45-0385 NEW→

Chloro[2-methyl{1,2-diphenyl-2-[(4-amidophenylsulfonyl) amido]ethyl}amino}phenyl]-2,3,4,5-tetramethylcyclo-pentadienyl]rhodium(III) Heterogenized Rh(III)-catalyst on a polyethylene sinter plate
yellow-orange plate
(1cm x 1cm x 1.5mm)
Note: Sold under license from PolyAn for research purposes only.
PCT/EP2010/060270



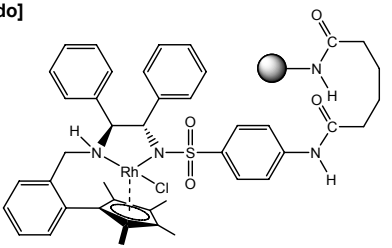
100mg
500mg

Rhodium content:	0.05 mass%
Support material:	Polyethylene
Weight of one plate:	100mg
Mean Particle Size:	30 microns

RHODIUM (Compounds)

45-0387 NEW→

Chloro[2-methyl{1,2-diphenyl-2-[(4-amidophenylsulfonyl)amido] ethyl}amino}phenyl]-2,3,4,5-tetramethylcyclopentadienyl] rhodium(III) Heterogenized Rh(III)-catalyst supported on ultra-high molecular weight polyethylene microparticles
yellow-orange pwdr.
Note: Sold under license from PolyAn for research purposes only. PCT/EP2010/060270



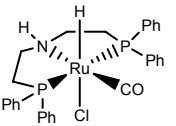
100mg
500mg

Rhodium content:	0.05 mass%
Support material:	Ultra-high molecular weight polyethylene
Specific volume:	2-4 ml/g
Mean Particle Size:	30 microns

RUTHENIUM (Compounds)

44-0071 NEW→

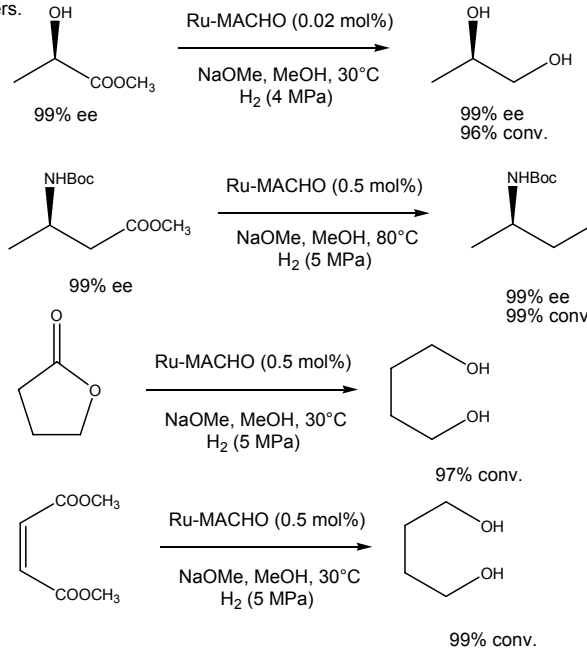
Carbonylchlorohydrido{bis[2-(diphenylphosphinomethyl)ethyl]amino}ruthenium(II), min.98% Ru-MACHO™
$C_{29}H_{30}ClNOP_2Ru$; FW: 607.03; white to yellow pwdr.
air sensitive
Note: Manufactured under license of Takasago patent. PCT/JP2010-004301.



250mg
1g
5g

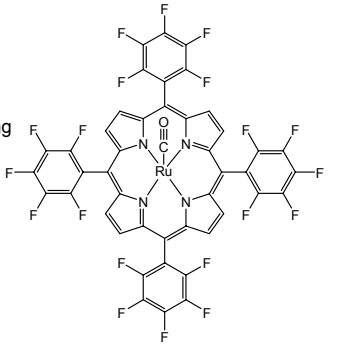
Technical Note:

1. Catalyst used in the hydrogenation of α-hydroxy esters, β-Boc-Amino esters, lactones and maleic acid esters.



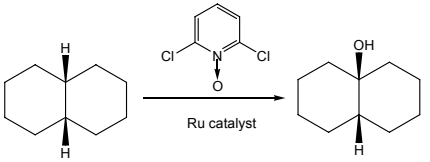
44-1030 NEW→ **Carbonyl[5,10,15,20-tetrakis(2,3,4,5,6-pentafluorophenyl)-21H,23H-porphinato] ruthenium(II), min. 98%** *[171899-61-9]*
$Ru(C_{44}H_8F_{20}N_4)CO$; FW: 1101.61; red xtl.

50mg
250mg



Technical Note:

1. Catalyst used for the hydroxylation of alkanes using 2,6-dichloropyridine-N-oxide as the oxidant under mild, nonacidic conditions.

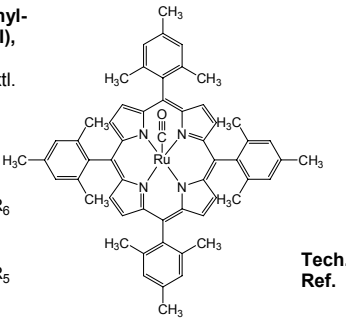


Reference:

1. *Inorg. Chem.,* **2006**, *45*, 4769.

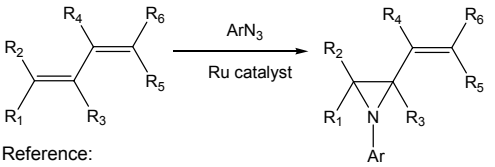
44-1025 NEW→ **Carbonyl[5,10,15,20-tetrakis(2,4,6-trimethylphenyl)-21H,23H-porphinato]ruthenium(II), min. 98%** *[92669-43-7]*
$Ru(C_{56}H_{52}N_4)CO$; FW: 910.12; red-orange xtl.

50mg
250mg



Technical Notes:

1. Catalyst used for the direct aziridination of conjugated dienes by aryl azides.
2. See 44-1020 (page 40).



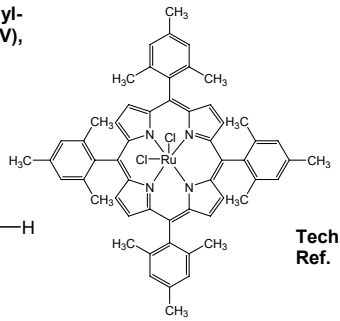
Tech. Note (1)
Ref. (1)

Reference:

1. *Eur. J. Org. Chem.,* **2007**, 743.

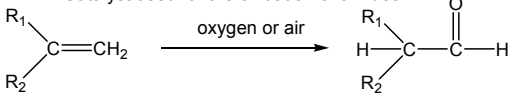
44-1020 NEW→ **Dichloro[5,10,15,20-tetrakis(2,4,6-trimethylphenyl)-21H,23H-porphinato]ruthenium(IV), min. 98%** *[145698-90-4]*
$Ru(C_{56}H_{52}N_4)Cl_2$; FW: 953.01; purple xtl.

25mg
100mg



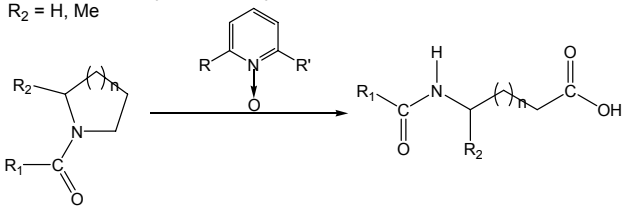
Technical Notes:

1. Catalyst used for the oxidation of 1-alkenes to aldehydes using air or oxygen.
2. Catalyst used for the oxidation of amides.



Tech. Note (1)
Ref. (1)

R_1 = Ph, 2-$MeOC_6H_4$, 4-$MeOC_6H_4$, 2-naphthyl
R_2 = H, Me



Tech. Note (2)
Ref. (2)

References:

1. *Angew. Chem. Int. Ed.,* **2008**, *47*, 6638.
2. *J. Am. Chem. Soc.*, **2005**, *127*, 834.

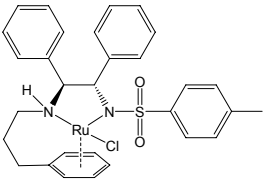
RUTHENIUM (Compounds)

44-0110 NEW→ **{N-[3-(η6-phenyl)propyl]-[(1S-2S)-1,2-diphenyl-1-4-methylbenzenesulfonyl-amidato(kN')-ethyl-2-amino-(kN)]} ruthenium(II) (S,S)-Teth-TsDpen RuCl**

[851051-43-9]

$C_{30}H_{31}ClN_2O_2RuS$; FW: 620.17; orange pwdr.

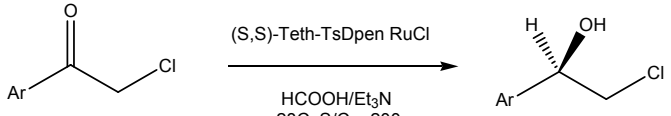
air sensitive



100mg
500mg

Technical Note:

1. Catalyst used for asymmetric -transfer hydrogenation.



Full conversion in 1.5 hr
97% ee

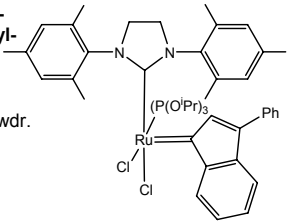
Reference:

1. *J. Org. Chem.*, **2006**, *71*, 7035.

RUTHENIUM (Compounds)

44-7783 NEW→ **Tri(i-propoxy)phosphine(3-phenyl-1H-inden-1-ylidene)[1,3-bis(2,4,6-trimethyl-phenyl)-4,5-dihydroimidazol-2-ylidene]ruthenium(II) dichloride, min. 95% cis-Caz-1**

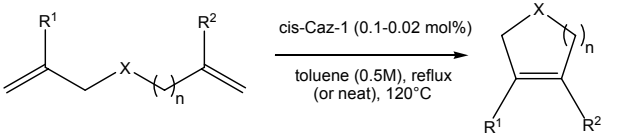
$C_{45}H_{57}Cl_2N_2O_3Ru$; FW: 876.89; brown pwdr.

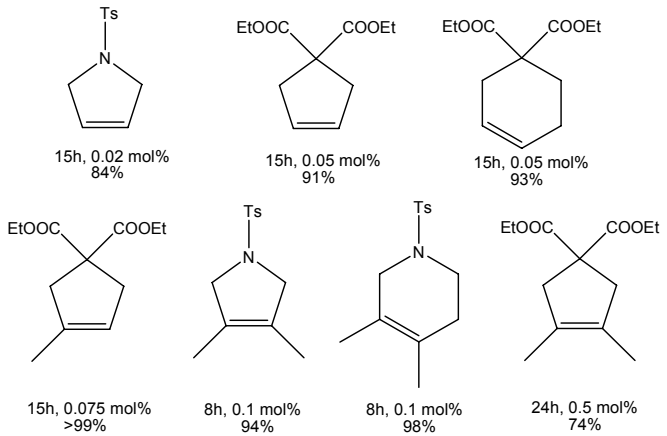


50mg
250mg

Technical Note:

1. Efficient catalyst for ring-closing metathesis.

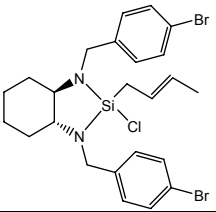


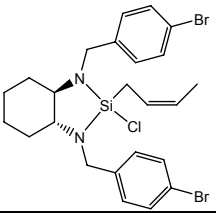


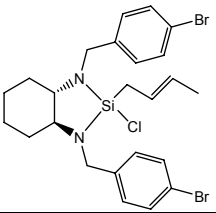
Reference:

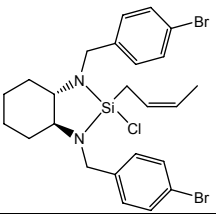
1. *Chem. Commun*, **2010**, 7115.

SILICON (Compounds)

14-1883 NEW→
(1R,2R)-(-)-[N,N'-Bis(4-bromobenzyl)-1,2-cyclohexanediamino][(2E)-2-buten-1-yl]chlorosilane, min. 98%
[804559-39-5]
$C_{24}H_{29}Br_2ClN_2Si$; FW: 568.85;
white solid; $[\alpha]_D$ -44.4° (c 1.1, CH_2Cl_2)
moisture sensitive
Note: Patent WO 03/074534, WO 06/062901.

250mg 1g

14-1887 NEW→
(1R,2R)-(-)-[N,N'-Bis(4-bromobenzyl)-1,2-cyclohexanediamino][(2Z)-2-buten-1-yl]chlorosilane, min. 98%
[804559-38-4]
$C_{24}H_{29}Br_2ClN_2Si$; FW: 568.85;
white solid; $[\alpha]_D$ -41.1° (c 1.0, CH_2Cl_2)
moisture sensitive
Note: Patent WO 03/074534, WO 06/062901.

250mg 1g

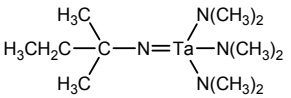
14-1884 NEW→
(1S,2S)-(+)-[N,N'-Bis(4-bromobenzyl)-1,2-cyclohexanediamino][(2E)-2-buten-1-yl]chlorosilane, min. 98%
[1072220-37-1]
$C_{24}H_{29}Br_2ClN_2Si$; FW: 568.85;
white solid; $[\alpha]_D$ +52.9° (c 1.3, CH_2Cl_2)
moisture sensitive
Note: Patent WO 03/074534, WO 06/062901.

250mg 1g

14-1888 NEW→
(1S,2S)-(+)-[N,N'-Bis(4-bromobenzyl)-1,2-cyclohexanediamino][(2Z)-2-buten-1-yl]chlorosilane, min. 98%
$C_{24}H_{29}Br_2ClN_2Si$; FW: 568.85;
white solid; $[\alpha]_D$ +45.8° (c 1.4, CH_2Cl_2)
moisture sensitive
Note: Patent WO 03/074534, WO 06/062901.

250mg 1g

SILVER (Compounds)

47-0650 NEW→
Silver bis(trifluoromethanesulfonyl)imide acetonitrile adduct, min. 97% *[189114-61-2]*
$Ag[(N(CF_3SO_2)_2]\cdot CH_3CN$; FW: 388.02; white to off-white solid
500mg 2g

TANTALUM (Compounds)

73-0490 NEW→
t-Amylimidotris(dimethylamido) tantalum(V) TAIMATA *[629654-53-1]*
$C_{11}H_{29}N_4Ta$; FW: 398.32
air sensitive, moisture sensitive

1g 5g

TUNGSTEN (Compounds)

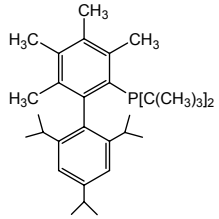
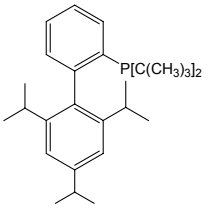
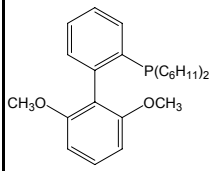
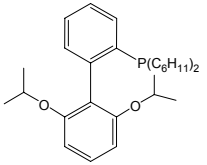
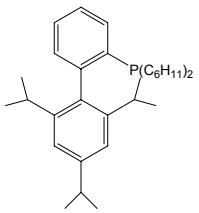
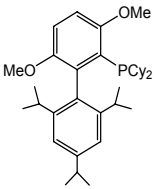
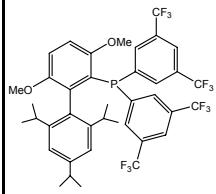
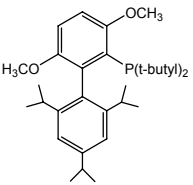
74-7435 NEW→
Tungsten(IV) oxide (99.9+%-W) (WO2.9 Blue Sub-oxide)
[12037-58-0]
$WO_{2.75-2.90}$; FW: 215.85; blue pwdr.
10g 50g

ZINC (Compounds)

30-1350 NEW→
Zinc bis(trifluoromethylsulfonyl)imide, min. 97% *[168106-25-0]*
$Zn[(CF_3SO_2)_2N]_2$; FW: 625.69; white pwdr.
hygroscopic
1g 5g

BUCHWALD BIARYL PHOSPHINE LIGAND MINI KIT 1

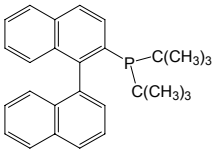
96-5485 Buchwald Biaryl Phosphine Ligand Mini Kit 1
(contains more recently developed ligands)
for aromatic carbon-heteroatom bond formation and Suzuki Coupling.
Patents: US 6,395,916, US 6,307,087.
Components available for individual sale.
Contains the following:

			
	t-butylXPhos	**SPhos**	**RuPhos**
15-1051 250mg	15-1052 500mg	15-1143 500mg	15-1146 500mg
			
XPhos	**BrettPhos**	**JackiePhos**	**t-butylBrettPhos**
15-1149 500mg	15-1152 250mg	15-1157 100mg	15-1164 100mg

15-1051	2-Di-t-butylphosphino-3,4,5,6-tetramethyl-2',4',6'-tri-i-propylbiphenyl, min. 98% *[857356-94-6]*	250mg	Visit www.strem.com
15-1052	2-Di-t-butylphosphino-2',4',6'-tri-i-propyl-1,1'-biphenyl, min. 98% t-butylXPhos *[564483-19-8]*	500mg	Visit www.strem.com
15-1143	2-Dicyclohexylphosphino-2',6'-dimethoxy-1,1'-biphenyl, min. 98% SPhos *[657408-07-6]*	500mg	Visit www.strem.com
15-1146	2-Dicyclohexylphosphino-2',6'-di-i-propoxy-1,1'-biphenyl, min. 98% RuPhos *[787618-22-8]*	500mg	Visit www.strem.com
15-1149	2-(Dicyclohexylphosphino)-2',4',6'-tri-i-propyl-1,1'-biphenyl, min. 98% XPhos *[564483-18-7]*	500mg	Visit www.strem.com
15-1152	2-(Dicyclohexylphosphino)-3,6-dimethoxy-2'-4'-6'-tri-i-propyl-1,1'-biphenyl, min. 98% BrettPhos *[1070663-78-3]*	250mg	Visit www.strem.com
15-1157	2-[3,5-Bis(trifluoromethyl)phenylphosphino]-3,6-dimethoxy-2'-4'-6'-tri-i-propyl-1,1'-biphenyl, min. 98% JackiePhos *[1160861-60-8]*	100mg	See page 32
15-1164	2-(Di-t-butylphosphino)-3,6-dimethoxy-2'-4'-6'-tri-i-propyl-1,1'-biphenyl, min. 98% t-butylBrettPhos	100mg	See page 35

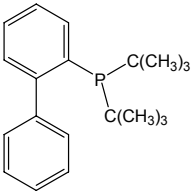
BUCHWALD BIARYL PHOSPHINE LIGAND MINI KIT 2

96-5490 **Buchwald Biaryl Phosphine Ligand Mini Kit 2**
NEW→ **(contains more mature ligands)**
for aromatic carbon-heteroatom bond formation and Suzuki Coupling and Negishi Cross-coupling.
Patents: US 6,395,916, US 6,307,087.
Components available for individual sale.
Contains the following:



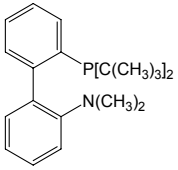
TrixiePhos

15-1043 250mg

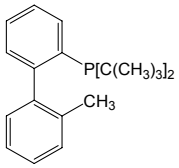


JohnPhos

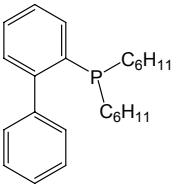
15-1045 500mg



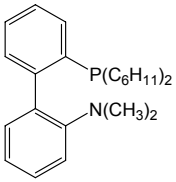
15-1048 500mg



15-1049 500mg

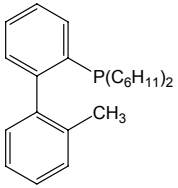


15-1140 500mg



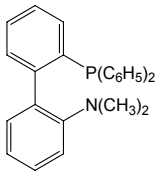
DavePhos

15-1145 500mg



MePhos

15-1148 500mg



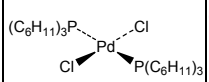
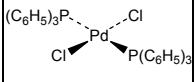
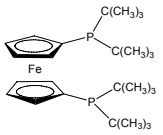
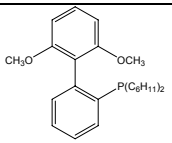
15-1745 500mg

15-1043 racemic-2-Di-t-butylphosphino-1,1'-binaphthyl, 98% TrixiePhos *[255836-67-0]*
Visit www.strem.com
15-1045 2-(Di-t-butylphosphino)biphenyl, 99% JohnPhos *[224311-51-7]*
15-1048 2-Di-t-butylphosphino-2'-(N,N-dimethylamino)biphenyl, 98% *[224311-49-3]*
15-1049 2-Di-t-butylphosphino-2'-methylbiphenyl, 99% *[255837-19-5]*
15-1140 2-(Dicyclohexylphosphino)biphenyl, 98% *[247940-06-3]*
15-1145 2-(Dicyclohexylphosphino)-2'-(N,N-dimethylamino)biphenyl, 98% DavePhos *[213697-53-1]*
15-1148 2-Dicyclohexylphosphino-2'-methylbiphenyl, min. 98% MePhos *[251320-86-2]*
15-1745 2-Diphenylphosphino-2'-(N,N-dimethylamino)biphenyl, 98% *[240417-00-9]*

CatKits – SINGLE USE VIALS for LOW CATALYST LOADING EXPERIMENTS

96-3790 **Kit of CatKits – Single-Use Vials for low catalyst loading experiments**

Components available for individual sale.

Components	46-2040	46-2038	46-2030	46-2033
Metal Precursor			$Pd(OAc)_2$	$Pd(OAc)_2$
Ligand	—	—		
Base	K_3PO_4	K_3PO_4	K_3PO_4	K_3PO_4

This Kit contains 4 different type of Single-Use Vials.
Each type has 5 x 1 vials.
Contains the following:

46-2040 NEW→	trans-Dichlorobis(tricyclohexylphosphino) palladium(II)/potassium phosphate admixture [CatKit single-use vials - 6.62 wt% Pd complex] *[29934-17-6]*	5 x 1vial	Visit www.strem.com
46-2038 NEW→	trans-Dichlorobis(triphenylphosphine) palladium(II)/potassium phosphate admixture [CatKit single-use vials - 6.32 wt% Pd complex] *[13965-03-2]*	5 x 1vial	
46-2030 NEW→	Palladium(II) acetate/1,1'-bis(di-t-butylphosphino) ferrocene/potassium phosphate admixture [CatKit single-use vials - 2.02 wt% $Pd(OAc)_2$] *[95408-45-0]*	5 x 1vial	
46-2033 NEW→	Palladium(II) acetate/2-dicyclohexylphosphino-2,6-dimethoxy-1,1'-biphenyl (SPhos)/potassium phosphate admixture [CatKit single-use vials - 1.96 wt% $Pd(OAc)_2$] *[1028206-58-7]*	5 x 1vial	

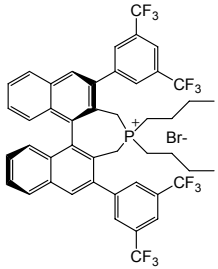
MARUOKA CHIRAL PHASE-TRANSFER PHOSPHONIUM ORGANOCATALYST KIT

96-3750 **Maruoka Chiral Phase-Transfer Phosphonium Organocatalyst Kit**

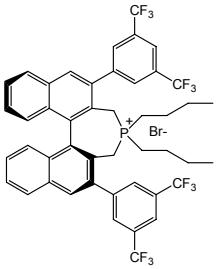
NEW→

Components available for individual sale.

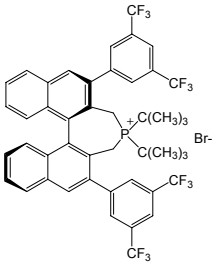
Contains the following:



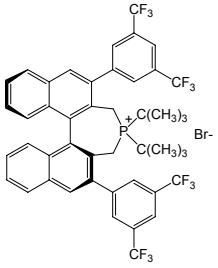
15-1457 50mg



15-1458 50mg



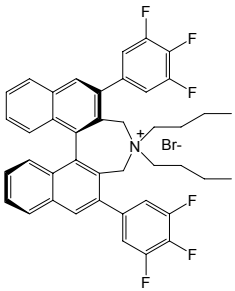
15-1464 50mg



15-1465 50mg

15-1457	(11bR)-(+)-4,4-Dibutyl-2,6-bis[3,5-bis(trifluoromethyl)phenyl]-4,5-dihydro-3H-dinaphtho[2,1-c:1',2'-e]phosphepinium bromide, 99% R-MARUOKA CAT P-NB	50mg	See page 34
15-1458	(11bS)-(-)-4,4-Dibutyl-2,6-bis[3,5-bis(trifluoromethyl)phenyl]-4,5-dihydro-3H-dinaphtho[2,1-c:1',2'-e]phosphepinium bromide S-Maruoka CAT P-NB *[1110813-90-5]*	50mg	See page 34
15-1464	(11bR)-(+)-4,4-Di-t-butyl-2,6-bis[3,5-bis(trifluoromethyl)phenyl]-4,5-dihydro-3H-dinaphtho[2,1-c:1',2'-e]phosphepinium bromide, 99% R-MARUOKA CAT P-TB	50mg	See page 34
15-1465	(11bS)-(-)-4,4-Di-t-butyl-2,6-bis[3,5-bis(trifluoromethyl)phenyl]-4,5-dihydro-3H-dinaphtho[2,1-c:1',2'-e]phosphepinium bromide S-MARUOKA CAT P-TB	50mg	See page 35

Also Available



07-0380 (R-shown)

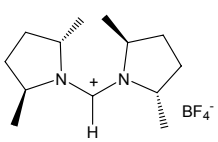
07-0381 (S-not shown)

NHC LIGAND KIT 1: CHIRAL N-HETEROCYCLIC CARBENES

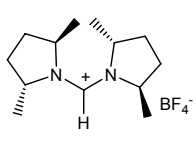
96-3760 **NHC Ligand Kit 1: Chiral N-Heterocyclic Carbenes**

NEW→ Components available for individual sale.

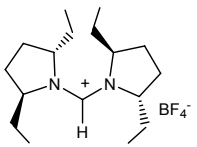
Contains the following:



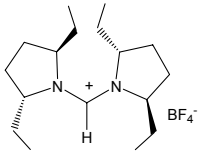
07-4021 100mg



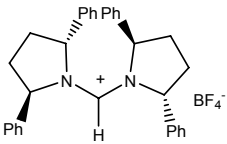
07-4022 100mg



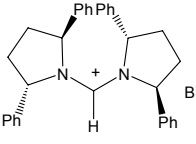
07-4024 100mg



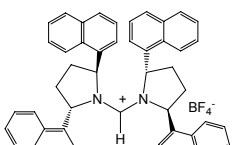
07-4025 100mg



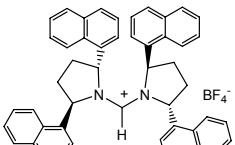
07-4026 100mg



07-4027 100mg



07-4029 100mg



07-4030 100mg

07-4021	(2S,5S)-1-{[(2S,5S)-2,5-Dimethylpyrrolidin-1-yl]methylene}-2,5-dimethylpyrrolidinium tetrafluoroborate, min. 97% *[1204324-12-8]*	100mg	Visit www.strem.com
07-4022	(2R,5R)-1-{[(2R,5R)-2,5-Dimethylpyrrolidin-1-yl]methylene}-2,5-dimethylpyrrolidinium tetrafluoroborate, min. 97% *[1204324-14-0]*	100mg	
07-4024	(2R,5R)-1-{[(2R,5R)-2,5-Diethylpyrrolidin-1-yl]methylene}-2,5-diethylpyrrolidinium tetrafluoroborate, min. 97% *[1204324-20-8]*	100mg	
07-4025	(2S,5S)-1-{[(2S,5S)-2,5-Diethylpyrrolidin-1-yl]methylene}-2,5-diethylpyrrolidinium tetrafluoroborate, min. 97% *[1204324-18-4]*	100mg	
07-4026	(2R,5R)-1-{[(2R,5R)-2,5-Diphenylpyrrolidin-1-yl]methylene}-2,5-diphenylpyrrolidinium tetrafluoroborate, min. 97% *[1204324-08-2]*	100mg	
07-4027	(2S,5S)-1-{[(2S,5S)-2,5-Diphenylpyrrolidin-1-yl]methylene}-2,5-diphenylpyrrolidinium tetrafluoroborate, min. 97% *[1204324-10-6]*	100mg	
07-4029	(2S,5S)-1-{[(2S,5S)-2,5-Di(naphthalen-1-yl])pyrrolidin-1-yl] methylene}-2,5-di(naphthalen-1-yl)pyrrolidinium tetrafluoroborate, min. 97% *[1204324-24-2]*	100mg	
07-4030	(2R,5R)-1-{[(2R,5S)-2,5-Di(naphthalen-1-yl)pyrrolidin-1-yl] methylene}-2,5-di(naphthalen-1-yl)pyrrolidinium tetrafluoroborate, min. 97% *[1204324-26-4]*	100mg	

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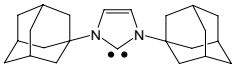
NHC LIGAND KIT 2: "FREE" CARBENES

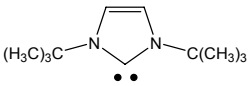
96-3765 **NHC Ligand Kit 2: "Free" Carbenes**

NEW→ Components available for individual sale.

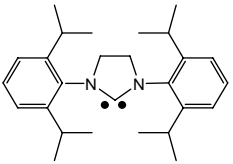
Contains the following:



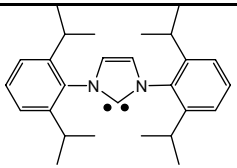
07-0324 250mg



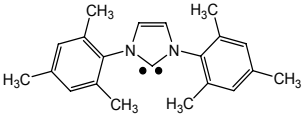
07-0333 250mg



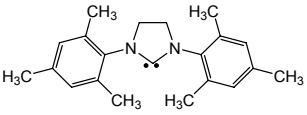
07-0593 500mg



07-0595 250mg



07-0600 500mg



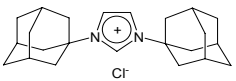
07-0605 500mg

07-0324	1,3-Bis(1-adamantyl)imidazol-2-ylidene, min. 98% ARDUENGO'S CARBENE *[131042-77-8]*	250mg	Visit www.strem.com
07-0333	1,3-Di-t-butylimidazol-2-ylidene, min. 98% *[157197-53-0]*	250mg	
07-0593	1,3-Bis(2,6-di-i-propylphenyl)-4,5-dihydroimidazol-2-ylidine, min. 98% *[258278-28-3]*	500mg	
07-0595	1,3-Bis(2,6-di-i-propylphenyl)imidazol-2-ylidene, min. 98% *[244187-81-3]*	250mg	
07-0600	1,3-Bis(2,4,6-trimethylphenyl)imidazol-2-ylidene, min. 98% *[141556-42-5]*	500mg	
07-0605	1,3-Bis(2,4,6-trimethylphenyl)-4,5-dihydroimidazol-2-ylidene, min. 98% *[173035-11-5]*	500mg	

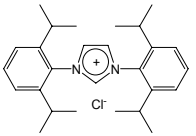
NHC LIGAND KIT 3: VARIETY of N-HETEROCYCLIC CARBENES

96-3770 NHC Ligand Kit 3: Variety of N-Heterocyclic Carbenes

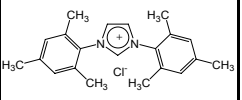
NEW→ Components available for individual sale. Contains the following:



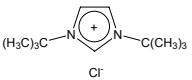
07-0322 250mg



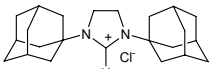
07-0590 500mg



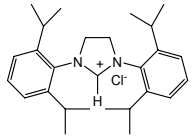
07-0299 1g



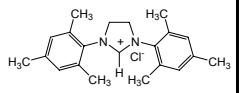
07-0368 250mg



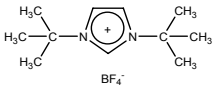
07-4007 500mg



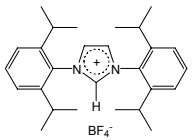
07-4009 500mg



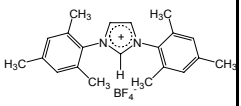
07-4011 500mg



07-0598 500mg

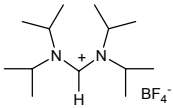


07-0587 1g

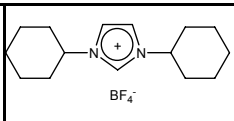


07-0302 1g

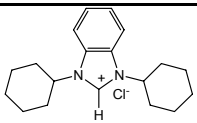
Also Available:



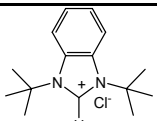
07-4020



07-0597



07-4015



07-4013

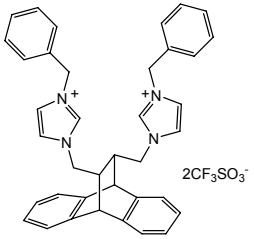
07-0322	1,3-Bis(1-adamantyl)imidazolium chloride, min. 97% *[131042-78-9]*	250mg	Visit www.strem.com
07-4007	1,3-Bis(1-adamantyl)-4,5-dihydroimidazolium chloride, min. 97% *[871126-33-9]*	500mg	
07-0590	1,3-Bis(2,6-di-i-propylphenyl)imidazolium chloride, min. 97% *[250285-32-6]*	500mg	
07-4009	1,3-Bis(2,6-di-i-propylphenyl)-4,5-dihydroimidazolium chloride, min. 97% *[258278-25-0]*	500mg	
07-0587	1,3-Bis(2,6-di-i-propylphenyl)-4,5-dihydroimidazolium tetrafluoroborate, min. 95% *[282109-83-5]*	1g	
07-0299	1,3-Bis(2,4,6-trimethylphenyl)imidazolium chloride, min. 97% *[141556-45-8]*	1g	
07-4011	1,3-Bis(2,4,6-trimethylphenyl)-4,5-dihydroimidazolium chloride, min. 97% *[173035-10-4]*	500mg	
07-0302	1,3-Bis(2,4,6-trimethylphenyl)-4,5-dihydroimidazolium tetrafluoroborate, min. 95% *[245679-18-9]*	1g	
07-0368	1,3-Di-t-butylimidazolium chloride, min. 98% *[157197-54-1]*	250mg	
07-0598	1,3-Bis(t-butyl)imidazolium tetrafluoroborate, min. 97% ItBuHBF$_4$ *[263163-17-3]*	500mg	

Also Available

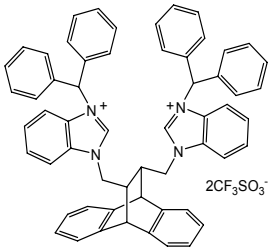
07-4020	Di-i-propylaminomethylene(di-i-propyl)aminium tetrafluoroborate, min. 97% *[369405-27-6]*	Visit www.strem.com
07-0597	1,3-Bis(cyclohexyl)imidazolium tetrafluoroborate, min. 97% ICyHBF$_4$ *[286014-38-8]*	
07-4015	1,3-Dicyclohexylbenzimidazolium chloride, min. 97% *[1034449-15-4]*	
07-4013	1,3-Di-t-butylbenzimidazolium chloride, min. 97% *[946607-10-9]*	

NHC LIGAND KIT 4: BIS CARBENES

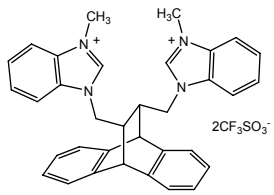
96-3775 **NHC Ligand Kit 4: Bis Carbenes**
NEW→ Components available for individual sale.
Contains the following:



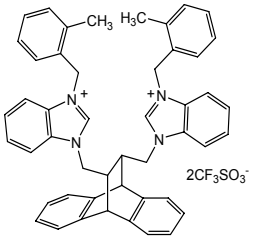
07-0076 100mg



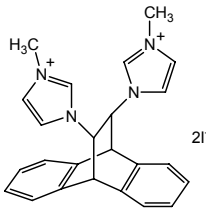
07-0078 100mg



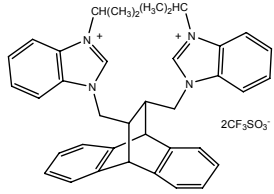
07-0080 100mg



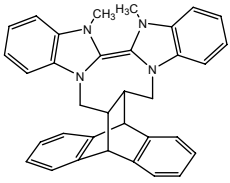
07-0082 100mg



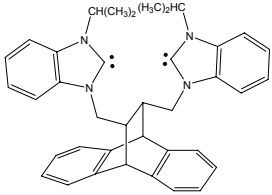
07-0083 100mg



07-0084 100mg



07-0086 100mg



07-0088 100mg

07-0076	11,12-Bis[N-benzyl-1H-imidazolium-3-methylene]-9,10-dihydro-9,10-ethanoanthracene bis(trifluoromethanesulfonate)	100mg	Visit www.strem.com
07-0078	11,12-Bis[N-(2,2-diphenyl-1-ethyl)-1H-benzimidazolium-3-methylene]-9,10-dihydro-9,10-ethanoanthracene bis(trifluoromethanesulfonate)	100mg	
07-0080	11,12-Bis[N-methyl-1H-benzimidazolium-3-methylene]-9,10-dihydro-9,10-ethanoanthracene bis(trifluoromethanesulfonate) *[958004-03-0]*	100mg	
07-0082	11,12-Bis[N-(2-methylbenzyl)-1H-benzimidazolium-3-methylene]-9,10-dihydro-9,10-ethanoanthracene bis(trifluoromethanesulfonate)	100mg	
07-0083	11,12-Bis[3-methylimidazolium]-9,10-dihydro-9,10-ethanoanthracene bis(iodide)	100mg	
07-0084	11,12-Bis[N-(i-propyl)-1H-benzimidazolium-3-methylene]-9,10-dihydro-9,10-ethanoanthracene bis(trifluoromethanesulfonate) *[958004-12-1]*	100mg	
07-0086	(12a,18a)-5,6,12,12a,13,18,18a,19-Octahydro-5,6-dimethyl-13,18[1',2']-benzenobisbenzimidazo [1,2-b:2',1'-d]benzo [i][2.5]benzodiazocine potassium triflate adduct *[958004-04-1]*	100mg	
07-0088	11,12-Bis[1,3-dihydro-3-(i-propyl)-2H-benzimidazol-2-ylidene-3-methylene]-9,10-dihydro-9,10-ethanoanthracene *[958004-05-2]*	100mg	

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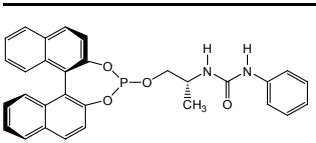
UREAPHOS AND METAMORPHOS LIGAND KIT FOR ASYMMETRIC HYDROGENATION

96-3740 **UREAphos and METAMORPhos Ligand Kit for Asymmetric Hydrogenation**

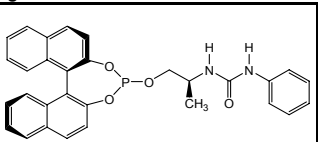
NEW→

Components available for individual sale.

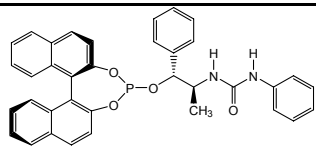
Contains the following:



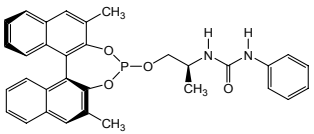
15-2200 50mg



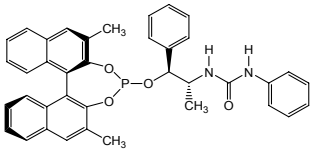
15-2201 50mg



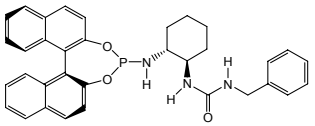
15-2202 50mg



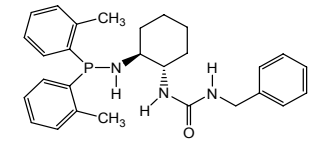
15-2204 50mg



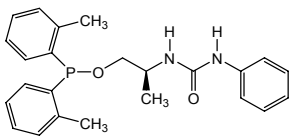
15-2206 50mg



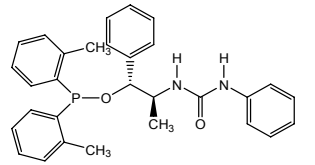
15-2208 50mg



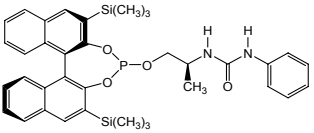
15-2210 50mg



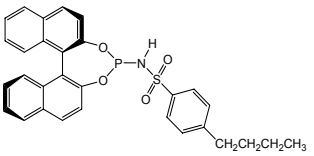
15-2212 50mg



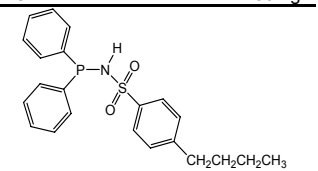
15-2214 50mg



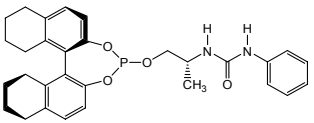
15-2216 50mg



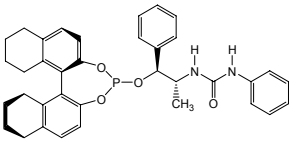
15-2218 50mg



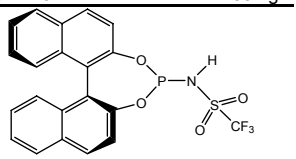
15-2220 50mg



15-2222 50mg



15-2224 50mg



15-2228 50mg

15-2200	1-{(2R)-1-[(11bR)-Dinaphtho[2,1-d:1',2'-f][1,3,2]dioxaphosphepin-4-yloxy]propan-2-yl}-3-phenylurea, min. 97% UREAPhos *[1198080-53-3]*	See page 36
15-2201	1-{(2S)-1-[(11bR)-Dinaphtho[2,1-d:1',2'-f][1,3,2]dioxaphosphepin-4-yloxy]propan-2-yl}-3-phenylurea, min. 97%	See page 37
15-2202	1-{(1R,2S)-1-[(11bR)-Dinaphtho[2,1-d:1',2'-f][1,3,2]dioxaphosphepin-4-yloxy]-1-phenylpropan-2-yl}-3-phenylurea, min. 97% *[1198080-55-5]*	See page 36
15-2204	1-{(2S)-1-[(11bS)-2,6-Dimethyldinaphtho[2,1-d:1',2'-f][1,3,2]dioxaphosphepin-4-yloxy]propan-2-yl}-3-phenylurea, min. 97%	See page 36
15-2206	1-{(1S,2R)-1-[(11bR)-2,6-Dimethyldinaphtho[2,1-d:1',2'-f][1,3,2]dioxaphosphepin-4-yloxy]-1-phenylpropan-2-yl}-3-phenylurea, min. 97%	See page 36
15-2208	1-Benzyl-3-{(1R,2R)-2-[(11bS)-dinaphtho[2,1-d:1',2'-f][1,3,2]dioxaphosphepin-4-ylamino]cyclohexyl}urea, min. 97%	See page 31
15-2210	1-Benzyl-3-[(1S,2S)-2-(di-o-tolylphosphinoamino)cyclohexyl]urea, min. 97%	See page 31

UREAPHOS AND METAMORPHOS LIGAND KIT for ASYMMETRIC HYDROGENATION (cont.)

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15-2212	1-[(2S)-1-(Di-o-tolylphosphinooxy)propan-2-yl]-3-phenylurea, min. 97%	See page 38
15-2214	1-[(1R,2S)-1-(Di-o-tolylphosphinooxy)-1-phenylpropan-2-yl]-3-phenylurea, min. 97%	See page 37
15-2216	1-{2S)-1-[(11bR)-2,6-Bis(trimethylsilyl)dinaphtho[2,1-d:1',2'-f] [1,3,2] dioxaphosphepin-4-yloxy]propan-2-yl}-3-phenylurea, min. 97%	See page 33
15-2218	4-Butyl-N-[(11bR)-dinaphtho[2,1-d:1',2'-f][1,3,2]dioxaphosphepin-4-yl]benzenesulfonamide triethylamine adduct, min. 97% *[1150592-91-8]*	See page 33
15-2220	4-Butyl-N-(diphenylphosphino)benzenesulfonamide, min. 97% *[1025096-61-0]*	See page 33
15-2222	1-{(2R)-1-[(11bR)-8,9,10,11,12,13,14,15-Octahydrodinaphtho[2,1-d:1',2'-f] [1,3,2]dioxaphosphepin-4-yloxy]propan-2-yl}-3-phenylurea, min. 97%	See page 38
15-2224	1-{(1S,2R)-1-[(11bR)-8,9,10,11,12,13,14,15-Octahydrodinaphtho[2,1-d:1',2'-f] [1,3,2]dioxaphosphepin-4-yloxy]-1-phenylpropan-2-yl}-3-phenylurea, min. 97%	See page 38
15-2228	N-[(11bS)-Dinaphtho[2,1-d:1',2'-f][1,3,2]dioxaphosphepin-4-yl]-1,1,1-trifluoromethanesulfonamide triethylamine adduct, min. 97% METAMORPhos	See page 37

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