

## Contents

### Special Issue: 16th International Conference on Phosphorus Chemistry

Preface ..... 2381

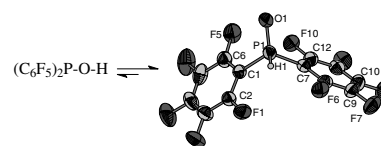
#### Accounts

**Berthold Hoge, Stefan Neufeind,  
Sonja Hettel, Waldemar Wiebe,  
Christoph Thösen**

*J. Organomet. Chem. 690 (2005) 2382*

Stable phosphinous acids

The bonding of two CF<sub>3</sub> groups to a phosphorus atom effects a drastically decreased basicity. That is the phosphorus atom is the least basic centre in the compound (CF<sub>3</sub>)<sub>2</sub>POH – the only known example of a phosphinous acid. The compound (C<sub>6</sub>F<sub>5</sub>)<sub>2</sub>POH, originally claimed as a phosphinous acid, is proved to exist in the tautomeric oxide form, (C<sub>6</sub>F<sub>5</sub>)<sub>2</sub>P(O)H.

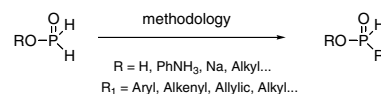


**Jean-Luc Montchamp**

*J. Organomet. Chem. 690 (2005) 2388*

Recent advances in phosphorus–carbon bond formation: synthesis of H-phosphinic acid derivatives from hypophosphorous compounds

This account summarizes our work on the development of novel phosphorus–carbon bond-forming reactions. Synthetic methodology for the preparation of H-phosphinic acid and esters from hypophosphorous compounds is more specifically discussed.

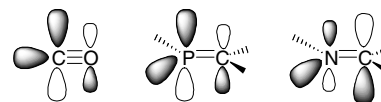


**Marjolaine Doux, Audrey Moores,  
Nicolas Mézailles, Louis Ricard, Yves Jean,  
Pascal Le Floch**

*J. Organomet. Chem. 690 (2005) 2407*

The CO/PC analogy in coordination chemistry and catalysis

This short account summarizes recent results obtained in the coordination chemistry of phosphinines and emphasizes their analogy with CO ligands.

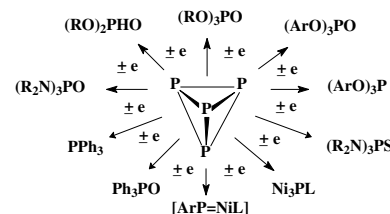


**Yulia H. Budnikova, Dmitry G. Yakhvarov,  
Oleg G. Sinyashin**

*J. Organomet. Chem.* 690 (2005) 2416

Electrocatalytic eco-efficient functionalization of white phosphorus

The potentialities of the electrochemical methods for organophosphorous compounds preparation from white phosphorous were shown.

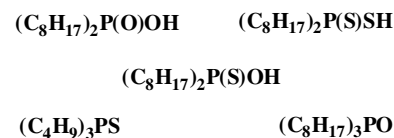


**Douglas S. Flett**

*J. Organomet. Chem.* 690 (2005) 2426

Solvent extraction in hydrometallurgy: the role of organophosphorus extractants

The development of very simple and highly efficient phosphorus-based extractants is presented with particular emphasis on the separation of cobalt from nickel in sulphate leach liquors. Examples of actual industrial operating plants are also given.

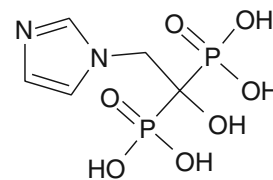


**Jonathan R. Green**

*J. Organomet. Chem.* 690 (2005) 2439

Zoledronic acid: pharmacologic profile of a potent bisphosphonate

Chemical structure of zoledronic acid.

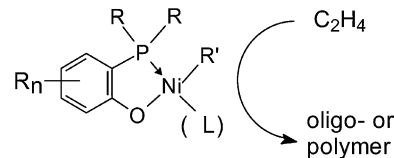


**Joachim Heinicke, Normen Peulecke,  
Martin Köhler, Mengzhen He, Wilhelm Keim**

*J. Organomet. Chem.* 690 (2005) 2449

Tuning of nickel 2-phosphinophenolates – catalysts for oligomerization and polymerization of ethylene

This short personal account summarizes recent work concerning the syntheses and structural aspects of neutral and cationic (organo)nickel and (organo) palladium 2-phosphinophenol(ate) complexes and catalysts for the oligo- or polymerization of ethylene.

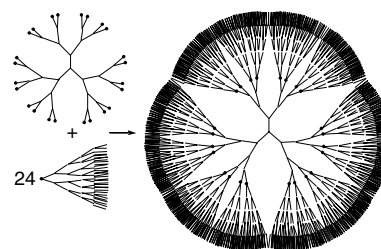


Valérie Maraval, Régis Laurent,  
Patrice Marchand, Anne-Marie Caminade,  
Jean-Pierre Majoral

*J. Organomet. Chem.* 690 (2005) 2458

Accelerated methods of synthesis of  
phosphorus-containing dendrimers

This paper reviews methods usable to multiply rapidly the number of end groups of phosphorus-containing dendrimers. Besides the one-step synthesis of hyperbranched polymers, it describes the use of large cores, of dendrons, or of branched monomer of types AB<sub>2</sub> and CD<sub>2</sub> or AB<sub>3</sub> and CD<sub>3</sub> for improved syntheses of dendrimers.

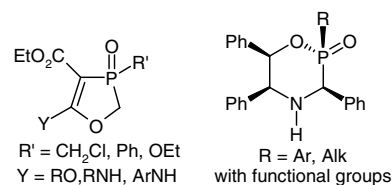


Henri-Jean Cristau, Jean-Luc Pirat,  
David Virieux, Jérôme Monbrun,  
Ciptadi Ciptadi, Yves-Alain Bekro

*J. Organomet. Chem.* 690 (2005) 2472

Synthesis, reactivity and stereochemistry of  
new phosphorus heterocycles with 5- or 6-  
membered rings

Syntheses of novel phosphorus heterocycles containing  $\alpha$ -amino or  $\alpha$ -hydroxyphosphonic or phosphinic acids motifs are developed. 2,3-dihydro-1,3-oxaphospholes (**1**) and 1,4,2-oxazaphosphinanes (**2**) exhibit a reactive part, respectively the enolether moiety and the P–H bond, which allows various structural modifications: (i) for **1a**, by introduction of amino substituents, (ii) for **2a**, by hydroxy- or aminoalkylation, by Michael addition or by P-arylation. These reactions present generally a good or even an excellent kinetic diastereoselectivity which can often be predicted by molecular models of the transition states.

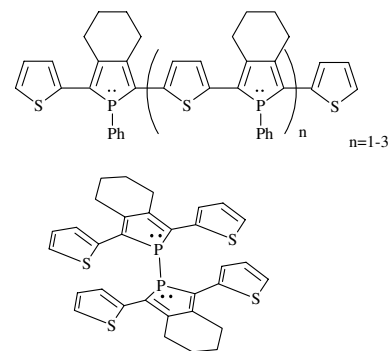


Muriel Hissler, Christophe Lescop,  
Régis Réau

*J. Organomet. Chem.* 690 (2005) 2482

Organophosphorus  $\pi$ -conjugated materials:  
the rise of a new field

An overview of the synthesis and properties of linear organic  $\pi$ -conjugated systems incorporating phosphole rings is presented. Applications in the field of OLED's and NLO are developed.

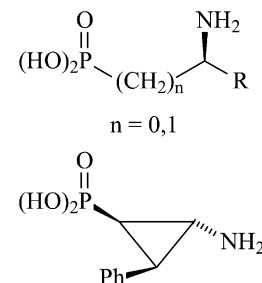


Marian Mikołajczyk

*J. Organomet. Chem.* 690 (2005) 2488

Acyclic and cyclic aminophosphonic acids:  
asymmetric syntheses mediated by chiral  
sulfinyl auxiliary

A new, general approach to enantiomerically pure  $\alpha$ - and  $\beta$ -aminoalkanephosphonic acids is described which involves in a key step a highly diastereoselective addition of phosphite anions and  $\alpha$ -phosphonate carbanions to enantiopure sulfinimines. This account discusses also the asymmetric cyclopropanation of enantiopure  $\alpha$ -phosphorylvinyl sulfoxides which paved the way to  $\beta$ -aminocyclopropanephosphonic acids. This new approach is exemplified by the total synthesis of  $\beta$ -amino- $\gamma$ -phenylcyclopropanephosphonic acid – a constrained analogue of the GABA<sub>B</sub> antagonist phaclofen.



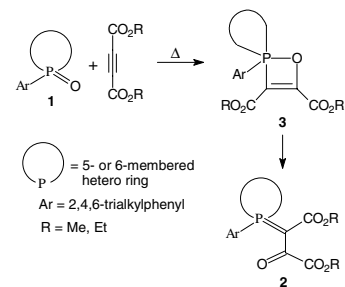
## Regular papers

György Keglevich, Tamás Körtvélyesi,  
Anikó Ujvári, Eszter Dudás

*J. Organomet. Chem.* 690 (2005) 2497

A quantum chemical study on the reaction of 1-aryl-1,2-dihydrophosphinine oxides with dimethyl acetylenedicarboxylate

The reaction of cyclic phosphine oxides (**1**) and dialkyl acetylenedicarboxylate giving the corresponding  $\beta$ -oxophosphorane/ylide (**2**) was studied by quantum chemical calculations. Relative energies of the transition states (**6** and **7**), intermediates (**3**) and possible products, such as oxophosphorane/ylide **2** or Diels Alder cycloadducts **5** were calculated for the potential pathways. Geometry of a few relevant species (**2a**<sup>\*</sup>, **3a**<sub>2</sub><sup>\*</sup>, **6** and **7**) was also evaluated.

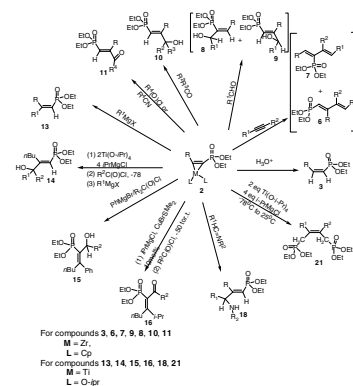


Abed Al-Aziz Al-Quntar, Morris Srebnik

*J. Organomet. Chem.* 690 (2005) 2504

Reactions of 1-alkynylphosphonates with group (IV) complexes

Group IV metallacycles of 1-alkynylphosphonates undergo regio- and stereoselective reactions to provide highly substituted vinylphosphonates. In addition, the amino phosphosphonates **18**, are very active matrix metalloprotease (MMP) inhibitors.

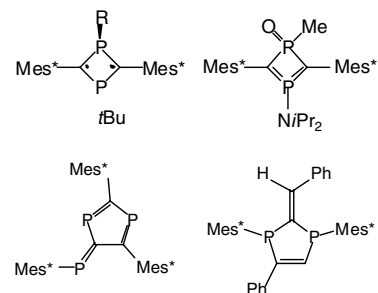


Masaaki Yoshifuji, Hiroki Sugiyama,  
Shigekazu Ito

*J. Organomet. Chem.* 690 (2005) 2515

Syntheses and reactivity of novel unsaturated cyclic compounds containing phosphorus atoms

Syntheses and reactivity of some novel unsaturated cyclic four- and five-membered compounds containing phosphorus are described, suggesting the usefulness of 2,4,6-tri-*t*-butylphenyl ( $\text{Mes}^*$ ) as a protecting group. The structure of a 1,3-diphosphacyclobutane-2,4-diyl was confirmed by X-ray crystallography and reactions were conducted to explore the character of the unusual bonding system.

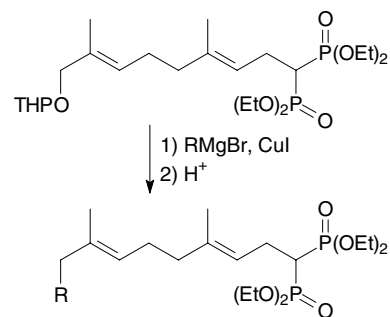


Larry W. Shull, David F. Wiemer

*J. Organomet. Chem.* 690 (2005) 2521

Copper-mediated displacements of allylic THP ethers on a bisphosphonate template

The copper-mediated displacement of an allylic THP ether by Grignard reagents proceeds in a system that contains a geminal bisphosphonate ester.

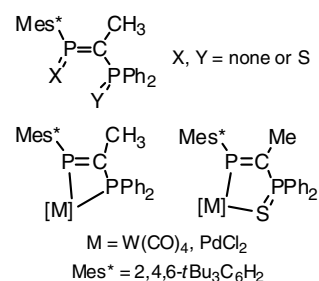


**Shigekazu Ito, Hongze Liang,  
Masaaki Yoshifuji**

*J. Organomet. Chem.* 690 (2005) 2531

1,3-Diphosphapropenes for novel chemistry  
of metal complexes

Several 1,3-diphosphapropene derivatives bearing the P=C–P or P=C–P=S skeleton were prepared and used as a chelate ligand for transition-metal complexes. Some palladium(II) complexes were used for catalytic reactions such as cross-couplings and direct aminations of allyl alcohol to allylaniline.

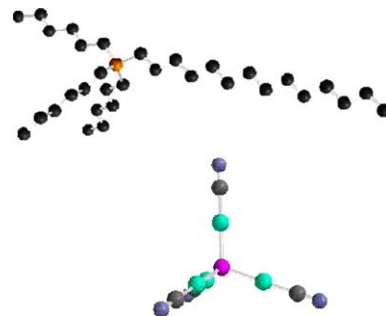


**Rico E. Del Sesto, Cynthia Corley,  
Al Robertson, John S. Wilkes**

*J. Organomet. Chem.* 690 (2005) 2536

Tetraalkylphosphonium-based ionic liquids

A new class of phosphonium-based room temperature ionic liquids (RTIL) has been synthesized and characterized. The salts contain conjugated organic anions, anionic dyes, and metal–ligand complexes. The viscosities and low temperature glass transitions can be controlled by cation size and symmetry, while the optical properties can be varied through selection of a number of anions.

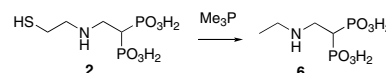


**Ivan S. Alferiev, Jeanne M. Connolly,  
Robert J. Levy**

*J. Organomet. Chem.* 690 (2005) 2543

A novel mercapto-bisphosphonate as an  
efficient anticalcification agent for bio-  
prosthetic tissues

Nucleophilic addition of cystamine to vinylidene-bisphosphonic acid followed by reduction of disulfide bonds with Me<sub>3</sub>P gives HSCH<sub>2</sub>CH<sub>2</sub>NHCH<sub>2</sub>(PO<sub>3</sub>H<sub>2</sub>)<sub>2</sub> (**2**) in a high yield. Bioprosthetic tissues stabilized with triglycidylamine in the presence of **2** demonstrate an almost complete inhibition of long-term in vivo calcification.

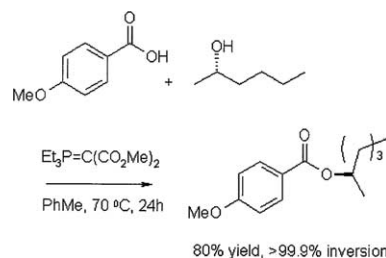


**J. Dyck, S. Zavorine, A.J. Robertson,  
A. Capretta, V. Larichev, J. Britten,  
J. McNulty**

*J. Organomet. Chem.* 690 (2005) 2548

Dimethylmalonyltrialkylphosphoranes: probing the steric effect on phosphorus and its stereochemical consequence in esterification reactions of chiral secondary alcohols

High chemical yields and high levels of stereochemical inversion are demonstrated in the phosphorane-mediated esterification reaction of chiral alcohols with non-hindered carboxylic acids through the incorporation of sterically non-hindered alkyl groups of phosphorus.

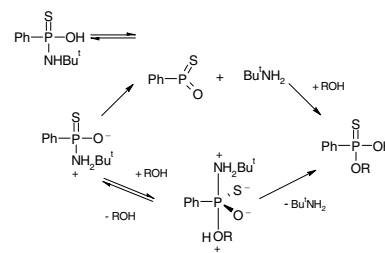


**Stefan Jankowski, Adam Mazur,  
Tomasz Nonas, Barbara Vokal**

*J. Organomet. Chem.* 690 (2005) 2553

Kinetic isotope effects of nitrogen and hydrogen in reaction of *N-tert-butyl-P*-phenylphosphonamidothioic acid with alcohols

The intermediacy of metathiophosphonate PhPSO in the reaction of *N-tert-butyl-P*-phenylphosphonamidothioic acid with alcohols (MeOH, BuOH, Pr<sup>i</sup>OH, Bu<sup>i</sup>OH) is proposed on the basis of nitrogen and hydrogen kinetic isotope effects, as well as semiempirical PM3 calculations. For the reaction with methanol the alternative addition-elimination mechanism cannot be excluded.

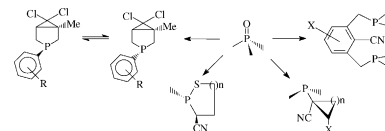


**Irina L. Odinets, Natalya M. Vinogradova,  
Ekaterina V. Matveeva, Denis D. Golovanov,  
Konstantin A. Lyssenko, György Keglevich,  
László Kollár, Gerd-Volker Roëschenthaler,  
Tatyana A. Mastryukova**

*J. Organomet. Chem.* 690 (2005) 2559

Novel functionalised P-ligands: advances and application

Novel endo- and exocyclic phosphine ligands possessing different functionalities obtained by reduction of the P=O precursors with desired stereochemistry are discussed. The diastereoselective deoxygenation including the catalytic reduction processes, the factors defining the reactivity and the role of the substituents on the stability of phosphorus atom configuration in a series of 3-aryl-3-phospha-bicyclo[3.1.0]hexanes are reported. The complexation features of the ligands with Rh(III) and Pd(II) were examined and Rh(III) complexes were tested in styrene hydroformylation showing the structure–activity dependence.

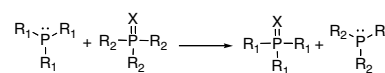


**Martin Kullberg, Jacek Stawinski**

*J. Organomet. Chem.* 690 (2005) 2571

Theoretical investigations on the mechanism of chalcogens exchange reaction between P(V) and P(III) compounds

Mechanistic pathways for chalcogens transfer from P(V) to P(III) compounds were explored using density functional theory calculations.



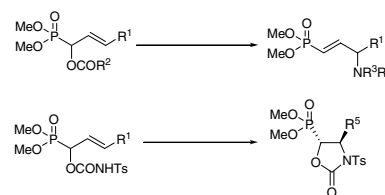
X = O, S, Se; R<sub>1</sub> = H, Me; R<sub>2</sub> = H, OMe

**Antonette De la Cruz, Anyu He,  
Anchalee Thanavaro, Bingli Yan,  
Christopher D. Spilling, Nigam P. Rath**

*J. Organomet. Chem.* 690 (2005) 2577

Allylic hydroxy phosphonates: versatile chiral building blocks

Allylic hydroxy phosphonates are converted into  $\beta$  and  $\gamma$  substituted amino phosphonates using a series of palladium-catalyzed reactions. The judicious selection of nitrogen nucleophile and palladium catalyst allow for excellent regio- and stereochemical control. Palladium(0)-catalyzed amine addition or tosyl carbamate rearrangement gives rise to the  $\gamma$ -substituted phosphonates, whereas, reaction of the tosyl carbamates with palladium (II) and base gives oxazolidinones ( $\beta$ -substitution).

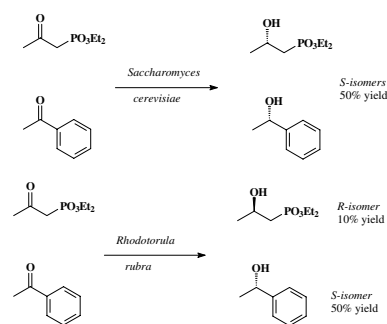


Ewa Żyłańczyk-Duda,  
Magdalena Klimek-Ochab,  
Paweł Kafarski, Barbara Lejczak

*J. Organomet. Chem.* 690 (2005) 2593

Stereochemical control of biocatalytic asymmetric reduction of diethyl 2-oxopropylphosphonate employing yeasts

Nonracemic diethyl 2-oxopropylphosphonate of *R* and *S* configuration and of high enantiomeric purity was obtained by stereocontrolled bioreduction using: *Rhodotorula rubra*, *Rhodotorula glutinis*, *Rhodotorula gracilis* and baker's yeast. The effect of the addition of chemical compounds influencing the stereoselectivity of biotransformation have been investigated.

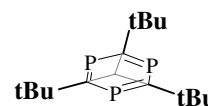


László Nyulászi

*J. Organomet. Chem.* 690 (2005) 2597

Substituent effect on low coordination phosphorus chemistry

The repulsion between the *t*Bu substituents is crucial in determining the stability of phosphorus compounds.

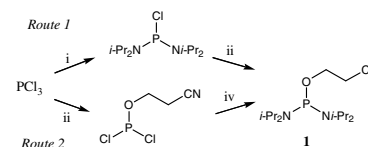


Ravi Gukathasan, Morteza Massoudipour,  
Indranil Gupta, Anwar Chowdhury,  
Siegmar Pulst, Sivakumar Ratnam,  
Yogesh S. Sanghvi, Scott A. Laneman

*J. Organomet. Chem.* 690 (2005) 2603

Large-scale synthesis of high purity "Phos reagent" useful for oligonucleotide therapeutics

A cost-effective synthesis of high purity 2-cyanoethyl-*N,N,N',N'*-tetraisopropylphosphorodiamidite (Phos Reagent) has been accomplished on a commercial scale. Two routes, which begin with  $\text{PCl}_3$ , furnished high purity Phos Reagent with purities 99% when several key factors are controlled.



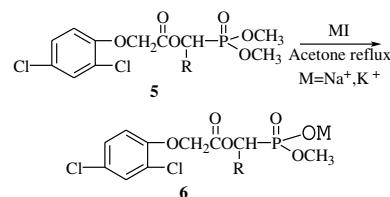
Reagents and Conditions: i, *i*-Pr<sub>2</sub>NH (2 equiv), THF, -10 °C; ii, HOCH<sub>2</sub>CH<sub>2</sub>CN (1 equiv), MeCN, 0 °C; iii, HOCH<sub>2</sub>CH<sub>2</sub>CN (1 equiv), MeCN, 0 °C; iv, *i*-Pr<sub>2</sub>NH (2 equiv), THF, -10 °C

Hong Wu He, Tao Wang, Jun Lin Yuan

*J. Organomet. Chem.* 690 (2005) 2608

Synthesis and herbicidal activities of methyl-1-(2,4-dichlorophenoxyacetoxy)alkylphosphonate monosalts

The phosphonate monosalts can be prepared from 1-(2,4-dichlorophenoxyacetoxy)alkylphosphonic acid dimethyl esters **5**, which were synthesized by the condensation of *O,O*-dimethyl-1-hydroxyalkylphosphonates with dichlorophenoxyacetic chloride. This method provides a simple and efficient procedure for the synthesis of phosphonate derivatives containing sensitive groups to acid, base or water such as carboxylate ester bond; and the herbicidal activity of title compounds was evaluated in a set of experiments in greenhouse. Most of the compounds exhibited notable herbicidal activity.



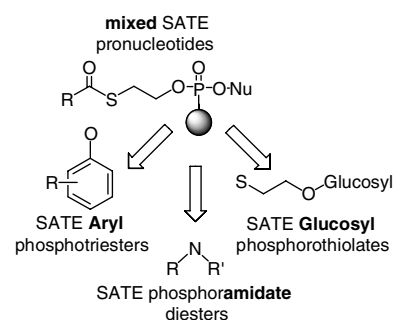
A series of 1-(2,4-dichlorophenoxyacetoxy)-alkylphosphonic acid dimethyl esters **5** and its corresponding phosphonate monosalts **6** were synthesized as potential herbicide.

Anne Jochum, Nathalie Schlienger,  
David Egron, Suzanne Peyrottes,  
Christian Périgaud

*J. Organomet. Chem.* 690 (2005) 2614

Biolabile constructs for pronucleotide design

Three series of biolabile constructs (mixed SATE pronucleotides) were designed for the delivery of the corresponding 5'-mononucleotide inside cells. Synthesis of these mononucleoside derivatives (phosphotriesters, phosphoramidates and phosphorothiolates) involves both P<sup>III</sup> and P<sup>V</sup> chemistries.

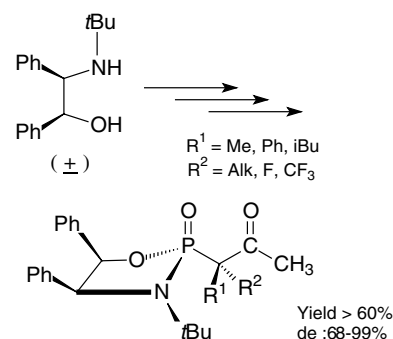


Jean-Luc Pirat, Xavier Marat,  
Ludovic Clarion, Arie Van der Lee,  
Jean-Pierre Vors, Henri-Jean Cristau

*J. Organomet. Chem.* 690 (2005) 2626

Diastereoselective synthesis of  $\alpha,\alpha'$ -disubstituted  $\beta$ -ketophosphonates derivatives as building blocks for automated syntheses

A convenient and efficient synthesis of  $\alpha,\alpha'$ -disubstituted  $\beta$ -ketophosphonic derivatives in good to excellent *de*'s and yields has been achieved by  $\alpha$ -acylation followed by diastereoselective  $\alpha$ -alkylation of chiral 5-membered cyclic phosphonamidates.

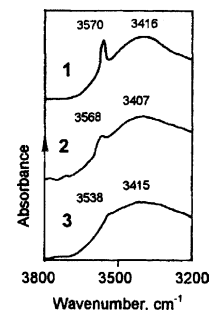


Mihkel Veiderma, Kaia Tnsuaadu,  
Rena Knubovets, Merike Peld

*J. Organomet. Chem.* 690 (2005) 2638

Impact of anionic substitutions on apatite structure and properties

A review of the results of the authors on single and coupled substitutions of F for OH, and of CO<sub>3</sub> and SO<sub>4</sub> for PO<sub>4</sub> in synthetic and natural apatites, their influence on apatite structure and properties, studied by peak fitting FTIR, XRD, TG/DTA and TG/EGA methods, is presented. Calcination of carbonate and sulphate substituted apatites leads to the formation of stable stoichiometric apatite.

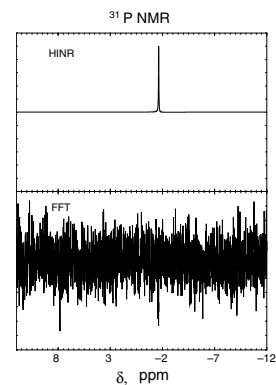


Sharif D. Kunikeev, Howard S. Taylor,  
Jian-Jung Pan, Allan Kershaw,  
Charles E. McKenna

*J. Organomet. Chem.* 690 (2005) 2644

A new signal processing method to observe weak <sup>31</sup>P and <sup>17</sup>O NMR peaks

A new harmonic inversion (HI) signal processing method provided better <sup>31</sup>P and <sup>17</sup>O NMR peak detection sensitivity than a conventional FFT approach when applied to several model samples.

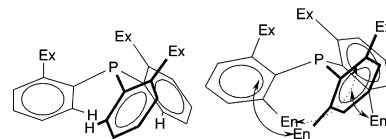




**René T. Boéré, Yuankui Zhang***J. Organomet. Chem.* 690 (2005) 2651

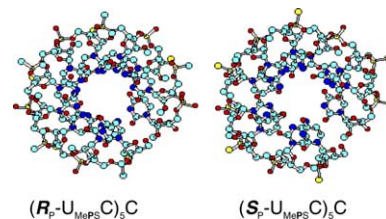
Extremely bulky triarylphosphines incorporating 2,6-diisopropylphenyl substituents; consideration of steric shielding and steric pressure

In *ortho* substituted triarylphosphines, substituents in the *exo* position (Ex) act as steric shields surrounding the phosphorus lone pairs electrons, whereas those in the *endo* position (En) exert steric pressure which can be sufficient to flatten the  $C_3P$  pyramid; when the two effects work together, the shielding of the phosphorus lone pair can be dramatically increased.

**L.A. Wozniak, M. Janicka, M. Bukowiecka-Matusiak***J. Organomet. Chem.* 690 (2005) 2658

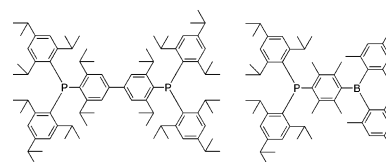
Chirality at phosphorus: hybrid duplexes of chimeric oligonucleotides containing methylphosphonothioate linkages with complementary DNA and RNA

Chimeric oligonucleotides with incorporated diastereomerically pure dinucleoside(3',5')-methylphosphonothioates and their oxo- and seleno-congeners of known absolute configuration are reported. The relation between stability of the hybrid duplexes with complementary DNA and RNA and their structure is analyzed in context of absolute configuration of the P-chiral internucleotide bonds.

**Shigeru Sasaki, Fumiki Murakami, Midori Murakami, Mariko Watanabe, Kiyotoshi Kato, Katsuhide Sutoh, Masaaki Yoshifuji***J. Organomet. Chem.* 690 (2005) 2664

Synthesis of crowded triarylphosphines carrying functional sites

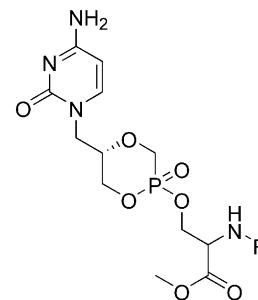
4,4'-Diphosphinobiaryls and borylphosphinobenzenes carrying crowded triarylphosphine moieties were synthesized. Two phosphorus atoms of 4,4'-diphosphinobiaryls were reversibly oxidized in two steps in spite of 4,4'-biarylene bridge. UV-Vis spectra of 1,4-borylphosphinobenzene suggested significant phosphorus-boron interaction.

**Charles E. McKenna, Boris A. Kashemirov, Ulrika Eriksson, Gordon L. Amidon, Phillip E. Kish, Stefanie Mitchell, Jae-Seung Kim, John M. Hilfinger***J. Organomet. Chem.* 690 (2005) 2673

Cidofovir peptide conjugates as prodrugs

Cidofovir (HPMPC, Vistide) is a broad-spectrum anti-viral agent that is used to treat AIDS-related CMV retinitis. Currently, cidofovir is of particular interest as a potential therapy for orthopox virus infections, including smallpox. An important limitation of cidofovir and analogous nucleotide drugs in a

therapeutic role is their low oral bioavailability and poor transport into cells. In principle, bioavailability of a drug can be improved by structural modification targeting transporters expressed in human intestine. To be effective, the transported prodrug must be cleaved by endogenous enzymes to its parent compound. In this work, three examples of novel cyclic cidofovir (cHPMPC) prodrugs incorporating dipeptides were synthesized and evaluated in a rat oral bioavailability model, in which the prodrugs showed significantly enhanced transport vs. HPMPC and cHPMPC. The prodrugs inhibited Gly-Sar uptake in a competitive binding assay using DC5 cells over-expressing hPepT1.



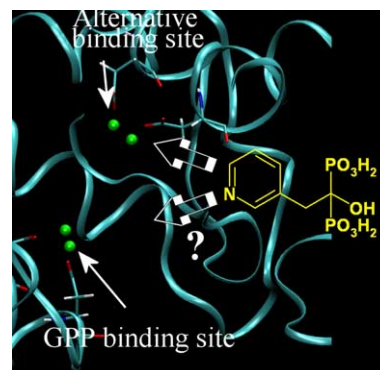
R = Val, Ala and Leu

Frank H. Ebetino, Christian N. Rozè,  
Charles E. McKenna, Bobby L. Barnett,  
James E. Dunford, R. Graham G. Russell,  
Glen E. Mieling, Michael J. Rogers

*J. Organomet. Chem.* 690 (2005) 2679

Molecular interactions of nitrogen-containing bisphosphonates within farnesyl diphosphate synthase

Bisphosphonates, known for their effectiveness in the treatment of osteoporosis, inhibit bone resorption via mechanisms that involve binding to bone mineral and cellular effects on osteoclasts. The major molecular target of nitrogen-containing bisphosphonates (N-BPs) in osteoclasts is farnesyl diphosphate synthase (FPPS).



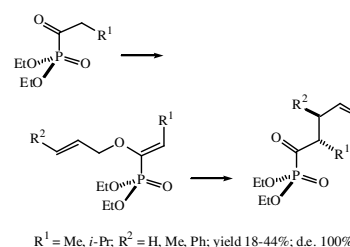
## Note

Kamyar Afarinkia, Andrew J. Twist,  
Hui-wan Yu

*J. Organomet. Chem.* 690 (2005) 2688

Preparation of  $\alpha$ -ketophosphonates by a [3,3]-sigmatropic shift of enolphosphonates

$\alpha$ -Ketophosphonates are prepared by a [3,3]-sigmatropic shift of enolphosphonates.



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