

In this issue...

The development of high oxidation state early transition metal catalysts for alkene and alkyne metathesis reactions has been reviewed. See Richard Schrock, pp. 2773–2777.



Chemical biology articles published in this journal also appear in the *Chemical Biology Virtual Journal*: www.rsc.org/chembiol



Cover

See E. W. Meijer *et al.*, page 2811. A 3D-presentation of our supramolecular target-specific MRI contrast agent is shown, where the Gd(III)DTPA complex creates contrast upon touching the water.

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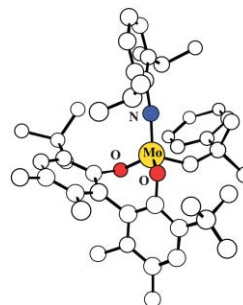
40TH ANNIVERSARY ARTICLE

2773

High oxidation state alkylidene and alkylidyne complexes

Richard R. Schrock

Electron deficient high oxidation state early transition metal complexes that contain metal–carbon double or triple bonds and bulky supporting ligands have been found to be highly reactive catalysts for the alkene and alkyne metathesis reactions, respectively.



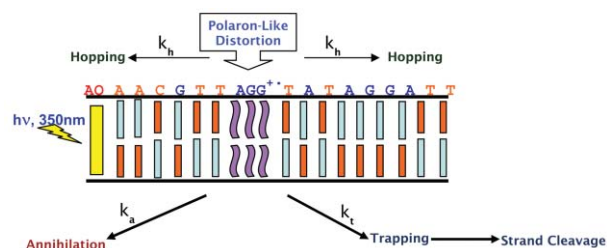
FEATURE ARTICLE

2778

Long-range radical cation migration in DNA: Investigation of the mechanism

Abraham Joy* and Gary B. Schuster

During the past decade long-range radical cation migration in DNA has been extensively investigated due to its potential to yield a deeper understanding of oxidative damage of genomic DNA and the potential for use of DNA architectures in molecular electronics. In this article we discuss various aspects of the radical cation migration process and present the plausible mechanism by which this process occurs.



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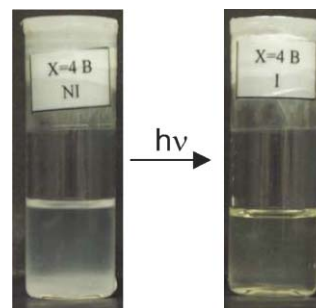
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Photo-stabilised microemulsions

Julian Eastoe,* Paul Wyatt,
Margarita Sánchez-Dominguez, Ana Vesperinas,
Alison Paul, Richard K. Heenan and Isabelle Grillo

Light-induced stabilisation of water-in-heptane microemulsions has been achieved with a UV-sensitive gemini photo-surfactant.

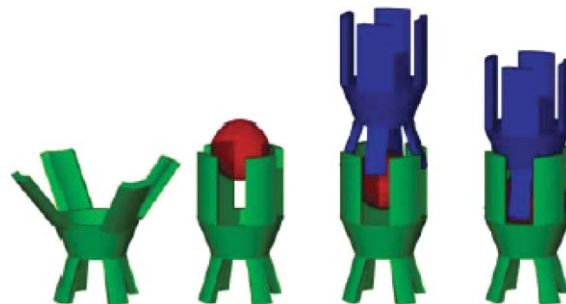


2787

Nano-dimensions for the pyrogallol[4]arene cavity

Gareth W. V. Cave, Matthew C. Ferrarelli and
Jerry L. Atwood*

The spontaneous self-assembly of pyrogallol[4]arene and four 4,4'-bipyridine building blocks yields an extended cup-like cavitand, capable of being stacked together. These stacked "nano-cups" produce a cavity that can completely enshroud a guest molecule.

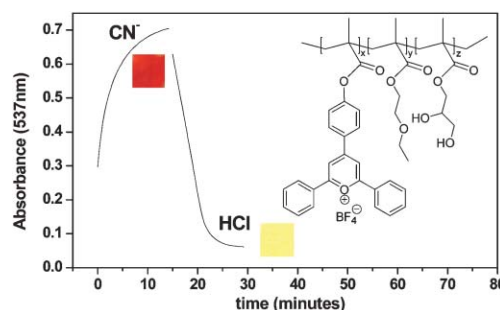


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Pyrylium-containing polymers as sensory materials for the colorimetric sensing of cyanide in water

Félix García,* José Miguel García, Beatriz García-Acosta,
Ramón Martínez-Máñez,* Félix Sancenón and Juan Soto

A sensory polymeric material for the colorimetric sensing of cyanide in water has been developed based on the reactivity of this anion with the pyrylium cation.

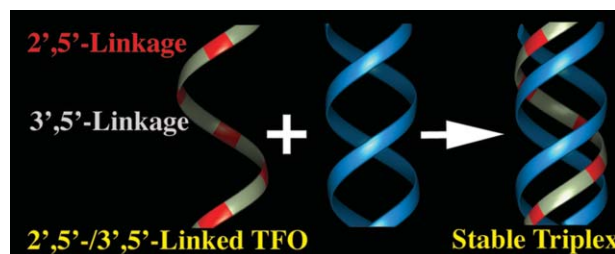


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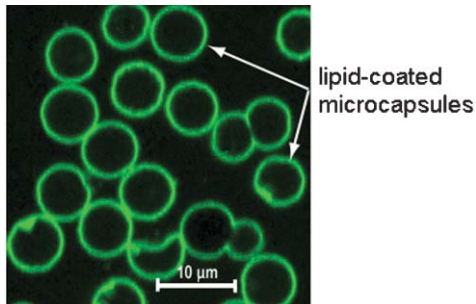
Promotion of stable triplex formation by partial incorporation of 2',5'-phosphodiester linkages into triplex-forming oligonucleotides

Satoshi Obika, Akiko Hiroto, Osamu Nakagawa and
Takeshi Imanishi*

Discontinuous replacement of the 3',5'-phosphodiester linkages in triplex-forming oligonucleotides by 2',5'-linkages significantly promotes parallel-motif triplex formation.



2796

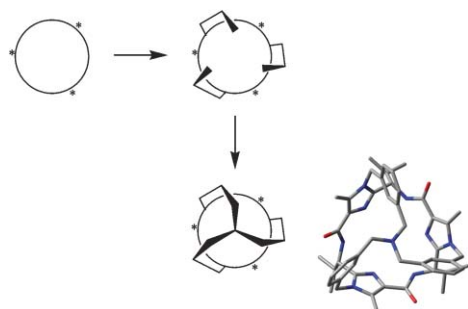


Lipid modified polyelectrolyte microcapsules with controlled diffusion

Gopal Krishna, Tatsiana Shutava* and Yuri Lvov

The lipid coating introduced directly on (polystyrene sulfonate/polyallylamine hydrochloride)₅ polyelectrolyte microcapsule surfaces significantly reduces the permeability of capsule walls estimated by fluorescence recovery after photobleaching (FRAP).

2799

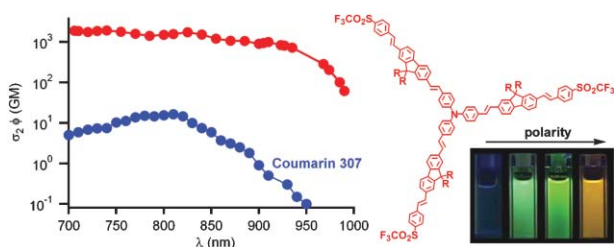


A widely applicable concept for predictable induction of preferred configuration in C₃-symmetric systems

Gebhard Haberhauer,* Thomas Oeser and Frank Rominger

Starting from a single chiral platform a widely applicable concept to introduce the preferred configuration of octahedral and tetrahedral centres in C₃-symmetric systems is described.

2802

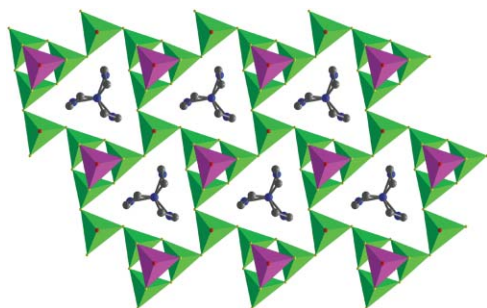


Towards “smart” multiphoton fluorophores: strongly solvatochromic probes for two-photon sensing of micropolarity

Céline Le Droumaguet, Olivier Mongin, Martinus H. V. Werts and Mireille Blanchard-Desce*

New fluorophores, combining broad, very high two-photon absorption in the near-infrared region with a marked dependence of their emission spectra on solvent polarity, have been designed as model probes for two-photon sensing of the chemical environment.

2805



Two-dimensional organization of [ZnGe₃S₉(H₂O)]⁴⁻ supertetrahedral clusters templated by a metal complex

Nanfeng Zheng, Xianhui Bu and Pingyun Feng*

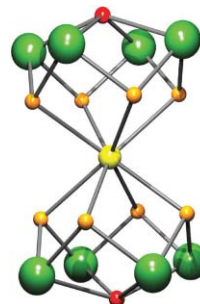
Under the structure-directing effect of a chiral metal complex, supertetrahedral [ZnGe₃S₉(H₂O)]⁴⁻ clusters are joined by Zn(H₂O)²⁺ into a two-dimensional wide-gap semiconductor that shows photocatalytic activity for hydrogen production from aqueous solution.

2808

Synthesis and characterisation of a {Ni₈} single molecule magnet and another octanuclear nickel cage

Aidan Bell, Guillem Aromí, Simon J. Teat, Wolfgang Wernsdorfer and Richard E. P. Winpenny*

Two new octanuclear nickel(II) cage complexes are reported, one of which has an $S = 8$ ground state and is a rare example of a nickel-based single molecule magnet.

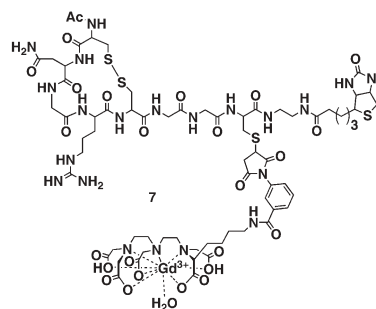


2811

A supramolecular approach to multivalent target-specific MRI contrast agents for angiogenesis

Anouk Dirksen, Sander Langereis, Bas F. M. de Waal, Marcel H. P. van Genderen, Tilman M. Hackeng* and E. W. Meijer*

The synthesis of a cyclic peptide–Gd(III)DTPA molecule equipped with biotin is presented, yielding a well-defined multivalent MRI contrast agent after its coupling to avidin.

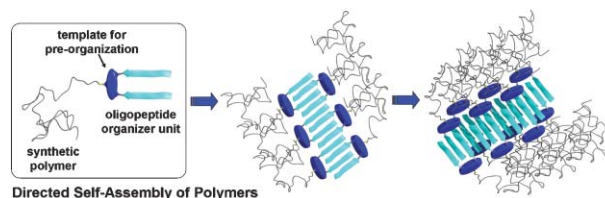


2814

Rational design of oligopeptide organizers for the formation of poly(ethylene oxide) nanofibers

Doreen Eckhardt, Matthijs Groenewolt, Eberhard Krause and Hans G. Börner*

Template pre-organized peptides were utilized to guide the processes of structure formation in synthetic polymers. Therefore, novel peptide-organizer units were designed and conjugated to poly(ethylene oxide). Driven by the formation of the peptide-motif, the building-blocks self-assemble into well-defined nanofibers.

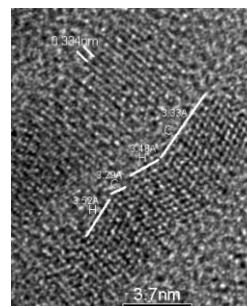


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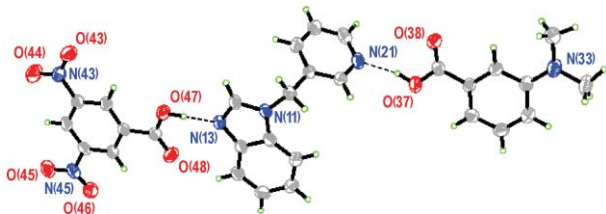
A new route to nanorods of cadmium sulfide

Paul Christian and Paul O'Brien*

Cadmium sulfide nanorods have been prepared of predominantly the cubic form. The presence of trace amounts of the hexagonal phase can result in an anisotropic nanostructure, even when the amount of the hexagonal phase present is too small to be observed by powder diffraction.



2820

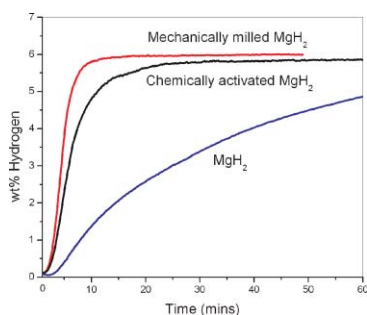


Supramolecular reagents: versatile tools for non-covalent synthesis

Christer B. Aakeröy,* John Desper and Joaquin F. Urbina

The rational hydrogen-bond directed assembly of ternary co-crystals (1:1:1) based upon asymmetric ditopic supramolecular reagents and pairs of carboxylic acids is presented.

2823

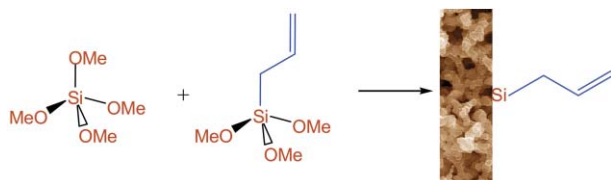


Chemical activation of MgH₂; a new route to superior hydrogen storage materials

Simon R. Johnson, Paul A. Anderson,* Peter P. Edwards,* Ian Gameson, James W. Prendergast, Malek Al-Mamouri, David Book,* I. Rex Harris, John D. Speight and Allan Walton

The activation of the hydrogen store MgH₂ by quite modest amounts of LiBH₄ results in a spectacular increase in the kinetics of hydrogen desorption/absorption.

2826

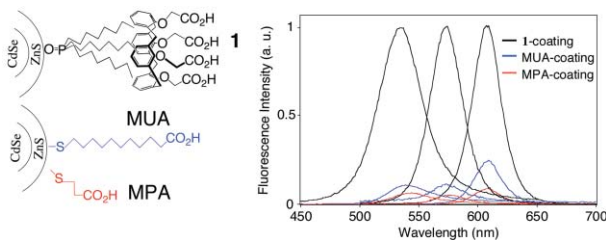


Allyl-functionalized hybrid silica monoliths

Héctor Colón, Xin Zhang, Jessica K. Murphy, José G. Rivera and Luis A. Colón*

A hybrid allyl-organosilica monolith was synthesized in a “one pot” reaction approach. This is a viable platform for producing silica-based, chromatographic, monolithic structures with the stationary phase bonded through a surface silicon–carbon bond instead of conventional siloxane bonding.

2829



Calixarene-coated water-soluble CdSe–ZnS semiconductor quantum dots that are highly fluorescent and stable in aqueous solution

Takashi Jin,* Fumihiko Fujii, Hiroshi Sakata, Mamoru Tamura and Masataka Kinjo

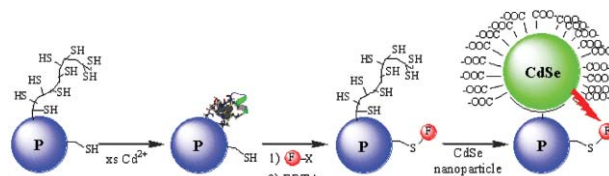
A simple method for the preparation of highly fluorescent and stable, water-soluble CdSe–ZnS quantum dots is reported using calix[4]arene carboxylic acids (**1**) as surface coating agents.

2832

General, high-affinity approach for the synthesis of fluorophore appended protein nanoparticle assemblies

Marinella G. Sandros, De Gao, Cagil Gokdemir and David E. Benson*

Metallothionein fusion proteins allow for site-specific, orthogonal functionalization with thiol reactive molecules and either CdSe, CdSe/ZnS core-shell, or Au nanoparticles. Assembly of the proposed scheme is confirmed by fluorescence resonance energy transfer.

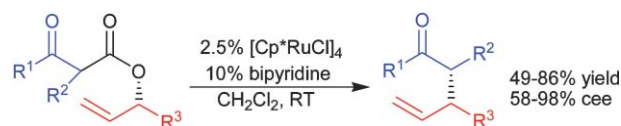


2835

Ruthenium-catalyzed stereospecific decarboxylative allylation of non-stabilized ketone enolates

Erin C. Burger and Jon A. Tunge*

Stereospecific decarboxylative allylation allows the synthesis of enantioenriched unsaturated ketones. The decarboxylative coupling of non-stabilized ketone enolates with allyl electrophiles is characterized by regioselective enolate formation, highly regioselective allylation, and good stereospecificity.

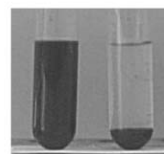
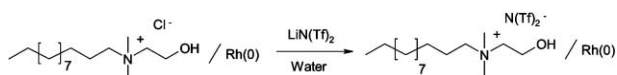


2838

Organic phase stabilization of rhodium nanoparticle catalyst by direct phase transfer from aqueous solution to room temperature ionic liquid based on surfactant counter anion exchange

Vincent Mévellec, Bastien Leger, Marc Mauduit and Alain Roucoux*

Addition of LiN(Tf)₂ transfers hydrosol nanocatalysts Rh(0)-HEA12Cl to an ionic liquid phase. Stabilized nanoparticles with an average diameter of 2.8 nm performed styrene hydrogenation in biphasic media.

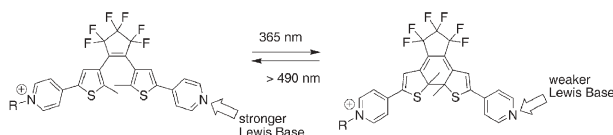


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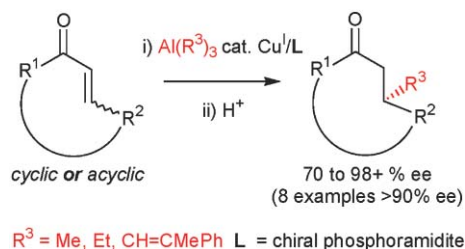
Photomodulation of Lewis basicity in a pyridine-functionalized 1,2-dithienylcyclopentene

Hema D. Samachetty and Neil R. Branda*

The ability of a pyridine ligand on the photoresponsive 1,2-dithienylethene backbone to coordinate to a ruthenium porphyrin is modulated by interconverting the compound between its electronically insulated ring-open and electronically connected ring-closed form.



2843

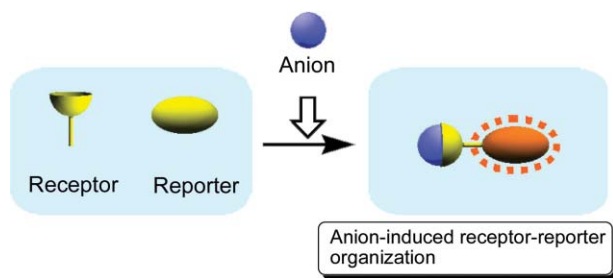


Highly enantioselective copper(I)-phosphoramidite-catalysed additions of organoaluminium reagents to enones

Alexandre Alexakis,* Victoria Albrow, Kallolmay Biswas, Magali d'Augustin, Oscar Prieto and Simon Woodward*

Technically simple and robust procedures offer good to exceptional levels of enantioselectivity in 1,4-additions of AlR_3 species to enones; sequential carboalumination-ACA cascades are possible.

2846

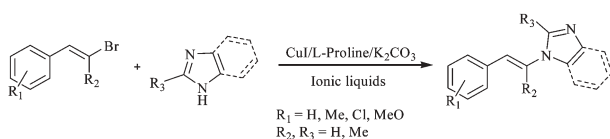


Detection of anions using a fluorescent alizarin-phenylboronic acid ensemble

Yuji Kubo,* Atsushi Kobayashi, Tomohisa Ishida, Yoshihiro Misawa and Tony D. James*

Selective anion-induced organization of phenylboronic acids and alizarin allows for developing a new TURN-ON fluorescent sensor of anions in MeOH.

2849

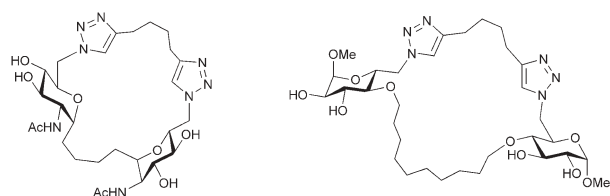


L-Proline promoted Ullmann-type reaction of vinyl bromides with imidazoles in ionic liquids

Zhiming Wang, Weiliang Bao* and Yong Jiang

The Ullmann-type coupling reaction of vinyl bromides and imidazoles in ILs at 90–110 °C gave the corresponding *N*-vinylimidazoles in good to excellent yields by using L-proline as the ligand.

2852



A short route for the synthesis of “sweet” macrocycles via a click-dimerization–ring-closing metathesis approach

Simon Dörner and Bernhard Westermann*

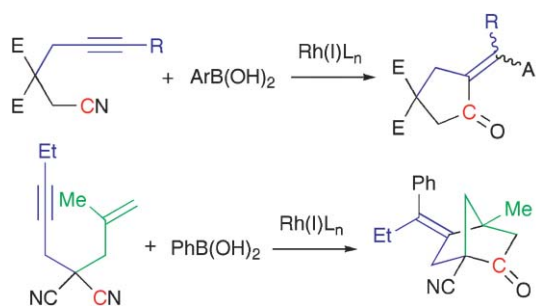
Macrocyclic molecules containing different carbohydrate moieties are prepared by a facile and flexible approach involving click-dimerization and ring-closing metathesis.

2855

Intramolecular nucleophilic addition of an organorhodium(I) to a nitrile

Tomoya Miura, Hiroki Nakazawa and Masahiro Murakami*

The rhodium-catalysed cyclisation reactions of cyano-substituted alkynes with arylboronic acids are developed, wherein an intermediate organorhodium(I) species undergoes nucleophilic addition to a nitrile.

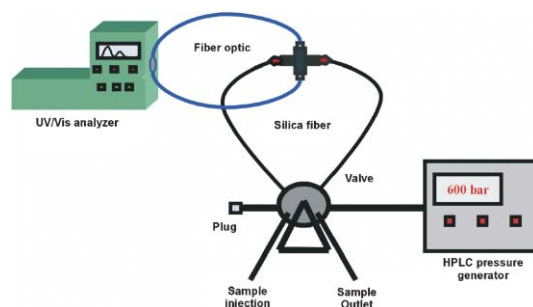


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Optical fiber-based on-line UV/Vis spectroscopic monitoring of chemical reaction kinetics under high pressure in a capillary microreactor

Fernando Benito-Lopez, Willem Verboom,* Masaya Kakuta, J. (Han) G. E. Gardeniers,* Richard J. M. Egberink, Edwin R. Oosterbroek, Albert van den Berg and David N. Reinhoudt

A miniaturized fiber-optics based system for on-line measurement by UV/Vis spectroscopy of chemical reaction kinetics under high pressure, up to 600 bar, is described.

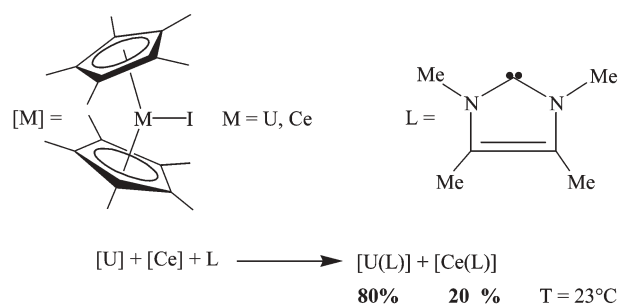


2860

The remarkable efficiency of *N*-heterocyclic carbenes in lanthanide(III)/actinide(III) differentiation

Thouraya Mehdoui, Jean-Claude Berthet,* Pierre Thuéry and Michel Ephritikhine*

A novel aspect of NHCs is their capacity to discriminate between trivalent lanthanide and actinide ions, as revealed by the competition reactions of analogous U(III) and Ce(III) organo-compounds with $C_3Me_4N_2$, and a comparison of the crystal structures of the corresponding carbene adducts.

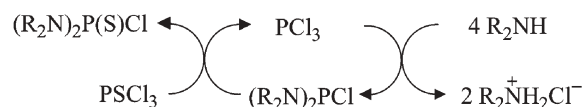


2863

A new mechanism for nucleophilic substitution at a thiophosphoryl centre revealed by the reaction of diisopropylamine with $PSCl_3$

Martin J. P. Harger

The reaction of $PSCl_3$ with Pr^i_2NH at 60 °C affords the disubstitution product $(Pr^i_2N)_2P(S)Cl$ without first forming the monosubstitution product $Pr^i_2NP(S)Cl_2$; a P^{III} compound, probably PCl_3 , generated *in situ* seems to be a crucial intermediate.




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