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IN THIS ISSUE

ISSN 1144–0546 CODEN NJCHES 34(8) 1493–1784 (2010)

Cover
See Brandi M. Cossairt and Christopher C. Cummins, pp. 1533–1536.
Organophosphorus compounds are obtained directly from white phosphorus (P_4) by taking advantage of the inherent ability of P–P bonds to trap radicals; the methodology extends also to products containing P–Si and P–Sn bonds.
Image reproduced by permission of Brandi M. Cossairt and Christopher C. Cummins from *New J. Chem.*, 2010, **34**, 1533.

Inside cover
See Shigehiro Yamaguchi *et al.*, pp. 1537–1540.
Highly emissive 1-aryl-2,3,4,5-tetraphenylphosphole oxides have been synthesized. Their Φ_F (0.25–0.91) in crystals depends not on the bulkiness or electronic effect of the 1-aryl groups, but on their packing modes.
Image reproduced by permission of Aiko Fukazawa, Yasunori Ichihashi and Shigehiro Yamaguchi from *New J. Chem.*, 2010, **34**, 1537.

EDITORIALS

1510

Introduction to the themed issue on Main Group Chemistry

Presenting a collection of articles on the theme of Main Group Chemistry

1511

Pascal Le Floch: 1958–2010

A tribute to Pascal Le Floch, the former co-Editor-in-Chief of *NJC*.

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E-mail njc@chem.ufl.edu

Dr Denise Parent
New Journal of Chemistry,
Université Montpellier II,
Place Eugène Bataillon C.C. 014,
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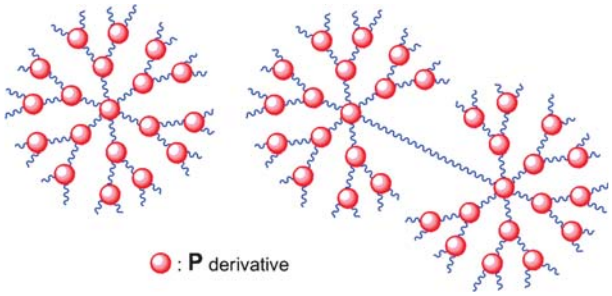
PERSPECTIVES

1512

Biological properties of phosphorus dendrimers

Anne-Marie Caminade,* Cédric-Olivier Turrin and Jean-Pierre Majoral*

Dendrimers built with phosphorus at each branching point have numerous biological properties.

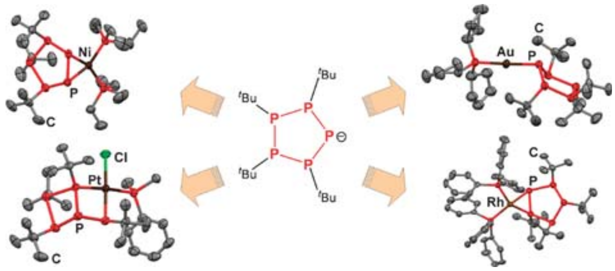


1525

The versatile reactivity of tetra-*tert*-butyl-cyclopentaphosphanide monoanions

Santiago Gómez-Ruiz and Evamarie Hey-Hawkins*

This review describes the versatile reactivity of *cyclo*-$(P_5{}^tBu_4)^-$ in reactions with main group and transition metal complexes. Such novel phosphorus-rich metal complexes may be useful precursors for the preparation of phosphorus-rich metal phosphides, which are expected to exhibit interesting properties for materials science.



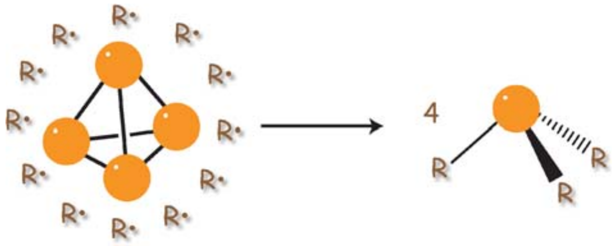
LETTERS

1533

Radical synthesis of trialkyl, triaryl, trisilyl and tristannyl phosphines from P_4

Brandi M. Cossairt and Christopher C. Cummins*

A reaction scheme has been developed that accomplishes the direct radical functionalization of white phosphorus without the intermediacy of PCl_3.

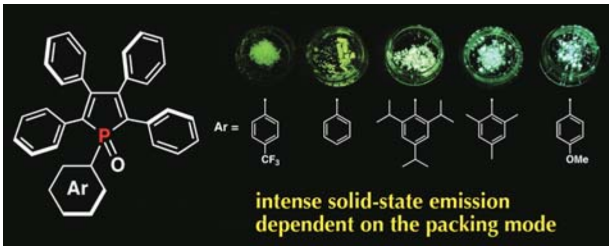


1537

Intense fluorescence of 1-aryl-2,3,4,5-tetraphenylphosphole oxides in the crystalline state

Aiko Fukazawa, Yasunori Ichihashi and Shigehiro Yamaguchi*

1-Aryl-2,3,4,5-tetraphenylphosphole oxides showed intense fluorescence in crystals. Their quantum yields (Φ_F 0.25–0.91) depend not on the steric bulkiness or electronic effect of the 1-aryl groups, but on their packing modes.



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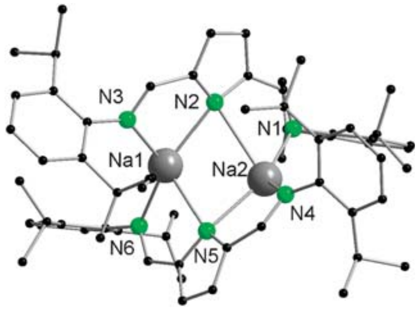
Dimeric complexes of lithium and sodium forming a tetrametallacyclobuta[1,2:1,4:2,3:3,4]tetracyclopentane structure

Jelena Jenter and Peter W. Roesky*

The reaction of 2,5-bis{*N*-(2,6-diisopropylphenyl)iminomethyl}pyrrole ($(DIP_2\text{-pyr})H$) with *n*BuLi and NaH resulted in the dimeric lithium and sodium compounds $[(DIP_2\text{-pyr})M]_2$ (M = Li, Na).

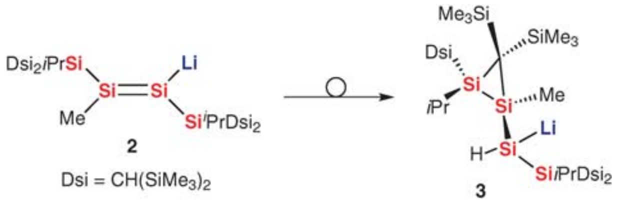


1544

Addition of methyllithium to disilyne RSi≡SiR (R = Si*i*Pr[CH(SiMe$_3$)$_2$]), giving a disilenyllithium, and its unexpected isomerization to a disilacyclopropylsilyllithium

Torahiko Yamaguchi, Masaaki Ichinohe and Akira Sekiguchi*

The reaction of disilyne RSi≡SiR (R = Si*i*Pr[CH(SiMe$_3$)$_2$]) **1** with MeLi produced the methyl-substituted disilenyllithium **2** as the primary product, however, it unexpectedly underwent isomerization to disilacyclopropylsilyllithium **3**.



1547

2-(2′-Pyridyl)-4,6-diphenylphosphinine *versus* 2-(2′-pyridyl)-4,6-diphenylpyridine: an evaluation of their coordination chemistry towards Rh(I)

Ariadna Campos Carrasco, Evgeny A. Pidko, Anna M. Masdeu-Bultó, Martin Lutz, Anthony L. Spek, Dieter Vogt and Christian Müller*

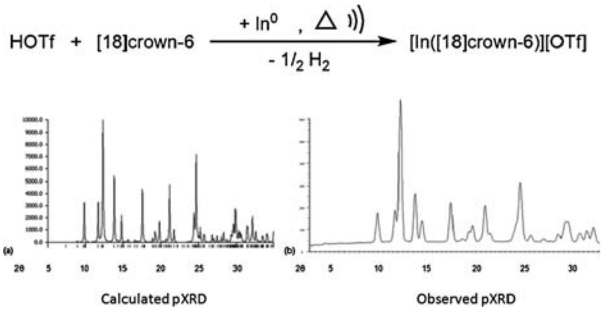
The coordination chemistry of the bidentate P,N hybrid ligand 2-(2′-pyridyl)-4,6-diphenylphosphinine towards Rh(I) has been investigated and compared to the structurally analogous 2,2′-bipyridine derivative.

1551

Alternative syntheses of univalent indium salts including a direct route from indium metal

Benjamin F. T. Cooper and Charles L. B. Macdonald*

Protonolysis of indium(I) reagents using an [18]crown-6 poly-ether pre-treated with trifluoromethanesulfonic acid (HOTf) provides an efficient route to the known salt [In([18]crown-6)][OTf] in good to excellent yield. The treatment of indium metal with HOTf, in the presence or absence of [18]crown-6, provides a high-yield synthetic approach to univalent indium salts that does not require the use of a pre-existing indium(I) reagent.



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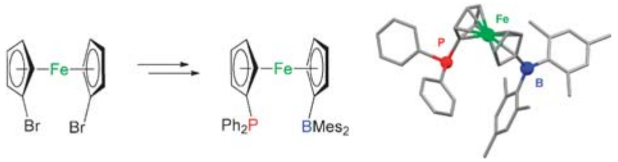
LETTERS

1556

A 1,1′-ferrocenyl phosphine-borane: synthesis, structure and evaluation in Rh-catalyzed hydroformylation

Magnus W. P. Bebbington, Sébastien Bontemps, Ghenwa Bouhadir, Martin J. Hanton, Robert P. Tooze, Hendrick van Rensburg and Didier Bourissou*

The ambiphilic ligand Ph_2P–(1,1′-ferrocenyl)–$BMes_2$ has been shown by NMR spectroscopy and X-ray diffraction analysis to adopt a monomeric structure free of dative P → B and Fe → B interactions.

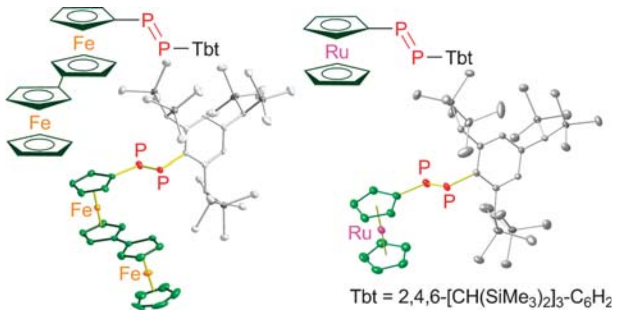


1560

Synthesis, structures and properties of biferrocenyl- and ruthenocenyl-substituted diphosphenes

Takahiro Sasamori,* Akimi Hori, Yoshikazu Kaneko and Norihiro Tokitoh*

Novel d-π electron systems of metallocenyldiphosphenes have been synthesized and characterized.



Tbt = 2,4,6-$[CH(SiMe_3)_2]_3$-C_6H_2

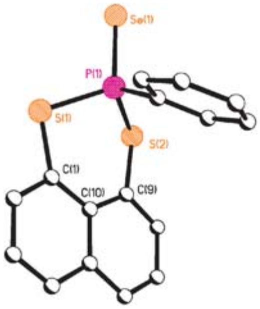
PAPERS

1565

Synthesis and X-ray structures of new phosphorus–selenium heterocycles with an E–P(Se)–E′ (E, E′ = N, S, Se) linkage

Guoxiong Hua, Amy L. Fuller, Yang Li, Alexandra M. Z. Slawin and J. Derek Woollins*

Simple routes to new 5–7 membered P–Se heterocycles have been developed.

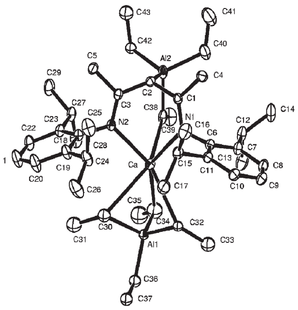


1572

Synthesis of β-diketiminato calcium silylamides and their reactions with triethylaluminium

Mark R. Crimmin, Michael S. Hill,* Peter B. Hitchcock and Mary F. Mahon

β-Diketiminato calcium silylamides react with triethylaluminium to yield a calcium aluminate complex in which coordination at calcium is provided by bridging interactions with the aluminate anion and a ligand derived from further reaction of the β-diketiminate with triethylaluminium.



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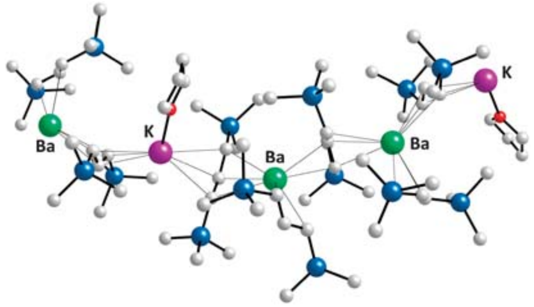


Allyl complexes of the heavy alkaline-earth metals: molecular structure and catalytic behavior

Keith T. Quisenberry, Rosemary E. White, Timothy P. Hanusa* and William W. Brennessel

The allyl complex $SrA'_2(thf)_2$ ($A' = 1,3\text{-}(SiMe_3)_2C_3H_3$) is a monomer with π-bound allyl ligands, but the same bulky allyl forms a polymeric barium/potassium species, $K(thf)Ba_2A'_5$. $CaA'_2(thf)_2$, $SrA'_2(thf)_2$ and $K(thf)Ba_2A'_5$ are initiators for methyl methacrylate polymerization.

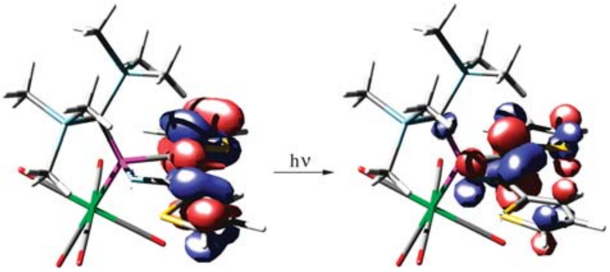
1585

Dithienophosphole-capped π-conjugated oligomers

Stefan Durben, Thomas Linder and Thomas Baumgartner*

The incorporation of two dithienophosphole end units within π-conjugated oligomers provides highly luminescent chromophores whose photophysical features can be tuned by the aromatic linker.

1593

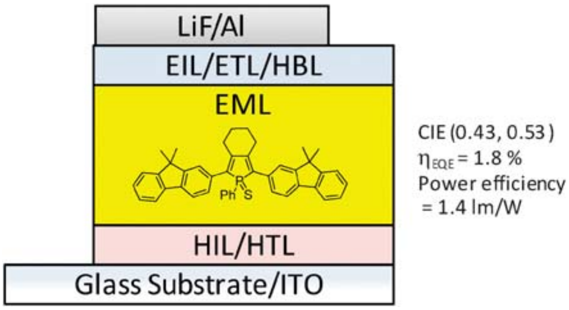


Extended π conjugation in 2*H*-1,4,2-diazaphosphole complexes

Holger Helten, Jörg Daniels, Martin Nieger and Rainer Streubel*

Syntheses, structures as well as the electronic and photophysical properties of planar, π conjugated thienyl substituted 2*H*-1,4,2-diazaphosphole complexes are presented, which show UV/Vis absorptions at very long wavelengths and pronounced acidichroism.

1603



Phosphole-based π-conjugated electroluminescent materials for OLEDs

Damien Joly, Denis Tondelier, Valérie Deborde, Bernard Geffroy,* Muriel Hissler* and Régis Réau*

Novel mixed phosphole–fluorene π-conjugated systems are stable electroluminescent materials, and the OLEDs incorporating these derivatives as emitters present very high performances.

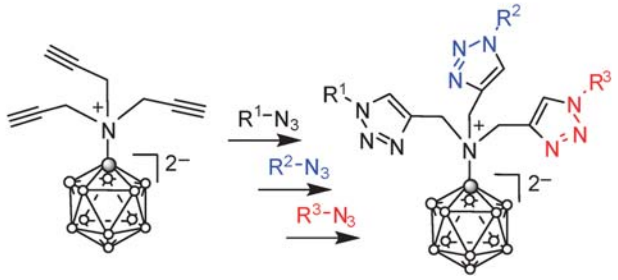
PAPERS

1612

Synthesis of triazolyl methyl-substituted amino- and oxy-undecahydrododecaborates for potential application in boron neutron capture therapy

Mohamed E. El-Zaria, Afaf R. Genady and Hiroyuki Nakamura*

A highly efficient route to the synthesis of triazole-based dodecaborate anions is now available by the CuI-catalyzed ligation of dodecaborate terminal alkynes and organic azides.

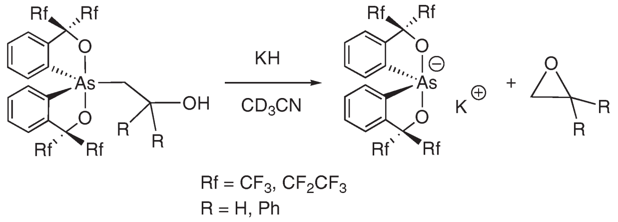


1623

Formation of epoxides from pentacoordinated organoarsenic compounds with a β-hydroxyethyl group

Xin-Dong Jiang, Shiro Matsukawa, Yuta Fukuzaki and Yohsuke Yamamoto*

A series of pentacoordinated organoarsenic compounds bearing a β-hydroxyethyl group were synthesized and characterized. Upon treatment of these compounds with KH in CD_3CN, decomposition reactions proceeded to quantitatively produce the corresponding epoxide.

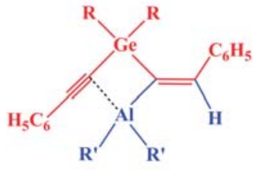


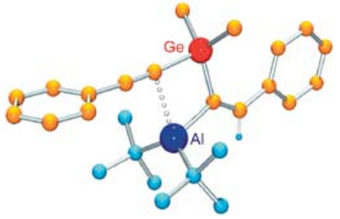
1630

Hydroalumination of dialkynylgermanes—synthesis of alkenyl–alkynylgermanes with intramolecular aluminium–carbon interactions

Werner Uhl,* Martina Rohling and Jutta Kösters

Hydroalumination of $R_2Ge(C{\equiv}C–Ph)_2$ (R = Me, C_6H_5) affords alkenyl–alkynylgermanes which show an intramolecular interaction between the coordinatively-unsaturated aluminium atom and the α-carbon atom of the triple bond.



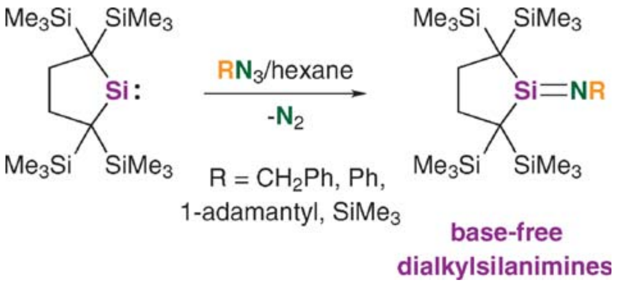


1637

Synthesis and structure of stable base-free dialkylsilanimines

Takeaki Iwamoto,* Nobuyoshi Ohnishi, Zhenyu Gui, Shintaro Ishida, Hiroyuki Isobe, Satoshi Maeda, Koichi Ohno and Mitsuo Kira*

Four base-free dialkylsilanimines were synthesized as air-sensitive crystals and their structures were characterised by X-ray analysis and UV-vis absorption spectroscopy.



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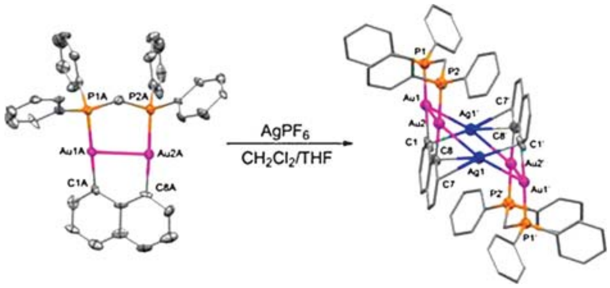
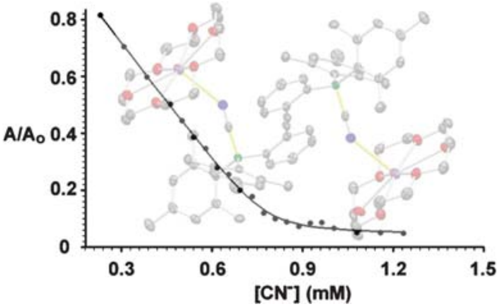


Synthesis, structure and luminescence of 1,8-diaurionaphthalenes

Casey R. Wade, Andrey A. Yakovenko and
François P. Gabbaï*

The synthesis and structural characterization of a new 1,8-diaurionaphthalene complex has been carried out along with its reaction with AgPF$_6$ resulting in formation of a novel dicationic metallocycle complex as the PF$_6^-$ salt.

1652

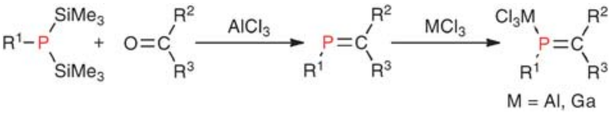


Comparative structural and thermodynamic studies of fluoride and cyanide binding by PhBMes$_2$ and related triarylborane Lewis acids

Christopher Bresner, Cally J. E. Haynes, David A. Addy, Alexander E. J. Broomsgrove, Philip Fitzpatrick, Dragoslav Vidovic, Amber L. Thompson, Ian A. Fallis and Simon Aldridge*

Comparative thermodynamic and structural parameters associated with fluoride and cyanide binding by simple triarylboranes have been determined experimentally.

1660

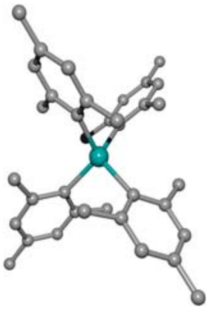


A Lewis acid-mediated synthesis of P-alkyl-substituted phosphaalkenes

Joshua I. Bates, Brian O. Patrick and Derek P. Gates*

The reaction of disilylphosphines with appropriate ketones or aldehydes in the presence of aluminum chloride affords phosphaalkenes in good yields.

1667



Organic heterobimetallic complexes of the alkaline earth metals (Ae = Ca, Sr, Ba) with tetrahedral metallate anions of three-valent metals (M = B, Al, Ga, and V)

Jens Langer, Sven Krieck, Helmar Görls, Günter Kreisel, Wolfgang Seidel and Matthias Westerhausen*

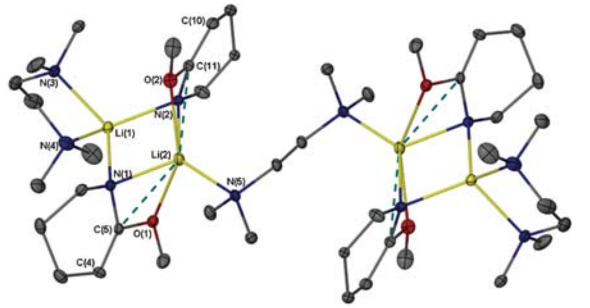
Heterobimetallic complexes of the heavy alkaline earth metals (Ae) often form solvent-separated ion pairs such as the solvent complexes of the type $[(L)_n\text{Ae}][\text{MR}_4]_2$ of trivalent metals M (V cyan, C grey).

1678

Homo- and heteroanionic alkali metal aza-enolate aggregates derived from *o*-methylvalerolactim ether

Philip C. Andrews,* Steven D. Bull and
Magdaline Koutsaplis

Reaction of *o*-valerolactim ether with BuM (M = Li, Na, K) in the presence of Lewis donors forms an aza-enolate anion, which is observed in a series of structurally characterised complex homoanionic, heteroanionic and heterobimetallic aggregates. In the absence of a Lewis donor nucleophilic substitution is thermodynamically favoured.

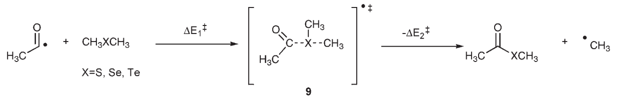


1692

An *ab initio* and DFT study of homolytic substitution reactions of acyl radicals at sulfur, selenium, and tellurium

Sonia M. Horvat* and Carl H. Schiesser

Ab initio and DFT calculations predict that homolytic substitution reactions of acetyl radicals at the heteroatom in dimethyl sulfide, dimethyl selenide and dimethyl telluride, with the expulsion of methyl radical, proceed *via* smooth transition states and without the involvement of hypervalent intermediates.

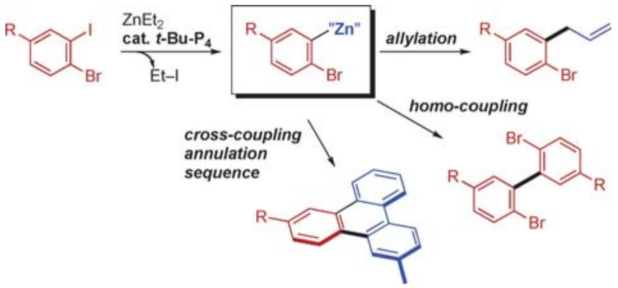


1700

Generation of arylzinc reagents through an iodine–zinc exchange reaction promoted by a non-metallic organic superbase

Hiroshi Naka,* Keisuke Ito, Masahiro Ueno,
Koji Kobayashi and Yoshinori Kondo*

A phosphazene base-promoted iodine–zinc exchange reaction yielded salt-free, functionalized arylzinc reagents from aryl iodides and diethylzinc. The resulting arylzinc compounds were found to be powerful synthetic precursors for complex aromatic compounds.

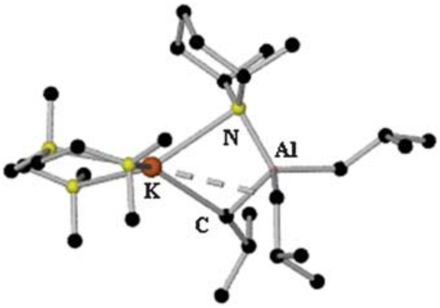


1707

Structural insights into mono-amido tris-alkyl potassium aluminates

Ben Conway,* Pablo García-Álvarez, Alan R. Kennedy,
Jan Klett, Robert E. Mulvey* and Stuart D. Robertson

Significant structural differences are revealed in a series of PMDETA stabilized trisalkylamido potassium aluminates formed by co-complexation of the parent potassium amide with $^{i}Bu_3Al$.



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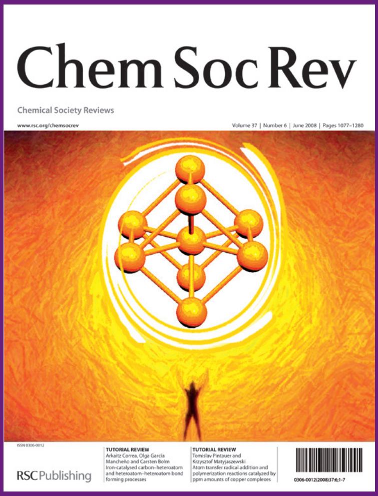
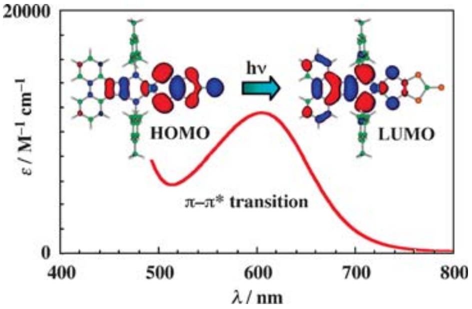


1713

Synthesis and structures of platinum diphenylacetylene and dithiolate complexes bearing diphosphinidenecyclobutene ligands (DPCB-Y)

Yumiko Nakajima, Mitsuharu Nakatani, Kyohei Hayashi, Yu Shiraishi, Ryo Takita, Masaaki Okazaki and Fumiyuki Ozawa*

Diphosphinidenecyclobutenes (DPCB-Y) as low-coordinate phosphorus ligands form platinum complexes having an extended π-conjugated system with dπ–pπ interaction.

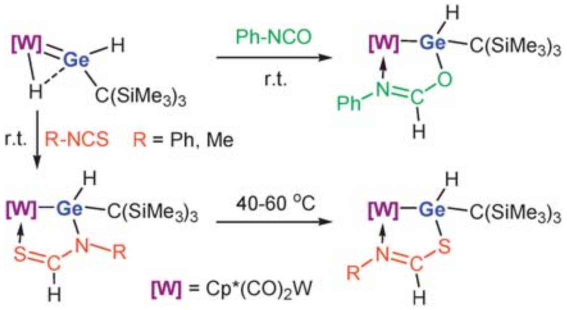


1723

Reactions of a hydrido(hydrogermylene)tungsten complex with some heterocumulenes: hydrogermylation and thermal rearrangement

Hisako Hashimoto,* Tetsuya Fukuda and Hiromi Tobita*

A hydrido(hydrogermylene)tungsten complex can carry out hydrogermylation of isocyanate and isothiocyanates at room temperature to give novel five-membered chelate complexes. On gentle heating in solution, the products of the isothiocyanates cleanly rearrange to isomeric chelate complexes.

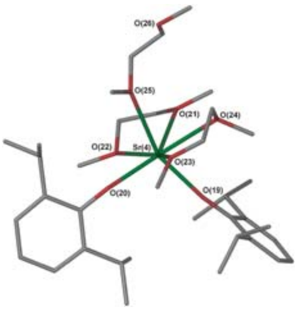


1731

Synthesis and structural characterisation of the heavier alkaline earth 2,6-di-iso-propylphenolate complexes

Glen B. Deacon,* Peter C. Junk* and Graeme J. Moxey

Redox transmetallation ligand exchange reactions were employed in the synthesis of 2,6-di-iso-propylphenolate complexes of the heavy alkaline earths; the resulting mononuclear complexes were structurally characterised.

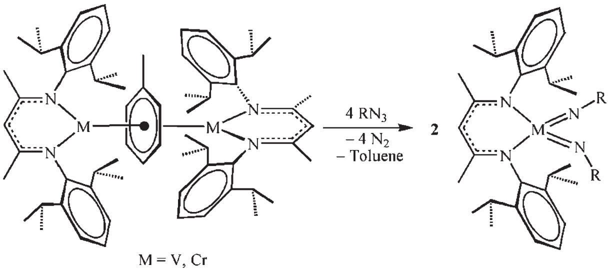


1737

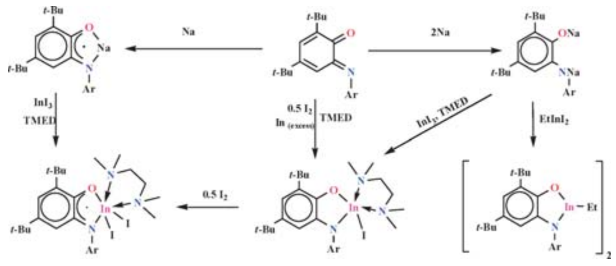
Reductive N–N bond cleavage and coupling of organic azides mediated by chromium(I) and vanadium(I) *β*-diketiminate

Kuan-Ming Lin, Po-Yang Wang, Yun-Jen Shieh, Hong-Zhang Chen, Ting-Shen Kuo and Yi-Chou Tsai*

Reactions of organic azides RN_3 with two univalent vanadium and chromium inverted-sandwich (μ-η^6:η^6-$C_6H_5CH_3$)[M(Nacnac)]$_2$ complexes (M = Cr (**1**) and V (**2**); Nacnac = HC(C(Me)NC$_6$H$_3$^{i}Pr$_2$)$_2$) have been investigated.



1746

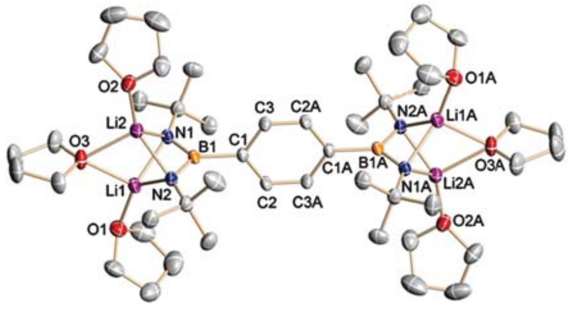


Indium(III) complexes with *o*-iminobenzoquinone in different redox states

Alexandr V. Piskunov,* Irina N. Mescheryakova, Georgy K. Fukin, Vladimir K. Cherkasov and Gleb A. Abakumov

Investigations of the synthesis and structure of indium(III) complexes with *o*-iminobenzoquinone in different redox states are presented.

1751

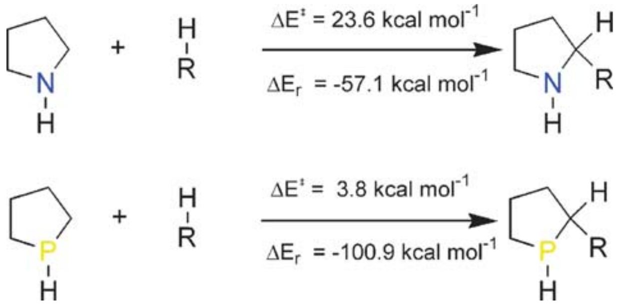


Syntheses and structures of new alkali-metal boraamidinates and ferrocenyl aminoboranes

Andrea M. Corrente and Tristram Chivers*

Syntheses and structural investigations of alkali-metal boraamidinates $[\{Li(THF)\}_4(\mu\text{-}THF)_2]$-$[1,4\text{-}(N^tBu)_2BC_6H_4B(N^tBu)_2]$, $[M(THF)_2][PhB[(NDipp)(N(H)Dipp)]$ (M = Li, K), and $[K_2(THF)_3][PhB(NDipp)_2]$, and ferrocenyl aminoboranes $FcB[N(H)R]_2$ (R = ^{t}Bu, Dipp) and $1,1'\text{-}Fc\{B[N(H)^tBu]_2\}_2$ are reported.

1760

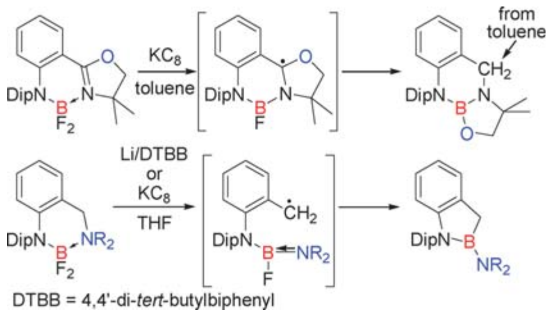


P-Heterocyclic carbenes as effective catalysts for the activation of single and multiple bonds. A theoretical study

Markus Rullich, Ralf Tonner and Gernot Frenking*

Quantum chemical calculations show that *P*-heterocyclic carbenes have substantially lower activation barriers than *N*-heterocyclic carbenes for breaking the single bonds H–H, O–H, N–H, C–H, C–F, C–Cl and Si–H, as well as the π-bonds in benzene, ethylene and acetylene.

1774



Reduction of base-stabilized difluoroboranes to induce rearrangement reactions

Makoto Yamashita,* Yoshitaka Aramaki and Kyoko Nozaki*

Lewis base-stabilized difluoroboranes **2**, **4-pyr** and **4-^{i}Pr** were synthesized and fully characterized. Reduction of these difluoroboranes afforded a complicated mixture. The major Dip-containing species, such as **5-H**, **13-pyr** or **13-^{i}Pr**, was probably formed *via* a skeletal rearrangement in each reaction with a radical intermediate.

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