

Dalton Transactions

An international journal of inorganic chemistry incorporating Acta Chemica Scandinavica

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Cover

See: Arne Baunemann, Younsoo Kim, Manuela Winter and Roland A. Fischer, pp. 121–128.

From molecules to materials: tailored precursors for the CVD of tantalum nitride.

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CHEMICAL BIOLOGY

B1

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Chemical Biology

January 2006/Volume 1/Issue 1

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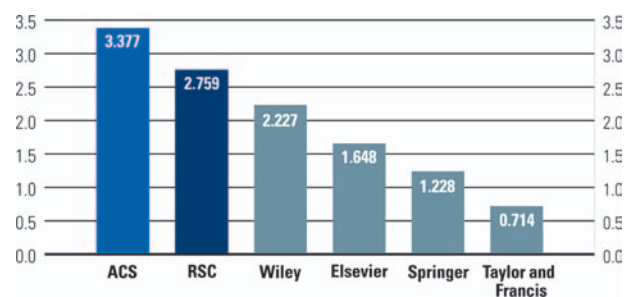
EDITORIAL

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Dalton Transactions: Developing for the Inorganic Community

Jamie Humphrey and Paul Walton

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To mark and celebrate the launch of weekly issues, and new issue format, this, the first issue, contains articles written by members of the Editorial and Advisory Board.

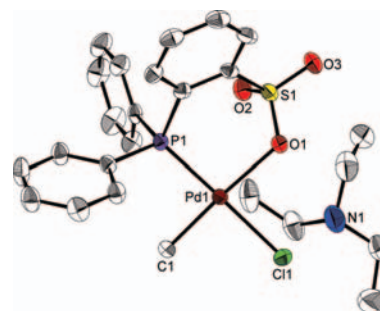


COMMUNICATIONS

Synthesis of anionic methylpalladium complexes with phosphine–sulfonate ligands and their activities for olefin polymerization

Takuya Kochi, Kenji Yoshimura and Kyoko Nozaki*

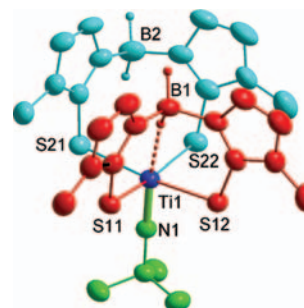
Anionic methylpalladium(II) complexes with bidentate phosphine–sulfonate ligands were prepared and their catalytic activities for copolymerization of ethylene with methyl acrylate were investigated.



Dihydrobis(methimazolyl)borate and methimazolyl complexes of titanium

Anthony F. Hill* and Matthew K. Smith

The first poly(methimazolyl)borato complex of group 4, $[\text{Ti}(=\text{NCMe}_3)\{\text{H}_2\text{B}(\text{mt})_2\}_2]$ (mt = methimazolyl), results from the reaction of $\text{Na}[\text{H}_2\text{B}(\text{mt})_2]$ with $[\text{Ti}(=\text{NCMe}_3)\text{Cl}_2(\text{py})_3]$ and features both $\kappa^2\text{-S,S'}$ and $\kappa^3\text{-H,S,S'}$ coordination of $\text{H}_2\text{B}(\text{mt})_2$ ligands coincident within the same molecule.

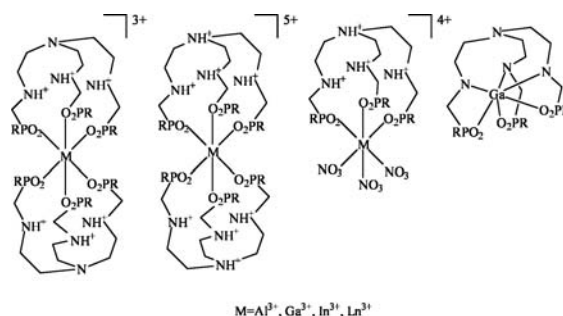


PAPERS

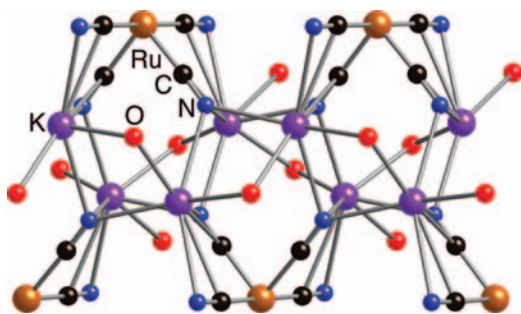
Lanthanide(III) and group 13 metal ion complexes of tripodal amino phosphinate ligands

Michael S. Kovacs, Vishakha Monga, Brian O. Patrick and Chris Orvig*

The tripodal amine-phosphinate ligands, tris(4-(phenylphosphinato)-3-benzyl-3-azabutyl)amine (H_3ppba) and tris(4-(phenylphosphinato)-3-azabutyl)amine (H_3ppa) form novel complexes upon reaction with Al^{3+} , Ga^{3+} , In^{3+} and the lanthanides (Ln^{3+}).



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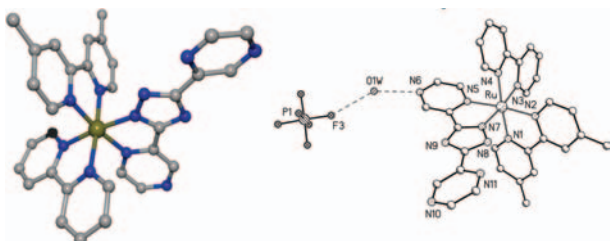


New members of the $[\text{Ru}(\text{diimine})(\text{CN})_4]^{2-}$ family: structural, electrochemical and photophysical properties

H. Adams, W. Z. Alsindi, G. M. Davies, M. B. Duriska, T. L. Easun, H. E. Fenton, J.-M. Herrera, M. W. George,* K. L. Ronayne, X.-Z. Sun, M. Towrie and M. D. Ward*

A series of complexes $[\text{Ru}(\text{NN})(\text{CN})_4]^{2-}$ (where NN is a bidentate diimine) has been prepared and characterised by electrochemical and photophysical techniques; structural studies with either K^+ or a lanthanide(III) cation reveal a range of coordination networks.

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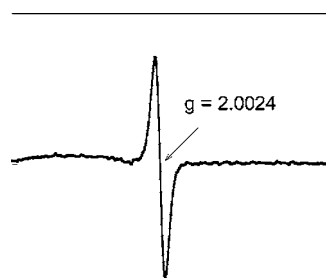


Synthesis of mononuclear and dinuclear ruthenium(II) tris(heteroleptic) complexes *via* photosubstitution in bis(carbonyl) precursors

Declan Mulhern, Sally Brooker, Helmar Görls, Sven Rau and Johannes G. Vos*

A new synthetic method for the preparation of tris heteroleptic ruthenium polypyridyl complexes is presented; the X-ray structures of some of these compounds are reported.

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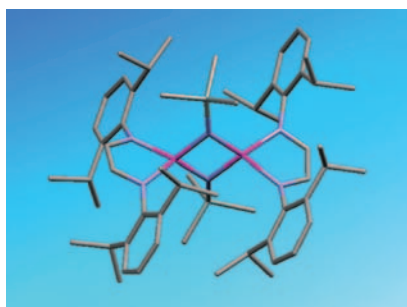


Ligand effect on the kinetics of hydroperoxochromium(III)–oxochromium(V) transformation and the lifetime of chromium(V)

Kelemu Lemma, Arkady Ellern and Andreja Bakac*

A macrocyclic hydroperoxochromium(III) complex converts spontaneously and rapidly to a Cr(V) species: $\text{L}^2(\text{H}_2\text{O})\text{CrOOH}^{2+} \rightarrow \text{L}^2\text{Cr}(\text{v})$.

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The reactivity of gallium-(I), -(II) and -(III) heterocycles towards Group 15 substrates: attempts to prepare gallium–terminal pnictinidene complexes

Robert J. Baker, Cameron Jones,* David P. Mills, Damien M. Murphy,* Evamarie Hey-Hawkins and Robert Wolf

The reactivity of a series of Ga(I), Ga(II) and Ga(III) heterocyclic compounds towards a number of Group 15 substrates has been investigated. This study has led to a variety of novel complexes containing gallium–pnictogen bonds.

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Hydride transfer reactivity of tetrakis(trimethylphosphine)-(hydrido)(nitrosyl)molybdenum(0)

Yin Zhao, Helmut W. Schmalle, Thomas Fox, Olivier Blacque and Heinz Berke*

The complex $\text{Mo}(\text{PMe}_3)_4(\text{H})(\text{NO})$ inserts a variety of unsaturated organic substrates such as ketones and imines, but also metal carbonyl functionalities. The imine insertion can be extended to become a catalytic hydrogenation cycle.

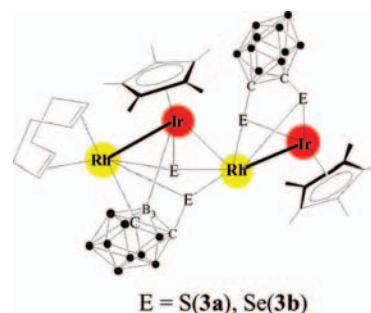


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Tetrametallic clusters (Ir_2Rh_2) through an ancillary *ortho*-carborane-1,2-dichalcogenolato ligands

Guo-Xin Jin* and Jian-Qiang Wang

Tetranuclear (Ir_2Rh_2) cluster complexes $\{\text{Cp}^*\text{Ir}[\text{E}_2\text{C}_2(\text{B}_{10}\text{H}_9)]\}\text{Rh}_2(\text{cod})\{\text{Cp}^*\text{Ir}[\text{E}_2\text{C}_2(\text{B}_{10}\text{H}_{10})]\}$ ($\text{E} = \text{S}$ (**3a**); Se (**3b**)) were obtained from the reactions of the 16-electron complex $\text{Cp}^*\text{Ir}[\text{E}_2\text{C}_2(\text{B}_{10}\text{H}_{10})]$ ($\text{E} = \text{S}$ (**1a**); Se (**1b**)) with $[\text{Rh}(\text{cod})(\mu\text{-OEt})]_2$, and characterized by X-ray crystallography.

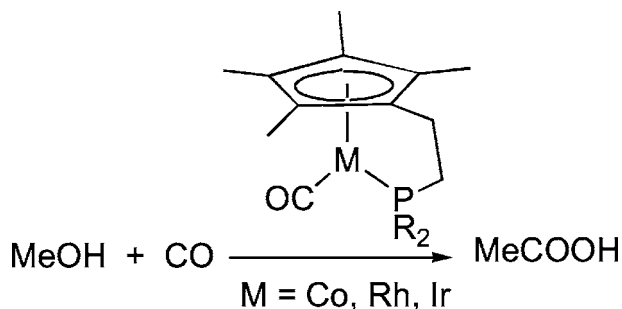


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The synthesis, characterisation and reactivity of 2-phosphanylcyclopentadienyl complexes of cobalt, rhodium and iridium

Ann C. McConnell, Peter J. Pogorzelec, Alexandra M. Z. Slawin, Gary L. Williams, Paul I. P. Elliott, Anthony Haynes, Andrew C. Marr and David J. Cole-Hamilton*

$[\text{M}(\text{C}_5\text{Me}_4(\text{CH}_2)_2\text{PR}_2)(\text{CO})]$ are synthesised from $\text{Li}[\text{C}_5\text{Me}_4(\text{CH}_2)_2\text{PR}_2]$ and suitable metal containing precursors; $[\text{Rh}(\text{C}_5\text{Me}_4(\text{CH}_2)_2\text{PETe}_2)(\text{CO})]$ is so electron rich that reductive elimination of $\text{MeC}(\text{O})\text{I}$ is rate determining in methanol carbonylation.

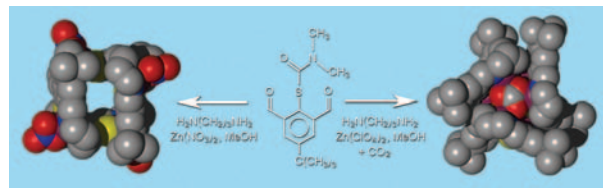


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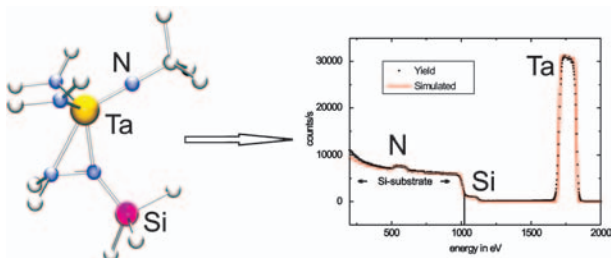
Controlled formation and topologies of thiophenolate-based macrocycles: rings, cylinders and bowls

Aase Christensen, Christoph Mayer, Frank Jensen, Andrew D. Bond* and Christine J. McKenzie*

The Ni^{2+} , Pd^{2+} or Zn^{2+} templated Schiff base condensation depicted yields controllably 2 + 2 and 4 + 4 thiophenolate hinged macrocyclic complexes with topologies dependent on the metal ions, anions and solvent.



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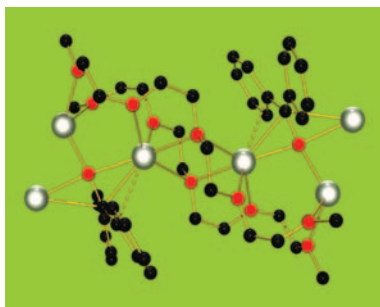


Mixed hydrazido amido/imido complexes of tantalum, hafnium and zirconium: potential precursors for metal nitride MOCVD

Arne Baunemann, Younsoo Kim, Manuela Winter and Roland A. Fischer*

Mixed imido-/amido-/hydrazido complexes of Zr, Hf and Ta have been synthesised by salt metathesis and transamination-type reactions. Preliminary MOCVD experiments to deposit TaN(Si) thin films are reported.

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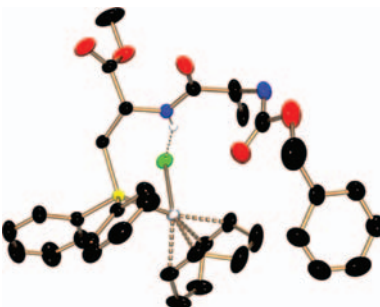


Sodium compounds of the benzophenone dianion (diphenyloxidomethanide)

Jens Geier,* Heinz Rügger and Hansjörg Grützmacher*

The benzophenone dianion, $(\text{Ph}_2\text{CO})^{2-}$, which occurs in the well known deeply violet sodium/benzophenone ether solutions frequently used as an *in situ* prepared self-indicating drying and deoxygenating agent for organic solvents, was crystallised with sodium cations in form of the polymeric chain compounds $[\text{Na}_2(\text{Ph}_2\text{CO})(\text{tetraglyme})]_\infty$ **1** and $[\text{Na}_2(\text{Ph}_2\text{CO})(\text{thf})_2]_\infty$ **2** (Na: silver, C: black, O: red).

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Coordination chemistry of phosphanyl amino acids: solid state and solution structures of neutral and cationic rhodium complexes

Christian Meyer, Markus Scherer, Hartmut Schönberg, Heinz Rügger, Sandra Loss, Volker Gramlich and Hansjörg Grützmacher*

Several Rh complexes with phosphanyl-substituted amino acids and dipeptides are prepared and structurally characterized. Some of the compounds are active catalyst precursors for the hydrogenation of alkenes (C: black; H: white; O: red; N: blue; P: yellow; Cl: green; Rh: silver).

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Solution-phase template approach for the synthesis of Cu_2S nanoribbons

Zhengquan Li, Huan Yang, Yue Ding, Yujie Xiong and Yi Xie*

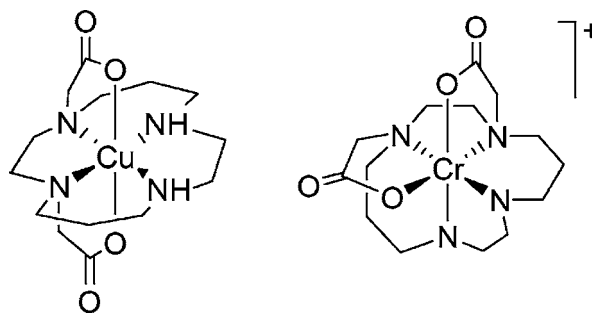
Cu_2S nanoribbons were synthesized through a solution-phase template approach, in which Bi_2S_3 nanoribbons acted as both template and reactant with the assistance of solvent.

152

Coordination chemistry of 1,4-bis-carboxymethylcyclam, $H_2(1,4\text{-bcc})$

Deborah M. Tonei, David C. Ware,* Penelope J. Brothers, Paul G. Plieger and George R. Clark

Reduction of the cobalt(III) complex $[Co(1,4\text{-bcc})]ClO_4$ (1,4-bcc = 1,4-bis-carboxymethylcyclam) with zinc amalgam gave the cobalt(II) complex, crystallised as the coordination polymer $\{[Co(1,4\text{-bcc})]ZnCl_2\}_n$. Removal of cobalt from $[Co(1,4\text{-bcc})]ClO_4$ allowed isolation of the free ligand salt $H_2(1,4\text{-bcc})\cdot 4HCl$, from which Cu(II), Ni(II), Zn(II) and Cr(III) complexes were prepared.

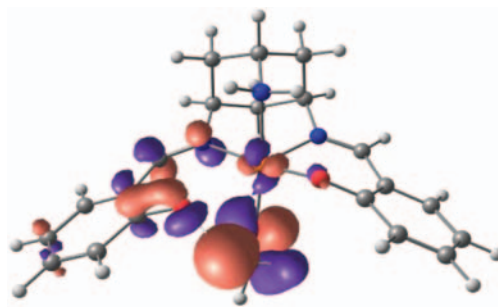


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Catalytic alcohol oxidation by an unsymmetrical 5-coordinate copper complex: electronic structure and mechanism

Ekaterina Zueva, Paul H. Walton and John E. McGrady*

Density functional theory reveals that, despite the structural and functional similarities between the model copper complex $Cu^{II}L$, $L = cis\text{-}1\text{-}(3',5'\text{-dimethoxy-benzylideneamino})\text{-}3,5\text{-}[2\text{-hydroxy-(}3',5'\text{-di-}tert\text{-butyl)benzylideneimino]cyclohexane}$, and the active site of galactose oxidase, the mechanism of alcohol oxidation is fundamentally different in the two cases.

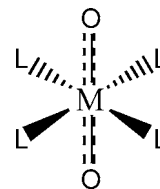


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Electronic structures of *trans*-dioxometal complexes

Patrick Hummel, Jay R. Winkler and Harry B. Gray*

We have employed computational methods based on density functional theory to elucidate the effects of equatorial ligands on the electronic structures of *trans*-dioxometal complexes.

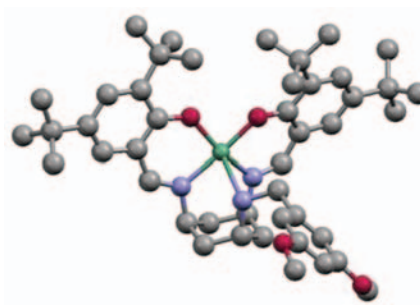


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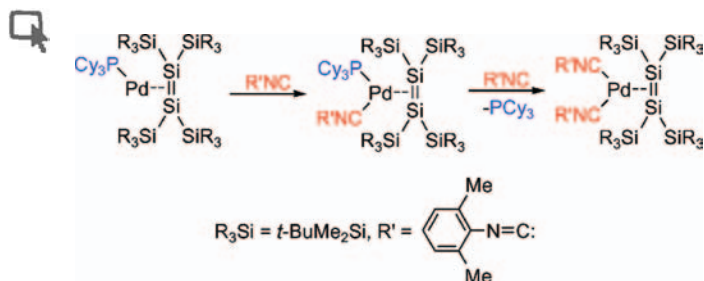
(*N*-Benzyl-bis-*N'*,*N''*-salicylidene)-*cis*-1,3,5-triaminocyclohexane copper(II): a novel catalyst for the aerobic oxidation of benzyl alcohol

Alison K. Nairn, Stephen J. Archibald, Rajiv Bhalla, Bruce C. Gilbert, Elizabeth J. MacLean, Simon J. Teat and Paul H. Walton*

Preparation and spectroscopic analysis of a novel tach based N_3O_2 complex $Cu^{II}L$ (where $H_2L = N\text{-benzyl-}N',N''\text{-di-}tert\text{-butyl-disalicyl-triaminocyclohexane}$) and the catalytic oxidation chemistry of its corresponding phenoxyl radical complex $[Cu^{II}L]^{\bullet}$.



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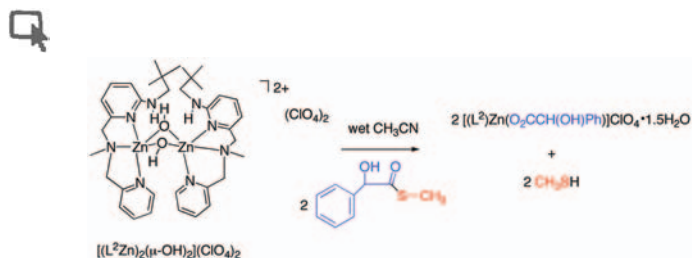


Ligand dependence of π -complex character in disilene–palladium complexes

Takeaki Iwamoto, Yumiko Sekiguchi, Naoki Yoshida, Chizuko Kabuto and Mitsuo Kira*

Bis- and mono(isocyanide)(disilene)palladium complexes, which are synthesized by the ligand exchange reactions of the corresponding 16-electron bis(phosphine)(disilene)palladium or 14-electron (phosphine)(disilene)palladium, show enhanced π -complex character compared with the corresponding bis(phosphine)(disilene)palladium complexes.

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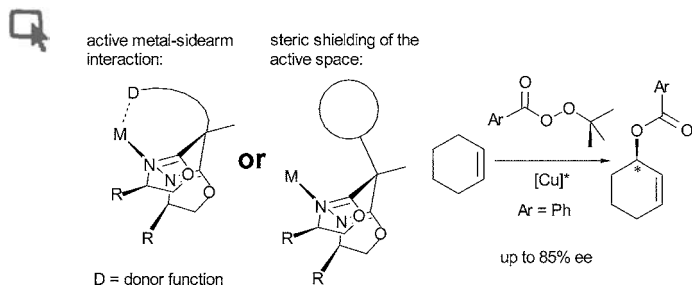


Thioester hydrolysis reactivity of zinc hydroxide complexes: investigating reactivity relevant to glyoxalase II enzymes

Lisa M. Berreau,* Amrita Saha and Atta M. Arif

A series of zinc hydroxide complexes have been investigated for thioester hydrolysis reactivity; complexes capable of forming a terminal Zn–OH moiety mediate thioester hydrolysis.

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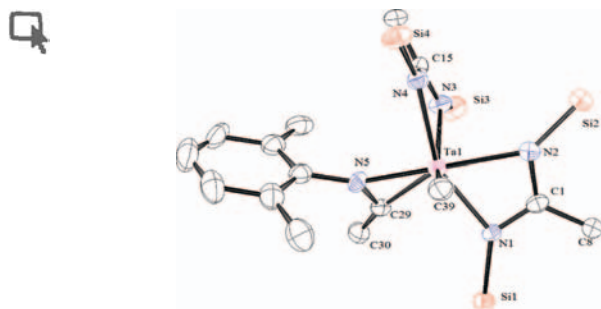


Bisoxazolines with one and two sidearms: stereodirecting ligands for copper-catalysed asymmetric allylic oxidations of alkenes

Markus Seitz, Carmine Capacchione, Stéphane Bellemin-Laponnaz, Hubert Wadepohl, Benjamin D. Ward and Lutz H. Gade*

A series of sidearm functionalized bisoxazoline ligands has been synthesized and tested in the copper catalyzed asymmetric allylic oxidation of cyclohexene. The sidearms do not interfere directly in this reaction and only play an indirect role by virtue of their steric demand.

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Olefination and group transfer reactions of an electron deficient tantalum methylene complex

Sarah M. Mullins, Robert G. Bergman* and John Arnold*

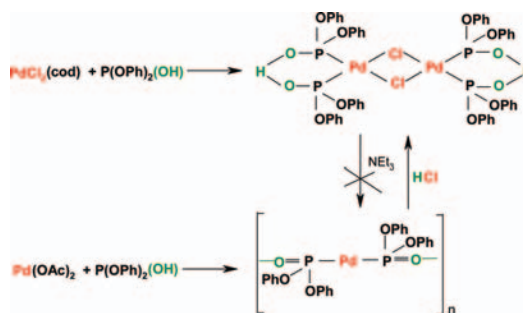
The reactivity of an electronically unsaturated tantalum methylene complex $[ToIC(NSiMe_3)_2]_2Ta(CH_2)CH_3$ (**1**) is described. Electrophilic addition and olefination reactions of the Ta=CH₂ functionality are reported. Addition of 2,6-dimethylphenyl isocyanide to **1** yields the η^2 -ketenimine complex **13**, the core structure of which is shown.

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Chemistry of palladium phosphinite ($\text{PPh}_2(\text{OR})$) and phosphonite ($\text{P}(\text{OPh})_2(\text{OH})$) complexes: catalytic activity in methoxycarbonylation and Heck coupling reactions

Iweta Pryjomska, Hubert Bartosz-Bechowski, Zbigniew Ciunik, Anna M. Trzeciak* and Józef J. Ziółkowski

Palladium complexes of the *trans*- $\text{PdCl}_2[\text{PPh}_2(\text{OR})]_2$ ($\text{R} = \text{C}_6\text{F}_5$, ^iBu , or *O*-menthyl), $[\mu\text{-ClPd}(\text{PPh}_2\text{OH})(\text{PPh}_2\text{O})]_2$, $[\text{Pd}(\text{P}(\text{O})\text{PPh}_2)_2]_n$, $[\mu\text{-ClPd}(\text{P}(\text{OPh})_2\text{OH})(\text{P}(\text{OPh})_2\text{O})]_2$ and $[\text{Pd}[\text{P}(\text{O})(\text{OPh})_2]_2]_n$ type are very good catalysts for methoxycarbonylation of iodobenzene and Heck cross-coupling reactions.

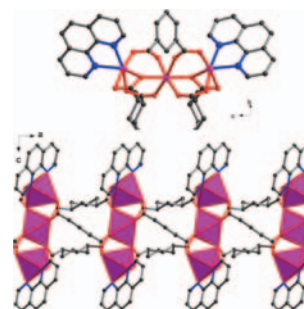


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1,2-, 1,3- and 1,4-Cyclohexanedicarboxylates of Cd and Mn with chain and layered structures

A. Thirumurugan, M. B. Avinash and C. N. R. Rao*

A systematic investigation of the three isomeric 1,2-, 1,3- and 1,4-cyclohexanedicarboxylates (CHDCs) formed by cadmium and manganese with the three isomeric dicarboxylic acids in the presence or absence of amines has been carried out. The ring conformation as well as the structural aspects of these carboxylates have been discussed.



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Single-walled carbon nanotube growth using $[\text{Fe}_3(\mu_3\text{-O})(\mu\text{-O}_2\text{CR})_6(\text{L})_3]^{n+}$ complexes as catalyst precursors

Douglas Ogrin, Ramon Colorado, Jr., Benji Maruyama, Mark J. Pender, Richard E. Smalley and Andrew R. Barron*

Spin coating of molecular precursors allows for the formation of catalyst nanoparticles suitable for growth of SWNTs with a high degree of uniformity in the diameter, without the formation of preformed clusters of a set diameter.

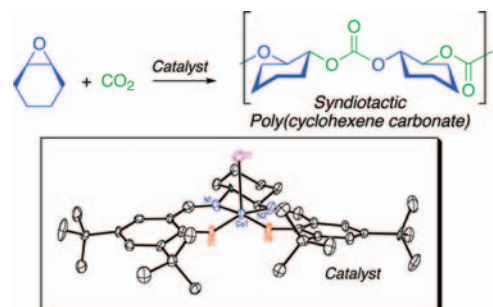


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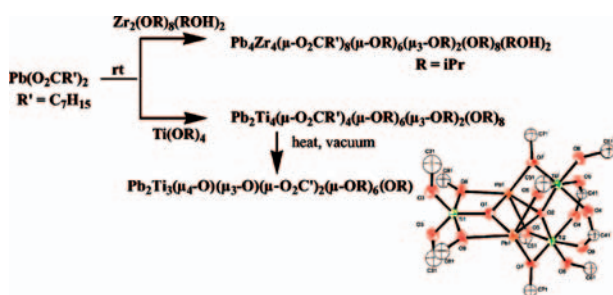
Copolymerization of cyclohexene oxide and carbon dioxide using (salen)Co(III) complexes: synthesis and characterization of syndiotactic poly(cyclohexene carbonate)

Claire T. Cohen, Christophe M. Thomas, Kathryn L. Peretti, Emil B. Lobkovsky and Geoffrey W. Coates*

Catalysts (salen)CoX (salen = *N,N'*-bis(salicylidene)-1,2-diamino-alkane; X = halide or carboxylate) have high activities for CHO/CO₂ copolymerization, yielding syndiotactic poly(cyclohexene carbonate) a previously unreported microstructure for this polymer.



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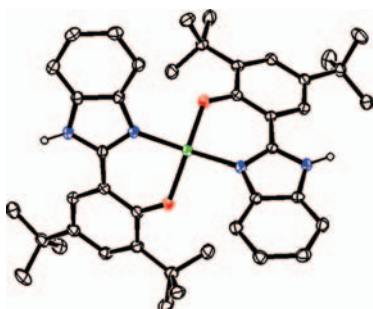


Interplay between lead carboxylate and Ti or Zr isopropoxides in solution routes to perovskites: synthesis, molecular structures and reactivity of single source non-oxo Pb–Zr and Pb–Ti carboxylatoalkoxides supported by 2-ethylhexanoate ligands

Anne Brethon, Liliane G. Hubert-Pfalzgraf* and Jean-Claude Daran

Reaction between Pb 2-ethylhexanoate and $\text{Ti}(\text{O}^i\text{Pr})_4$ or $\text{Zr}_2(\text{O}^i\text{Pr})_8(\text{PrOH})_2$ afforded the first non-oxo Pb–Zr and Pb–Ti carboxylatoalkoxides.

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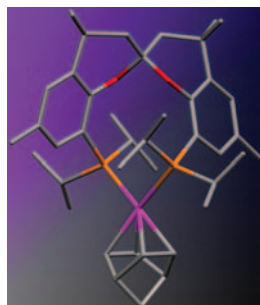


Phenoxyl radicals: H-bonded and coordinated to Cu(II) and Zn(II)

Laurent Benisvy,* Eckhard Bill, Alexander J. Blake, David Collison, E. Stephen Davies, C. David Garner,* Graeme McArdle, Eric J. L. McInnes, Jonathan McMaster,* Stephanie H. K. Ross and Claire Wilson

Two phenol-imidazole pro-ligands (^RLH) undergo a reversible, one-electron, oxidation to form a phenoxyl radical stabilised by an intramolecular N–H \cdots O hydrogen bond; the $[\text{M}(\text{II})(^R\text{L})_2]$ ($\text{M} = \text{Cu}$ or Zn) complexes undergo two, one-electron, ligand-based oxidations.

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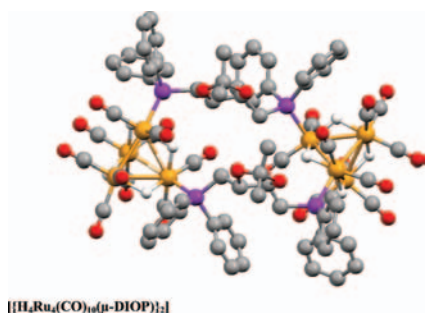


SPANphos: *trans*-spanning diphosphines as *cis* chelating ligands!

Cristina Jiménez-Rodríguez, Francesc X. Roca, Carles Bo, Jordi Benet-Buchholz, Eduardo C. Escudero-Adán, Zoraida Freixa and Piet W. N. M. van Leeuwen*

SPANphos diphosphine ligands, based on a spirobichroman backbone, introduced as putative *trans* ligands, form compounds of the type $[\text{Rh}(\text{nbd})(\text{SPANphos})]\text{BF}_4$ in which both norbornadiene and SPANphos act as *cis* chelating ligands.

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Synthesis, characterization and reactivity of tetranuclear ruthenium hydrido clusters containing chiral phosphine ligands

Viktor Moberg, Pertti Homanen, Simona Selva, Roger Persson, Matti Haukka, Tapani A. Pakkanen, Magda Monari* and Ebbe Nordlander*


Five new tetrahydrido tetranuclear carbonyl clusters containing a chiral phosphine (NMDPP, DUPHOS, DIOP or DIPAMP) were found to catalyse the (asymmetric) hydrogenation of tiglic acid (*trans*-2-methyl-2-butenoic acid).

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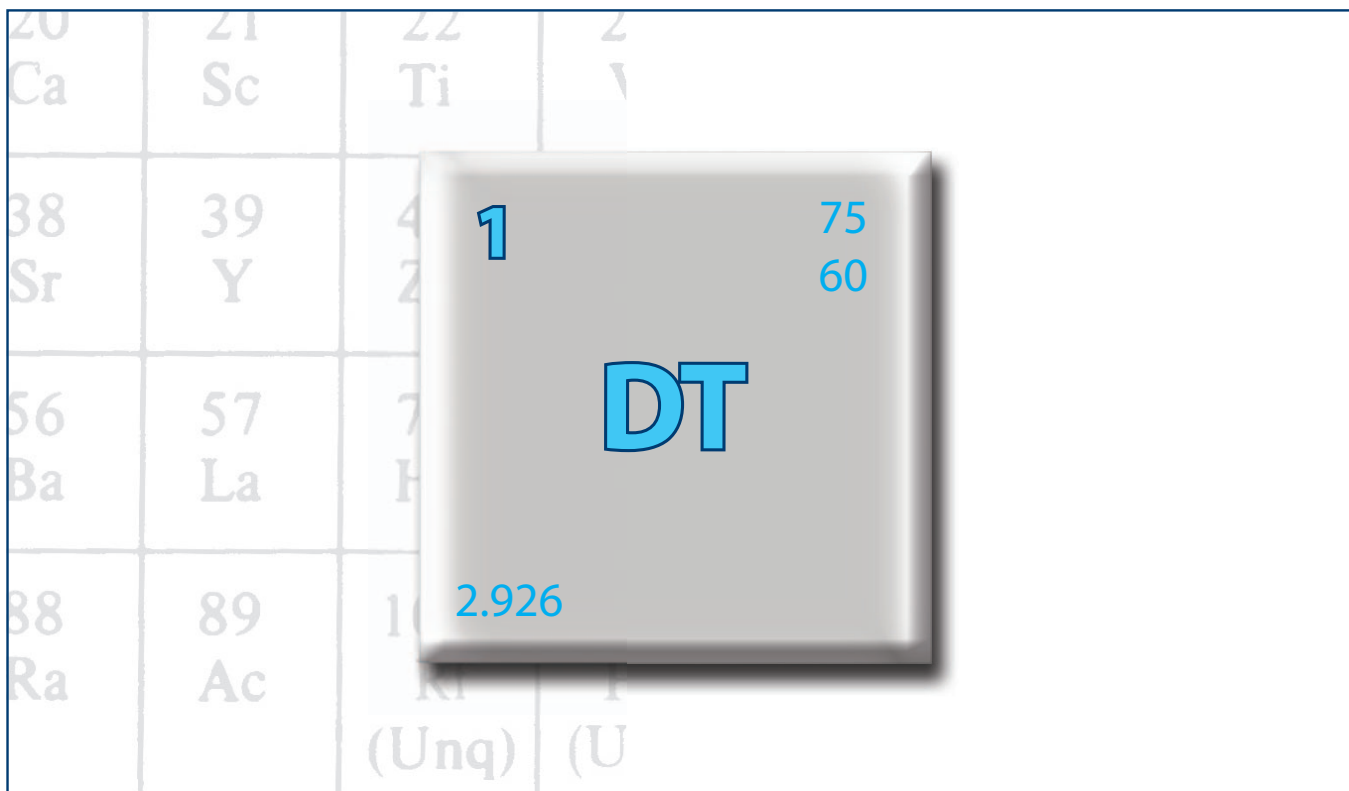
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