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# Contents

Special Issue: Molecular Architecture	s, dedicated to professor	Gyula Pályi
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#### Review

### **R.B.** King

Preface

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Supraicosahedral polyhedra in carboranes and metallacarboranes: The role of local vertex environments in determining polyhedral topology and the anomaly of 13-vertex *closo* polyhedra Metal-free carboranes having 13 vertices are anomalous since their *closo* polyhedra having the expected 28 skeletal electrons are not the usual deltahedra with exclusively triangular faces but instead polyhedra with one or two trapezoidal faces obtained by removal of one or more edges from the corresponding 13vertex deltahedron. The 12-vertex tetracarbon carborane (CH<sub>3</sub>)<sub>4</sub>C<sub>4</sub>B<sub>8</sub>H<sub>8</sub> with a *nido* skeletal electron count of 28 skeletal electrons but with two quadrilateral faces can be derived from a 13-vertex *closo* polyhedron with one quadrilateral face by removal of a degree 4 vertex.



#### Communication

### Itaru Sato, Yasushi Ohgo, Hirotaka Igarashi, Daisuke Nishiyama, Tsuneomi Kawasaki, Kenso Soai

J. Organomet. Chem. 692 (2007) 1783

Determination of absolute configurations of amino acids by asymmetric autocatalysis of 2alkynylpyrimidyl alkanol as a chiral sensor The absolute configurations of 20 amino acids, even when the enantiomeric excess of amino acid is as low as 0.1%, are determined by asymmetric autocatalysis of 2-alkynyl-5-pyrimidyl alkanol with amplification of enantiomeric excess using as a chiral sensor.



#### **Regular Papers**

#### M. Ronchi, M. Pizzotti, A. Orbelli Biroli, P. Macchi, E. Lucenti, C. Zucchi

J. Organomet. Chem. 692 (2007) 1788

Synthesis and structural characterization of functionalized cyclotetrasiloxane rings [4- $RC_6H_4Si(O)OR'$ ]<sub>4</sub> (R = Cl, Br, CH=CH<sub>2</sub>, CH<sub>2</sub>Cl; R' = Na, SiMe<sub>3</sub>) as scaffolds for the synthesis of models of a silica bound monolayer of fluorescent or second order NLO active organic chromophores

A series of sodium cyclotetrasiloxanolates properly functionalized in the *para* position of the aromatic rings such as  $[4\text{-}RC_6H_4\text{Si}(\text{O})\text{ONa}]_4$  and the corresponding trimethylsiloxycyclotetrasiloxanes  $[4\text{-}RC_6H_4\text{Si}(\text{O})\text{OSiMe}_3]_4$  (R = Cl, Br,  $\text{CH}=\text{CH}_2$ , CH<sub>2</sub>Cl) have been prepared. The crystalline structures of some of them have been characterized by single crystal X-ray diffraction analysis at low temperature. All the compounds contain the aryl rings in an all *cis* arrangement respect to the oligosiloxane cycle and almost parallel among them.



#### Diána Lantos, María Contel, Sergio Sanz, Andrea Bodor, István T. Horváth

J. Organomet. Chem. 692 (2007) 1799

Vladimir Nesterov, Bhaskar Poola,

propan-2-ol]

Xiaoping Wang, Michael G. Richmond

J. Organomet. Chem. 692 (2007) 1806

Pincer ligand coordination at a triosmium

cluster: X-ray structures of 1,2-Os<sub>3</sub>(CO)<sub>10</sub>[4,6-

bis(diphenylphosphinomethyl)-m-xylene] and

1,2-Os<sub>3</sub>(CO)<sub>10</sub>[1-diphenylphosphino-1-{(2,4-

dimethyl-5-diphenylphosphinomethyl)phenyl}-

Homogeneous gold-catalyzed hydrosilylation of aldehydes

The catalytic hydrosilylation of aldehydes in the presence of PBu<sub>3</sub> modified Au(I)-complexes was investigated. In situ IR and NMR experiments have revealed that both, the ligand PBu<sub>3</sub> and the substrate aldehyde play an important role in stabilizing the gold catalyst and/or forming the catalytically active species. In their absence the reducing power of silane destabilizes the gold (I) catalyst giving rise to gold clusters or particles. Several side reactions involving water and oxygen were also investigated. A plausible reaction pathway as an alternative to the well-accepted mechanism for the transition-metal homogeneously catalyzed hydrosilylation of aldehydes has been proposed to accommodate the experimental observations

The reaction of the triosmium cluster  $1,2-Os_3-(CO)_{10}(MeCN)_2$  with the pincer ligand 4,6-bis-(diphenylphosphinomethyl)-*m*-xylene (dppx) furnishes the diphosphine-bridged clusters  $1,2-Os_3(CO)_{10}(dppx)$  (2) and  $1,2-Os_3(CO)_{10}[1-di$  $phenylphosphino-1-{(2,4-dimethyl-5-diphenyl$  $phosphinomethyl)phenyl}-propan-2-ol] (3) as$ the major and minor products, respectively.Both clusters have been structurally characterized, and the origin of the functionalized dppxligand in the minor product is traced to theethanol solvent that was used in the recrystallization of the parent diphosphine ligand.





# Raffaello Lazzaroni, Roberta Settambolo, Silvia Rocchiccioli, Giuditta Guazzelli

J. Organomet. Chem. 692 (2007) 1812

From chiral and prochiral *N*-allylpyrroles to stereodefined pyrrole fused architectures: A particular application of the rhodiumcatalyzed hydroformylation A short review is given on the rhodiumcatalyzed hydroformylation of chiral and prochiral *N*-allylpyrroles as a synthetic route to stereodefined 5,6-dihydro- and 5,6,7,8-tetrahydroindolizines. In the key step, the carbonyl group of a 4-pyrrolylbutanal, the *oxo* product, becomes the starting point for an intramolecular cyclization reaction generating the C8–C9 indolizine bond.



#### Attila Sisak, Erzsébet Halmos

J. Organomet. Chem. 692 (2007) 1817

Reactions of early–late heterobimetallics with oxiranes: New examples for cooperative reactivity

Cobalt-containing early-late heterobimetallic (ELHB) compounds react with oxiranes to give acyl-cobaltteracarbonyls. We have demonstrated that the ELHB compounds containing Group 4 metals and silyl-cobalttetracarbonyls exhibit analogous reactivity with oxiranes. The studied heterobimetallic systems mediated the rearrangement of monosubstituted oxiranes to ketones.



#### Tamás Kégl, Ferenc Ungváry

J. Organomet. Chem. 692 (2007) 1825

Internal carbon monoxide exchange and CO dissociation in cobalt carbonyl carbene complexes. A density functional study

Dicobalt-carbonyl mono- and biscarbene complexes have been investigated by the means of DFT calculations. Their structures, the intramolecular rearrangements and the dissociation of the carbonyl group are reported.

#### Tomoyuki Mochida, Fumiko Shimizu, Hirotaka Shimizu, Kazuya Okazawa, Fuminori Sato, Daisuke Kuwahara

J. Organomet. Chem. 692 (2007) 1834

Attila C. Bényei, Henrik Gulyás,

Yoshiki Ozawa, Kimihiro Kimura,

J. Organomet. Chem. 692 (2007) 1845

Molecular architecture of a water-soluble sulfonated phosphane with propeller chirality

Ferrocenylpyrazole-A versatile building block for hydrogen-bonded organometallic supramolecular assemblies

The crystal architectures of 5-ferrocenylpyrazole (FcPz) and its metal complexes were investigated. FcPz forms a zigzag onedimensional architecture via NH···N hydrogen bonds. The reaction of FcPz with metal salts provided metal-centered ferrocenyl clusters, which are joined via hydrogen bonds to form supramolecular chains in the crystal.

Koshiro Toriumi, Tamás Kégl, József Bakos X-ray structures of the tris(2,4-xylyl)phosphane and its trisulfonated derivative:

The structure of tris(2,4-xylyl)phosphane (1) is reported and supramolecular assembly of gua<sup>+</sup> salt of tris(2,4-dimethyl-5-sulfonatophenyl)phosphane co-crystal with guanidine chloride (2) is analyzed in detail. The high barrier of concerted ring rotation opens the possibility of resolving the enantiomers through hydrogen bonds to chiral donors.

In platinum-diphosphine complexes, the iodo-

## Tamás Kégl, László Kollár

J. Organomet. Chem. 692 (2007) 1852

Iodo-methyl ligand exchange reaction in platinum complexes: A density functional study

methyl ligand exchange reaction has been investigated by the means of gradientcorrected DFT calculations. The reaction energy profile, and the electronic structures of species involved in the reaction are reported.











#### Laura de Quadras, Jürgen Stahl, Fedor Zhuravlev, John A. Gladysz

J. Organomet. Chem. 692 (2007) 1859

Monophosphine and diphosphine ligands for diplatinum polyynediyl complexes: Efficient syntheses of new functionality-containing systems and model compounds A variety of oxygen- fluorine-, geminal dimethyl-, and alkene-containing monophosphines and diphosphines are prepared that are useful precursors to diplatinum polyynediyl complexes in which two flexible sp<sup>3</sup> chains span the termini. Model platinum complexes are also reported.





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