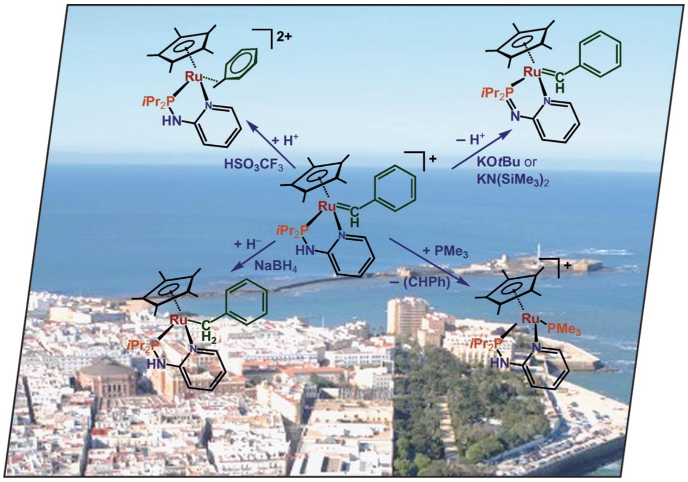
COVER PICTURE

The cover picture shows various reactions of the carbene complex $[Ru(\eta^5\text{-}C_5Me_5)\{\kappa^2\text{-P,N-P}i\text{Pr}_2NHC_5H_4N\}(=CHC_6H_5)]^+$ over a view of Cádiz (phoenician Gadir), one of the oldest european continuously inhabited cities. These processes illustrate its ambiphilic character. It reacts as a nucleophile with Brønsted acids, yielding a complex with an η^2-benzyl ligand. There are some previously described examples of this coordination mode for early transition metal benzylidene complexes, but this represents the first example of a structural characterization in the case of ruthenium complexes. The electrophilic behaviour of $[Ru(\eta^5\text{-}C_5Me_5)\{\kappa^2\text{-P,N-P}i\text{Pr}_2NHC_5H_4N\}(=CHC_6H_5)]^+$ has been shown by reaction with hydride, giving rise to an η^1-benzyl complex. Normally, NMR studies allow unambiguous characterization of the η^1 coordination of a benzyl ligand. However, especially for late transition metal complexes, distinction between the usually disregarded η^2 and the generally considered η^3 mode is difficult. We propose, from this study, that the presence of an η^2-benzyl ligand in metal complexes should not be ruled out only on the basis of their NMR spectra. The carbene complex also reacts with other bases like KO*t*Bu, $KN(SiMe_3)_2$ and PMe_3. Details are discussed in the article by I. Macías-Arce, M. C. Puerta and P. Valerga on p. 1767 ff.



CONTENTS

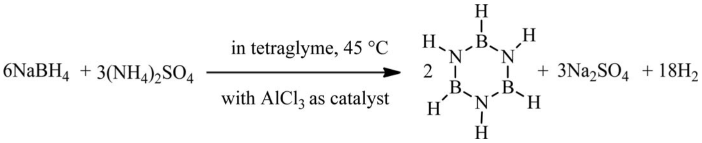
SHORT COMMUNICATION

Borazine

J.-s. Li,* C.-r. Zhang, B. Li,
F. Cao, S.-q. Wang 1763–1766

An Improved Synthesis of Borazine with Aluminum Chloride as Catalyst

Keywords: Boron / Heterocycles / Aluminum / Synthetic methods / Nitrides



Borazine is an excellent precursor for boron nitride. An improved synthesis procedure was disclosed, which involved the use of aluminum chloride as a catalyst in the reaction of sodium borohydride with ammonium sulfate. An improved yield of borazine was obtained in comparison to the reaction without a catalyst.

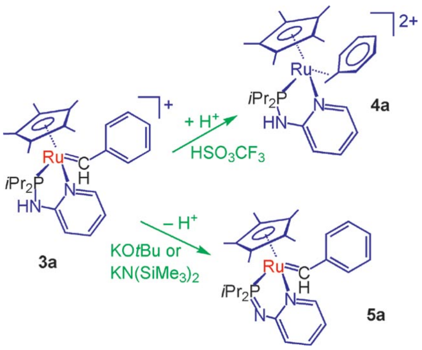
FULL PAPERS

Hybrid Ligand Ru Complexes

I. Macías-Arce, M. C. Puerta,*
P. Valerga* 1767–1776

Half-Sandwich Benzylidene Ruthenium Complexes Bearing Phosphanyl-Pyridine Ligands: Reactivity towards Nucleophiles and Electrophiles

Keywords: Carbenes / Ruthenium / Half-sandwich complexes / P,N ligands / β-Elimination



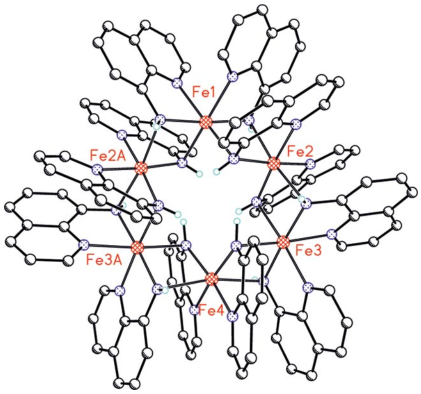
The synthesis and characterization of carbenes [Ru(η^5-C_5Me_5)(κ^2-*P*,*N*-P*i*Pr_2X-C_5H_4N)(=CHC_6H_5)][BAr′$_4$] (X = NH **3a**, S **3b**) that contain chelating hemilabile phosphanyl-pyridine ligands are reported. Compound **3a** shows ambiphilic character when reacting with Brønsted acids and hydride. Reaction of **3b** with $LiCH_3$ yields a 2-phenylethyl ruthenium complex stable towards β elimination.

Wheel-Like Magnetic Complexes

A. Malassa, C. Agthe,
H. Görls, M. Podewitz, L. Yu,
C. Herrmann, M. Reiher,*
M. Westerhausen* 1777–1790

Synthesis, Structures, and Magnetic Properties of *N*-Trialkylsilyl-8-amidoquinoline Complexes of Chromium, Manganese, Iron, and Cobalt as well as of Wheel-Like Hexanuclear Iron(II) and Manganese(II) Bis(8-amidoquinoline)

Keywords: Amides / Wheel structures / Chromium / Manganese / Cobalt / Iron / Magnetic properties

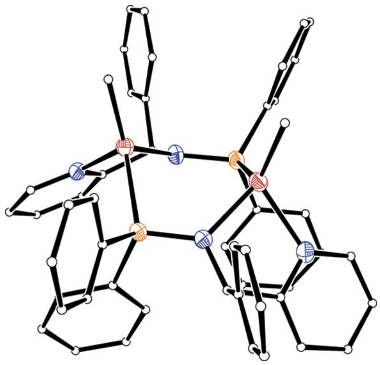


The 8-amidoquinoline complexes of Fe^{II} and Mn^{II} form hexanuclear wheels. Surprisingly, the magnetic properties differ: the Fe^{II} complex is ferromagnetic, whereas the Mn^{II} wheel shows an antiferromagnetic coupling. In contrast to these cage compounds, the Co^{II} complex is a mononuclear compound.

(2-Pyridylmethyl)amide Anions

D. Olbert, H. Görls, D. Conrad, M. Westerhausen* 1791–1797

Coordination Behavior of the (Diphenylphosphanyl)[α-(2-pyridyl)benzyl]amide Anion toward Lithium and Zinc Cations



(2-Pyridylmethyl)amide anions act as bidentate chelate ligands. *N*-(Diphenylphosphanyl) substitution extends the coordination behavior. The hard lithium cation exclusively binds to the nitrogen donors, whereas methylzinc (diphenylphosphanyl)-(2-pyridylmethyl)amide dimerizes through bridging amide and phosphanyl moities (Zn red, P orange, N blue; C hollow spheres; H omitted).

Keywords: Pyridylmethylamines / Lithium / Zinc / Metalation reactions / C–C coupling reactions

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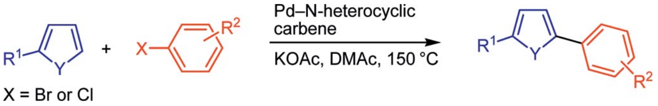
Pd–N-Heterocyclic Carbenes

I. Ozdemir,* Y. Gök, Ö. Özeroğlu, M. Kaloğlu, H. Doucet,* C. Bruneau 1798–1805

N-Heterocyclic Carbenes: Useful Ligands for the Palladium-Catalysed Direct C5 Arylation of Heteroaromatics with Aryl Bromides or Electron-Deficient Aryl Chlorides



N-Heterocyclic carbene ligands attached to palladium generate useful catalyst precursors for the direct arylation of heteroaromatics by using challenging aryl halides such as deactivated or congested aryl bromides and also activated aryl chlorides.

Keywords: Aryl halides / Atom economy / C–H activation / Carbenes / Heteroaromatics / Palladium

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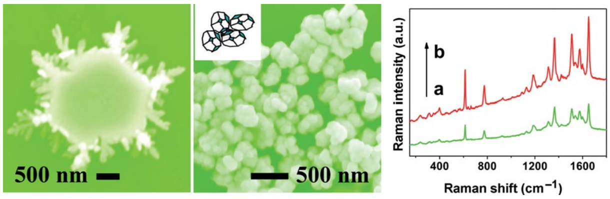
Silver Nanoparticles

X. Li, J. Wang, Y. Zhang, M. Li, J. Liu* 1806–1812

Surfactantless Synthesis and the Surface-Enhanced Raman Spectra and Catalytic Activity of Differently Shaped Silver Nanomaterials



The transition of shape-selective silver nanostructures from nanoplates to nanodendrites and to nanospheres made up of primary nanoparticles can be controlled by changing the molar ratio of vitamin C to $AgNO_3$ with a range of about 800. Compared with the other Ag nanomaterials presented here, the nanospheres show excellent surface-enhanced effects and catalytic activity.

Keywords: Silver / Nanostructures / Raman spectroscopy / Catalytic activity

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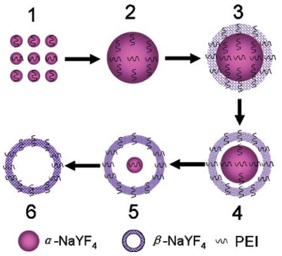
Hollow Nanosphere Synthesis

J. Zhao, X. Liu, D. Cui, Y. Sun, Y. Yu, Y. Yang, C. Du, Y. Wang, K. Song, K. Liu, S. Lu, X. Kong,* H. Zhang* 1813–1819

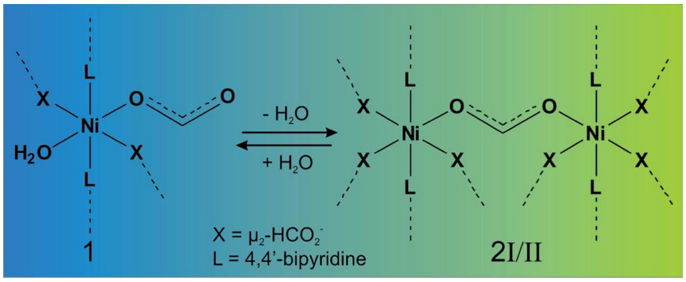
A Facile Approach to Fabrication of Hexagonal-Phase $NaYF_4$:Yb^{3+}, Er^{3+} Hollow Nanospheres: Formation Mechanism and Upconversion Luminescence



A hydrothermal route has been developed for preparation of $NaYF_4$ hollow nanospheres (HNS) with PEI as a surfactant. The formation is related to the localised Ostwald ripening mechanism. The obtained $NaYF_4$: 20 mol-% Yb^{3+}, 2 mol-% Er^{3+} HNS have excellent porous properties and demonstrate superior upconversion luminescence.

Keywords: Hydrothermal synthesis / Rare earths / Crystal growth / Polymers / Luminescence / Ostwald ripening

Polymorphic Modifications



J. Boeckmann, M. Wriedt, C. Näther* 1820–1828

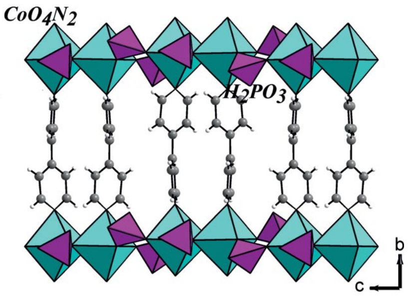
Thermal Decomposition Reactions as a Tool for the Synthesis of New Thermodynamic Metastable Modifications: Synthesis, Structures, and Properties of (Formato)nickel(II) Coordination Polymers Based on 4,4′-Bipyridine

Keywords: Coordination polymers / Transition metals / Crystal structures / Thermal properties / Magnetic properties / Solid-state structures

Two new polymorphic modifications **2I** and **2II** based on nickel(II) formate and 4,4′-bipyridine were prepared and investigated. On heating, the light blue, hydrated compound **1** transformed into the light green, metastable anhydrous intermediate **2II**, which transformed on further heating into the thermodynamic stable modification **2I**. Their magnetic properties are different.

Transition-Metal Phosphites

Open-framework transition-metal phosphite compounds have been prepared by using solvothermal methods, and all compounds were fully characterized. The figure shows the structure of a two-dimensional cobalt phosphite structure.



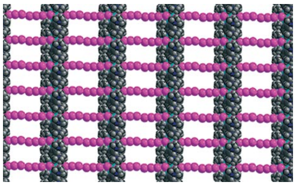
P. Ramaswamy, S. Mandal, N. N. Hegde, R. Prabhu, D. Banerjee, S. V. Bhat, S. Natarajan* 1829–1838

Synthesis, Structure, and Magnetic Properties of Amine-Templated Transition-Metal Phosphites

Keywords: Solvothermal synthesis / X-ray diffraction / Transition metals / Phosphorus / Open frameworks

Metastable Semiconductors

Coordination polymers hane been formed as intermediates in the course of oxidation of dinuclear Cu^I complexes featuring bridging, redoxactive guanidine ligands.

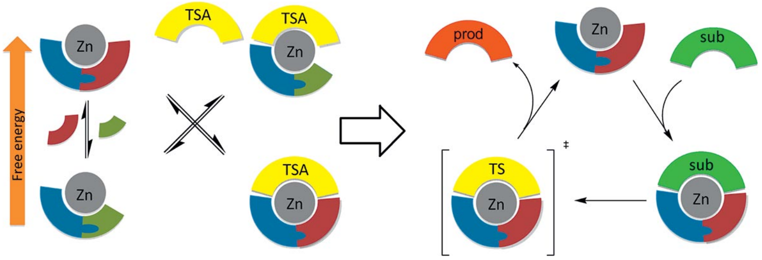


D. Emeljanenko, A. Peters, N. Wagner, J. Beck, E. Kaifer, H.-J. Himmel* 1839–1846

Successive Ligand and Metal Oxidation: Redox Reactions Involving Binuclear Cu^I Complexes of Chelating Guanidine Ligands

Keywords: Binuclear complex / Oxidation / Copper / Guanidine / Semiconductors / Redox chemistry

Catalyst Evolution



M. Matsumoto, D. Estes, K. M. Nicholas* 1847–1852

Evolution of Metal Complex-Catalysts by Dynamic Templating with Transition State Analogs

Keywords: Catalyst evolution / Templating / Transition state analogs / Zinc catalysts / Ester hydrolysis

Sets of equilibrating (imine)Zn complexes respond differentially to templating with coordinating hydrolytic transition state analogs. The LZn species amplified by the *pro*-TSA is the most active catalyst for ester hydrolysis.

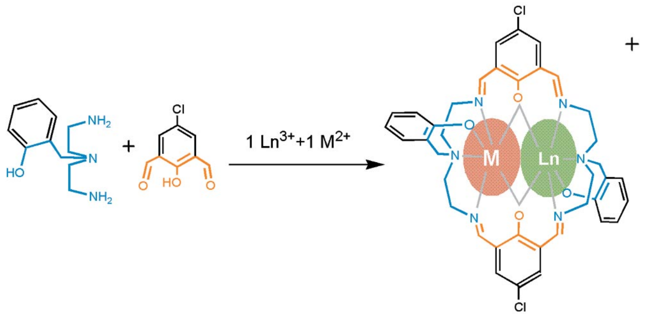
CONTENTS

Dinuclear Ln Complexes

S. Tamburini,* V. Peruzzo, F. Benetollo, P. A. Vigato 1853–1864

💻 f,f Homodinuclear and d,f or f,f′ Heterodinuclear Complexes with a [2+2] Macrocyclic Compartmental Schiff Base

Keywords: Lanthanides / Schiff bases / Macrocycles / Heteronuclear complexes



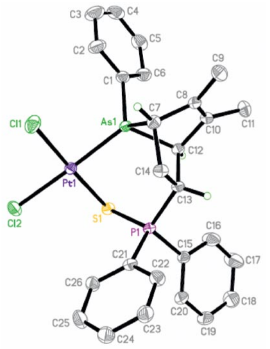
A [2+2] symmetric compartmental macrocycle bearing two -$CH_2C_6H_4OH$ pendant arms and the related d,f heterodinuclear, f,f homodinuclear, and f,f′ heterodinuclear complexes were obtained through a template or step-by-step procedure. Their properties were investigated in the solid state and in solution.

Chiral Arsane Ligand

M. Ma, S. A. Pullarkat, Y. Li, P.-H. Leung* 1865–1871

Metal Effects on the Asymmetric Synthesis of a New Heterobidentate As/P=S Ligand

Keywords: As ligands / P ligands / S ligands / Palladium / Platinum / Asymmetric synthesis / Cycloaddition



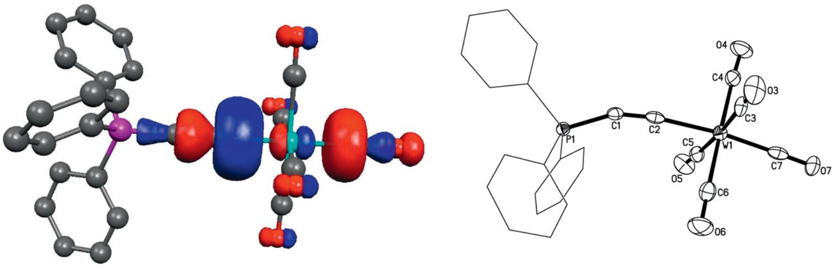
A chiral Pt complex has been successfully applied to the resolution of a new chiral bidentate As/P=S hemilabile ligand via the asymmetric cycloaddition reaction between 3,4-dimethyl-1-phenylarsole and diphenylvinylphosphane sulfide. The difference in reactivity and ease of resolution as compared to the palladium analogue was studied.

Tungsten Phosphonioacetylides

W. Petz,* B. Neumüller,* R. Tonner* 1872–1880

💻 Reaction of Double Ylide $C(PPh_3)_2$ with $[W(CO)_6]$ – Crystal Structures of $[(CO)_5W(CCPPh_3)]$ and $[(CO)_5W\{\eta^1\text{-}O_2C_2(PPh_3)_2\}]$ and Bonding Analyses of $[TM(CCPR_3)]$ Compounds

Keywords: Tungsten / Carbodiphosphorane / Structure elucidation / Carbonyl ligands / Density functional calculations



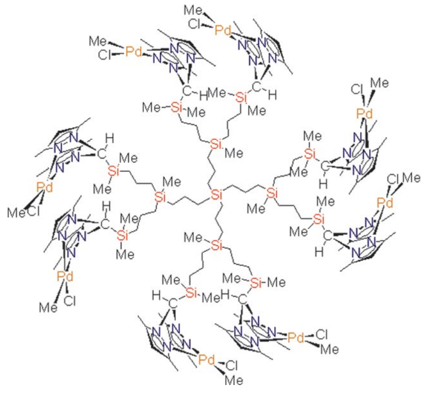
The tungsten phosphonioacetylide complex $[(CO)_5W(CCPPh_3)]$ is one of the reaction products of $C(PPh_3)_2$ and $[W(CO)_6]$, and its structure is confirmed by an X-ray diffraction analysis. Theoretical studies on bonding analyses of $[TM(CCPPh_3)]$ (TM: transition metal) complexes are presented.

Dendritic Metal Complexes

A. Sánchez-Méndez, E. de Jesús,* J. C. Flores,* P. Gómez-Sal 1881–1887

[Bis(pyrazolyl)methane]palladium Complexes with a Carbosilane Dendritic Structure

Keywords: Dendrimers / N ligands / Palladium / Heck reaction / Heterocycles



Discrete and dendritic (scorpionato)Pd^{II} complexes have been synthesized, overcoming the steric and solubility issues that previously limited the synthesis of polymetallic dendrimers containing poly(pyrazolyl)methane complexes.

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* Author to whom correspondence should be addressed.

💻 Supporting information on the WWW (see article for access details).