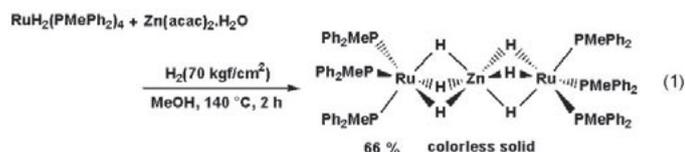


were prepared in good yield from the reaction of $\text{Ru}(\text{acac})_3$ and the corresponding phosphine under dihydrogen in the presence of excess zinc. When MePPh_2 was employed as a phosphine, an analogous trinuclear complex $[(\text{MePPh}_2)_3\text{Ru}(\mu\text{-H})_3]_2\text{Zn}$ was prepared only in 17% yield and could not be isolated in a pure state. We therefore looked for a new general procedure for the synthesis of this type of complexes and we could develop a new procedure. The reaction of $\text{RuH}_2(\text{MePPh}_2)_4$ and an excess of $\text{Zn}(\text{acac})_2 \cdot \text{H}_2\text{O}$ under dihydrogen gave the $[(\text{MePPh}_2)_3\text{Ru}(\mu\text{-H})_3]_2\text{Zn}$ in 66% isolated yield (eq. 1). We herein report the synthesis, characterization, structure, and catalytic activity of heterometallic hydride complexes, $[(\text{L})_3\text{Ru}(\mu\text{-H})_3]_2\text{Zn}$.



Keywords: cluster compounds, ruthenium zinc hydride compounds, catalytic hydrogenation

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Syntheses, characterization and DFT investigations of iridium complexes and diprotonated terpyridines

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Terpyridine complexes in the form of $[\text{IrCl}(\text{L})(\text{terpy})](\text{PF}_6)_2$ and $[\text{IrCl}(\text{L})(\text{tterpy})](\text{PF}_6)_2$ were prepared (L = bipyridine derivatives, terpy = 2,2':6',2''-terpyridine, tterpy = 4''-(4-tolyl)-2,2':6',2''-terpyridine). They were characterized by ESI-MS spectrometry, UV-vis spectroscopy, and cyclic voltammetry (CV). The electronic properties of some complexes were studied by using the B3LYP functional calculations and their optimized geometries were discussed in comparison with those of the experimentally observed ones. The ground and the excited triplet states were also examined by using density-functional-theory (DFT). A series of metal-free new blue emissive compounds of the type $[\text{terpyH}_2]\text{Cl} \cdot \text{PF}_6$, $[\text{tterpyH}_2]\text{Cl} \cdot \text{PF}_6$, $[\text{ClterpyH}_2]\text{Cl} \cdot \text{PF}_6$, and $[\text{BterpyH}_2](\text{PF}_6)_2$ (Clterpy = 4''-chloro-2,2':6',2''-terpyridine and Bterpy = 4,4''-tert-butyl-2,2':6',2''-terpyridine) were also prepared and characterized by electrospray ionization mass spectrometry, UV-vis spectroscopy, and CV. The $\pi\text{-}\pi^*$ bands in the UV region for the diprotonated ligands in acetonitrile were red-shifted relative to those of the corresponding neutral ligands. The CVs for all of the diprotonated ligands showed the first reduction wave at around -0.6 V, being more positive than those of the neutral ligands. The DFT approach was used to interpret remarkably large proton affinity of the terpy ligand.

Keywords: terpyridine, proton affinity, DFT calculation

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Iridium and zirconium formamidinates as precursors for novel stable carbenes

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Amidines are bidentate nitrogen ligands displaying a rich coordination chemistry towards main group and transition elements. These ligands have been extensively used for the stabilization of multiple bonded transition metal moieties and as components in catalytic systems, and an extensive body of work is available on the subject. The formamidinate skeleton is also a fragment of the imidazolium precursors for the well-known N-heterocyclic carbenes, and in this case the backbone closing the heterocyclic ring has always been a main group fragment, most frequently carbon. A combination of the two fields of research for the purpose of synthesizing N-heterocyclic carbenes with transition metal backbones is an appealing target, because the transition metal backbone is expected to impart superior σ -donating and π -accepting properties to the carbene ligand. The crystal structural of the following Ir/Zr formamidinates that are potential precursors to N-heterocyclic carbenes with Ir/Zr backbones will be presented: (1) $\text{C}_{29}\text{H}_{34}\text{N}_2\text{O}_{0.25}\text{Zr}$, FW = 505.80, triclinic, *P*-1, $a = 8.128(1)$, $b = 11.515(2)$, $c = 28.177(6)$ Å, $\alpha = 86.880(8)$, $\beta = 85.367(10)$, $\gamma = 72.953(11)^\circ$, $V = 2511.8(8)$ Å³, $Z = 4$, $R = 0.046$. (2) $\text{C}_{58}\text{H}_{64}\text{BfIrN}_3\text{O}_{0.5}$, FW = 1014.13, triclinic, *P*-1, $a = 12.086(3)$, $b = 13.590(2)$, $c = 15.939(4)$ Å, $\alpha = 85.705(13)$, $\beta = 72.829(9)$, $\gamma = 89.110(14)^\circ$, $V = 2494.2(10)$ Å³, $Z = 2$, $R = 0.037$. (3) $\text{C}_{56}\text{H}_{59}\text{BfIrN}_3 \cdot 2 \text{CH}_2\text{Cl}_2$, FW = 1146.92, triclinic, *P*-1, $a = 12.625(3)$, $b = 12.948(4)$, $c = 17.065(3)$ Å, $\alpha = 97.194(15)$, $\beta = 98.857(15)$, $\gamma = 110.250(11)^\circ$, $V = 2537.6(11)$ Å³, $Z = 2$, $R = 0.039$.

Keywords: chelates, iridium compounds, zirconium compounds

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Synthesis and characterization of an N-heterocyclic carbene palladium-based complex

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A number of simple N-heterocyclic carbene (NHC) palladium-based complexes have recently emerged as effective catalysts for a variety of cross-coupling reactions [1]. Also some of the NHC ligands have proved to be particularly useful in olefin metathesis reactions [2]. Based on these findings and our continuing interest in developing more efficient and stable catalysts, we now report the straightforward preparation of the title type complex and its structural and spectroscopic characterization. The Pd atom lies on a center of inversion and is coordinated by two chloride anions and two C atoms from two carbene ligands and the ligands are therefore arranged in a trans-geometry. The Cl-Pd-C angles are $91.31(7)^\circ$ and $88.69(7)^\circ$, and the Cl-Pd-Cl' and C-Pd-C' angles are precisely 180° [symmetry

code: (i) $-x+1, -y+1, -z$]. These structural parameters imply a perfect square-planar geometry around the palladium centre. The Pd-Cl and Pd-C lengths are 2.3052(9) Å and 2.035(2) Å, respectively. These bond lengths are comparable to those observed in literature [3]. In addition, the Pd-Cl bond in the complex is somewhat shorter than the average of 2.33(4) Å calculated for 2151 Pd-Cl lengths in 1306 complexes reported to the Cambridge Structural Database [4,5]. The Pd-Cl lengths in these 1252 complexes span the range 2.222-2.516 Å; therefore, the Pd-Cl separation in the investigated complex is within the expected range. The equivalent Pd-C lengths are consistent with Pd-C single bonds [3].

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Keywords: N-heterocyclic carbenes, palladium, crystal structure

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Structural studies on Ag(I) N-heterocyclic carbene complexes: From monomers to polymers

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N heterocyclic carbenes (NHCs) have shown to equal, if not exceed, phosphines in their ability to bind to many transition metal complexes. Due to this bonding strength, the synthesis of NHC complexes for catalytic applications has received a great deal of interest. Ag(I) carbene complexes are good carbene transfer agents for the synthesis of Ni, Pd, Pt, Cu, Au, Rh, Ir and Ru carbene complexes. A revision of the literature shows that N heterocyclic carbene complexes of silver are able to generate very complex bonding motifs in the solid state, especially with halide anions.[1] In the course of our current studies on group 10 NHC catalysts, we have prepared a series of Ag(I) N-heterocyclic carbenes (NHCs) by reaction of the corresponding N,N disubstituted imidazolium salts with silver oxide in dichloromethane. These carbenes, of general formula (NHC)AgBr, differ in the substituents at the nitrogen atoms. In this report, we will compare three different molecular structures, determined by X ray diffraction methods, of (NHC)AgBr complexes bearing, at the nitrogen atoms, two benzyl groups (1), a benzyl and a mesityl group (2), or two first generation poly(benzyl ether) dendrons (3). Complex 1 is monomeric with an NHC-Ag-Br angle close to the linearity and a Ag – Br distance of 2.51 Å. Complex 2 consists of a dimeric structure, with an asymmetrical bridge and a NHC-Ag-Br angle of 135 deg and Ag – Br distances of 2.61 to 2.77 Å. Complex 3 has an unprecedented polymeric structure constituted by a zigzag chain of alternating silver and bromo atoms (Ag – Br distance = 2.66 Å) with pending carbene ligands coordinated to the Ag centers (NHC-Ag-Br angle of 129.1 deg).

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Keywords: silver compounds, polymer structure, dendrimers

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Structural analysis of the rare earth metal hydride complexes

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Rare earth metal hydride complexes are fundamental components in a wide range of stoichiometric and catalytic reactions. Heterometallic Mo-Y₄ hydride complex can be proceeded hydrogen addition reaction without degradation of a single crystal form. Moreover, it is thought to exist lattice H₂ in the Mo-Y₄ crystal lattice. In order to clarify the mechanism of the hydrogen addition reaction the determination of the position of lattice H₂ in the crystal lattice is studied by the precise charge density study of Mo-Y₄ complex in SPring-8. The crystals had to be encapsulated in the glass capillary due to the volatile solvent, toluene, being unstable in air, and being exposed in hydrogen gas. Single crystal X-ray diffraction measurements in as high counting statistics as possible were carried out by imaging plate detector to ensure data accuracy in the maximum-entropy method (MEM) analysis. The determined lattice structures are monoclinic $P2_1/n$, $a = 13.25 \text{ \AA}^3$, $b = 30.41 \text{ \AA}^3$, $c = 18.11 \text{ \AA}^3$, $\beta = 91.9^\circ$ (without hydrogen gas) and $a = 13.27 \text{ \AA}^3$, $b = 30.79 \text{ \AA}^3$, $c = 17.84 \text{ \AA}^3$, $\beta = 92.3^\circ$ (under hydrogen gas exposure). The reliability factors of structure refinement by SHELXL were $R = 4.80 \%$ ($R_{\text{free}} = 4.82 \%$) and $R = 6.59 \%$ ($R_{\text{free}} = 7.22 \%$), respectively. By the MEM charge density, the hydride ligands are clearly identified and the mechanism of the hydrogen addition reaction will be described with a help of the further advanced technique, that is, the MEM electrostatic potential imaging

Keywords: crystallographic analysis, maximum entropy method, metal-hydrogen interactions

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Structural challenges of giant bismuth oxo-diketonate clusters

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New method for the preparation of polymetallic oxo-diketonates has been developed. Fluorinated bis(gem-diol), 1,1,1,5,5,5-hexafluoropentane-2,2,4,4-tetraol, can be obtained by hydration of hexafluoroacetylacetone (Hhfac). We have shown that in the presence of proton acceptor the tetraol is capable to act as a controlled source of both diketonate and oxo-groups by undergoing a facile cleavage of the two C-O bonds. The first bismuth oxo-diketonate, Bi₉O₇(hfac)₁₃, has been obtained in quantitative yield using triphenylbismuth as a starting material in reaction with tetraol. The structure of the bismuth oxo-diketonate features metal atoms in two distinctly different chemical and coordination environments: the [Bi₆O₇] central oxo-core and three Bi(hfac)_x arms attached to its periphery. In coordinating solvents, this molecule irreversibly dissociates to give Bi(hfac)₃ and high-nuclearity bismuth oxo-diketonates. A giant oxo-cluster [Bi₃₈O₄₅(hfac)₂₄] has been isolated and fully characterized. Its [Bi₃₈O₄₅]²⁴⁺ core capped by 24 diketonate ligands, has a size larger than 2 nm and may serve as a model for