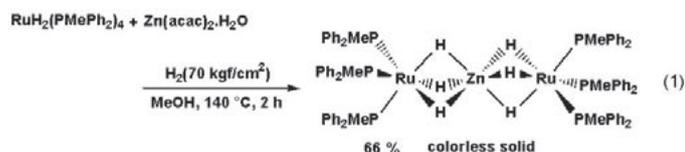


were prepared in good yield from the reaction of $\text{Ru}(\text{acac})_3$ and the corresponding phosphine under dihydrogen in the presence of excess zinc. When MePPh_2 was employed as a phosphine, an analogous trinuclear complex $[(\text{MePPh}_2)_3\text{Ru}(\mu\text{-H})_3]_2\text{Zn}$ was prepared 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