

Abstract

In this work some heteroarylsubstituted alkenol-ligands (N,O-ligands) have been used to synthesize new homo- and heteroleptic palladium- ($[\text{Pd}(\text{N},\text{O})_2]$, $[\text{Pd}(\text{Allyl})(\text{N},\text{O})]$), platinum- ($[\text{Pt}(\text{N},\text{O})(\text{CH}_3)(\text{DMSO})]$), gold- ($[\text{Au}(\text{N},\text{O})(\text{CH}_3)_2]$), and aluminium-complexes ($[\text{Al}(\text{N},\text{O})_3]$, $[\text{MeAl}(\text{N},\text{O})_2]$). The various possible coordination sites of the heterocycles in the N,O-ligands was in the focus of this work. It was found that in all synthesized compounds the ligands coordinate to the metal center through the enolate-oxygen as well as the lewis-basic nitrogen of the heterocycles, regardless of the additional oxygen-, nitrogen or sulfur atom present in the heterocycles. All compounds have been thoroughly investigated by multinuclear NMR analyses in solution and single-crystal X-ray diffraction analyses in the solid-state. Supplementary EI-MS measurements have been conducted to examine the fragmentation of the compounds in the gas-phase.

The perfluoroalkyl groups of the N,O-ligands ensure an adequate thermal stability and a high volatility of the complexes, which is significantly influenced by the chain length of the perfluoroalkyl groups. Especially the synthesized heteroleptic allyl-alkenolate-palladium complexes ($[\text{Pd}(\text{allyl})(\text{N},\text{O})]$) as well as the dimethyl-alkenolate-gold complexes ($[\text{Au}(\text{N},\text{O})(\text{CH}_3)_2]$) show an outstanding volatility which makes them interesting precursors for the application in chemical vapor deposition-techniques.

These compounds have been applied and the parameters optimized in the material synthesis of elemental noble metal films *via* thermal and PECVD-methods. The thereby gained findings were employed in the deposition of palladium-particles on porous carbonized wood substrates (BioC) which then, in the scope of more sustainable syntheses, were used as recyclable heterogeneous catalysts in C-C-coupling reactions (*Heck-Mizoroki*- and *Suzuki-Miyaura*-reaction). These investigations showed that particularly the *via* PECVD-methods coated Pd@BioC catalysts are easily recycled and 30 successive catalytic cycles in the *Suzuki-Miyaura*-reaction were catalyzed with excellent conversion rates.

The conversion of the various N,O-ligands with $[\text{AlMe}_3]$ and $[\text{Al}(\text{O}^t\text{Bu})_3]_2$ showed the different reactivity of the ligands, whereby homoleptic octahedral $[\text{Al}(\text{N},\text{O})_3]$, hetero-

leptic $[\text{MeAl}(\text{N},\text{O})_2]$ as well as heteroleptic $[\text{Al}(\text{N},\text{O})(\text{O}^t\text{Bu})_2]_2$ compounds could be synthesized. Additionally the gas phase structures as well as possible fragmentation mechanisms of some of the aluminium complexes could be elucidated by a combination of IRMPD-spectroscopy and computational modelling.