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Certificate

Mr. Christian KNOLL

(Vienna University of Technology)

This is to certify that you presented in
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CNC-Tetrazolylidene Complexes Of Group 8 Metals

Christian Knoll^a, Danny Müller^a, Gerald Giester^b, Peter Weinberger^a

^a Institute of Applied Synthetic Chemistry, Vienna University of Technology, Getreidemarkt 9/163-AC, A-1060 Vienna, Austria

^b Institute of Mineralogy and Crystallography, University of Vienna, Althanstr. 14, 1090 Vienna, Austria

E-mail: christian.knoll@tuwien.ac.at

Introduction:

The variety of CNC-ligands used in reactivity and structural studies is very ample. Nevertheless, the examples dealing with carbene complexes of substituted 1*H*-tetrazoles are rather scarce.^[1] In the present study, we present a dual experimental and theoretical approach on the investigation of group 8 metal CNC complexes of 1,1'-(4-*t*-butyl-pyridyl)-4-methyl-tetrazol-5-ylidene (tBuPy(MeTz)₂) and of 1,1'-(4-*t*-butyl-pyridyl)-4-ethyl-tetrazol-5-ylidene (tBuPy(EtTz)₂) with focus on their structural properties and further reactivity.



Fig. 1/2: Calculated structures of different Fe-CNC-tetrazolyl-pyridine complexes

Due to the insolubility of the attempted 2,6-bis(tetrazol-1-yl)pyridine-fragment (Fig.3), a *t*-Bu substituted pyridine ligand system was used to enhance solubility. In figure 3 the synthetic pathway of the ligands is illustrated.

Synthesis of the ligands:

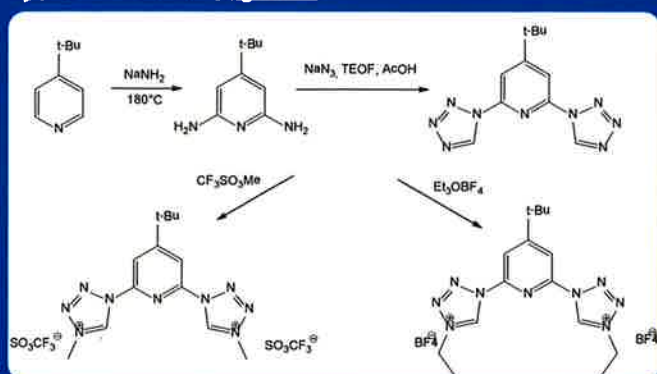


Fig. 3: Reaction scheme of the ligand synthesis

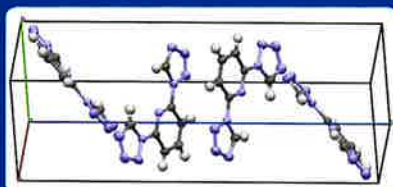


Fig. 4a,b: Single crystal X-ray diffraction structure of 2,6-bis(1*H*-tetrazolyl)pyridine

Synthesis of the complexes:

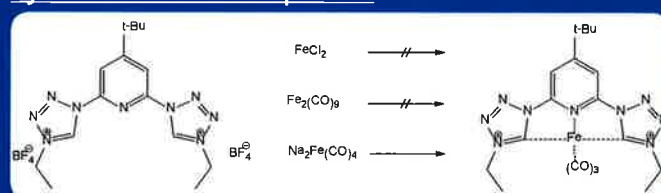


Fig. 5: Reaction scheme of the complex synthesis

Methods of characterization:

The compounds were analyzed using ¹H-NMR, ¹³C-NMR, ATR mid-range-FTIR, powder X-ray diffraction and single-crystal X-ray diffraction.

For qualitative interpretation of the IR spectra of the compounds also DFT optimisation followed by frequency analysis with Gaussian 09 was performed. Level of theory: DFT B3LYP, Basis set: 6-311++g(d,p) for the ligands and SDD for the complexes.

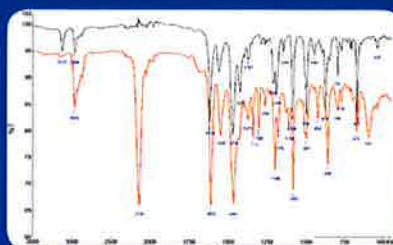


Fig. 6: comparison of measured IR spectra of 4-(*t*-Bu)-2,6-di(1*H*-tetrazol-1-yl)pyridine (black) and the complex of 4-(*t*-Bu)-2,6-di(4-ethyl-1*H*-tetrazol-1-yl)(BF₄) + Na₂Fe(CO)₄ (red)



Fig. 7: calculated IR spectrum of cationic 4-(*t*-Bu)-2,6-di(4-ethyl-1*H*-tetrazol-1-yl)pyridine



Fig. 8: calculated IR spectrum of 4-(*t*-Bu)-2,6-di(1*H*-tetrazol-1-yl)pyridine

The strong vibrational mode at 2136 cm⁻¹ in the red spectrum above is the CO-band of the iron CO₃ complex.

Conclusion:

We demonstrated the successful synthesis of tetrazole containing pyridine CNC carbene ligands and the complexation with Iron. The insertion of a *t*-Bu group in 4 position at the pyridine ring avoided solubility issues of the complexes, which prevented any reaction.

Outlook:

Further synthesis of Iron and Ruthenium complexes will be carried out for testing of possible catalytic activity of hydride complexes for transfer hydrogenation reactions. Additionally we will study the influence of the tetrazolyl group via comparison to other complexes with similar motifs.

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