A Spectroscopic Investigation of Low-Coordinate, Phosphanylphosphido Iron Complexes

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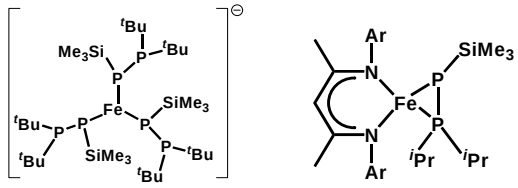
Introduction

Coordinatively unsaturated iron compounds are of great interest not only because they exhibit unusual magnetic properties but also because they function as structural model complexes of technologically important enzymes such as nitrogenases and hydrogenases. Consequently, the study of these complexes might lead to greater insights in the reaction mechanisms of these enzymes. We have focused our efforts on synthesizing novel low-valent phosphorous compounds, in particular nucleophilic phosphanylphosphinidenes and phosphanylphosphides.[1] Up to date the synthesis of low-coordinate iron(II) complexes relied on using sterically demanding ligands such as β-diketiminates.[2,3] Therefore, to stabilize the phosphanylphosphido complexes **2**, we used as starting material a β-diketiminate complex of iron(II) which we reacted with lithiated diphosphanes R_2P-P($SiMe_3$)Li (R= *t*Bu, *i*Pr). Interestingly, the presence of a diphosphane excess leads to the formation of the homoleptic complex **1** through an unprecedented elimination of the β-diketiminate ligand.



Scheme 1. Drawings of the molecular structure of the homoleptic (**1**) and heteroleptic (**2**) phosphanyl-phosphido complexes under investigation.

Experimental

In order to investigate the electronic structure of complexes **1** - **2** we have recorded a series of field- and temperature-dependent ^{57}Fe Mössbauer spectra using constant acceleration spectrometer outfitted with a 8 T superconducting magnet available at the EMR facility of NHFML.

Results and Discussion

Analysis of the ^{57}Fe Mössbauer spectra recorded for ground solid samples of **1** and **2** demonstrates that the iron sites of these complexes adopt a +2 oxidation state and a high-spin electronic configuration. Moreover, the investigation of the field-dependent behavior of these spectra indicates that while the quintet ground state of **1** can be well described by a rhombic zero-field splitting (ZFS) tensor, the ZFS tensor describing the fine structure of **2**'s ground state is rather axial**.**

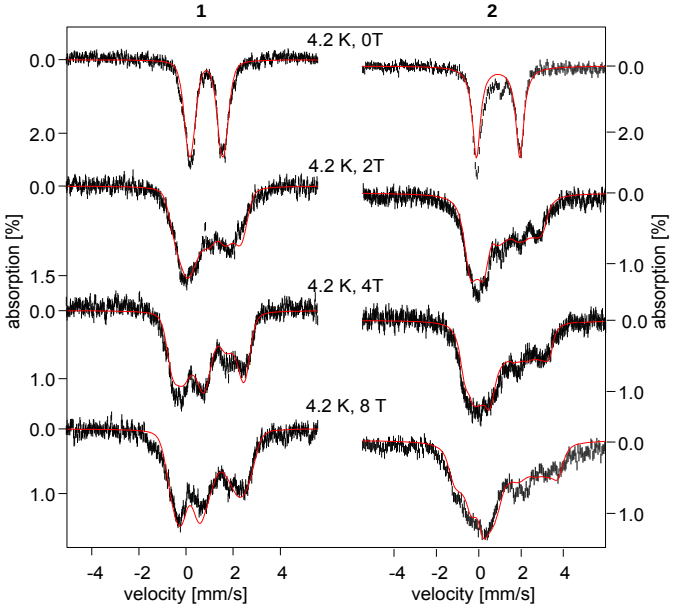


Fig 1. Variable-field ^{57}Fe Mössbauer spectra recorded at 4.2 K for **1** (*left*) and **2** (*right*). The solid red lines are simulations obtained using an *S* = 2 spin-Hamiltonian.

Conclusions

The iron(II) sites of **1** and **2** are found to adopt a high-spin electronic configuration that lacks the large unquenched orbital momenta observed for similar compounds.

Acknowledgements

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References

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