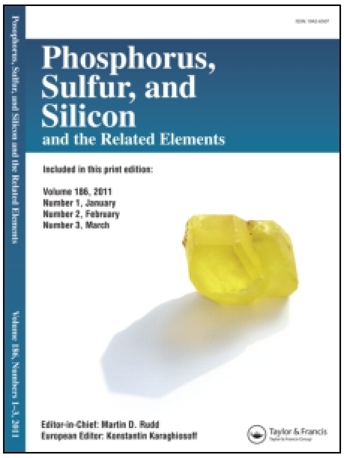

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NH-Phosphanylamido- and PH-Phosphoraneiminato Transition-Metal Complexes: Syntheses, Structures and Computational Studies

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NH-PHOSPHANYLAMIDO- AND PH-PHOSPHORANEIMINATO TRANSITION-METAL COMPLEXES: SYNTHESES, STRUCTURES AND COMPUTATIONAL STUDIES

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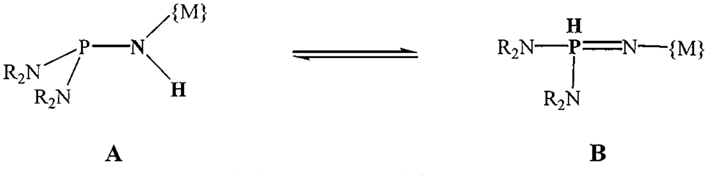
Within our investigations on phosphazene chemistry, we report about systematic studies of reactions of $(R_2N)_2PNH_2$ with several group IV (Ti, Zr, Hf) transition-metal halides [M]—Cl ([M] = Cp_2MCl, $CpMCl_2$, MCl_3), leading to $(R_2N)_2PN(H)[M]$ and $(R_2N)_2P(H)N[M]$, respectively. These experiments demonstrate the great influence of electronic effects of the metal fragment on the equilibrium between the (NH)-phosphanylamido- (**A**) and the tautomeric (PH)-phosphoraneiminato form (**B**).



SCHEME 1

A stronger Lewis-acidic character of the metal center stabilizes the PH-form. Computational studies on high DFT-level unambiguously confirm the experimental results.[1]

Furthermore, complexes **A** can be used as precursors for the generation of the first phosphaneiminato transition-metal complexes of the type $(R_2N)PN[M]$.

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[1] M. Raab, A. Sundermann, G. Schick, A. Loew, M. Nieger, W. W. Schoeller, and E. Niecke, *Organometallics*, **19,** 2616 (2001).