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

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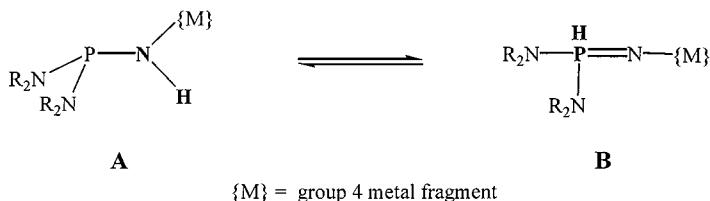
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## NH-PHOSPHANYLAMIDO- AND PH-PHOSPHORANEIMINATO TRANSITION-METAL COMPLEXES: SYNTHESSES, STRUCTURES AND COMPUTATIONAL STUDIES

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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.<sup>1</sup>

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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