Lewis Acid Catalyzed Z to E Isomerization of 1,2-Bis(diphenylphosphino)ethene

Marcus Sigl, Annette Schier, Hubert Schmidbaur*

Anorganisch-chemisches Institut der Technischen Universität München, Lichtenbergstrasse 4, D-85747 Garching, Germany

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Z-1,2-Bis(diphenylphosphino)ethene, cis-Ph₂PCH=CHPPh₂, forms 1:2 adducts with GaBr₃ and GaI₃, the former of which has been identified in an X-ray diffraction study as the complex of the isomerized ligand, E-Ph₂PCH=CHPPh₂. The GaI₃ complex is believed to be analogous on the basis of analytical and spectroscopic data. InBr₃ affords a 1:1 complex with an ionic structure [(Ph₂PCH=CHPPh₂)₂InBr₃]⁺ [InBr₄]⁻ in which the cation contains the original cis-ligand. With InI₃ also a 1:1 adduct is obtained, where the metal triiodide unit is attached to only one phosphorus atom of the non-isomerized (cis) ligand in the solid state. There is rapid site exchange of the InI₃ unit in chloroform solution as followed by NMR spectroscopy. The metal halide induced Z/E isomerization of Ph₂PCH=CHPPh₂ has been studied in various solvents and at variable temperature with stoichiometric and catalytic amounts of AlX₃ and GaX₃ Lewis-acids. InX₃ compounds proved ineffective (X = Cl, Br, I). Anhydrous AlBr₃ was found to be most efficient, giving a 90% Z/E conversion in 10 min at 100°C in toluene. A mechanism is proposed which is compatible with the experimental data.

* Reprint requests to Prof. Dr. H. Schmidbaur.