Untersuchungen an Systemen des Typs PCl_3/MCl_3/Aren (M = Al, Ga), I. Reaktionen mit Monohalogenbenzolen; Multikern-NMR-spektroskopische Charakterisierung von Aryldichlorhydrogenphosphoniumsalzen; Struktur des *para*-Fluorphenyldichlorphosphonium-tetrachloroaluminats

Investigations on Systems of the Type PCl_3/MCl_3/Arene (M = Al, Ga), I. Reactions with Monohalobenzenes; Multinuclear NMR Spectroscopic Characterization of Aryldichlorohydrogenphosphonium Salts; Crystal Structure of *para*-Fluorophenyldichlorophosphonium Tetrachloroaluminate

Walter Frank*, Björn Gelhausen, Guido J. Reiß, Risto Salzer

Universität Kaiserslautern, Fachbereich Chemie, Postfach 3049, D-67653 Kaiserslautern

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The reactions of the monohalobenzenes with $AlCl_3$ ($GaCl_3$) and PCl_3 have been monitored by ^{31}P NMR spectroscopy. Primary product of the reaction with fluorobenzene and $AlCl_3$ is the thermolabile *para*-fluorophenyldichlorophosphonium tetrachloroaluminate, which was characterized by ^{1}H, ^{13}C, ^{19}F, ^{27}Al and ^{31}P NMR spectroscopy as well as by a crystal structure analysis (space group $P2_1/c$, a = 7.0720(10), b = 12.659(3), c = 15.413(3) Å, β = 90.93(3)°, Z = 4, T = –110 °C). For the phosphonium ion we found a very good agreement of the experimental structural parameters and those obtained by *ab initio* quantum chemical calculations at the B3LYP 6-31++G(d,p) level of theory. Both, the experimentally determined and the calculated structure show a significant chinoid distortion of the *para*-disubstituted benzene ring. From the primary product the reaction proceeds to give exclusively *para*-fluorophenyl-(phenyl)dichlorophosphonium tetrachloroaluminate. With $GaCl_3$ and fluorobenzene analogous tetrachlorogallates were observed, however, some by-products were recognized: *para*-fluorophenylchlorofluorophosphonium and *para*-fluorophenyldifluorophosphonium tetrachlorogallate at the beginning of the reaction, bis(*para*-fluorophenyl)chlorophosphonium tetrachlorogallate at a later stage of the reaction. The reaction of chlorobenzene with PCl_3 and $AlCl_3$ yields analogous products as compared to the reaction with fluorobenzene. However, appreciable amounts of *ortho*- and some *meta*-chlorophenyldichlorophosphonium tetrachloroaluminate are by-products. If $GaCl_3$ is used instead of $AlCl_3$, numerous by-products and reaction intermediates are detectable. The major one is *para*-chlorophenyldihydrogenchlorophosphonium tetrachlorogallate. No principal differences were observed, when $AlCl_3$ and $GaCl_3$, respectively, reacted with bromobenzene and PCl_3 giving phenylbromodichlorophosphonium and *para*-bromophenylbromodichlorophosphonium salts as well as some amounts of the *ortho*- and *meta*-bromophenyl derivatives. With iodobenzene the corresponding reactions exclusively give phenyldichloroiodophosphonium tetrachloroaluminate and -gallate, respectively.

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