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Complex Chemical Synthesis of Unstable Sulfinyl- and Sulfonyl Derivatives of Phosphorus(III)

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Complex Chemical Synthesis of Unstable Sulfinyl- and Sulfonyl Derivatives of Phosphorus(III)

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The phosphorus(III) homologues of sulfonamides, $R'_2P-S(0)_2R$, are hitherto unknown. This is also in the case of phosphorus(V) derivatives: sulfinylphosphinates undergo symmetrization reactions to the homogeneous anhydrides. Sulfinylphosphinites, the O-isomers of sulfonylphosphanes, can only be built up as unstable ligands in the coordination sphere of transition metals, where the $Br(CO)_4Mn$ -fragment seems to be more stable than the $(CO)_5M$ -fragment (M = Cr, Mo, W). Thus, we now synthesized the iodo complexes $I(CO)_4Mn[P(C_6H_5)_2X]$ (X = H, SiMe3) as suitable starting material for the synthesis of SO-, SO_2 -, RSO- and RSO_2 -derivatives of coordinated phosphorus(III). Because of the surprising cis-position of the iodo and silyl group (x-ray structure analysis) the silyl-phosphane complex 2 is also of high interest to 1,2-elimination reactions to give metal-phosphorus double bonds.

$$IMn(CO)_{5} + P(C_{6}H_{5})_{2}X \longrightarrow cis-I(CO)_{4}Mn[P(C_{6}H_{5})_{2}X]$$

$$X = H/\frac{1}{2}, SiMe_{3}/\frac{2}{2}$$

$$\frac{1}{2} + RSO_{2}C1 \longrightarrow I(CO)_{4}Mn - \frac{1}{P} - 0 - \frac{S}{2} - R$$

$$sulfinylphosphinito-P$$

$$I(CO)_{4}Mn - \frac{1}{P} - \frac{S}{2} - R$$

$$sulfinylphosphane$$

$$Sulfinylphosphane$$

$$1/2 [I(CO)_{4}Mn - \frac{1}{P} - \frac{1}{2}SO_{n}$$

$$thionyl- or sulfuryldiphosphane$$

$$\frac{1}{2} - Me_{3}SiI - CO)_{4}Mn = P \longrightarrow [(CO)_{4}Mn - P - \frac{1}{2}SO_{n}]$$