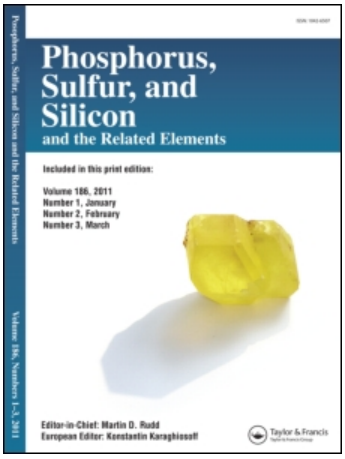

Phosphorus, Sulfur, and Silicon and the Related Elements
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713618290

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

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To cite this Article Lorenz, Ingo-Peter and Effinger, Guido(1987) 'Complex Chemical Synthesis of Unstable Sulfinyl- and Sulfonyl Derivatives of Phosphorus(III)', Phosphorus, Sulfur, and Silicon and the Related Elements, 30: 3, 702
To link to this Article: DOI: 10.1080/03086648708079196
URL: http://dx.doi.org/10.1080/03086648708079196

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

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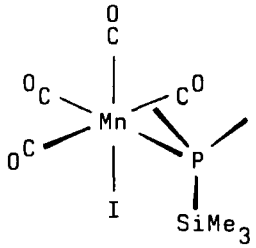
The phosphorus(III) homologues of sulfonamides, $R'_2P\text{-}S(O)_2R$, are hitherto unknown. This is also in the case of phosphorus(V) derivatives: sulfinylphosphinates undergo symmetrization reactions to the homogeneous anhydrides. Sulfinylphosphinites, the O-isomers of sulfonylphosphanes, can only 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, $SiMe_3$) 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 silylphosphane complex 2 is also of high interest to 1,2-elimination reactions to give metal-phosphorus double bonds.

$$IMn(CO)_5 + P(C_6H_5)_2X \longrightarrow \text{cis-}I(CO)_4Mn[P(C_6H_5)_2X]$$

X = H/1, $SiMe_3$/2

$$1 + RSO_2Cl \longrightarrow I(CO)_4Mn\text{—}P(\text{—}O\text{—}S(=O)\text{—}R)\text{—}$$

sulfinylphosphinito-P



2

+ RSO_2Cl → $I(CO)_4Mn\text{—}P(\text{—}S(=O)_2\text{—}R)\text{—}$

sulfinylphosphane

+ SO_nCl_2 → 1/2 $[I(CO)_4Mn\text{—}P\text{—}]_2SO_n$

thionyl- or sulfuryldiphosphane

- Me_3SiI → $(CO)_4Mn{=}P\text{—}[Mn(CO)_4\text{—}P\text{—}]_2$