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## Phosphorus, Sulfur, and Silicon and the Related Elements

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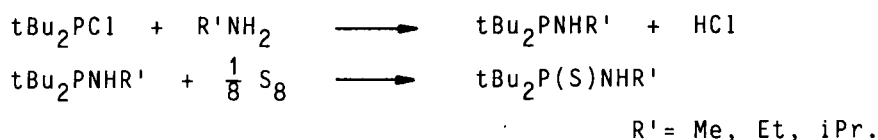
## Preparation, Properties and Complexation Behaviour of P,P-Di-tert. Butylphosphinothioic Amides

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Starting from  $t\text{Bu}_2\text{PCl}$ , the title compounds  $t\text{Bu}_2\text{P(S)NHR'}$  ( $\text{R}' = \text{Me}, \text{Et}, i\text{Pr}, t\text{Bu}$ ) may be easily prepared according to



With  $\text{R}' = t\text{Bu}$  the amine has to be substituted by its Li-salt  $[\text{tBuNH}]^-\text{Li}^+$ .

The amides  $t\text{Bu}_2\text{P(S)NHR'}$  are colourless crystals which are only slowly hydrolysed. On heating  $t\text{Bu}_2\text{P(S)NhtBu}$  loses butene to form  $t\text{Bu}_2\text{P(S)NH}_2$  in quantitative yield.

One of the most interesting features of phosphinothioic amidates  $\text{R}_2\text{P(S)NR}'^-$  is the variety of their transition metal complexes, all of which contain four-membered chelate rings and  $\text{MS}_2\text{N}_2$ -chromophores. Thus, depending on R and  $\text{R}'$ ,  $\text{Ni(II)}$ -chelates may be monomer or catenated, planar or tetrahedral. With some of them in solution equilibria of these forms are observed. The outstanding effect of tBu in this regard is shown.

In paramagnetic  $[t\text{Bu}_2\text{P(S)NtBu}]_2\text{Ni}$  the rotation round the P-C-bond can be frozen at low temperatures. Rate constant and activation parameters have been determined by NMR-spectroscopy.