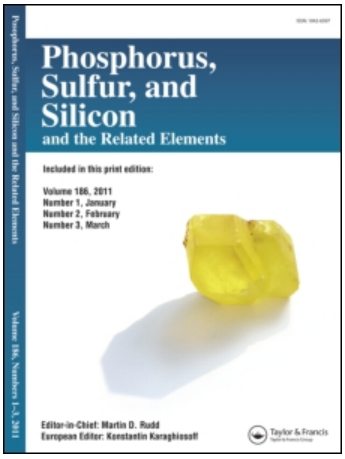

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The Reactivity of Mn(II) and Ti(IV) Dialkylamides with Organophosphorus Esters

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The Reactivity of Mn(II) and Ti(IV) Dialkylamides with Organophosphorus Esters

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Treatment of dialkyl (or diaryl) phosphites with titanium tetrakis-(diethylamide) at room temperature resulted in a smooth displacement of both ester functions by the diethylamino groups to give bis(diethylamino) phosphorus acid (58-65%). The same results are obtained at -40° and no evidence of an intermediate product was detected using ^{1}H n.m.r. techniques. Treatment of dimethyl phosphite with titanium tetrakis(*n*-dibutylamide) resulted in isolation of two products which were identified as bis-(*n*-dibylamino) phosphorus acid (52%) and methyl-(*n*-dibutylamino) phosphorus acid (21%). On the other hand, trialkyl (triaryl) phosphates are inert to the titanium reagents.

In contrast, however, treatment of trialkyl (or triaryl) phosphates with manganese bis(diethylamide) resulted in isolation of *N*,*N*-diethyl dialkyl (or diaryl) phosphoramidate (63-84%) with no evidence of the disubstituted [i.e. $(RO)P(O)(NEt_2)_2$] or trisubstituted [i.e. $(NEt_2)_3PO$] analogues. Manganese bis(diethylamide) proved unreactive towards *N*,*N*-diethyl diethyl-phosphoramidate which indicates that the reaction stops at the mono-substitution stage. Treatment of diethyl phosphite with manganese bis(diethylamide) gave a mixture of unreacted diethylphosphite, ethyl-(diethylamino) phosphorus acid and bis(diethylamino) phosphorus acid in a ratio of 2:4:1.

The amination of the above phosphorus di- and tri-esters using titanium(IV) and manganese(II) reagents represent the first examples of the direct displacement of a phosphorus ester function by an amino group.