REACTIONS OF COORDINATED TRIMETHYLPHOSPHITE WITH BINARY FLUORIDES

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Fluorination of free trimethylphosphite by phosphorus pentafluoride or tungsten hexafluoride involves complex formation followed by rapid F-for-OCH_3 exchange and Michaelis-Arbusov rearrangement reactions (D.W.A. Sharp et al., J. Chem. Soc. A, 1969, 872; J.M. Winfield et al., ibid, 1970, 501). Reactions between WF_6 or PF_5 and $P(OCH_3)_3$, coordinated to Fe^{II} (low spin d^6-inert) or Cu^I (d^{10} -labile) cations in CH_3CN, counter anions PF_6^- or AsF_6^-, are very different as evidenced by an n.m.r. study.

Reactions between Fe^{II}-$P(OCH_3)_3$ and WF_6 are very slow at room temperature; the major products are CH_3PF_4 and $WOF_4.NCCH_3$. Reactions between Cu^I-$P(OCH_3)_3$ and WF_6 or PF_5 are rapid, even below room temperature, and depend on the stoicheiometry. The major products are $W_2O_2F_9^-$ and a PF_5X^- species, or OPF_3, minor products include CH_3OPF_2, $(CH_3O)_2PF$, and PF_3. When the mole ratio coordinated $P(OCH_3)_3$:WF_6 is 1:1, additional $W_2O_2F_9$ and PF_5X n.m.r. signals are observed.

The reactions involve fluorination of free $P(OCH_3)_3$ whose concentration in solution is limited by the metal cation, and in the reaction between PF_5 and Cu^I-$P(OCH_3)_3$ $PF_5.P(OCH_3)_3$ has been identified as the initial product. Conventional Michaelis-Arbusov rearrangements are of minor importance as CH_3CN acts as a sink for CH_3^+, but the final step in the formation of CH_3PF_4 is of this type.