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Synthesis of 2-Mercapto- and 2-Hydroxy-Substituted Diphenylphosphines for use as Dianionic Bidentate Ligands and Polydentate Ligand Precursors

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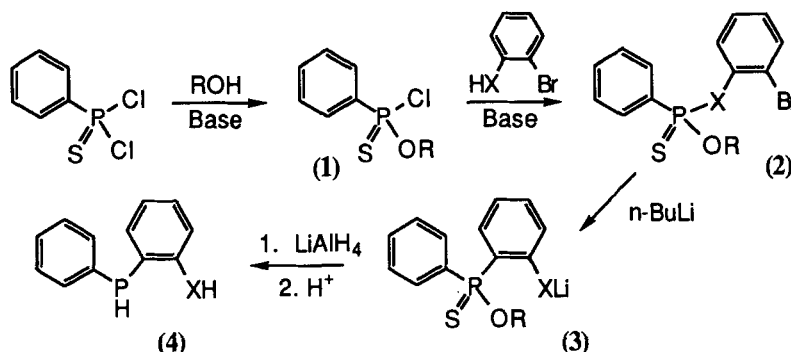
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SYNTHESIS OF 2-MERCAPTO- AND 2-HYDROXY-SUBSTITUTED DIPHENYLPHOSPHINES FOR USE AS DIANIONIC BIDENTATE LIGANDS AND POLYDENTATE LIGAND PRECURSORS

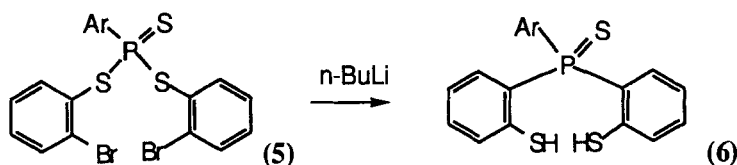
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As part of our studies into the synthesis of polydentate phosphine-containing ligands, we have investigated the preparation of the phosphines (**4**; X=O) and (**4**; X=S). These are of interest both as potential dianionic bidentate ligands and as useful precursors of more complex polydentate ligand systems. A synthesis of the thiol system (**4**; X=S) from 1,2-dinitrobenzene has been previously reported [1], but the observation [2], that 2-bromoaryl esters of phosphoric acid rearrange to give esters of arylphosphonic acids in the presence of alkyl lithiums, led us to consider whether a similar type of rearrangement might provide a convenient approach to both (**4**; X=S) and (**4**; X=O).



We have now confirmed this and have also shown that it is possible to extend this approach to bring about the simultaneous rearrangements of two 2-bromoaryl ester groups, such as in the conversion of (**5**; Ar=Ph) to (**6**; Ar=Ph). This offers a potential route to a range of tridentate and phosphine-capped tripodal tetradentate ligand systems.



[1] E.P. Kyba and C.N. Clubb, *Inorg. Chem.*, **23**, 4766, (1984).

[2] J. Heinicke, I. Böhle and A. Tzschach, *J. Organomet. Chem.*, **317**, 11, (1986).