

Tetrapodal Pentadentate Ligands with NS₄ and NP₄ Donor Sets, An Elusive Tetrathiol, and a Sterically Encumbered Tetraphosphane

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Z. Naturforsch. **57 b**, 1256–1264 (2002); received August 5, 2002

Tetrapodal Pentadentate Ligand, Polythiols, Polyphosphanes

With the intention of preparing tetrapodal pentadentate ligands having NS₄ or NP₄ donor sets, we investigated reactions of the previously reported tetratosylate 2,6-C₅H₃N[CMe(CH₂OTs)₂]₂ (**2**) with thiourea or diphenylphosphide, but found them not to proceed cleanly, and to give mixtures of products. A derivative of **2** better suited to nucleophilic substitution is the corresponding tetrabromide 2,6-C₅H₃N[CMe(CH₂Br)₂]₂ (2,6-bis-(2-bromo-1-bromomethyl-1-methyl-ethyl)-pyridine, **3**), which is obtained in excellent yield from **2** by treatment with LiBr in dimethylsulfoxide. The reaction of **3** with 4 eq of thiourea in refluxing ethanol gives a single product. Substitution is not quantitative, however, and the product likely is a bis(thiouonium) bis(bromide) salt. Similarly, the reaction of **3** with 4 eq of potassium *O*-ethyl xanthogenate displaces only two out of the four bromo substituents under the chosen conditions; workup then leads to what is formulated as a bis(thietane) derivative formed by intramolecular cyclisation. By contrast, nucleophilic substitution with NaSet in ethanol is quantitative, and the thioether 2,6-C₅H₃N[CMe(CH₂SET)₂]₂ (2,6-bis-(2-ethylsulfanyl-1-ethyl-sulfanylmethyl-1-methyl-ethyl)-pyridine, **4**) has been isolated in close to 60% yield. Likewise, and in spite of the considerable steric bulk amassed in the molecule, the reaction of **3** with an excess of KPPH₂ in THF proceeds smoothly (even at –50 °C), to give the tetraphosphane 2,6-C₅H₃N[CMe(CH₂PPh₂)₂]₂ (2,6-bis-{2-(diphenyl-phosphanyl)-1-[(diphenyl-phosphanyl)-methyl]-1-methyl-ethyl}-pyridine, **5**) in 65% yield. In order to assess possible pathways of oxidative degradation relevant to the coordination chemistry of this ligand, **5** was treated with NO in CH₂Cl₂ or ether at different temperatures. In two cases, reaction was observed to produce the oxide 2,6-C₅H₃N[CMe(CH₂P(=O)Ph₂)₂]₂ (**6**) as a colourless solid in near quantitative yield, with concomitant formation of N₂O. All compounds have been characterised by ¹H, ¹³C and ³¹P NMR spectroscopy (as applicable); IR spectroscopic and elemental analysis data are reported, and the crystal structure of **6** has been determined.