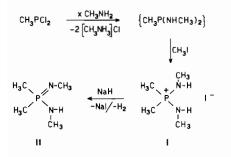
## N,N',P,P-Tetramethylamino-iminophosphorane: A New Bidentate Chelate Ligand

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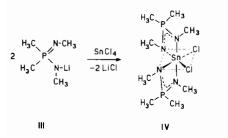
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In contrast to the well known dithiophosphate<sup>1</sup> and dithiophosphinate<sup>2</sup> bis(bidentate) complexes, the few synthesized compounds with the isoelectronic  $R_2P(NR)NR^-$  ligand have been only described and studied as dynamic monobidentate compounds,<sup>3</sup> to our knowledge.

Starting with  $CH_3PCl_2$  and  $CH_3NH_2$  we have synthesized the title ligand (II) according to the reaction scheme:



II, which can be purified by sublimation, is extremely sensitive to moisture. Metallation with  $n-C_4H_9Li$  affords the corresponding lithium salt (III), which reacts with SnCl<sub>4</sub> with formation of the new chelate complex (IV):



All compounds have been identified by elemental analyses, MS, <sup>31</sup>P- and <sup>1</sup>H NMR data. IV: <sup>31</sup>P NMR (20% solution in CH<sub>2</sub>Cl<sub>2</sub>, 85% H<sub>3</sub>PO<sub>4</sub> as external standard):  $\delta = -49.1$  ppm, <sup>2</sup>J<sup>117,119</sup>Sn<sup>31</sup>P = 52/54 Hz. The room temperature <sup>1</sup>H NMR spectrum (60 MHz, 10% solution in CH<sub>2</sub>Cl<sub>2</sub>, TMS as internal

standard) of IV exhibits two doublets with an additional tin coupling.  $\delta CH_3(P) = -1.44 \text{ ppm(d)}, {}^2J_{PH} = 12.9 \text{ Hz}, {}^4J^{117,119}SnH = 3.8 \text{ Hz}; \delta CH_3(N) = 2.72 \text{ ppm(d)}, {}^3J_{PH} = 16.8 \text{ Hz}, {}^3J^{117,119}SnH = 64.4/67.6 \text{ Hz}.$ Variable temperature proton NMR studies show that in solution IV is stereochemically mobile. At --60 °C  $(CH_2Cl_2)$  the CH<sub>3</sub>N doublet is split into two doublets  $(\delta CH_3(P) \text{ remains a doublet})$  with slightly different coupling constants ( ${}^{3}J_{PH} = 16.0/17.6$  Hz). This is strong evidence that at low temperature IV adopts the cis geometrical structure, a result which is in good agreement with studies on tin(IV) acetylacetonates.<sup>4</sup> The concentration-independent coalescence temperature ( $T_c = -45$  °C, a full line shape analysis will be carried out to obtain kinetic parameters for the exchange process) and the preservation of 117,119Sn-NCH<sub>3</sub> coupling during the dynamic process confirm an intramolecular configurational rearrangement. On the basis of the above evidence, terminal group exchange in IV must proceed via an intramolecular twist or bond rupture mechanism.<sup>5</sup>

Mass spectrum (18 eV): m/e = 393 (4% M<sup>\*</sup> – Cl), 119 (100%) and further peaks < 393. IV is a white crystalline solid, m.p. 151 to 153 °C (decomp.) soluble in dichloromethane and chloroform, but insoluble in petroleum ether and benzene. It is very sensitive to moisture.

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