A New Application of the Tetramethylphospholyl (η^5-C_4Me_4P) π-Ligand. Synthesis of η^5-Tetramethylphospholyl Complexes of Yttrium and Lutetium

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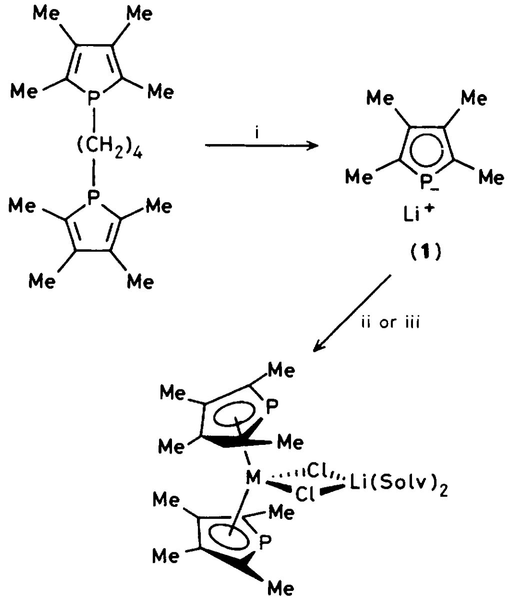
Reaction of lithium 2,3,4,5-tetramethylphospholide with MCl_3 gives η^5-$(C_4Me_4P)_2{\cdot}MCl{\cdot}LiCl{\cdot}(solvent)_2$ [solvent = Et_2O, 1,2-dimethoxyethane (DME), M = Y, Lu], which are the first reported π-heterocyclopentadienyl compounds of group 3 metals.

Since we have recently been successful in preparing η^5-phospholyl complexes of Zr[1] and Ti,[2,3] we wanted to try to synthesise η^5-phospholyl complexes of the early transition metals, those in group 3, because, to our knowledge, no π-heterocyclopentadienyl complexes of rare earths have ever been made. We selected the C_4Me_4P ligand because this ligand, which is peralkylated on the phospholyl ring, gave a much more tractable π-complex with Zr than the less substituted phospholyl ligand.[4] Thus, when a pure solution of lithium 2,3,4,5-tetramethylphospholide (**1**) [obtained from 1,4-bis(2′,3′,4′,5′-tetramethylphospholyl)butane][5] was treated with anhydrous YCl_3 or $LuCl_3$, bis(phospholyl) complexes were isolated after work-up. With yttrium, we got white crystals of composition $(C_4Me_4P)_2YCl{\cdot}LiCl{\cdot}(DME)_2$ (DME = 1,2-dimethoxyethane), (**2**), whereas with lutetium, white $(C_4Me_4P)_2LuCl{\cdot}LiCl{\cdot}(Et_2O)_2$, (**3**), was obtained.[†]



(**2**): M = Y, Solv. = DME
(**3**): M = Lu, Solv. = Et_2O

Scheme 1. *Reagents and conditions*: i, Li (excess), tetrahydrofuran (THF), room temp., 2 h; ii, YCl_3 powder, THF, room temp. 30 min, extract Et_2O, then DME, cryst. at −30 °C in DME (35%); iii, $LuCl_3$ powder, THF, room temp., 30 min, extract Et_2O (twice), cryst. at −30 °C in Et_2O (26%).

[†] Compound (**2**), n.m.r. (C_4D_8O): ^1H [200 MHz, p.p.m. from int. tetramethylsilane (TMS), J in Hz] 1.98 (s, CH_3–C_3), 2.21 (m, $^3J_{PH} \approx 10$, $^2J_{PP} \approx 20$, CH_3–C_2), 3.28 (s, CH_3 of DME), 3.44 (s, CH_2 of DME); $^{31}P\{^1H\}$ (32.4 MHz, H_3PO_4 84% ext.) 84.0 (d, $^1J_{PY}$ 6.4); $^{13}C\{^1H\}$ (50 MHz, int. TMS) 14.88 (s, CH_3–C_3), 17.34 (ps. t., $^2J_{PC} \approx 31$, CH_3–C_2), 58.80 (s, CH_3 of DME), 72.59 (s, CH_2 of DME), 134.97 (ps. t., $^2J_{PC} \approx 3.6$, C_3), 142.02 (dm, $^1J_{PC} \approx 46$, $^1J_{PY} \approx 1$, C_2); ^7Li (31.1 MHz, satd. LiCl in C_4H_8O/C_4D_8O) −1 (s); ^{89}Y (19.6 MHz, 3 M YCl_3 in D_2O) 38.4 (t, $^1J_{PY}$ 6.4).

Compound (**3**), n.m.r. (C_4D_8O): ^1H 1.23 (t, J 7, CH_3 ether), 2.06 (s, CH_3–C_3), 2.33 (m, $^3J_{PH} \approx 10$, CH_3–C_2), 3.50 (q, J 7, CH_2 ether); $^{31}P\{^1H\}$ 78.6; $^{13}C\{^1H\}$ 15.01 (s, CH_3–C_3), 15.66 (s, CH_3 ether), 17.61 (ps.t., $^2J_{PC} \approx 32$, CH_3–C_2), 66.28 (s, CH_2 ether), 134.34 (ps. t., $^2J_{PC} \approx 3$, C_3), 141.26 (m, $^1J_{PC} \approx 45.5$, C_2); ^7Li −1 (s).

Evidence for the η^5 structure of the phospholyl ligand in (**2**) and (**3**) comes from i, the high characteristic value of the $^1J_{PC}$ coupling constant ($\approx$45 Hz) which has the same value as in $(\eta^5\text{-}C_4Me_4P)_2TiCl_2$[3] and $(\eta^5\text{-}C_4Me_4P)_2ZrCl_2$,[1] of which the *X*-ray crystal structure has been determined, and ii in (**2**) the low value of the $^1J_{PY}$ coupling constant (6.4 Hz), which was determined from the doublet observed in the ^{31}P n.m.r. spectrum, and confirmed by observation of a 1 : 2 : 1 triplet in the ^{89}Y n.m.r. spectrum; two recently prepared σ-bonded yttrium–phosphine complexes had $^1J_{PY} \approx 50$ Hz.[6,7] Thus, a plausible structure for (**2**) and (**3**) is presented in Scheme 1.

As in the aforementioned Ti and Zr π-phospholyl complexes, the P atoms on the two phospholyl rings are magnetically nonequivalent and this gives rise to second-order effects on the ^1H and ^{13}C n.m.r. signals of the C atom α to phosphorus and of the methyl group attached to it. From these signals, one can extract a value of $^2J_{PP'}$ of about 20 Hz, somewhat smaller than in $(\eta^5\text{-}C_4Me_2H_2P)_2TiCl_2$ ($\approx$37 Hz).[3] The yttrium complex (**2**) could be recrystallised in ether without loss of co-ordinated DME. An attempt was made to obtain a phospholyl complex with lanthanum by the same route; however, no reaction took place when a mixture of (**1**) and $LaCl_3$ was refluxed for 16 h.

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