Phosphorus–Heteroatom Bond Cleavage by Ytterbium Metal. Synthesis of Mono(η^5-tetramethylphospholyl)ytterbium(II) Chloride and Thiolate Complexes and Structural Characterisation of $[Yb(\mu\text{-}Cl)(\eta^5\text{-}C_4Me_4P)(thf)_2]_2$ and $[Yb(\mu\text{-}SPh)(\eta^5\text{-}C_4Me_4P)(thf)_2]_2$

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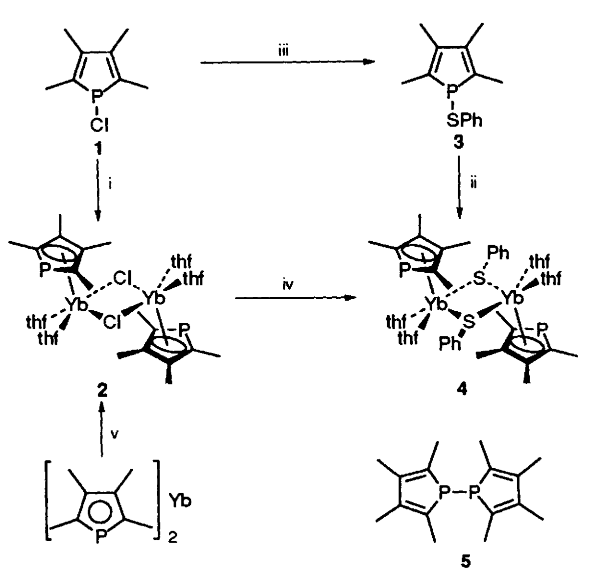
The structurally characterised $[Yb(\mu\text{-}Cl)(\eta^5\text{-}C_4Me_4P)(thf)_2]_2$ **2** and $[Yb(\mu\text{-}SPh)(\eta^5\text{-}C_4Me_4P)(thf)_2]_2$ **4** can be easily prepared by direct cleavage of the P–Cl or P–S bonds of respectively 1-chloro- and 1-phenylthio-2,3,4,5-tetramethylphosphole by ytterbium metal in thf at room temperature, while **4** can also be prepared by reaction of **2** with NaSPh.

Divalent lanthanide organometallic compounds are receiving much attention at present; much of the chemistry of these compounds has been concerned with the synthesis and reactivity of substituted bis(cyclopentadienyl)samarium, ytterbium and europium complexes.[1] On the other hand, very few monocyclopentadienyl lanthanide(II) complexes are known to exist,[2–4] and only one has been structurally characterised.[4] Having demonstrated that Sm and Yb metals were able to insert into the P–P bonds of substituted 1,1′-biphospholyls, thus yielding bis(phospholyl)samarium(II) and ytterbium(II) complexes,[5] we reasoned that cleavage of a P–Z bond (Z being a heteroatom residue) of a substituted phosphole with Yb or Sm would lead to Z-substituted monophospholylsamarium(II) or ytterbium(II) complexes.

We thus mixed equimolecular amounts of Yb metal [activated with *ca.* 2–5% (m/m) $HgCl_2$] and of the readily available 1-chloro-2,3,4,5-tetramethylphosphole[6] **1** in tetrahydrofuran (thf) at room temperature. A reaction occurred, as indicated by an increase in temperature and turbidity of the solution. At this stage, when the reaction mixture was checked by ^{31}P NMR, the only detected product was the known P–P bonded 2,3,4,5,2′,3′,4′,5′-octamethyl-1,1′-biphospholyl,[6] **5**. After a variable period (0–6 days), further evolution occurred as indicated by the increasing red colour of the solution followed by gradual precipitation of an orange-red solid within 24 h; this solid was purified by extraction and crystallisation from warm thf. A 75% yield of $[Yb(\mu\text{-}Cl)(\eta^5\text{-}C_4Me_4P)(thf)_2]_2$ **2**† was thus obtained (Scheme 1). Initial reaction of **1** with Yb would then give **5** and $YbCl_2$; subsequently, the P–P bond of **5** would be cleaved by Yb in excess, affording $[Yb(C_4Me_4P)_2]$ which, by comproportionation with the produced $YbCl_2$, would yield **2**. Support for this hypothesis is provided by the fact that **2** can also be obtained by reaction of isolated $[Yb(C_4Me_4P)_2]$[5] with $YbCl_2$; Evans *et al.* also obtained $[Sm(\mu\text{-}I)(\eta^5\text{-}C_5Me_5)(thf)_2]_2$ by reaction of $[Sm(C_5Me_5)_2]$ with SmI_2.[4]

Insertion of Yb into a P–S bond was also successful. When activated Yb metal and 1-phenylthio-2,3,4,5-tetramethylphosphole **3**, readily obtained in 72% yield from **2** and NaSPh in thf, were reacted together at room temperature in thf, dark red crystals appeared after 24 h. These crystals were purified by extraction with thf and a 62% yield of $[Yb(\mu\text{-}SPh)(\eta^5\text{-}C_4Me_4P(thf)_2]_2$ **4** was obtained. **4** could also be obtained by functionalisation of the Yb–Cl bond of **2**: reaction of equimolecular quantities of **2** and NaSPh in thf gave **4** in 34% yield. Reaction of **2** with $KOBu^t$ or reaction of Yb with the P–Sn bond of 1-trimethylstannyl-2,3,4,5-tetramethylphosphole did not yield the expected monophospholyl Yb derivatives, but instead led to disproportionation and formation of $[Yb(C_4Me_4P)_2]$.

The structures of **2** and **4** have been determined by X-ray crystallography‡ (Figs. 1 and 2). **2** and **4** are respectively chloride- and thiolate-bridged centrosymmetric dimers with a planar M_2X_2 core (M = Yb, X = Cl, S), a structure akin to that found in $[Sm(\mu\text{-}I)(\eta^5\text{-}C_5Me_5)(thf)_2]_2$[4] and $[Sm(\mu\text{-}SPh)(\eta^8\text{-}C_8H_8)(thf)_2]_2$.[7] In **4**, there are two independent molecules in the unit cell with similar geometries. The phospholyl rings



Scheme 1 Synthesis of monophospholyl ytterbium(II) chloride and thiolate complexes. *Reagents and conditions*: i, Yb, thf, room temp., 7 d; ii, Yb, thf, room temp., 24 h; iii, NaSPh, thf, room temp., 1 h; iv, NaSPh, thf, room temp., 24 h; v, $YbCl_2$, thf, room temp., 7 d

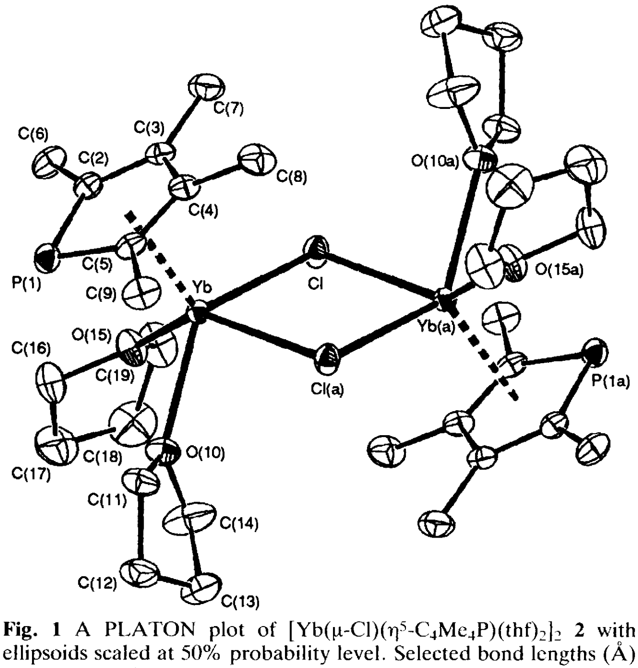


Fig. 1 A PLATON plot of $[Yb(\mu\text{-}Cl)(\eta^5\text{-}C_4Me_4P)(thf)_2]_2$ **2** with ellipsoids scaled at 50% probability level. Selected bond lengths (Å) and angles (°): Yb–Cl 2.7724(8), Yb–Cl(a) 2.7554(9), Yb–O(10) 2.414(2), Yb–O(15) 2.425(3), Yb–P(1) 2.911(1), Yb–C(av.) 2.77, Cl–Yb–Cl(a) 82.94(3), Cl–Yb–O(15) 84.86(6), Cl(a)–Yb–O(10) 80.71(3), O(10)–Yb–O(15) 77.25(9), Yb–Cl–Yb(a) 97.06(3).

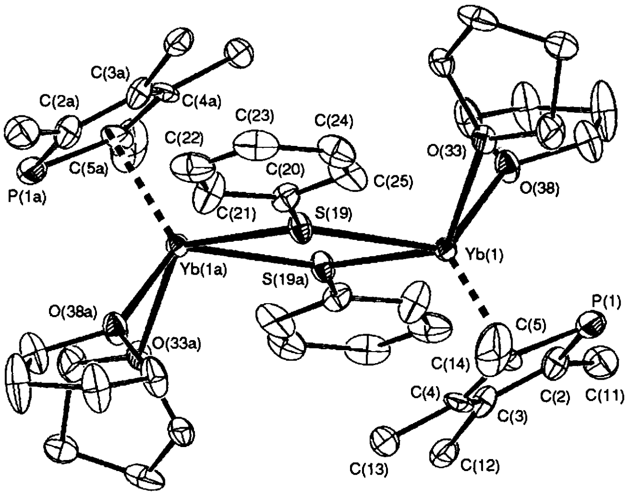


Fig. 2 A PLATON plot of $[Yb(\mu\text{-}SPh)(\eta^5\text{-}C_4Me_4P)(thf)_2]_2$ **4** with ellipsoids scaled at 40% probability level. Selected bond lengths (Å) and angles (°): Yb(1)–S(19) 2.834(4) [2.816(4)], Yb(1)–S(19a) 2.827(4) [2.789(4)], Yb(1)–O(33) 2.39(1) [2.41(1)], Yb(1)–O(38) 2.42(1) [2.43(1)], Yb(1)–P(1) 2.931(4) [2.955(5)], Yb(1)–C(av.) 2.75 [2.78], S(19)–Yb(1)–S(19a) 68.9(1) [69.8(1)], S(19)–Yb(1)–O(33) 83.9(3) [86.3(3)], S(19a)–Yb(1)–O(38) 87.0(3) [85.2(3)], O(33)–Yb(1)–O(38) 79.0(4) [78.2(4)], Yb(1)–S(19)–Yb(1a) 111.1(1) [110.2(1)]; parameters in brackets are those of the second half-dimer.

of **2** and **4** are planar and η^5-bonded to Yb. Their geometry is not significantly different to that of other η^5-bonded complexes containing the phospholyl ligand,[8] although some of the ligand C–C bonds in **4** are inaccurate, due to the poor quality of the crystal. The Yb–C, Yb–P and Yb–O distances in **2** and **4** are similar to those found in $[Yb(\eta^5\text{-}C_4H_2Ph_4P)_2(thf)_2]$, whereas the Yb–Cl bonds in **2** (av. 2.73 Å) are significantly longer than in Yb^{III} dimers also containing the Yb_2Cl_2 unit such as $[Yb(\mu\text{-}Cl)(\eta^5\text{-dienyl})]_2$ (range of Yb–Cl bonds 2.62–2.65 Å);[9] this due to the fact that Yb^{II} is bigger than Yb^{III}. The Yb–S bonds in **4** (av. 2.82 Å) seem to be slightly longer than in $[Yb^{II}(SCH_2Bu^t{}_3\text{-}2,4,6)_2(dme)_2]$[10] (2.76 Å) or $[Li(tmeda)]_3[Yb^{III}(SBu^t{}_3)]$ (2.74 Å).[11]

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Footnotes

† For **2**: Satisfactory elemental analysis (C, H, Cl, P) was obtained for $C_{24}H_{40}Cl_2O_2Yb_2$ (after loss of 2 moles of thf by **2**). NMR (C_4D_8O): ^1H (200 MHz, ppm from int. Me_4Si, J in Hz) 1.57 (thf), 1.99 (s, CH_3), 2.18 (d, J_{PH} *ca.* 10, CH_3), 3.65 (thf); $^{31}P\{^1H\}$ (81 MHz, ppm from ext. 85% H_3PO_4) 81.4. For **3**: Satisfactory analysis (C, H) was obtained for $C_{14}H_{17}PS$. bp 170 °C/0.1 mm. NMR ($CDCl_3$): ^1H 1.70 (d, J_{PH} *ca.* 3, CH_3) 2.01 (d, J_{PH} *ca.* 10.5, CH_3), 7.20 (m, C_6H_5); $^{31}P\{^1H\}$ 33.1. For **4**: NMR (C_4D_8O): ^1H 1.57 (thf), 2.07 (s, CH_3), 2.27 (d, J_{PH} *ca.* 11, CH_3), 3.65 (thf), 6.75 (ps.t., $J = 8$, H para), 6.91 (ps.t., $J = 8$, H meta), 7.38 (ps. d., $J = 8$, H ortho); $^{31}P\{^1H\}$ 82.5. No meaningful elemental analysis could be obtained for this compound.

‡ *Crystal data*: structure determination details (data collected at −150 ± 0.5 °C on an Enraf Nonius CAD4 diffractometer using Mo-Kα radiation (λ = 0.71073 Å) and a graphite monochromator). For **2**: $C_{16}H_{28}ClO_2PYb$ (half-dimer), $M = 491.87$; space group: monoclinic, $P2_1/n$ (No. 14); $a = 11.662(1)$, $b = 13.980(1)$, $c = 11.927(1)$ Å, $\beta = 107.86(1)°$; $V = 1850.81(55)$ Å^3; $Z = 4$; $\rho_{calc} = 1.768$ g cm^{-3}; $\mu = 52.8$ cm^{-1}; $F(000) = 968$; $2\theta_{max} = 56°$; number of reflections 5384 unique, 4294 with $F_o{}^2 > 3.0\sigma(F_o{}^2)$. Final agreement factors $R = 0.026$, $R_w = 0.036$, g.o.f. = 0.99. For **4**: $C_{44}H_{66}O_4P_2S_2Yb_2$ (two independant half-dimers). $M = 1131.17$; space group: monoclinic, $P2_1/c$ (No. 14); $a = 15.783(1)$, $b = 19.696(2)$, $c = 15.005(1)$ Å, $\beta = 90.49(1)°$; $V = 4664.3(1.1)$ Å^3; $Z = 4$; $\rho_{calc} = 1.611$ g cm^{-3}; $\mu = 41.7$ cm^{-1}; $F(000) = 2256$; $2\theta_{max} = 50°$; number of reflections 8173 unique, 5399 with $F_o{}^2 > 3.0\sigma(F_o{}^2)$. Final agreement factors $R = 0.070$, $R_w = 0.103$, g.o.f. = 2.08. The poor quality of the crystal is reflected by the relatively large agreement factors and the bad definition of some of the thermal ellipsoids. Crystal structures were solved and refined using the Enraf Nonius MOLEN package. Positions of the ytterbium atoms were determined from Patterson maps and all other atoms were located in subsequent difference Fourier maps. In **2**, hydrogen atoms were included as fixed contributions in the final stages of least-squares refinement while using anisotropic temperature factors for all other atoms. In **4**, the contribution of the hydrogen atoms was neglected.

Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Information for Authors, Issue No. 1.

References

1 Recent reviews: R. D. Rogers and L. M. Rogers, *J. Organomet. Chem.*, 1993, **457**, 41; 1992, **442**, 225; 1992, **442**, 83; 1991, **416**, 201; W. J. Evans, *Polyhedron*, 1987, **5**, 803.

2 S. J. Swamy and H. Schumann, *J. Organomet. Chem.*, 1987, **334**, 1.

3 F. G. N. Cloke, C. I. Dalthy, P. B. Hitchcock, H. Karamallakis and G. A. Lawless, *J. Chem. Soc., Chem. Commun.*, 1991, 779.

4 W. J. Evans, J. W. Grate, H. W. Choi, I. Bloom, W. E. Hunter and J. L. Atwood, *J. Am. Chem. Soc.*, 1985, **107**, 941.

5 F. Nief, L. Ricard and F. Mathey, *Polyhedron*, 1993, **12**, 19.

6 K. Theopold and H. Douglas, *Angew. Chem., Int. Ed. Engl.*, 1989, **28**, 1367.

7 K. Mashima, Y. Nakayama, N. Kanehisa, Y. Kai and A. Nakamura, *J. Chem. Soc., Chem. Commun.*, 1993, 1847.

8 F. Mathey, *New J. Chem.*, 1987, **11**, 585.

9 J. Gräper, R. D. Fischer and G. Paolucci, *J. Organomet. Chem.*, 1994, **471**, 47; T. Akhnoukh, J. Müller, K. Xiao, X.-F. Li and R. D. Fischer, *J. Organomet. Chem.*, 1991, **408**, 87; H. Luecken, J. Schmitz, W. Lamberts, P. Hannibal and K. Handrick, *Inorg. Chim. Acta*, 1989, **156**, 119; N. Höck, W. Oroschin, G. Paolucci and R. D. Fischer, *Angew. Chem., Int. Ed. Engl.*, 1986, **25**, 738; M. F. Lappert, A. Singh, J. L. Atwood and W. E. Hunter, *J. Chem. Soc., Chem. Commun.*, 1981, 1191; E. C. Baker, L. D. Brown and K. N. Raymond, *Inorg. Chem.*, 1975, **14**, 1376.

10 B. Çetinkaya, P. B. Hitchcock, M. F. Lappert and R. G. Smith, *J. Chem. Soc., Chem. Commun.*, 1992, 932.

11 K. Tatsumi, T. Amemiya, H. Kawaguchi and K. Tani, *J. Chem. Soc., Chem. Commun.*, 1993, 773.