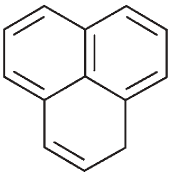
The synthesis, X-ray structure and fluxional behaviour of an ytterbium(II) phenalenide complex

David J. Berg,*[a] Jianlong Sun[a] and Brendan Twamley[b]

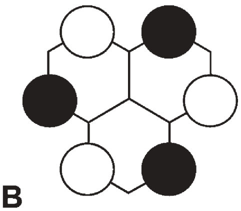
Received (in Berkeley, CA, USA) 26th June 2006, Accepted 25th July 2006
First published as an Advance Article on the web 16th August 2006
DOI: 10.1039/b609084b

The first lanthanoid complexes containing delocalized phenalenide anions are reported and the rapid migration of the η^3-bonded metal centre between the three rings of the π-system is the first report of a degenerate haptotropic rearrangement in organolanthanoid chemistry.

Cyclopentadienide (Cp) anion and its derivatives are the mostly widely used ligands in organometallic chemistry. Given that the pK_a of phenalene (**A**) is similar to cyclopentadiene at *ca.* 19,[1] it is somewhat surprising that the phenalenide anion (Pn) has received so little study as an ancillary ligand. In fact, metal complexes of this anion are limited to the Group 10 metals and only one complex, $[(\eta^3(4\text{–}6)\text{-1-ethoxyphenalenyl})Pt(PPh_3)_2]^+BF_4^-$, has been characterized crystallographically.[2]



A



B

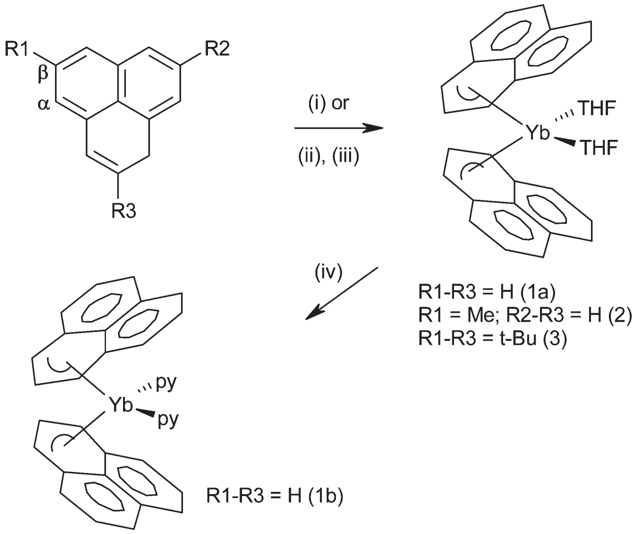
Charge density in the phenalenide anion is equally distributed over the six α-carbon positions consistent with the symmetrical nature of the HOMO (**B**). Since bonding in lanthanoid complexes is regarded as ionic,[3] the mode of bonding between a lanthanoid cation and a phenalenide anion is not necessarily established *a priori*. We therefore set out to determine whether phenalenide anions are suitable ligands for the lanthanoids and to determine their preferred bonding mode with these metals. Our initial efforts focusing on the phenalenide complexes of Yb(II) are reported here.

The most efficient synthesis of Yb(II) phenalenide complexes (**1–3**) uses the acid–base reaction between the appropriate substituted phenalene[4] and $Yb[N(SiMe_3)_2]_2(THF)_2$[5] in toluene, although salt metathesis between pre-formed Li^+Pn^- and YbI_2 in THF generates the same complexes, albeit in poorer yields (Scheme 1). All complexes are deep red in colour and readily soluble in toluene; only complex **3** dissolves appreciably in saturated hydrocarbons. ^{1}H NMR integrations and elemental analyses indicate that **1–3** are bis(THF) solvates. The complexes melt with some decomposition but we were unable to obtain mass spectroscopic data on these highly oxygen and moisture senstive compounds.†

The ^{1}H NMR spectra of complexes **1–3** show chemical shifts and line widths consistent with diamagnetic Yb(II) complexes. However, at room temperature the ^{1}H NMR spectra of **1a/b** are highly symmetrical with only one resonance each for the α and β protons. The $^{13}C\{^1H\}$ NMR similarly indicates a highly symmetric ligand environment. On cooling to 200 K in d_8-toluene or d_8-thf, the phenalenide resonances for **1–2** broaden considerably but do not decoalesce before the complex precipitates from solution (*ca.* 190–195 K).

The bulkier tris(*tert*-butyl) substituted phenalenide in **3** also shows single sharp resonances for the α-aryl and t-butyl protons at 5.63 and 1.21 ppm, respectively, in d_8-toluene. In this case, decoalescence appears to occur at about 190 K, just *before* the complex precipitates from solution (Fig. 1). No change in coalescence temperature or line widths was observed when the solvent was changed from d_8-toluene to d_8-thf or when the concentration of the complex was varied threefold suggesting that the dynamic process involved is unimolecular in nature.

The averaged chemical shifts of the phenalenide protons observed in the ^{1}H NMR spectra of **1–3** are remarkably far upfield. By comparison, the α-allylic (5.45–6.04 ppm) and α-naphthalenic (7.4–8.0 ppm) protons observed in the slow exchange spectra of known group 10 η^3-phenalenyl complexes



Scheme 1 Synthesis of **1–3**; reagents and conditions: (i) $Yb[N(SiMe_3)_2]_2[THF]_2$ (0.5 equiv.), toluene, 18 h; (ii) n-BuLi (1 equiv.), THF, 0 °C; (iii) YbI_2 (0.5 equiv.), THF, 18 h; (iv) excess pyridine, 1 h, RT.

---

[a] *Department of Chemistry, University of Victoria, P.O. Box 3065, Victoria, British Columbia, Canada V8W 3V6. E-mail: djberg@uvic.ca, jianlong@uvic.ca; Fax: +1 250-721-7147; Tel: +1 250-721-7161*
[b] *University Research Office, 109 Morrill Hall, University of Idaho, Moscow, Idaho, USA 83844-3010. E-mail: btwamley@uidaho.edu; Fax: +1 208-885-6198; Tel: +1 208-885-2847*

This journal is © The Royal Society of Chemistry 2006

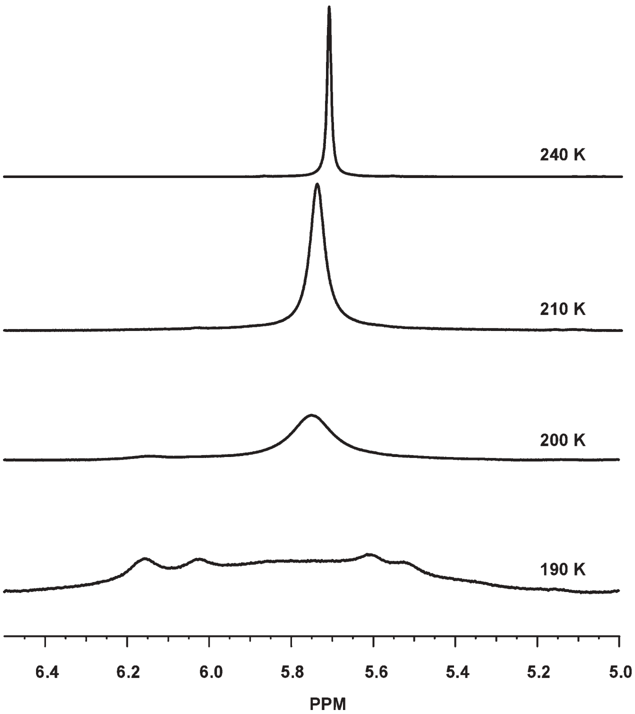


Fig. 1 Variable temperature ^{1}H NMR spectra (500 MHz, d_8-toluene) of **3** showing the α-phenalenyl proton resonances.

differ by at least 1.9 ppm and predict a coalescence averaged position of 6.7–7.4 ppm. In fact, the average α-proton was observed at 7.32 ppm in $[Pd(\eta^3\text{-phenalenyl})(tmeda)]^+PF_6^-$, the only previous case where the high temperature limiting ^{1}H NMR spectrum was observed for a fluxional metal phenalenyl complex.[2d]

The ^{1}H NMR experiments above strongly suggest an asymmetric bonding mode for the phenalenide ligand but in the absence of a low temperature limiting spectrum, it is not possible to determine precisely what that mode might be. After many attempts, a single crystal of **3** suitable for X-ray crystallography was eventually obtained from hexane at −30 °C.‡ The ORTEP3[6] plot of **3** (Fig. 2) indicates that the phenalenide ligand is bonded to Yb(II) in η^3-allylic fashion, although there are some minor differences between the bonding of the two phenalenide groups. For one phenalenide ligand, the η^3 bonding mode is highly symmetrical with Yb(1)–C(1–3) bond distances ranging from 2.808(3)–2.838(3) Å and non-bonded Yb(1)–C(4–6) contacts ranging from 2.996(3)–3.049(3) Å. The internal allyl C–C bond distances in this ligand are 1.390(4) and 1.399(4) Å, illustrating the symmetrical allylic bonding mode.

The Ln-allyl carbon distances are at the long end of the range found in symmetrically bonded, 8-coordinate lanthanoid allyls (2.682–2.839 Å, median 2.76 Å).[7] In a formal sense, **3** could be viewed as a 6-coordinate complex but if this is taken to be the case, then the Ln-C bond distances observed here would fall well beyond the normal range. Even as an 8-coordinate complex, **3** is clearly more crowded than most lanthanoid allyls as a result of the 'fused' naphthalene unit that makes up the remainder of the phenalenide ring system. This crowding is evident in the long Yb–O distances (2.435(2) and 2.436(2) Å) compared to 8-coordinate, Yb(II) indenyl (Ind) complexes, $Yb(Ind)_2(THF)_2$ (2.348–2.431 Å, median 2.386 Å)[8] and the observation that **3** readily loses one THF molecule on exposure to vacuum.

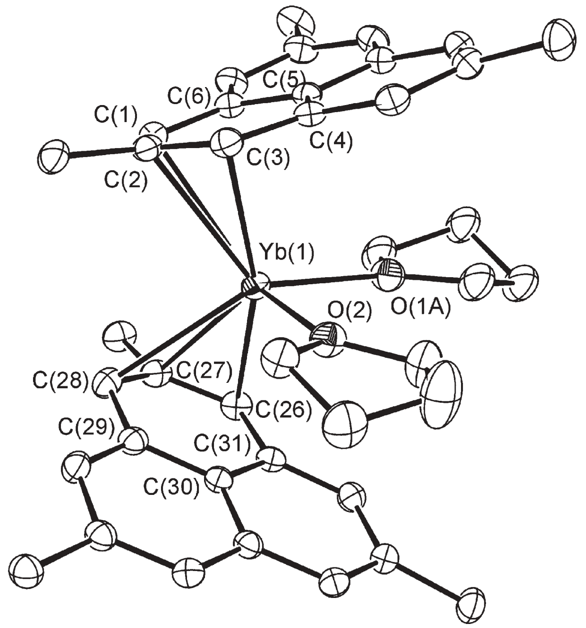


Fig. 2 ORETP3[6] drawing of **3** (30% probability thermal ellipsoids, H-atoms and t-Bu methyl groups omitted for clarity). Selected bond distances (Å) and angles (°): Yb(1)–C(1) 2.817(3), Yb(1)–C(2) 2.838(3), Yb(1)–C(3) 2.808, Yb(1)–C(26) 2.789(3), Yb(1)–C(27) 2.869(3), Yb(1)–C(28) 2.864(3), Yb(1)–O(1A) 2.435(2), Yb(1)–O(2) 2.436(2), C(1)–C(2) 1.390(4), C(2)–C(3) 1.399(4), C(26)–C(27) 1.396(4), C(27)–C(28) 1.393(4); O(1A)–Yb(1)–O(2) 94.73(8), C(1)/C(3) Centroid–Yb(1)–C(26)/C(28) Centroid 117.1.

The other phenalenide ligand is bonded less symmetrically with Yb(1) slipped towards the C(26)–C(31) bond. This leads to a Yb(1)–C(31) '*non-bonded*' distance that is only marginally longer at 2.886(3) Å than the Yb(1)–C(27/28) bond distances of 2.869(3) and 2.864(3) Å, respectively. An additional effect of this slippage is that the Yb(1)–C(26) distance is the shortest Yb–C bond distance observed in the molecule at 2.789(3) Å. Despite this distortion, the internal allylic C–C bond distances are very similar for both phenalenide ligands suggesting that it is best to regard both as η^3 bonded.

The dihedral (fold) angles, defined as the angle between the least square planes of the allylic and naphthalene subunits, is 12.0 and 12.6° for allylic units involving C(1–3) and C(26–28), respectively. This angle is much less pronounced in **3** than in $[(\eta^3\text{(4–6)-1-ethoxyphenalenyl})Pt(PPh_3)_2]^+BF_4^-$ (30.1°).[2a] The smaller fold angle in **3** may result in more delocalization of negative charge to the naphthalenic subunit. This would presumably result in an upfield shift of the proton resonances for this subunit and therefore explain why the averaged resonances of **3** occur further upfield than those in the Group 10 complexes.

The lower symmetry structure of **3** indicated by the variable temperature ^{1}H NMR spectra (Fig. 1) is consistent with an η^3 allylic ground state in solution as well as in the solid state. Although the low temperature limit was not reached in Fig. 1, the observed coalescence temperature indicates an upper limit for ΔG^* of *ca.* 10 kcal mol^{-1} for the degenerate haptotropic rearrangement shown in Fig. 3.[9–12] This value is far less than the

This journal is © The Royal Society of Chemistry 2006

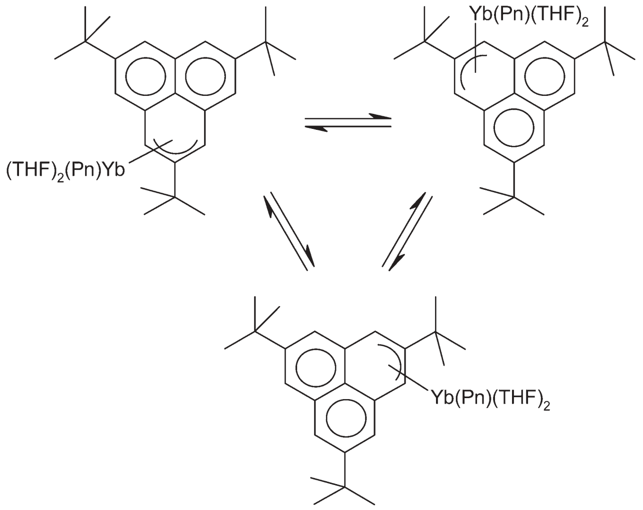


Fig. 3 The degenerate haptotropic rearrangement of **3** (Pn = η^3-2,5,8-tri-*tert*-butylphenalenyl).

21.6 ± 0.4 kcal mol^{-1} barrier reported for [(η^3-2,6,10-trimethylphenalenyl)Pd(tmeda)]$^+$PF$_6^-$.[2d] The low barrier to metal migration in **3** is perhaps not surprising given the expectation of ionic bonding in lanthanoid complexes and the absence of orbital barriers. However, as far as we are aware, this is the first demonstrated example of a rapid and reversible haptotropic rearrangement by a lanthanoid ion on a delocalized π system.[13]

Attempts to oxidize the divalent ytterbium centers in **1–3** with stoichiometric amounts of *tert*-butylchloride, *p*-tolyl disulfide or mercuric chloride resulted in decomposition with loss of the free phenalene. Phenalenyl systems have relatively stable cation, anion and radical oxidation states so decomposition may well involve ligand-based redox chemistry.[14] Nevertheless, we have successfully prepared phenalenide complexes of trivalent lanthanoids by metathesis routes; these complexes will be the subject of a forthcoming publication.

Notes and references

† Spectroscopic data for **1–3**. **1a**: red crystals; mp 86 °C (decomp.); ^{1}H NMR (C$_6$D$_6$, 500 MHz): δ 6.32 (br s, 6H, β-Pn*H*), 5.61 (br s, 12H, α-Pn*H*), 3.26 (br m, 8H, THF), 1.31 (br m, 8H, THF); ^{13}C NMR (C6D6, 125.7 MHz): δ 142.5 (β-Pn*C*H), 106.4 (α-Pn*C*H), 70.5, 26.0 (THF). **1b**: brown powder; ^{1}H NMR (C$_6$D$_6$, 300 MHz): δ 7.97 (br s, 4H, py), 6.90 (br s, 2H, py), 6.52 (br s, 4H, py), 6.23 (t, J = 7.3Hz, 6H, β-Pn*H*), 5.49 (d, J = 7.3Hz, 12H, α-Pn*H*); a satisfactory elemental analysis could not be obtained for **1a** or **1b**. **2**: red powder; mp 81 °C (decomp.); ^{1}H NMR (C$_6$D$_6$, 300 MHz): δ 6.33 (br s, 4H, β-Pn*H*), 5.52–5.59 (br m, 12H, α-Pn*H*), 3.28 (br m, 8H, THF), 1.86 (s, 6H, Me), 1.31 (br m, 8H, THF); ^{13}C NMR (C$_6$D$_6$, 125.7 MHz): δ 142.5 (β-Pn*C*H), 109.2, 106.2, 104.5 (α-Pn*C*H), 70.1, 26.0 (THF), 22.2 (Me); Anal. for $C_{36}H_{38}O_2Yb$. Found (Calcd): C, 62.60 (63.99); H, 5.27 (5.67%). **3**: red crystals; mp 192 °C (decomp.); ^{1}H NMR (C$_6$D$_6$, 500 MHz): δ 5.63 (s, 12H, α-Pn*H*), 3.55 (br m, 4H, THF), 1.35 (br m, 4H, THF), 1.21 (s, 54H, t-Bu); complex **3** loses one equivalent of THF on prolonged exposure to vacuum; ^{13}C NMR (C$_6$D$_6$, 125.7 MHz): δ 141.2 (quaternary-β-Pn), 104.1 (α-Pn*C*H), 34.4 (*C*Me$_3$), 31.0 (C*Me$_3$*); Anal. for $C_{58}H_{82}O_2Yb$. Found (Calcd): C, 71.31 (70.78); H, 9.22 (8.40%).

‡ Crystal data for **3**: $C_{58}H_{82}O_2Yb$, M = 984.28, monoclinic, *C*2/*c*, a = 41.067(2) Å, b = 12.0077(7) Å, c = 21.7474(12) Å, α = 90°, β = 104.579(1)°, γ = 90°, V = 10378.7(10) Å^3, T = 235(2) K, μ = 1.841 mm^{-1}, Z = 8, reflections measured = 78 029, independent reflections = 9400, R_1 = 0.0283, wR_2 (all data) = 0.0726. CCDC 612504. For crystallographic data in CIF or other electronic format see DOI: 10.1039/b609084b

1 K. Bowden and A. F. Cockerill, *J. Chem. Soc. B*, 1970, 173.

2 (*a*) A. Keasey, P. M. Bailey and P. M. Maitlis, *J. Chem. Soc., Chem. Commun.*, 1978, 142; (*b*) S. Lin and P. Boudjouk, *J. Organomet. Chem.*, 1980, **187**, C11; (*c*) K. Nakasuji, M. Yamaguchi, I. Murata, K. Tatsumi and A. Nakamura, *Organometallics*, 1984, **3**, 1257; (*d*) K. Nakasuji, M. Yamaguchi and I. Murata, *J. Am. Chem. Soc.*, 1986, **108**, 325.

3 P. M. Zeimentz, S. Arndt, B. R. Elvidge and J. Okuda, *Chem. Rev.*, 2006, **106**, 2404.

4 (*a*) Phenalene: P. Boudjouk and P. D. Johnson, *J. Org. Chem.*, 1978, **43**, 3979; (*b*) 2-Methylphenalene: L. K. Fieser and F. C. Novello, *J. Am. Chem. Soc.*, 1940, **62**, 1855; (*c*) 2,5,8-Tri-*tert*-butylphenalene: K. Goto, T. Kubo, K. Y. Yamamoto, K. Nakasuji, K. Sato, D. Shiomi, T. Takui, M. Kubota, T. Kobayashi, K. Yakusi and J. Ouyang, *J. Am. Chem. Soc.*, 1999, **121**, 1619.

5 (*a*) T. D. Tilley, R. A. Andersen and A. Zalkin, *J. Am. Chem. Soc.*, 1982, **104**, 3725; (*b*) Y. F. Rad'kov, E. A. Fedorova, S. Y. Khorshev, G. S. Kalinina, M. N. Bochkarev and G. A. Razuvaev, *Russ. J. Gen. Chem.*, 1985, **55**, 1911.

6 L. J. Farrugia, ORTEP3 for Windows, *J. Appl. Crystallogr.*, 1997, **30**, 565.

7 (*a*) R. Taube, H. Windisch, H. Hemling and H. Schumann, *J. Organomet. Chem.*, 1998, **555**, 201; (*b*) W. J. Evans, T. A. Ulibarri and J. W. Ziller, *J. Am. Chem. Soc.*, 1990, **112**, 2314; (*c*) R. Taube, S. Maiwald and J. Siefer, *J. Organomet. Chem.*, 2001, **621**, 327; (*d*) R. Taube, H. Windisch, H. Weisenborn, H. Hemling and H. Schumann, *J. Organomet. Chem.*, 1997, **548**, 229; (*e*) S. Maiwald, R. Taube, H. Hemling and H. Schumann, *J. Organomet. Chem.*, 1998, **552**, 195; (*f*) R. Taube, H. Windisch, S. Maiwald, H. Hemling and H. Schumann, *J. Organomet. Chem.*, 1996, **513**, 49; (*g*) E. Kirillov, C. W. Lehmann, A. Razavi and J.-F. Carpentier, *J. Am. Chem. Soc.*, 2004, **126**, 12240.

8 (*a*) A. V. Khvostov, B. M. Bulychev, V. K. Belsky and A. I. Sizov, *J. Organomet. Chem.*, 1999, **584**, 164; (*b*) M. Qi, Q. Shen, X. Gong, Z. Shen and L. Weng, *Chin. J. Chem.*, 2002, **20**, 564; (*c*) J. Jin, Z. Jin, W. Chen and Y. Zhang, *Jiegou Huaxue*, 1993, **12**, 241; (*d*) R. E. Marsh, *Acta Crystallogr., Sect. B: Struct. Sci.*, 1997, **53**, 317; (*e*) S. W. Ng and S. Hu, *Wuli Huaxue Xuebao*, 2000, **16**, 879.

9 Assuming a separation between the allylic and naphthalenic proton resonances of *ca.* 500 Hz at 500 MHz.

10 (*a*) NMR linewidths were simulated using DNMR3 from within SpinWorks to obtain a very rough estimate for k in a three site mutual exchange process; (*b*) K. Marat, *SpinWorks, Version 2.6*, University of Manitoba, Winnipeg, MB, 2005.

11 In principle, intermolecular ligand exchange could explain the solution behaviour observed for **1**–**3**. We regard this as unlikely because the fluxional process shows no noticeable dependence on complex concentration or the donor ability of the solvent (d$_8$-THF *vs.* d$_8$-toluene). Additionally, mixing **1** and **2** together in d$_8$-THF produced no change in the ^{1}H NMR spectra of either complex, strongly suggesting that intermolecular ligand exchange does not take place on the NMR timescale.

12 Intermolecular cyclopentadienyl exchange between lanthanoids and uranium centres has been shown to take place on a timescale far longer (minutes) than the NMR experiment: T. Mehdoui, J.-C. Berthet, P. Thuéry and M. Ephritikhine, *Dalton Trans.*, 2005, 1263.

13 For an example of an irreversible haptotropic rearrangement, see: H. Nakamura, Y. Nakayama, H. Yasuda, T. Maruo, N. Kanehisa and Y. Kai, *Organometallics*, 2000, **19**, 5392.

14 I. Murata, *Pure Appl. Chem.*, 1993, **65**, 97.