SUPPORTING INFORMATION

to

for

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[S2] NMR spectroscopy
Fig. 11 $^1$H NMR spectrum of 2d (500 MHz, C$_6$D$_6$, 25ºC).

Fig. 12 $^{13}$($^1$H) NMR spectrum of 2d (202 MHz, C$_6$D$_6$, 25ºC)
S3 Single-crystal X-ray structure determinations

Suitable single crystals were sealed under N₂ in thin-walled glass capillaries. X-ray diffraction data of compounds 2a, 4b and 5c were collected on a SMART APEX CCD diffractometer (graphitemonochromated Mo-Kα radiation, ϕ-ω-scan technique, λ= 0.71073 Å). The intensity data were integrated by means of the SAINT program. SADABS was used to perform area-detector scaling and absorption corrections. The structures were solved by direct methods and were refined against $F^2$ using all reflections with the aid of the SHELXTL package. All non-hydrogen atoms were refined anisotropically. The H atoms were included in calculated positions with isotropic thermal parameters related to those of the supporting carbon atoms but were not included in the refinement. All non-hydrogen atoms were found from the difference Fourier syntheses. All calculations were performed using the Bruker Smart program. CCDC 1881753(2a), 1881754 (4b) and 1881758(5c) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.
Fig. 14. Thermal ellipsoid (30%) plot of complex 2a. Hydrogen atoms are omitted for clarity except for H1A. The solvent molecule was omitted. Selected bond lengths (Å) and angles (°):
P(1)–Yb(1) 2.903(4), P(1)–C(8) 1.717(4), P(1)–C(1) 1.779(5), N(1)–C(8) 1.357(6), N(1)–C(6) 1.386(6), C(1)–C(6) 1.410(7), C(8)–P(1)–C(1) 90.6(2), C(8)–P(1)–Yb(1) 139.21(15), C(1)–P(1)–Yb(1) 129.83(16), C(8)–N(1)–C(6) 115.1(4), C(6)–C(1)–P(1) 110.1(3), N(1)–C(6)–C(1) 111.7(4), N(1)–C(8)–P(1) 112.5(3).

Table 1. Crystal and Data Collection Parameters of Complex (2a)₂-toluene.

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<td>Mo-Kα</td>
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<tr>
<td>Temperature (K)</td>
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Scan type \( \omega-20 \)
\( \theta \) range (deg) 1.876 to 27.493
\( h,k,l \) range \(-20 \leq h \leq 20\)
\(-19 \leq k \leq 19\)
\(-32 \leq l \leq 33\)
No. of reflections measured 55943
No. of unique reflections 14043 \( [R_{int}=0.0611] \)
Completeness to \( \theta \) 99.8\% \( [\theta=25.242] \)
Refinement method Full-matrix least-squares on \( F^2 \)
Data / restraints / parameters 14043 / 80 / 740
Goodness-of-fit on \( F^2 \) 1.061
Final R indices \([I>2\sigma(I)]\) 1.061
\( R_1 = 0.0408 \)
\( wR_2 = 0.1001 \)
\( R_1 = 0.0554 \)
\( wR_2 = 0.1062 \)
Largest diff. peak and hole (e\( \cdot \)Å\(^{-3} \)) 1.381 and -1.263

Figure 15. Thermal ellipsoid (30\%) plot of complex 4b. Hydrogen atoms are omitted for clarity.

Selected bond lengths (Å) and angles (°):
- P(1)–C(8) 1.741(10), P(1)–C(1) 1.774(10), N(1)–C(8) 1.371(12), N(1)–C(6) 1.395 (11), C(9)–C(14) 1.394(14), N(1)–Yb(1) 2.309(8), P(1)–Yb(2) 3.005(3), Yb(1)–C(14) 2.862(11), Yb(1)–C(9) 2.957(10), C(1)–C(6) 1.395(11), C(8)–C(9) 1.483(13), C(8)–P(1)–C(1) 89.0(5), C(8)–P(1)–Yb(2) 141.2(4), C(1)–P(1)–Yb(2) 122.7(4), C(8)–N(1)–C(6) 112.3(8), C(8)–N(1)–Yb(1) 107.9(6), C(6)–N(1)–Yb(1) 129.4(7), N(1)–Yb(1)–C(14) 66.0(3), C(6)–C(1)–P(1) 111.2(7), N(1)–C(6)–C(1) 112.7(9), N(1)–C(8)–C(9) 114.6(8), N(1)–C(8)–P(1) 114.9(7), C(9)–C(8)–P(1) 130.4(8), N(1)–C(8)–Yb(1) 46.6(5), C(9)–C(8)–Yb(1) 73.1(5), P(1)–C(8)–Yb(1) 147.4(5).
Table 2. Crystal and Data Collection Parameters of Complex 4b.

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<td>θ range (deg)</td>
<td>2.51 to 25.02</td>
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<tr>
<td>No. of reflections measured</td>
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<td>No. of unique reflections</td>
<td>5785[R int = 0.0626]</td>
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<td>Completeness to θ</td>
<td>99.3% [θ = 25.02]</td>
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<td>Refinement method</td>
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<td>Goodness-of-fit on F²</td>
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<td>Largest diff. peak and hole</td>
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<td>(e. Å⁻³)</td>
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The solvent molecule was omitted. Selected bond lengths (Å) and angles (°): P(1)–C(1) 1.793(3), P(1)–C(2) 1.794(3), N(1)–C(1) 1.326(3), N(1)–C(3) 1.414(3), C(2)–C(3) 1.406(4), N(1)–Yb(1) 2.354(2), P(1)–B(1) 2.090(3), Yb(1)–C(27) 2.740(3), Yb(1)–C(26) 3.077(10), C(1)–N(1)–Yb(1) 114.22(17), C(1)–N(1)–C(3) 111.4(2), C(3)–N(1)–Yb(1) 133.41(17), N(1)–C(1)–P(1) 115.33(19), C(1)–P(1)–C(2) 88.06(13), C(1)–P(1)–B(1) 105.65(12), C(2)–P(1)–B(1) 110.62(13), C(3)–C(2)–P(1) 109.9(2), C(2)–C(3)–N(1) 115.0(2), C(8)–B(1)–C(14) 106.4(2), C(8)–B(1)–C(20) 119.3(2), C(20)–B(1)–C(14) 112.4(2).

Table 3. Crystal and Data Collection Parameters of Complex 5c-toluene.

<table>
<thead>
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<th>Parameter</th>
<th>5c-toluene</th>
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</table>
CCDC 1881758
Formula C_{48}H_{27}BF_{15}NPYb
Molecular weight 1117.52
Crystal color Red
Crystal system Monoclinic
Space group P21/c

Unit cell dimensions
\[
a (\text{Å}) = 13.2386(6) \\
b (\text{Å}) = 21.6434(10) \\
c (\text{Å}) = 15.4959(7) \\
\beta (\text{deg}) = 102.1000 (10) \\
V (\text{Å}^3) = 4341.4(3)
\]

\[Z = 4\]
\[D_c (\text{g.cm}^{-3}) = 1.710\]
\[\mu (\text{mm}^{-1}) = 2.292\]
\[F(000) = 2188\]

Radiation (\(\lambda = 0.710730\text{Å}\)) Mo-K\(\alpha\)
Temperature (K) 100.2
Scan type \(\omega\)-2\(\theta\)

\[\theta \text{ range (deg)} = 2.461 \text{ to } 27.637\]
\[h,k,l \text{ range} = -15 \leq h \leq 16, -25 \leq k \leq 26, -20 \leq l \leq 9\]

No. of reflections measured 25978
No. of unique reflections 9750
Completeness to \(\theta_{9750}\) \(R_{int} = 0.0232\]
Completeness to \(\theta\) 99.9% \([\theta = 25.242]\]
Refinement method Full-matrix least-squares on \(F^2\)

Data / restraints / parameters 9750 / 0 / 605
Goodness-of-fit on \(F^2\) 1.032
Final R indices \([I>2\sigma (I)]\) \(R_1 = 0.0264\)
\(wR_2 = 0.0604\)

\(R\) indices (all data) \(R_1 = 0.0360\)
\(wR_2 = 0.0645\)

Largest diff. peak and hole \(0.872\) and \(-0.690\) (e.Å\(^{-3}\))

S4 References

1. Bruker (2013) SAINTPlus Data Reduction and Correction Program v. 8.34 a, Bruker AXS, Madison, Wisconsin, USA.