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Supporting Information

NH3 and (NH2)1− as Ligands in Yttrium Metallocene Chemistry

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Table of Contents

Table S1. Crystallographic details for $(C_5Me_5)_2Y(NH_2)(THF)$, **1** and $[(C_5Me_5)_2Y(NH_3)(THF)][BPh_4]$, **2**.

	1	**2**
Empirical formula	$C_{24}H_{40}YNO$	$C_{48}H_{61}BYNO$
Formula weight	447.48	767.69
Temperature (K)	88(2)	128(2)
Space group	$P2_1$	$P2_{1/n}$
a (Å)	8.3916(3)	11.7992(9)
b (Å)	16.1829(6)	22.5790(18)
c (Å)	9.2225(3)	15.3847(12)
α (°)	90	90
β (°)	111.3610(4)	91.7762(10)
γ (°)	90	90
Volume (Å^3)	1166.38(7)	4096.7(6)
Z	2	4
ρ_{calcd} (Mg/m^3)	1.274	1.254
μ (mm^{-1})	2.513	1.460
$R1^a$	0.0212	0.0336
$wR2^b$	0.0517	0.0894

$^aR1 = \Sigma||F_o|-|F_c|| / \Sigma|F_o|$. $^bwR2 = [\Sigma[w(F_o^2-F_c^2)^2] / \Sigma[w(F_o^2)^2]]^{1/2}$

Table S2. Selected bond lengths (Å) and angles (°) for $(C_5Me_5)_2Y(NH_2)(THF)$, **1**.

Y(1)-Cnt1	2.402
Y(1)-Cnt2	2.407
Y(1)-N(1)	2.226(2)
Y(1)-O(1)	2.3857(18)
Y(1)-C(1)	2.668(3)
Y(1)-C(15)	2.669(3)
Y(1)-C(11)	2.671(3)
Y(1)-C(5)	2.672(3)
Y(1)-C(2)	2.683(3)
Y(1)-C(14)	2.695(3)
Y(1)-C(4)	2.702(3)
Y(1)-C(3)	2.708(3)
Y(1)-C(13)	2.713(3)
Y(1)-C(12)	2.713(2)
Cnt1-Y(1)-N(1)	104.4
Cnt1-Y(1)-O(1)	104.5
Cnt1-Y(1)-N(1)	105.3
Cnt1-Y(1)-O(1)	103.9
Cnt1-Y(1)-Cnt2	137.8
N(1)-Y(1)-O(1)	91.71(8)

Table S3. Selected bond lengths (Å) and angles (°) for $[(C_5Me_5)_2Y(NH_3)(THF)][BPh_4]$, **2**.

Y(1)-Cnt1	2.358
Y(1)-Cnt2	2.366
Y(1)-O(1)	2.3530(12)
Y(1)-N(1)	2.4757(16)
Y(1)-C(4)	2.6356(18)
Y(1)-C(12)	2.6386(18)
Y(1)-C(3)	2.6402(18)
Y(1)-C(1)	2.6552(19)
Y(1)-C(11)	2.6552(18)
Y(1)-C(5)	2.6567(18)
Y(1)-C(13)	2.6605(18)
Y(1)-C(2)	2.6630(18)
Y(1)-C(14)	2.6639(18)
Y(1)-C(15)	2.6671(18)
Cnt1-Y(1)-N(1)	103.3
Cnt1-Y(1)-O(1)	104.0
Cnt2-Y(1)-N(1)	105.1
Cnt2-Y(1)-O(1)	104.7
Cnt1-Y(1)-Cnt2	138.8
O(1)-Y(1)-N(1)	90.93(5)

X-ray Data Collection, Structure Solution and Refinement

For $(C_5Me_5)_2Y(NH_2)(THF)$, **1:** A colorless crystal of approximate dimensions 0.275 x 0.312 x 0.426 mm was mounted on a glass fiber and transferred to a Bruker SMART APEX II diffractometer. The APEX2[1] program package was used to determine the unit-cell parameters and for data collection (20 sec/frame scan time for a sphere of diffraction data). The raw frame data was processed using SAINT[2] and SADABS[3] to yield the reflection data file. Subsequent calculations were carried out using the SHELXTL[4] program. The diffraction symmetry was 2/*m* and the systematic absences were consistent with the monoclinic space groups $P2_1$ and $P2_1/m$. It was later determined that space group $P2_1$ was correct. The structure was solved by direct methods and refined on F^2 by full-matrix least-squares techniques. The analytical scattering factors[5] for neutral atoms were used throughout the analysis. Hydrogen atoms H(1) and H(2) were located from a difference-Fourier map and refined (x,y,z and U_{iso}) with d(N-H) = 0.88Å. The remaining hydrogen atoms were included using a riding model. At convergence, wR2 = 0.0517 and Goof = 1.050 for 262 variables refined against 5132 data (0.78 Å), R1 = 0.0212 for those 4939 data with $I > 2.0\sigma(I)$. The absolute structure was assigned by refinement of the Flack[6] parameter.

For $[(C_5Me_5)_2Y(THF)(NH_3)][BPh_4]$, **2**: A colorless crystal of approximate dimensions 0.504 x 0.509 x 0.536 mm was mounted on a glass fiber and transferred to a Bruker SMART APEX II diffractometer. The APEX2[1] program package was used to determine the unit-cell parameters and for data collection (10 sec/frame scan time for a sphere of diffraction data). The raw frame data was processed using SAINT[2] and SADABS[3] to yield the reflection data file. Subsequent calculations were carried out using the SHELXTL[4] program. The diffraction symmetry was 2/*m* and the systematic absences were consistent with the monoclinic space group

$P2_1/n$ that was later determined to be correct. The structure was solved by direct methods and refined on F^2 by full-matrix least-squares techniques. The analytical scattering factors[5] for neutral atoms were used throughout the analysis. Hydrogen atoms H(1), H(2) and H(3) were located from a difference-Fourier map and refined (x,y,z and U_{iso}). The remaining hydrogen atoms were included using a riding model. At convergence, wR2 = 0.0894 and Goof = 1.027 for 491 variables refined against 9027 data (0.78Å), R1 = 0.0336 for those 7807 data with $I > 2.0\sigma(I)$.

Definitions:

$$wR2 = [\Sigma[w(F_o^2-F_c^2)^2] / \Sigma[w(F_o^2)^2]]^{1/2}$$

$$R1 = \Sigma||F_o|-|F_c|| / \Sigma|F_o|$$

$$Goof = S = [\Sigma[w(F_o^2-F_c^2)^2] / (n-p)]^{1/2}$$ where n is the number of reflections and p is the total number of parameters refined.

References

(1) Bruker AXS, Inc.: Madison, WI 2014.

(2) Bruker AXS, Inc.: Madison, WI 2013.

(3) Sheldrick, G. M. Bruker AXS, Inc.: Madison, WI 2014.

(4) Sheldrick, G. M. Bruker AXS, Inc.: Madison, WI 2014.

(5) *International Tables for Crystallography*, Vol. C.; Kluwer Academic Publishers: Dordrecht, 1992.

(6) Parsons, S.; Flack, H. D.; Wagner, T. *Acta Crystallogr. Sect. B Struct. Sci. Cryst. Eng. Mater.* **2013**, *B69*, 249.