Supporting Information for

Structural Complexity in the Rare Earth Metallocene Hydride Complexes, [(C$_5$Me$_5$)$_2$LnH]$_2$

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X-ray Data Collection, Structure Solution and Refinement for $(C_5Me_5)_2Gd(\mu$-$H)_2Gd(C_5Me_5)_2$, 1.

A yellow crystal of approximate dimensions 0.144 x 0.226 x 0.363 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 Cc and $C2/c$. It was later determined that space group $C2/c$ was correct.

The structure was solved using the coordinates of the terbium analogue and refined on F^2 by full-matrix least-squares techniques[5]. The analytical scattering factors[6] for neutral atoms were used throughout the analysis. The molecule was located on a two-fold rotation axis. The bridging hydrides could not be located and were not included in the refinement. The remaining hydrogen atoms were included using a riding model.

At convergence, $wR_2 = 0.0677$ and Goof = 1.106 for 201 variables refined against 4429 data (0.75Å), $R_1 = 0.0269$ for those 4071 data with $I > 2.0\sigma(I)$.

X-ray Data Collection, Structure Solution and Refinement for $(C_5Me_5)_2Tb(\mu$-$H)_2Tb(C_5Me_5)_2$, 2.

A yellow crystal of approximate dimensions 0.11 x 0.29 x 0.30 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 groups Cc and $C2/c$. It was later determined that space group $C2/c$ was correct.

The structure was solved by direct methods and refined[5] on F^2 by full-matrix least-squares techniques. The analytical scattering factors[6] for neutral atoms were used throughout the analysis. The molecule was located on a two-fold rotation axis. Hydrogen atom H(1) was 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, $wR_2 = 0.0550$ and Goof = 1.043 for 205 variables refined against 4334 data (0.74Å), $R_1 = 0.0209$ for those 3905 data with $I > 2.0\sigma(I)$.

X-ray Data Collection, Structure Solution and Refinement for $(C_5Me_5)_2Dy(\mu$-H)DyH$(C_5Me_5)_2$·toluene, 3B.

A yellow crystal of approximate dimensions 0.192 x 0.338 x 0.495 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 (15 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 using the coordinates of the yttrium analogue and refined on F^2 by full-matrix least-squares techniques[5]. The analytical scattering factors[6] for neutral atoms were used throughout the analysis. The hydride atoms 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. There was one molecule of toluene solvent present per formula-unit.

At convergence, wR_2 = 0.0440 and Goof = 1.202 for 471 variables refined against 10376 data (0.75Å), R_1 = 0.0216 for those 9889 data with $I > 2.0\sigma(I)$.

X-ray Data Collection, Structure Solution and Refinement for $(C_5Me_5)_2Dy(\mu$-H)DyH$(C_5Me_5)_2$, 3C.

A pale pink crystal of approximate dimensions 0.232 x 0.275 x 0.333 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. There were no systematic absences nor any diffraction symmetry other than the Friedel condition. The centrosymmetric triclinic space group $P\bar{1}$ was assigned and later determined to be correct.

The structure was solved by direct methods and refined on F^2 by full-matrix least-squares techniques[5]. The analytical scattering factors[6] for neutral atoms were used throughout the analysis. Hydride atoms H(1) and H(2) atoms 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. The pentamethylcyclopenadienyl ligand defined by atoms C(31)-C(40) was disordered and included using multiple components, partial site-occupancy-factors and isotropic thermal parameters.

At convergence, wR_2 = 0.0484 and Goof = 1.017 for 403 variables refined against 8455 data (0.74Å), R_1 = 0.0200 for those 7765 data with $I > 2.0\sigma(I)$.

References

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Definitions:

$$wR_2 = [\Sigma[w(F_o^2 - F_c^2)^2] / \Sigma[w(F_o^2)^2]]^{1/2}$$

$$R_1 = \Sigma||F_o| - |F_c|| / \Sigma|F_o|$$

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.