Supporting Information for

Structural Complexity in the Rare Earth Metallocene Hydride Complexes, [(C₅Me₅)₂LnH]₂

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X-ray Data Collection, Structure Solution and Refinement for (C₅Me₅)₂Gd(μ-H)₂Gd(C₅Me₅)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 APEX2¹ 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 SAINT² and SADABS³ to yield the reflection data file. Subsequent calculations were carried out using the SHELXTL⁴ 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 F² by full-matrix least-squares techniques⁵. The analytical scattering factors⁶ 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, wR² = 0.0677 and Goof = 1.106 for 201 variables refined against 4429 data (0.75Å), R₁ = 0.0269 for those 4071 data with I > 2.0σ(I).

X-ray Data Collection, Structure Solution and Refinement for (C₅Me₅)₂Tb(μ-H)₂Tb(C₅Me₅)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 APEX2¹ 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 SAINT² and SADABS³ to yield the reflection data file. Subsequent calculations were carried out using the SHELXTL⁴ 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 refined⁵ on F² by full-matrix least-squares techniques. The analytical scattering factors⁶ 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 Uiso). The remaining hydrogen atoms were included using a riding model.

At convergence, wR² = 0.0550 and Goof = 1.043 for 205 variables refined against 4334 data (0.74Å), R₁ = 0.0209 for those 3905 data with I > 2.0σ(I).
X-ray Data Collection, Structure Solution and Refinement for (C₅Me₅)₂Dy(μ-H)DyH(C₅Me₅)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 APEX2¹ 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 SAINT² and SADABS³ to yield the reflection data file. Subsequent calculations were carried out using the SHELXTL⁴ program. The diffraction symmetry was 2/m and the systematic absences were consistent with the monoclinic space group P2₁/n that was later determined to be correct.

The structure was solved using the coordinates of the yttrium analogue and refined on F² by full-matrix least-squares techniques⁵. The analytical scattering factors⁶ for neutral atoms were used throughout the analysis. The hydride atoms were located from a difference-Fourier map and refined (x,y,z and Uᵢso). The remaining hydrogen atoms were included using a riding model. There was one molecule of toluene solvent present per formula-unit.

At convergence, wR₂ = 0.0440 and Goof = 1.202 for 471 variables refined against 10376 data (0.75Å), R₁ = 0.0216 for those 9889 data with I > 2.0σ(I).

X-ray Data Collection, Structure Solution and Refinement for (C₅Me₅)₂Dy(μ-H)DyH(C₅Me₅)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 APEX2¹ 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 SAINT² and SADABS³ to yield the reflection data file. Subsequent calculations were carried out using the SHELXTL⁴ program. There were no systematic absences nor any diffraction symmetry other than the Friedel condition. The centrosymmetric triclinic space group P1̅ was assigned and later determined to be correct.

The structure was solved by direct methods and refined on F² by full-matrix least-squares techniques⁵. The analytical scattering factors⁶ 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 Uᵢso). The remaining hydrogen atoms were included using a riding model. The pentamethylcyclopentadienyl 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, wR₂ = 0.0484 and Goof = 1.017 for 403 variables refined against 8455 data (0.74Å), R₁ = 0.0200 for those 7765 data with I > 2.0σ(I).
References


Definitions:

\[ wR_2 = \left[ \frac{\sum [w(F_o^2 - F_c^2)^2]}{\sum [w(F_o^2)^2]} \right]^{1/2} \]

\[ R_1 = \frac{\sum |F_o| - |F_c|}{\sum |F_o|} \]

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