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Scandium and Yttrium Metallocene Borohydride Complexes: Comparisons of $(BH_4)^{1-}$ vs $(BPh_4)^{1-}$ Coordination and Reactivity

Selvan Demir, Nathan A. Siladke, Joseph W. Ziller, and William J. Evans*

Department of Chemistry, University of California

Irvine, California 92697-2025 (U.S.A.)

Fax: 949-824-2210

E-mail: wevans@uci.edu

Synthesis of $(C_5Me_5)_2Sc(\mu\text{-}H)_2BC_8H_{14}$, 10. In a nitrogen-filled glovebox free of coordinating solvents, a yellow solution of $(C_5Me_5)_2Sc(\eta^3\text{-}C_3H_5)$ (0.169 g, 0.47 mmol) in toluene (15 mL) was added to $(HBC_8H_{14})_2$ (0.116 g, 0.47 mmol). After the mixture was stirred for 24 h, the yellow solution was evaporated to dryness to yield a yellow tacky solid. This was extracted with hexane (15 mL) and evaporated to dryness to yield **10** as a tacky yellow residue (0.17 g, 82%). Yellow crystals suitable for X-ray analysis were grown from a concentrated hexane solution of **10** at −35 °C over the course of 48 h. ^{1}H NMR (benzene-d_6): δ 2.40-1.51 (m, α- β- and γ-H of $(\mu\text{-}H)_2BC_8H_{14}$), 1.57 (s, 30H, C_5Me_5), 1.04 (bs, 2H, $(\mu\text{-}H)_2BC_8H_{14}$).

X-ray Data Collection, Structure Solution and Refinement for $(C_5Me_4H)_2Y(THF)(\mu\text{-}H)_3BH$, 1. A colorless crystal of approximate dimensions 0.11 x 0.12 x 0.28 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 (30 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. The analytical scattering factors[5] for neutral atoms were used throughout the analysis. There were two molecules of the formula-unit present (Z = 4). Hydrogen atoms H(1)-H(8) 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. Carbon atoms C(42) and C(43) were disordered and included using multiple components with partial site-occupancy-factors. At convergence, wR2 = 0.0666 and Goof = 1.018 for 498 variables refined against 10477 data (0.75Å), R1 = 0.0274 for those 8804 data with I > 2.0σ(I).

X-ray Data Collection, Structure Solution and Refinement for $(C_5Me_5)_2Y(THF)(\mu\text{-}H)_2BH_2$, 2. A colorless crystal of approximate dimensions 0.19 x 0.23 x 0.27 mm was mounted on a glass fiber and transferred to a Bruker SMART APEX II diffractometer. The APEX2[6] program package was used to determine the unit-cell parameters and for data collection (25 sec/frame scan time for a sphere of diffraction data). The raw frame data was processed using SAINT[7] and SADABS[3] to yield the reflection data file. Subsequent calculations were carried out using the SHELXTL[8] 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. The analytical scattering factors[5] for neutral atoms were used throughout the analysis. Hydrogen atoms H(1)-H(8) 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 = 0.0766 and Goof = 1.044 for 539 variables refined against 10240 data, R1 = 0.0324 for those 8393 data with $I > 2.0\sigma(I)$.

X-ray Data Collection, Structure Solution and Refinement for $(C_5Me_4H)_2Sc(\mu\text{-}H)_2BH_2$, 5. A colorless crystal of approximate dimensions 0.27 x 0.29 x 0.36 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[8] 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 were located from a difference-Fourier

map and refined (x,y,z and U_{iso}). At convergence, wR2 = 0.0765 and Goof = 1.029 for 301 variables refined against 4209 data (0.75Å), R1 = 0.0272 for those 3940 data with I > 2.0σ(I).

X-ray Data Collection, Structure Solution and Refinement for $(C_5Me_5)_2Sc(THF)(\mu\text{-}H)_2BH_2$ and $(C_5Me_5)_2ScCl(THF)$, 6a. A colorless crystal of approximate dimensions 0.21 x 0.30 x 0.36 mm was mounted on a glass fiber and transferred to a Bruker SMART APEX II diffractometer. The APEX2[6] program package was used to determine the unit-cell parameters and for data collection (25 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. The analytical scattering factors[5] for neutral atoms were used throughout the analysis. Hydrogen atom associated with the BH_4 ligands were initially located from a difference-Fourier map and refined (x,y,z and U_{iso}) with fixed boron-hydrogen distances. The remaining hydrogen atoms were included using a riding model. There were two molecules of the formula-unit present. In both molecules the BH_4 and chloride ligands were disordered resulting in a refinement with each group assigned site-occupancy-factors of 0.50. The refinement is consistent with a composition of an equal number of the BH_4 and chloride complexes. At convergence, wR2 = 0.1053 and Goof = 1.012 for 530 variables refined against 10304 data (0.75Å), R1 = 0.0399 for those 9494 data with I > 2.0σ(I).

X-ray Data Collection, Structure Solution and Refinement for $(C_5Me_4H)_2Sc(\mu\text{-}H)_2BC_8H_{14}$, 9. A colorless crystal of approximate dimensions 0.17 x 0.21 x 0.23 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[8] 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. The analytical scattering factors[5] for neutral atoms were used throughout the analysis. Hydrogen atoms H(1)-H(4) 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 were two molecules of the formula unit present. One of the tetramethylcyclopentadienyl ligands on each of the independent molecules was disordered. The disordered ligands were included using multiple components and partial site-occupancy-factors. At convergence, wR2 = 0.1210 and Goof = 1.037 for 617 variables refined against 10393 data (0.78Å), R1 = 0.0468 for those 8670 data with $I > 2.0\sigma(I)$.

X-ray Data Collection, Structure Solution and Refinement for $(C_5Me_5)_2Sc(\mu\text{-}H)_2BC_8H_{14}$, 10. A yellow crystal of approximate dimensions 0.10 x 0.10 x 0.31 mm was mounted on a glass fiber and transferred to a Bruker SMART APEX II diffractometer. The APEX2[6] program package was used to determine the unit-cell parameters and for data collection (40 sec/frame scan time for a sphere of diffraction data). The raw frame data was processed using SAINT[9] 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. The analytical scattering factors[5] for neutral atoms were used throughout the analysis. Hydrogen atoms H(1a), H(1b), H(2a) and H(2b) were located from a difference-Fourier map and refined (x,y,z and U_{iso}). It was necessary to fix the hydrogen-hydrogen distances during refinement to

maintain a reasonable geometry about the boron atoms. The remaining hydrogen atoms were included using a riding model. At convergence, wR2 = 0.1225 and Goof = 1.030 for 577 variables refined against 11549 data (0.74Å), R1 = 0.0463 for those 9163 data with I > 2.0σ(I).

X-ray Data Collection, Structure Solution and Refinement for $[(C_5Me_4H)_2Sc]_2(\mu$-η^2:η^2-$N_2)$, 13'. An orange crystal of approximate dimensions 0.08 x 0.10 x 0.20 mm was mounted on a glass fiber and transferred to a Bruker SMART APEX II diffractometer. The APEX2[10] program package was used to determine the unit-cell parameters and for data collection (45 sec/frame scan time for a sphere of diffraction data). The raw frame data was processed using SAINT[9] 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. The analytical scattering factors[5] for neutral atoms were used throughout the analysis. Hydrogen atoms were included using a riding model. At convergence, wR2 = 0.1140 and Goof = 1.020 for 377 variables refined against 5625 data (0.85Å), R1 = 0.0453 for those 3961 data with I > 2.0σ(I). The crystal diffracted poorly requiring a long scan time (45s) and a data cutoff of 0.85Å.

References

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