

Supporting Information

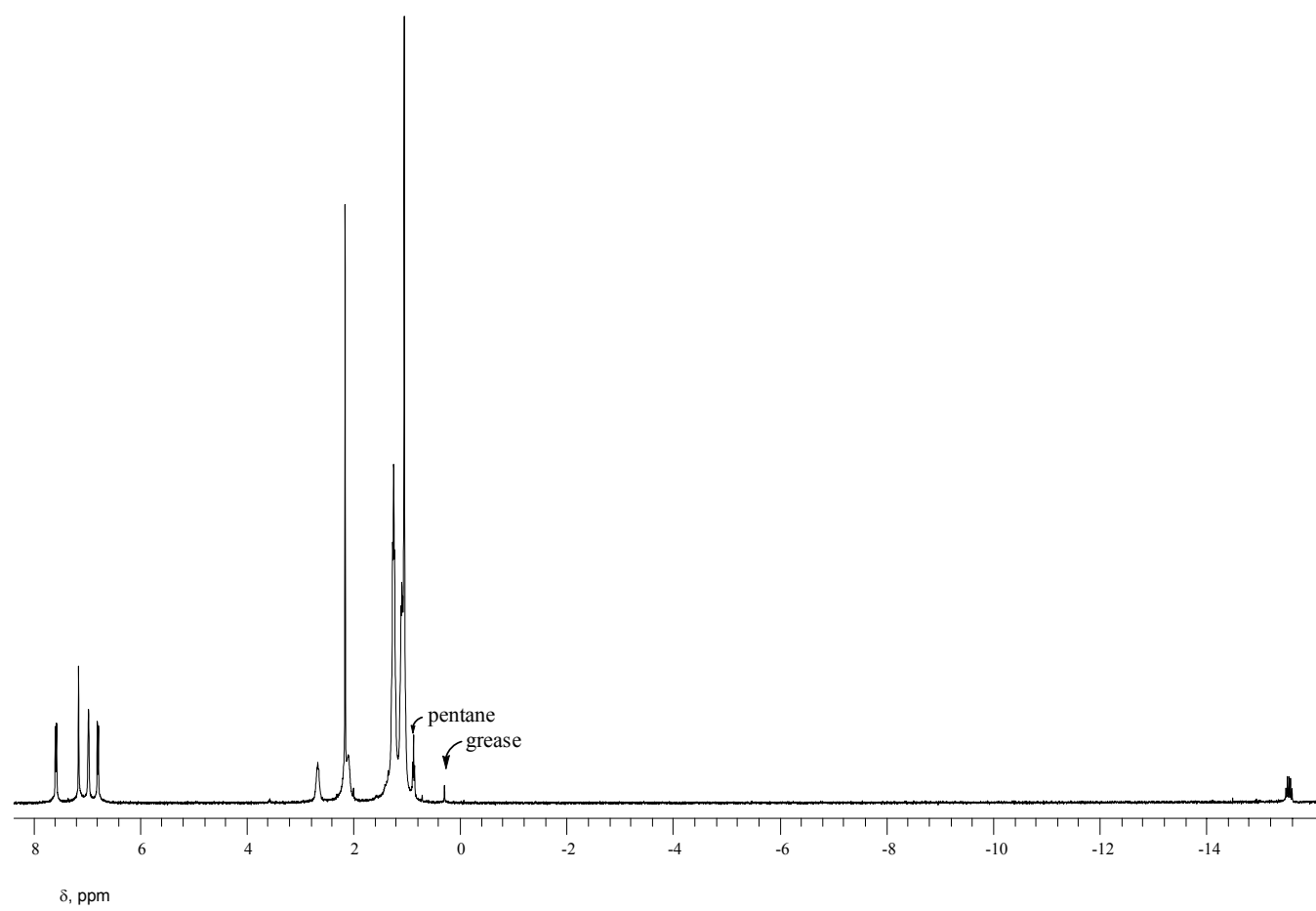
Oxidative Addition Reactions of Silyl Halides with the (PNP)Rh fragment

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Figure S-1. ^1H NMR spectrum of $(\text{PNP})\text{Rh}(\text{H})(\text{SiClMe}_2)$ (**15**) in C_6D_6 .



X-Ray data collection, solution, and refinement for 7. All operations were performed on a Bruker-Nonius Kappa Apex2 diffractometer, using graphite-monochromated MoK α radiation. All diffractometer manipulations, including data collection, integration, scaling, and absorption corrections were carried out using the Bruker Apex2 software.¹ Preliminary cell constants were obtained from three sets of 12 frames. Data collection was carried out at 120K, using a frame time of 10 sec and a detector distance of 60 mm. The optimized strategy used for data collection consisted of nine phi scan sets, with 0.5° steps in phi or omega; completeness was 98.2%. A total of 4453 frames were collected. Final cell constants were obtained from the xyz centroids of 9076 reflections after integration.

From the systematic absences, the observed metric constants and intensity statistics, space group $P2_1/n$ was chosen initially; subsequent solution and refinement confirmed the correctness of this choice. The structures were solved using SIR-92,² and refined (full-matrix-least squares) using the Oxford University *Crystals for Windows* program.³ All ordered non-hydrogen atoms were refined using anisotropic displacement parameters; hydrogen atoms were fixed at calculated geometric positions and allowed to ride on the corresponding carbon atoms.

The crystal structure of **7** contained disorder of a methine carbon atom on one of the PNP isopropyl groups, which was resolved successfully. The two-component disorder was described with a constraint that the occupancies of the major and minor components sum to 1.0. Major component atoms were refined by using anisotropic displacement parameters, while minor component atoms were refined by using isotropic displacement parameters. The atom C(21) was disordered, with the occupancy of the major component at 0.778(11). The final least-squares refinement converged to $R_1 = 0.0375$ ($I > 2\sigma(I)$, 6510 data) and $wR_2 = 0.112$ (F^2 , 9076 data, 321 parameters).

X-Ray data collection, solution, and refinement for 15. All operations were performed on a Bruker-Nonius Kappa Apex2 diffractometer, using graphite-monochromated MoK α radiation. All diffractometer manipulations, including data collection, integration, scaling, and absorption corrections were carried out using the Bruker Apex2 software.¹ Preliminary cell constants were obtained from three

sets of 12 frames. Data collection was carried out at 120K, using a frame time of 20 sec and a detector distance of 60 mm. The optimized strategy used for data collection consisted of six phi and omega scan sets, with 0.5° steps in phi or omega; completeness was 98.9%. A total of 2874 frames were collected. Final cell constants were obtained from the xyz centroids of 8785 reflections after integration.

From the systematic absences, the observed metric constants and intensity statistics, space group *C2/c* was chosen initially; subsequent solution and refinement confirmed the correctness of this choice. The structure was solved using SIR-92,² and refined (full-matrix-least squares) using the Oxford University *Crystals for Windows* program.³ The hydride ion was located on an electron density difference map, and refined by using isotropic displacement parameters. The final Rh-H distance, 1.50(2) Å, is consistent with other Rh-H distances found in the Cambridge Structural Database.⁴ All ordered non-hydrogen atoms were refined using anisotropic displacement parameters; other hydrogen atoms were fixed at calculated geometric positions and allowed to ride on the corresponding carbon atoms.

Compound **15** contained significant disorder, which was resolved successfully. The chlorodimethylsilyl moiety is rotationally disordered; however, the disorder is not statistical. Resolution of the disorder was achieved by restraining the occupancies of the Cl atoms to sum to 1.0, and constraining the occupancies of each of the three carbon-chlorine pairs to sum to 1.0. Major component atoms were refined by using anisotropic displacement parameters, while minor component atoms were refined by using isotropic displacement parameters. The disordered pairs Cl1/C29, Cl11/C27, Cl12/C28 had Cl atom occupancies of 0.766(4), 0.071(3) and 0.163(3), respectively. The final least-squares refinement converged to $R_1 = 0.0271$ ($I > 2\sigma(I)$, 7553 data) and $wR_2 = 0.0644$ (F^2 , 8785 data, 326 parameters).

Supporting information references.

- (1) Apex2, Version 2 User Manual, M86-E01078, Bruker Analytical X-ray Systems, Madison, WI, June 2006.
- (2) Altomare, A; Cascarano, G; Giacovazzo, G.; Guagliardi, A.; Burla, M. C.; Polidori, G.; Camalli, M. *J. Appl. Cryst.* **1994**, 27, 435.
- (3) Betteridge, P. W.; Carruthers, J. R.; Cooper, R. I.; Prout, K.; Watkin, D. J. *J. Appl. Cryst.* **2003**, 36, 1487.
- (4) Allen, F. H. *Acta Crystallogr., Sect. B*, **2002**, 58, 380-388.