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Intramolecular B−H Bond Activation from a Dihydridobis(dimethylpyrazolyl)borate Ligand: Formation of a Rhodium(III) Carbene Hydride and a Rare Example of Reverse α-Hydride Migration

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*Summary: The new complex $Bp^{Me_2}Rh(CO)(pyridine)$ (**1**) has been prepared and reacts with CH_3I to yield the novel Rh carbene hydride complex $HB(Me_2pz)_2Rh(H)(I)(C_5H_5N)(C(O)Me)$ (**3**), resulting from formal addition of CH_3I across the Rh−C bond concomitant with hydride transfer from B to Rh. Thermolysis of **3** induces migration of the Rh hydride to the α-carbon to give $HB(Me_2pz)_2Rh(I)(C_5H_5N)(CH(O)Me)$ (**6**), and a crossover study supports intramolecular mechanisms for both hydride transfer steps.*

The hydridotris(3,5-dimethylpyrazolyl)borate (Tp^{Me_2}) fragment, isoelectronic with though structurally distinct from cyclopentadienyl, has become a versatile and well-studied ancillary ligand in organometallic chemistry.[1−3] In contrast, the bidentate dihydridobis(3,5-dimethylpyrazolyl)borate (Bp^{Me_2}) ligand and its variously substituted derivatives have been utilized less often.[4−9] While most applications of the ligand have relied on the innocence of the BH_2 moiety, this functionality is intriguing in light of the proximity to the coordinated metal center of two potentially reactive hydrides and a latent Lewis acidic center at boron; several instances of B−H reactivity have already been described.[10−14] Here we report the preparation of $Bp^{Me_2}Rh(CO)(pyridine)$ (**1**) and its unexpected reaction with CH_3I, involving transfer of the boron-bound hydrogen in the Bp^{Me_2} ligand to Rh. This activation of the ancillary ligand leads to a novel boron-stabilized Rh carbene hydride complex, which upon thermolysis undergoes a reverse α-hydride migration to leave a stable 5-coordinate, electronically unsaturated Rh(III) center.

Our starting point in the preparation of **1** was the known $Bp^{Me_2}Rh(CO)_2$ complex **2**.[15] Consistent with literature observations,[15] while displacement of a CO ligand in **2** by triphenylphosphine was rapid at room temperature, the analogous substitution by pyridine did not proceed thermally, nor did it proceed in our initial attempts at photochemical activation.[16] As an alternate means of effecting the reaction with pyridine, we elected to activate **2** with trimethylamine *N*-oxide, which has been shown in many cases to labilize CO ligands by oxidation to CO_2.[17] Treatment of a yellow pyridine solution of dicarbonyl **2** with a stoichiometric amount of trimethylamine *N*-oxide results in a color change to bright orange. The reaction proceeds over the course of 1 h at room temperature, leading to yellow-orange $Bp^{Me_2}Rh(CO)(pyridine)$ (**1**) in 77% yield after crystallization (Scheme 1).[18] The complex exhibits a single CO stretch in the IR at 1972 cm^{-1} (cyclohexane), and the ^1H NMR spectrum of **1** in benzene solution is characterized by four methyl singlets at 1.50, 2.33, 2.35, and 2.53 ppm, two methyne singlets at 5.50 and 5.66 ppm, and three pyridine resonances at 6.03, 6.50, and 8.45 ppm. The inequivalence of the four pyrazolyl methyl groups and two methyne protons is indicative of a square-planar geometry at the metal center.

Interestingly, the CO stretching frequency of **1** in cyclohexane is the same as that observed for the closely related transient (η^3-Tp^{Me_2})Rh(CO) alkane adduct, which Bromberg et al. identified spectroscopically on the pathway for photoinduced C−H bond activation by $Tp^{Me_2}Rh(CO)_2$.[19] We were therefore somewhat surprised to find that complex **1** does not react with C−H

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[13] Gorrell, I. B.; Looney, A.; Parkin, G.; Rheingold, A. L. *J. Am. Chem. Soc.* **1990**, *112*, 4068 and references therein.

[14] Recently Hill and co-workers reported intramolecular B−H oxidative addition at Ru from the related hydridotris(2-sulfanyl-1-methylimidazolyl)borate ligand: Hill, A. F.; Owen, G. R.; White, A. J. P.; Williams, D. J. *Angew. Chem., Int. Ed.* **1999**, *38*, 2759.

[15] Bonati, F.; Minghetti, G.; Banditelli, G. *J. Organomet. Chem.* **1975**, *87*, 365.

[16] Complex **1** can be prepared by photolysis of pyridine solutions of $Bp^{Me_2}Rh(CO)_2$ with a vigorous N_2 purge to prevent CO recombination, but yields in this case are highly dependent on the purge rate, and several unidentified impurities formed in this procedure proved very difficult to separate from the product.

[17] Crabtree, R. H. *The Organometallic Chemistry of the Transition Metals*, 2nd ed.; Wiley: New York, 1994; p 77.

[18] The reaction does not proceed with pyridine *N*-oxide as oxidant, even upon heating to 75 °C. Treatment of $Bp^{Me_2}Rh(CO)_2$ with trimethylamine *N*-oxide in solvents other than pyridine (benzene, CH_2Cl_2, THF) results in decomposition.

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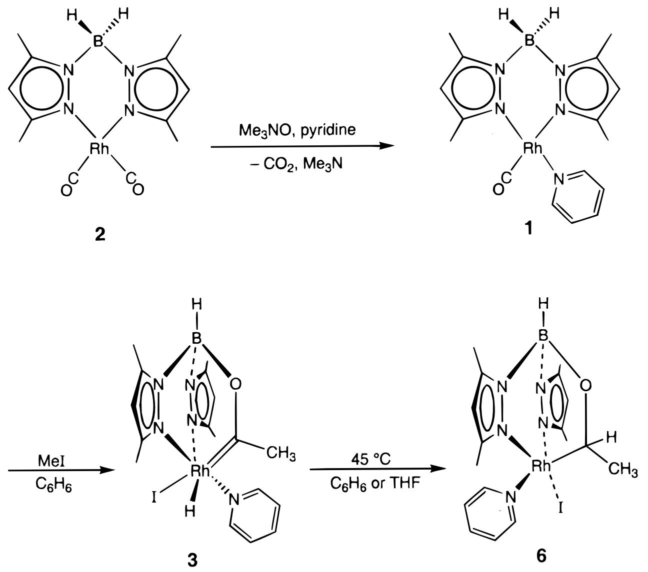
Scheme 1



or Si−H bonds at 45 °C.[20] However, treatment of a benzene solution of **1** with iodomethane results in immediate reaction at room temperature to form a new product quantitatively, as judged by ^{1}H NMR.[21] The ^{1}H NMR spectrum of this species exhibits a doublet at −14.2 ppm characteristic of a hydride bound to Rh. The IR spectrum exhibits a Rh−H stretch at 2060 cm^{-1}. Because we were unable to come to a definitive decision about the structure on the basis of these spectroscopic data, an X-ray diffraction analysis was carried out on crystals obtained from a THF/pentane solution. The product was shown to have the structure **3**, as illustrated in Scheme 1 and Figure 1. Formation of **3** involves a surprisingly deep-seated series of overall bonding changes: addition of the C−I bond across the M−C bond of a CO ligand to give an acyl or oxycarbene functionality, which is presumably stabilized by coordination of its oxygen atom to the Bp^{Me_2} boron atom, and transfer of a hydrogen from the boron center to rhodium.

The Rh═C−O moiety in **3** bears significant Fischer carbene character, as evidenced by a 300 ppm downfield chemical shift for this carbon in the ^{13}C{^{1}H} NMR spectrum (J_{Rh-C} = 35 Hz),[22] and by its relatively short Rh−C bond length (1.91 Å). For comparison, typical Rh−C single bond lengths in Rh(III) acyl moieties range from 1.93 to 2.06 Å.[23−25]

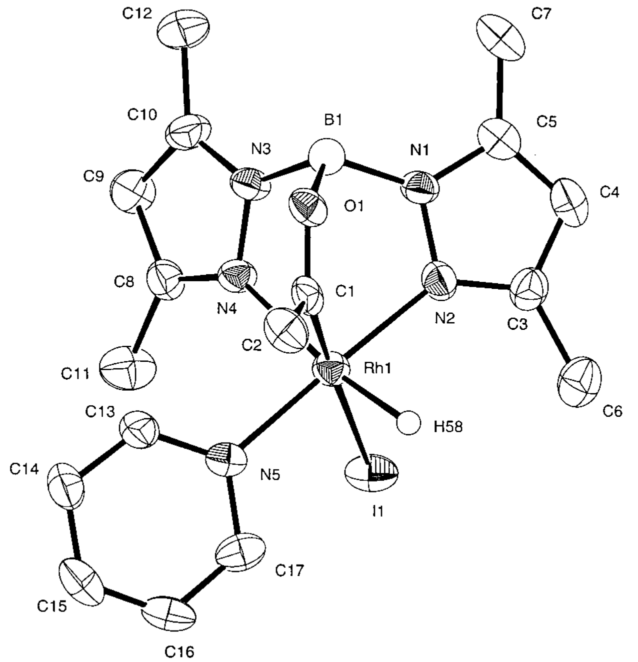


Figure 1. ORTEP diagram of **3**.

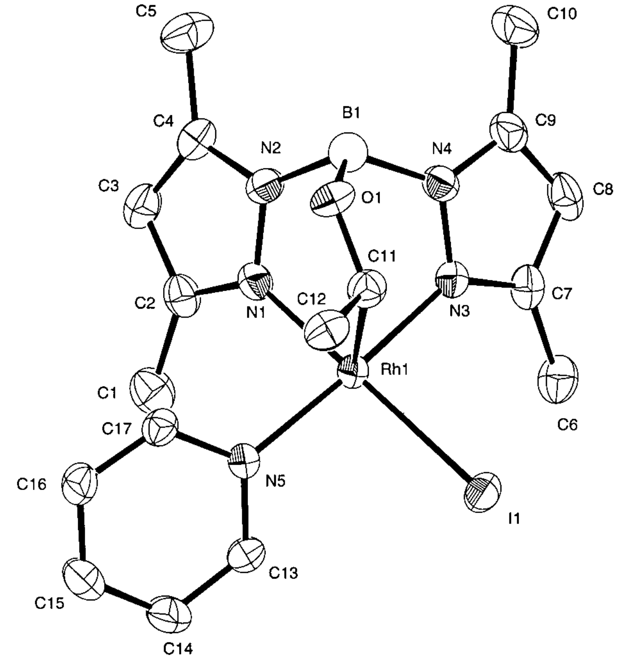


Figure 2. ORTEP diagram of **6**.

Further transformation of **3** yields a second unexpected result. Thermolysis of the carbene complex in benzene or THF at 45 °C for 36 h results in formation of a new product in 71% NMR yield (Scheme 1). Crystals of this product, obtained in 60% yield by vapor diffusion of pentane into a toluene solution at −35 °C, were analyzed by X-ray diffraction and shown to have the structure **6**, illustrated in Scheme 1 and Figure 2. Formation of **6** from **3** thus entails migration of the hydride ligand from the metal center to the carbene carbon (the α-carbon bound to oxygen), leading to a coordinatively unsaturated Rh bearing a boron-stabi-

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(19) Bromberg, S. E.; Yang, H.; Asplund, M. C.; Lian, T.; McNamara, B. K.; Kotz, K. T.; Yeston, J. S.; Wilkens, M.; Frei, H.; Bergman, R. G.; Harris, C. B. *Science* **1997**, *278*, 260.

(20) We suspect that the reactivity differences between **1** and the isoelectronic Tp^{Me_2}Rh(CO) fragment may in large part be due to the different geometries of the two species. The chelating nature of the Tp^{Me_2} ligand enforces a tetrahedral coordination environment around the Rh center, whereas the Bp^{Me_2} and pyridine ligands permit a (presumably) more stable square planar geometry. Analogous group 9 square-planar complexes such as Vaska's complex and Wilkinson's catalyst are similarly inert toward aliphatic hydrocarbons.[35]

(21) Neither the dicarbonyl complex **2** nor the phosphine carbonyl complex Bp^{Me_2}Rh(CO)PPh$_3$ reacts with iodomethane, even upon prolonged heating of benzene solutions at 75 °C. This reactivity difference between the pyridine-substituted Rh complex and the phosphine- and carbonyl-substituted complexes raises the question of whether pyridine dissociation is involved in the mechanism of reaction with iodomethane. Unfortunately, this hypothesis could not easily be tested by addition of free pyridine to the reaction mixture, since under those conditions quaternization of the pyridine by iodomethane is a competitive process.

(22) Dötz, K. H.; Fischer, E. O. *Transition Metal Carbene Complexes*; Verlag Chemie: Weinheim, Germany, 1983.

(23) Adams, H.; Bailey, N. A.; Mann, B. E.; Manuel, C. P. *Inorg. Chim. Acta* **1992**, *198*, 111.

(24) Bennett, M. A.; Jeffery, J. C.; Robertson, G. B. *Inorg. Chem.* **1981**, *20*, 323.

(25) Moloy, K. G.; Petersen, J. L. *Organometallics* **1995**, *14*, 2931.

lized 1-alkoxyethyl group. In the $^{13}C\{^1H\}$ NMR spectrum of **6**, the α-carbon resonance now appears as a doublet at 89 ppm ($J_{Rh-C} = 20$ Hz), while the proton bound to this carbon evidences a surprisingly downfield multiplet at 7.97 ppm ($J_{Rh-H} = 5$ Hz, $J_{H-H} = 4$ Hz) in the ^1H NMR spectrum. As shown in Figure 2, complex **6** exhibits a square-pyramidal geometry about the 5-coordinate Rh center (the sum of the angles formed by I, the pyridine nitrogen, and the pyrazolyl nitrogens with Rh at the vertex is 359.7°). Conversion of **3** to **6** results in a lengthening of the Rh−C and C−O bonds (from 1.91 to 2.11 Å and 1.28 to 1.36 Å, respectively) and concomitant shortening of the O−B bond from 1.55 to 1.45 Å.[26]

To distinguish intermolecular and intramolecular mechanisms of hydride transfer, both in the conversion of **1** to **3** and **3** to **6**, we performed a crossover experiment employing unlabeled **1** and doubly labeled d_2-$B[(CH_3)_2pz]Rh(^{13}CO)(py)$.[27] In a reaction mixture of these two complexes and iodomethane, an intermolecular hydride migration would lead to a statistical mixture of H and D bound to ^{12}C and ^{13}C in the final product **6**, while an intramolecular mechanism would yield only $^{12}C-H$ and $^{13}C-D$ products. A slight complication resulted from the fact that the deuterated Bp^{Me_2} ligand, prepared from dimethylpyrazole and $NaBD_4$,[28] could not be isolated without significant hydride incorporation at the boron (perhaps from the glassware surface), despite prior deuteration of the pyrazole nitrogen and attempts to deuterate the glassware. This exchange process was no longer active once the ligand was bound to Rh: IR analysis of doubly labeled **1** revealed >93% ^{13}C incorporation and 60% deuterium incorporation at boron. Equimolar amounts of this complex and unlabeled **1** were dissolved together in benzene and treated with iodomethane, after which the solution was thermolyzed to form **6**.[29] Analysis of the product mixture by ^1H and ^2H NMR spectroscopy supported a strictly intramolecular mechanism for both hydride migrations (B to Rh and Rh to C). The ^1H spectrum of the thermolyzed solution exhibited one resonance at 7.97 ppm with an integral of 0.5, corresponding to the proton on the unlabeled α-carbon; additionally, two ^{13}C-coupled satellites of this resonance ($J_{C-H} = 170$ Hz) were integrated together to 0.2, consistent with the initial 40% H incorporation at B in the ^{13}C-labeled starting material. In the ^2H spectrum, only a ^{13}C-coupled doublet was evident for the deuterium bound to the α-carbon, indicating that no intermolecular transfer had proceeded to place deuterium on a ^{12}C.

We do not yet have additional information about the mechanisms of these processes. However, we believe that formation of **3** from **1** proceeds by initial oxidative addition of iodomethane across the Rh center, followed by migratory insertion of the methyl group. The hydride transfer step remains intriguing. Several Bp-substituted transition-metal complexes show evidence of an agostic interaction between the boron-bound hydride and the metal center,[30−32] which supports a low-energy transition-state geometry for hydride migration in the formation of **3**. It is thus unclear whether the hydride transfer precedes or follows the methyl migration. Shriver and co-workers have demonstrated dramatic acceleration of migratory insertions upon coordination of Lewis acids to metal-bound CO ligands.[33,34] If hydride transfer preceded methyl migration in the formation of **3**, the boron could serve effectively as a tethered Lewis acid to catalyze the methyl migratory insertion.

The conversion of **3** to **6** is a rare instance of reverse α-hydride migration. There have been very few direct observations of 1,2-migration from a metal center to a carbene carbon, despite the fact that migration in the opposite direction to form the carbene is quite common.[35−38] In the present case, it is particularly notable that the hydride transfer to carbon is irreversible, despite its resulting in a coordinatively and electronically unsaturated metal center. Once again, coordination of the oxygen to the Lewis acidic boron may help to drive the migration. The overall transformation from **1** to **6** is not unprecedented: Carmona and co-workers showed in 1995 that thermolysis of $Bp^{Me_2}Mo(PMe_3)(CO)_2(C(O)Me)$ at 70 °C results in hydride migration from the boron to the acyl carbon.[12] In that case the Mo center remains coordinatively saturated throughout the reaction.

Acknowledgment. We are grateful to Dr. Dana Caulder and Dr. Fred Hollander of the UC Berkeley CHEXRAY facility for X-ray structure determinations of **3** and **6**. Dr. Peter Alaimo and Mr. David Tellers are gratefully acknowledged for helpful discussions. This work was supported by the Director, Office of Energy Research, Office of Basic Energy Sciences, Chemical Sciences Division, U.S. Department of Energy, under contract No. DE-AC03-76SF00098. We also appreciate a fellowship to R.G.B. from the John Simon Guggenheim Memorial Foundation.

Supporting Information Available: Text giving experimental details for the preparation and full spectroscopic and analytical characterization data for **1**, **3**, and **6** and figures and tables giving X-ray crystallographic data for **3** and **6**. This material is available free of charge via the Internet at http://pubs.acs.org.

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(26) The bond lengths given here for **3** are averaged for two inequivalent molecules in the unit cell. The bond lengths and angles for each individual molecule are given in the Supporting Information.

(27) ^{13}CO incorporation was achieved by stirring a benzene solution of $[Rh(CO)_2Cl]_2$ under 1 atm of ^{13}CO for 8 h prior to preparation of **2**. See: Adams, H.; Bailey, N. A.; Mann, B. E.; Manuel, C. P.; Spencer, C. M.; Kent, A. G. *J. Chem. Soc., Dalton Trans.* **1988**, 489.

(28) The deuterated $NaBp^{Me_2}$ salt was prepared using the published procedure for preparation of unlabeled KBp^{Me_2}: Trofimenko, S. *Inorg. Chem.* **1970**, *9*, 2493.

(29) The carbene product **3**-d_2 was independently characterized and exhibited a Rh−D resonance at −14.2 ppm in the ^2H NMR spectrum and a Rh−D stretch at 1448 cm^{-1} in the IR spectrum.

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(37) For an example of reversible α-hydride migration, see: Parkin, G.; Bunel, E.; Burger, B. J.; Trimmer, M. S.; Van Asselt, A.; Bercaw, J. E. *J. Mol. Catal.* **1987**, *41*, 21.

(38) For a recent example of alkyl migration from a metal center to an alkylidene carbon, see: Muir, J. E.; Haynes, A.; Winter, M. J. *Chem. Commun.* **1996**, 1765 and references therein.