[(^{t}Bu$_2$PCH$_2$SiMe$_2$)$_2$N]Rh^I? Rapidly Reversible H−C(sp^3) and H−C(sp^2) Bond Cleavage by Rhodium(I)

Alexander Y. Verat, Maren Pink, Hongjun Fan, John Tomaszewski, and Kenneth G. Caulton*

Department of Chemistry, Indiana University, Bloomington, Indiana 47405

Received November 20, 2007

Summary: The product of the reaction of (^{t}Bu$_2$PCH$_2$SiMe$_2$)$_2$N$^-$ (MgCl$^+$ salt) with [RhCl(cyclooctene)$_2$]$_2$ is a Rh^{III} complex where one ^{t}Bu methyl C−H bond has oxidatively added to Rh: (PNP)RhH. This is in rapid exchange among all 9 × 4 C−H bonds of the four ^{t}Bu groups. (PNP*)RhH undergoes oxidative addition equilibrium with the C−H bonds of benzene at ∼10^3 s^{-1} at 25 °C and oxidatively adds the ring C−H of other arenes. (PNP*)RhH forms η^2-olefin complexes with several olefins and dehydrogenates allylic C−H bonds to form (PNP)Rh(H)$_2$.*

Following the synthesis and characterization[1,2] of the unusual three-coordinated, T-shaped molecule [(^{t}Bu$_2$PCH$_2$SiMe$_2$)$_2$N]Co, or (PNP)Co, we became interested in whether a rhodium analogue could be produced in order to compare its reactivity (3d vs 4d metal). While there are several examples which might qualify as precedents, among them [Rh(PPh$_3$)$_3$]$^+$,[3] and [(^{t}Bu$_2$P)$_2$CH$_2$]Rh(CH$_2$^{t}Bu),[4] and (nacnac)Rh(olefin),[5,6] all but the last involve agostic interactions which occupy a fourth coordination site. Moreover, achieving a 3-coordinate, 14-valence-electron species for cobalt might have been due in part to the presence of two singly occupied valence orbitals (triplet ground state) in (PNP)Co, a feature we doubted would be true of (PNP)Rh. We report here on the synthesis and characterization of "(PNP)Rh", a molecule of exceptional reactivity, together with its selectivity for C−H bond cleavage. As such, this contributes observational evidence on the general class of molecules which have previously been characterized only by DFT methods during the course of mechanistic studies of catalytic alkane dehydrogenation by (pincer)Ir species.[7–11]

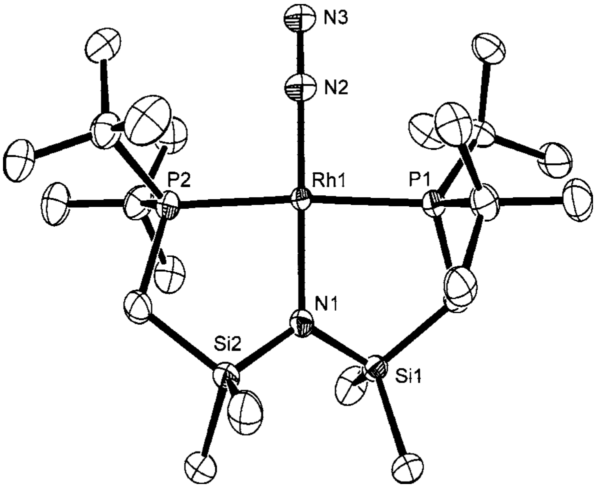


Figure 1. ORTEP view (50% probability ellipsoids) of the non-hydrogen atoms of (PNP)Rh(N$_2$), showing selected atom labeling. Unlabeled atoms are carbon.

Reaction[12] of (PNP)MgCl with [RhCl(cyclooctene)$_2$]$_2$ (2:1) in cyclohexane at 23 °C for 50 min gives olefin-free **1**, which reacts in the time of mixing at 23 °C with N$_2$ and with H$_2$ to form (PNP)Rh(N$_2$) (Figure 1)[12] and (PNP)Rh(H)$_2$, respectively. The dihydride (not η^2-dihydrogen) assignment of the latter product relies on a J_{HD} value measured as 6 Hz, which is too small[13] for H$_2$. Both products bind their gaseous ligand tightly enough to survive vacuum drying to solids, unlike the case for their cobalt analogues.[2] The NN stretching frequency of (PNP)Rh(N$_2$), 2092 cm^{-1}, is the lowest among known Rh(I) N$_2$ complexes[14] and supports the PNP anion as enhancing the π-basicity of Rh(I).

Proton and ^{31}P NMR spectra of **1** in d_{12}-cyclohexane at 25 °C are in agreement with C_{2v} symmetry. The ^{31}P{^{1}H} NMR signal (45 ppm) of (PNP)Rh in d_{14}-methylcyclohexane in the temperature range −10 to −60 °C shows increasing broadening and then decoalescence by −50 °C into two equally intense (but still 6 ppm broad) signals separated by 38 ppm, but averaging to the 25 °C value; thus the phosphorus nuclei are not equivalent in the ground-state structure. Because this observed ^{31}P chemical shift difference (38 ppm) was large compared to the difference calculated (DFT) from agostic conformers of (PNP)Rh^I, we looked harder for a hydride resonance. Only at −60 °C is an extremely broad ^{1}H NMR (500 MHz) hydride signal seen (−13.0 ppm), and this becomes

---

* To whom correspondence should be addressed. E-mail: caulton@indiana.edu.

[1] Ingleson, M. J.; Pink, M.; Caulton, K. G. *J. Am. Chem. Soc.* **2006**, *128*, 4248.

[2] Ingleson, M.; Fan, H.; Pink, M.; Tomaszewski, J.; Caulton, K. G. *J. Am. Chem. Soc.* **2006**, *128*, 1804.

[3] Yared, Y. W.; Miles, S. L.; Bau, R.; Reed, C. A. *J. Am. Chem. Soc.* **1977**, *99*, 7076.

[4] Urtel, H.; Meier, C.; Eisentrager, F.; Rominger, F.; Joschek, J. P.; Hofmann, P. *Angew. Chem., Int. Ed.* **2001**, *40*, 781.

[5] Budzelaar, P. H. M.; De Gelder, R.; Gal, A. W. *Organometallics* **1998**, *17*, 4121.

[6] Budzelaar, P. H. M.; Moonen, N. N. P.; De Gelder, R.; Smits, J. M. M.; Gal, A. W. *Eur. J. Inorg. Chem.* **2000**, 753.

[7] Wang, K.; Goldman, M. E.; Emge, T. J.; Goldman, A. S. *J. Organomet. Chem.* **1996**, *518*, 55.

[8] Xu, W.-w.; Rosini, G. P.; Krogh-Jespersen, K.; Goldman, A. S.; Gupta, M.; Jensen, C. M.; Kaska, W. C. *Chem. Commun.* **1997**, 2273.

[9] Gupta, M.; Hagen, C.; Flesher, R. J.; Kaska, W. C.; Jensen, C. M. *Chem. Commun.* **1996**, 2083.

[10] Zhu, K.; Achord, P. D.; Zhang, X.; Krogh-Jespersen, K.; Goldman, A. S. *J. Am. Chem. Soc.* **2004**, *126*, 13044.

[11] Liu, F.; Pak, E. B.; Singh, B.; Jensen, C. M.; Goldman, A. S. *J. Am. Chem. Soc.* **1999**, *121*, 4086.

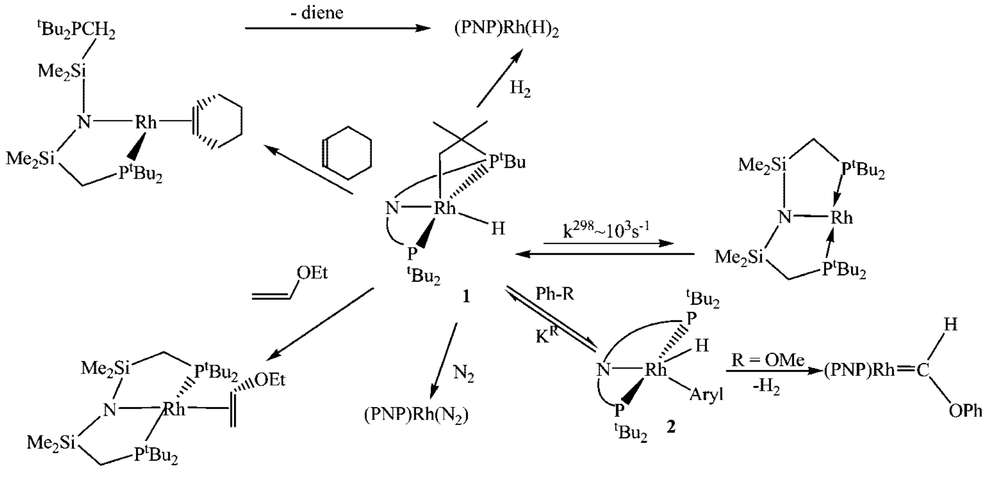
[12] See the Supporting Information.

[13] Kubas, G. J. *Dihydrogen and σ-Bond Complexes*; Kluwer Academic/Plenum Publishers: New York, 2001.

[14] Masuda, J. D.; Stephan, D. W. *Can. J. Chem.* **2005**, *83*, 324.

10.1021/om701165n CCC: $40.75

Scheme 1



sharper at lower temperatures, and finally becomes persuasive at −90 to −110 °C; the SiMe region also decoalesces into four signals. “(PNP)Rh” thus actually has the oxidatively added ground-state structure (PNP*)RhH (**1**; Scheme 1), where PNP* is tetradentate on Rh^{III}, via N, 2P, and one formerly ^{t}Bu CH$_3$ carbon. Fluxionality, cycling among 36 different ^{t}Bu C−H bonds, accounts for the unobservability of the hydride resonance at room temperature in this rapidly (~10^3 s^{-1}) reversible alkyl C−H oxidative addition, and thus **1** is a functional source of “(PNP)Rh”.[15,16]

In d_6-benzene, the ^{31}P{^{1}H} chemical shift (55 ppm) differs remarkably from the value (45 ppm) in cyclohexane, pentane, THF, 1,3,5-C$_6$H$_3$Me$_3$, and SiMe$_4$. Vacuum removal of the volatiles from a benzene solution and then dissolution in cyclohexane returns the 45 ppm ^{31}P chemical shift characteristic of virgin **1**. This unusual chemical shift change is also observed in d_8-toluene, in PhOMe, and in PhNMe$_2$. The ^{1}H NMR of **1** plus equimolar benzene at and below approximately −30 °C shows a hydride signal for (PNP)Rh(H)(C$_6$H$_5$) in d_8-THF at −23.0 ppm. The ^{1}H and ^{31}P NMR spectra of (PNP*)RhH in the presence of fluorobenzene (1:1 mol ratio) in d_8-THF below 0 °C shows evidence for two species, each with C_s symmetry. The ^{19}F NMR spectrum also shows two peaks in addition to free PhF; seeing free PhF indicates incomplete (~40%) conversion of (PNP*)RhH. The hydride region at −40 °C shows two (~equimolar) hydride doublets (Rh) of triplets (from P), one with additional doublet splitting due to coupling to F, consistent with the other spectra. While we cannot identify the position of the F on the aryl ring in the two isomers, the reaction is C−H cleavage and is selective for only two isomers. When this sample is vacuum-dried and then dissolved again in deuterated THF or cyclohexane, the populations of (PNP*)RhH and (PNP)Rh(H)(C$_6$H$_4$F) are unchanged. Consistent with this, even at 25 °C, one sees separate ^{31}P NMR signals for these two molecules, indicating that they are not in rapid (half-life <1 s) equilibrium at that temperature. We propose that arenes oxidatively add to (PNP*)RhH (Scheme 1) and that the NMR spectra reflect varying populations of **1** and **2** under conditions of fast exchange (i.e., dynamically averaged NMR spectra). By measuring the average ^{31}P chemical shift in cyclohexane/benzene mixtures at 25 °C, it is possible to evaluate K. This yielded $K°_{298} = 1.16 \pm 0.05$; thus, $\Delta G° \approx 0$ and, with $\Delta H° \approx T\Delta S°$ (a typical value[17] of this entropy term is 10 ± 2 kcal/mol), $\Delta H°$ for benzene C−H oxidative addition is ~10 kcal/mol. In pure benzene, the (aryl)Rh^{III}H product achieves a mole fraction of about 93%.

When the ^{31}P NMR is measured in a coaxial NMR tube, with **1** in both the inner tube, in C$_6$H$_6$, and in the outer tube, in C$_6$D$_6$, the ^{31}P chemical shift difference is 1.3 ppm. For comparison, the ^{31}P chemical shifts of (PNP)Rh(N$_2$) in the two solvents differ by only 0.05 ppm. We attribute this large change for **1** to a dynamically averaged case where the D isotope effect on the incomplete (see above) equilibrium shifts the equilibrium populations, with a resulting change in the population-weighted average ^{31}P chemical shift (“isotopic perturbation of resonance”).[18–20] The ^{31}P chemical shift in C$_6$D$_6$ shows that the heavy isotope forms less **2**.

Consistent with the idea of arene C−H oxidative addition (OA) to **1**, we find that addition of naphthalene or acenaphthalene to **1** in cyclohexane causes analogous ^{31}P NMR chemical shift changes, at arene to Rh mole ratios of 16:1 and 12:1, respectively. Arene oxidative addition is thus a general phenomenon; it is not merely “solvation.” While anisole gives the 55 ppm ^{31}P chemical shift characteristic of a C−H OA product, upon heating (90 °C, 12 h), anisole is dehydrogenated at the methyl hydrogens, to give (PNP)Rh(=C(OPh)H) with liberation of H$_2$ (Scheme 1).

We next probed whether **1** would cleave the C−H bonds of isolated vinyl groups. Mixing **1** with the prochiral olefin ethyl vinyl ether (1:4 mole ratio) at 25 °C in benzene gives a 1:1 Rh^I adduct whose ^{31}P{^{1}H} NMR spectrum is an ABX pattern (X = Rh), indicative of C_1 symmetry (Scheme 1). Both J_{PRh} values are large enough to indicate direct Rh−P bonding, four SiMe and four ^{t}Bu (doublet) ^{1}H NMR signals are observed, and the ethyl CH$_2$ protons are diastereotopically inequivalent in the species (PNP)Rh[η^2-H$_2$C=CH(OEt)]. Heating in C$_6$D$_6$ at 90 °C for 12 h gives no change; thus, there is no conversion to any carbene, as occurred with anisole.

In a complete change of behavior, when it is dissolved in neat cyclohexene, **1** gives >80% conversion to a product with an AMX ^{31}P{^{1}H} NMR pattern (X = Rh), where M has nearly the chemical shift of the free ligand and M shows no resolvable

---

(15) Kanzelberger, M.; Singh, B.; Czerw, M.; Krogh-Jespersen, K.; Goldman, A. S. *J. Am. Chem. Soc.* **2000**, *122*, 11017.

(16) Gatard, S.; Celenligil-Cetin, R.; Guo, C.; Foxman, B. M.; Ozerov, O. V. *J. Am. Chem. Soc.* **2006**, *128*, 2808.

(17) Watson, L. A.; Eisenstein, O. *J. Chem. Educ.* **2002**, *79*, 1269.

(18) Heinekey, D. M.; van Roon, M. *J. Am. Chem. Soc.* **1996**, *118*, 12134.

(19) Kozerski, L.; von Philipsborn, W. *Helv. Chim. Acta* **1982**, *65*, 2077.

(20) Saunders, M.; Kates, M. R.; Wiberg, K. B.; Pratt, W. *J. Am. Chem. Soc.* **1977**, *99*, 8072.

coupling to Rh^I or to the other phosphorus. The steric impact of a 1,2-disubstituted olefin is thus sufficient to displace one P^tBu_2 arm (Scheme 1) of the PNP ligand.[21] Nevertheless, over 12–24 h at 23 °C, this (η^2-PNP)Rh^I(olefin) adduct disappears, with formation of (PNP)Rh$(H)_2$, by apparent dehydrogenation of the allylic hydrogens. This same "arm-off" adduct formation is observed with neat 1,4-cyclohexadiene, and conversion to (PNP)Rh$(H)_2$ occurs even more quickly at 23 °C than with cyclohexene; 1,3-cyclohexadiene behaves analogously.

It is thus clear that the PNP ligand offers access to a 3-coordinated, but electron-rich (!) 14-electron Rh species which permits observation and quantification of dynamically averaged NMR of methyl H−C(sp^3) oxidative addition/reductive elimination. Related dynamic observations have been made[15] for the pincer (PCP)IrH(aryl); C−H bond cleavage generally has more favorable thermodynamics for Ir than for Rh, but an Rh precedent has been reported.[22] The lack of bimolecular cleavage of unactivated H−C(sp^3) bonds observed here is due to the less favorable thermodynamics for this reaction (i.e., the M−aryl bond is stronger than M−alkyl),[23] but the near-accessibility of this reaction is seen in the case of benzylic (anisole) and allylic (the C_6 mono- and dienes) C−H bonds. The generally greater M−H bond strength (vs M−C) leaves (PNP)Rh$(H)_2$ stable to vacuum, but (PNP)RhH(phenyl) loses arene under vacuum at 25 °C, which makes the latter challenging to characterize.

The facile reversibility observed here for H−aryl cleavage directly compares the free energies of H−aryl and H−C(sp^3) bonds, but only the former suffers the ~11 kcal/mol entropic penalty for a bimolecular process at 298 K. In this way, an intramolecular H−C(sp^3) cleavage can compete with a bimolecular H−aryl cleavage, but our results establish that the low barriers for both allow them to be coalesced by ^{1}H NMR even at ~0 °C. While H−C(sp^3) cleavage with the ligand is favored over alkane solvent conversion for reasons of entropy, arene σ(CH) bonds are still more favored.

Acknowledgment. We thank Prof. V. G. Shtyrlin for assistance in determining the equilibrium binding constant. This work was supported by the NSF (Grant No. CHE 05 44829). ChemMatCARS Sector 15 is principally supported by the National Science Foundation/Department of Energy under Grant No. CHE0087817. The Advanced Photon Source is supported by the U.S. Department of Energy, Basic Energy Sciences, Office of Science, under Contract No. W-31-109-Eng-38.

Supporting Information Available: Text, tables, and figures giving full computational and experimental details and spectroscopic data and a CIF file giving crystal data for (PNP)Rh(N_2). This material is available free of charge via the Internet at http://pubs.acs.org.

OM701165N

---

(21) Dani, P.; Richter, B.; van Klink, G. P. M.; van Koten, G. *Eur. J. Inorg. Chem.* **2001**, 125.

(22) Canepa, G.; Brandt, C. D.; Ilg, K.; Wolf, J.; Werner, H. *Chem. Eur. J.* **2003**, *9*, 2502.

(23) Wick, D. D.; Jones, W. D. *Organometallics* **1999**, *18*, 495.