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Half-Sandwich Iminophosphonamide Rhodium Complexes as Highly Efficient Catalysts for Dehydrogenation of Dimethylamine-Borane

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Abstract—The dehydrogenation of dimethylamine-borane (DMAB) catalyzed by the iminophosphonamide rhodium(III) complexes [Cp*RhCl{Ph_2P(N–*p*-Tol)(NR)}] (**Ia**, R = *p*-Tol; **Ib**, R = Me) as well as their in situ formed fulvene [(η^4-$C_5Me_4CH_2$)Rh(NPN)] (**IIa**, **IIb**) and diene [(η^4-C_5Me_5H)Rh(NPN)] (**IIIa**, **IIIb**) rhodium(I) derivatives is studied. Catalysts **IIIa** and **IIIb** turn out to be the most active and demonstrate a TOF activity of 110 (**IIIa**) and 540 h^{-1} (**IIIb**) at 40°C in toluene. The activity decreases significantly in more polar and coordinating THF. At the same time, the rate of DMAB dehydrogenation by complexes **Ia** and **Ib** is lower by 10–30 times, and fulvene complexes **Ia** and **Ib** are rapidly deactivated after the active initial period (<20% conversion). The kinetic studies show that the reaction has the first order with respect to the substrate and the catalyst. The model ^{11}B NMR experiments confirm that the reaction proceeds via the intermediate formation of a monomer $Me_2N{=}BH_2$, which rapidly dimerizes to $(Me_2N{-}BH_2)_2$. The mechanism of DMAB dehydrogenation with the formation of unstable hydride intermediate [Cp*RhH{Ph_2P(N–*p*-Tol)(NR)}] (**IVa**, **IVb**) is proposed on the basis of the preliminarily ^{31}P NMR results and published data.

Keywords: iminophosphonamide rhodium complexes, dehydrogenation of amine-boranes, catalysis, reaction mechanism

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INTRODUCTION

Amine-boranes RR'NH·BH_3 are considered as compounds for chemical hydrogen storage and as precursors for the fabrication of BN ceramics and new polymer materials: so-called inorganic polymers [1–5]. The catalytic dehydrogenation (dehydrocoupling and dehydropolymerization) of amine-boranes is the subject of active research, since the development of reliable, stable, and controlled processes remains a largely unsolved problem. Numerous catalysts developed for dehydrogenation act via various mechanisms of the metal–ligand interaction [6–13], and new complexes continue to be described in the literature [14–16]. Reversible switching over different coordination modes found in these compounds shows diverse variants of the activation and formation of polar and nonpolar bonds via both a sequence of oxidative addition/reductive elimination and without changing the oxidation state of the central metal atom.

In this work, the preliminary results of the dehydrogenation of dimethylaminoborane (DMAB, $Me_2NH{-}BH_3$) catalyzed by the rhodium(III) iminophosphonamide complexes [Cp*RhCl(NPN)] (**Ia**, NPN = Ph_2P(N–*p*-Tol)$_2$; **Ib**, NPN = Ph_2P(N–*p*-Tol)(NMe)), in situ formed rhodium(I) fulvene complexes [(η^4-$C_5Me_4CH_2$)Rh(NPN)] (**IIa**, **IIb**), and presumably diene complexes [(η^4-C_5Me_5H)Rh(NPN)] (**IIIa**, **IIIb**) are presented.

EXPERIMENTAL

All experiments were carried out in argon atmosphere using the Schlenk technique in solvents purified by standard methods. ^{1}H, ^{31}P{^{1}H}, and ^{11}B{^{1}H} NMR spectra were recorded on Bruker AMX 400 and Varian iNova 400 spectrometers. Chemical shifts in the NMR spectra are indicated in ppm (δ) relative to tetramethylsilane as the internal standard (^{1}H NMR spectra) and 85% H_3PO_4 and $BF_3{\cdot}OEt_2$ as the external standards (^{31}P and ^{11}B NMR, spectra, respectively). Prior to use the deuterated solvents C_6D_6 and toluene-d_8 were dried from traces of moisture and oxygen over sodium benzophenone ketyl. The complexes [Cp*$RhCl_2$]$_2$ [17] and [Cp*RhCl(NPN)] (**Ia**, **Ib**) [18] were synthesized using known procedures. DMAB was purchased at Sigma-Aldrich and additionally purified by sublimation in vacuo. Sodium hexamethyl

disilazide $Na[N(SiMe_3)_2$ was synthesized using a known procedure [19].

Catalytic studies were carried out in standard experiments. The preliminarily prepared solution of DMAB (0.163 M in toluene, 1.85 mL, 0.30 mmol) was transferred into a two-neck round-bottom 30-mL flask equipped with a three-way valve and tight rubber septa. The temperature of the mixture was maintained at 40°C. A necessary amount of the catalyst (1–4 mol %, 3–12 μmol) in the solid form (**Ia**, **Ib**) either was transferred into a DMAB solution with stirring, or syringed as a freshly prepared solution of complexes **IIa**, **IIb** or **IIIa**, **IIIb** (0.025 M in toluene, 0.24 mL). Hydrogen evolution from DMAB was monitored with the Man on the Moon 203 X102 kit instrument connected via wireless network to the software, which displayed in the online mode the time dependence of the pressure within 2–6 h [10]. The time reading was started from the moment of catalyst introduction. The final kinetic data points were taking into account the toluene pressure in a blank experiment at 313 K and used in the calculation of the number of H_2 equivalents. The calculation was performed in the ideal gas approximation ($pV = nRT$).

Synthesis in situ of [(η⁴-$C_5Me_4CH_2$)Rh{Ph_2P(N–*p*-Tol)(NR)}] (IIa, R = *p*-Tol; IIb, R = Me). Chloride complex **Ia** (**Ib**) (15 μmol) in toluene (0.55 mL) was suspended in a Schlenk flask, a solution of NaHMDS (0.38 M in toluene, 40 μL, 15 μmol) was added dropwise, and the mixture was stirred for 15 min. Then freshly prepared in situ solution of compound **IIa** (**IIb**) was used in catalytic experiments within 2–4 h.

Synthesis in situ of catalyst IIIa (IIIb). Chloride complex **Ia** (75 mg, 110 μmol) in toluene (3 mL) was suspended in a Schlenk flask, a solution of $NaBHEt_3$ in THF (110 μL, 1.0 M, 110 μmol) was added dropwise at –20°C, and the mixture was stirred for 15 min and then warmed to room temperature. A yellow-green solution was evaporated to dryness and dried for 15 min in a vacuum of an oil pump without heating. The dry residue was dissolved in toluene (4.4 mL) to prepare a 0.025 M solution of complex **IIIa** or **IIIb** for the use in the catalytic experiments. ^{31}P NMR (C_6D_6): **IIIa**: 40.4 ppm (d, J_{PRh} = 13.4 Hz); **IIIb**: 47.2 ppm (d, J_{PRh} = 13.1 Hz).

RESULTS AND DISCUSSION

The activity of the bipyridyl complexes $[Cp^*Rh(Bipy)(THF)](OTf)_2$ in the catalytic dehydrogenation of DMAB has recently been shown by Nozaki, and the participation of the hydride $Cp^*Rh(III)H$ complexes and η⁴-cyclopentadiene rhodium(I) complexes as intermediates of the catalytic cycle was proposed [20]. We have recently shown that the reaction of the rhodium(III) iminophosphonamide complexes [Cp*RhCl{Ph_2P(N–*p*-Tol)(NR)}] (**Ia**, **Ib**) with the base in isopropanol does not lead to the expected hydride complexes [Cp*RhH{Ph_2P(N–*p*-Tol)(NR)}] (**IVa**, R = *p*-Tol; **IVb**, R = Me) but affords the fulvene complexes [(η⁴-$C_5Me_4CH_2$)Rh{Ph_2P(N–*p*-Tol)(NR)}] (**IIa**, **IIb**) [18]. The attempt to synthesize Rh(III) hydrides **IVa** and **IVb** using $NaHBEt_3$, resulted in the rearrangement product **IIIa** and **IIIb**, respectively. The synthesized complexes **III**, as well as complexes **I** and **II**, were tested in DMAB dehydrogenation.

The treatment of a suspension of complexes **Ia** and **Ib** in toluene or THF with a solution of $NaHBEt_3$ (THF) at low temperature results in the formation of new complexes **IIIa** and **IIIb**, respectively. The ^{31}P NMR spectra of new compounds exhibit a doublet at 40.4 (**IIIa**) and 47.2 ppm (**IIIb**) with the characteristic large coupling constant J_{PRh} = 13.1–13.4 Hz. For instance, for the rhodium(III) iminophosphonamide complexes, the J_{PRh} constant does not exceed 9 Hz and strongly correlates with the NRhN chelate angle equal to 68°–69°. The value of J_{PRh} observed for complexes **IIIa** and **IIIb** is characteristic of rhodium(I) iminophosphonamide complexes **IIa** and **IIb** (J_{PRh} = 13.6–13.8 Hz) and of the 16ē complexes $[Cp^*Rh(NPN)]^+(PF_6^-)$ (**Va**, **Vb**) (J_{PRh} = 13.0–14.4 Hz) [18] in which the NRhN angle is considerably larger (about 72°). The ^1H NMR spectrum (C_6D_6) of complex **IIIa** also exhibits two types of methyl groups of the Cp* ring at 2.20 ppm (s, 6H) and 0.90 (s, 6H) and one doublet of halved intensity from the methyl group at 2.06 ppm (d, $^3J_{HH}$ = 6.8 Hz, 3H), which is spin–spin-coupled to the quartet at 1.64 ppm (q, J = 6.8 Hz, 1H). The NPN ligand in complex **IIIa** is symmetric and presented by one set of resonances from the *p*-tolyl substituents at 2.22 (s, 6H, Me_{Tol}) and 6.95 ppm (s, 8H, H_{Tol}), and the resonances from the Ph rings are observed as two broadened humps at 7.8–8.2 (4H) and 7.0–7.3 ppm (6H). These complexes are likely the rhodium(I) diene complexes [(η⁴-C_5Me_5H)Rh(NPN)] (Scheme 1). Complexes **IIIa** and **IIIb** are formed as a single isomer, but the NMR spectra do not allow an unambiguous determination of the endo-H or exo-H configuration of the diene ligand. All attempts to isolate complexes **IIIa** and **IIIb** in pure form were unsuccessful because of their high sensitivity to moisture or air traces and, therefore, these compounds were synthesized only in situ without isolation. However, the replacement of the solvent with complete removal of THF traces was required for the catalytic experiments (see below).

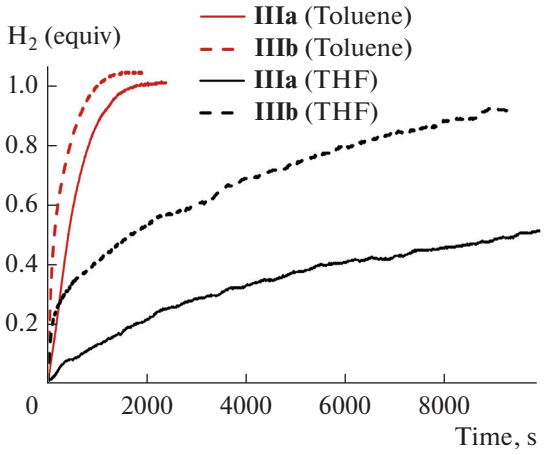


Fig. 1. Dehydrogenation of DMAB catalyzed by complexes **IIIa** and **IIIb** in toluene and THF. Conditions: T = 40°C, [Rh] = 5.8 mM, [DMAB] = 0.145 M, $V_{solution}$ = 2.1 mL.

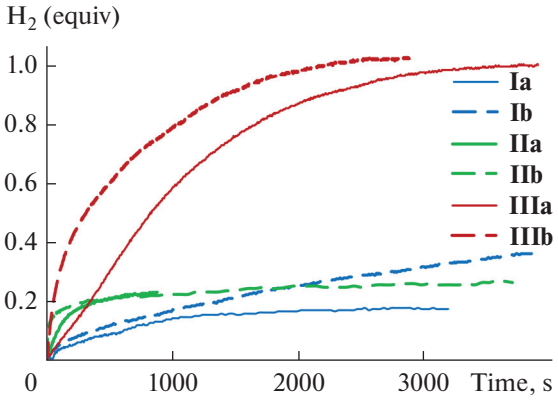
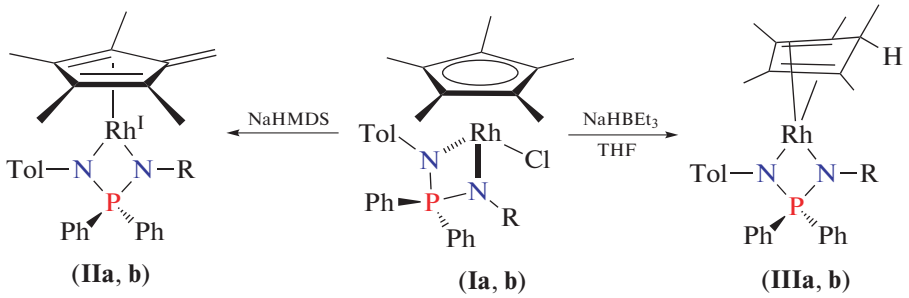


Fig. 2. Dehydrogenation of DMAB catalyzed by complexes **Ia**, **Ib** and **IIa**, **IIb** in toluene compared to complexes **IIIa** and **IIIb**. Conditions: T = 40°C, [Rh] = 2.9 mM, [DMAB] = 0.145 M, $V_{solution}$ = 2.1 mL.



Scheme 1. Synthesis of complexes **IIa**, **IIb** and **IIIa**, **IIIb**.

It is most likely that the reactions of compounds **Ia** and **Ib** with $NaHBEt_3$ preliminary afford hydride complexes **IVa** and **IVb** that further undergo rearrangement to complexes **IIIa** and **IIIb**. Unfortunately, no hydride resonances were detected by the NMR method even at –20°C because of the high rearrangement rate. Recently a similar rearrangement was reported for the arene iminophosphonamide ruthenium complexes with the successful characterization of the hydride intermediates [(η^6-arene)RuH(NPN)] and η^5-cyclohexadienyl products [(η^5-areneH)Ru(NPN)] of the intramolecular attack of the hydride ligand to the η^6-arene ring exclusively resulting in the endo-H complexes [21].

Complexes **Ia**, **Ib**, **IIa**, **IIb**, **IIIa**, and **IIIb** (4 mol %) were studied as catalysts of DMAB dehydrogenation at 40°C in toluene and THF. In toluene η^4-cyclopentadiene complexes **IIIa** and **IIIb** demonstrate very high activity in this process reaching TOF = 110 (**IIIa**) and 540 h^{-1} (**IIIb**), and the reaction completes within <0.5 h (Fig. 1). In both cases, the reaction occurred completely with the evolution of 1 equiv H_2. However, the use of more polar and coordinating solvent THF decreases the catalyst activity by nearly an order of magnitude, and the full conversion is not achieved even in 3 h. It is important to note that the more basic nitrogen atom in complex **IIIb** considerably (by 5 times) increases the initial activity of the catalyst (<30% conversion) in both toluene and THF. The observed activities are higher by an order of magnitude than those found previously for the Cp*Rh(III) complexes with the κ^1-*N*-pyrazolate (TOF = 28 h^{-1} at 45°C) [22] and 2,2'-bipyridine (TOF = 52 h^{-1} at 50°C) [20] ligands and are comparable with the efficiency of the most active catalysts [($Ph_2P(CH_2)_nPPh_2$)-$Rh(H_3B{-}NR_3)$] (TOF = 1250 h^{-1} at 25°C) [23] and *fac*-[$(CO)_3$(bis(NHC))MnBr] (TOF = 1200 h^{-1} at 60°C) [24] reported so far.

At the same time, the catalytic activity of the corresponding chloride complexes **Ia** and **Ib** and fulvene complexes **IIa** and **IIb** in toluene turned out to be much lower than that of **IIIa** and **IIIb** (Fig. 2): complexes **Ia** and **Ib** are by 10–30 times less active (TOF = 25–30 h^{-1}), and fulvene complexes **IIa** and **IIb** are rapidly deactivated even at 20% conversion in spite of the high initial activity.

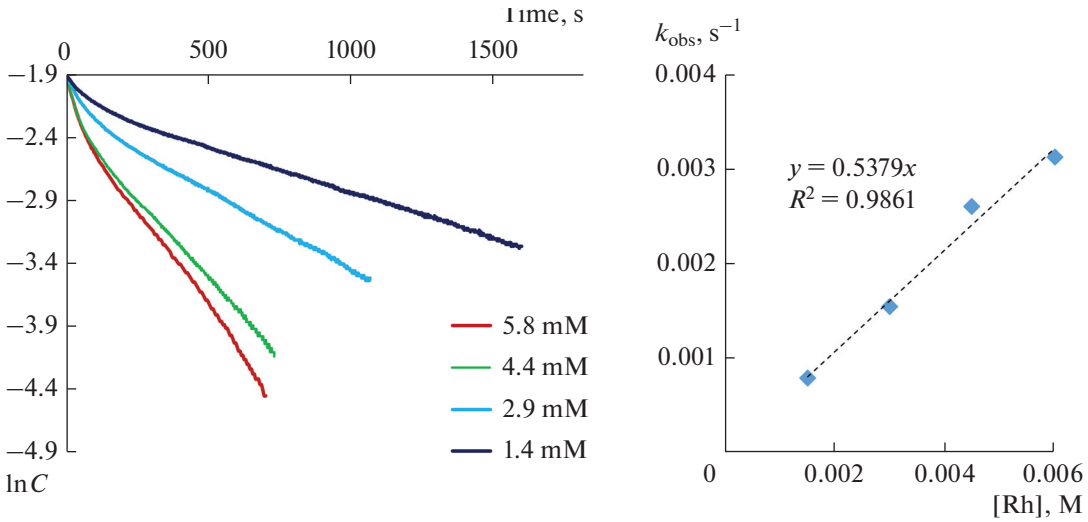


Fig. 3. Dehydrogenation of DMAB (0.145 M) catalyzed by complex **IIIb** at 40°C in toluene at different catalyst concentrations: the first-order kinetic curves (left) and dependence of k_{obs} on [Rh].

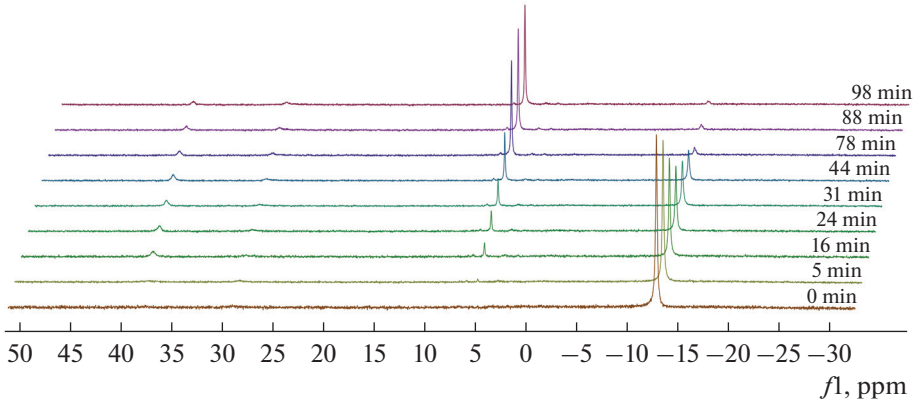


Fig. 4. Kinetics of DMAB dehydrogenation (0.085 M, δ_B = 13 ppm) catalyzed by complex **IIIa** (0.008 M) at 18°C in toluene-d_8. Changes in the ^{11}B NMR spectrum of the mixture.

The reaction kinetics was studied with the variation of the concentration of complex **IIIb** at a constant DMAB concentration (Fig. 3). The reaction has the first order with respect to DMAB and catalyst, and the determined second-order rate constant is k_2 = 0.54 M^{-1} s^{-1} at 40°C.

The kinetics of DMAB dehydrogenation with the ^{11}B NMR monitoring of the reaction products was studied for complex **IIIa** (Fig. 4) and confirms the first order reaction rate with respect to the substrate (Fig. 5). The reaction expectedly affords the dimer $(Me_2N{-}BH_2)_2$ (δ_B = 5.2 ppm) with the primary accumulation of small amounts of the $Me_2N{=}BH_2$ monomer (δ_B = 38.1 ppm), which indicates the dimerization of $Me_2N{=}BH_2$ outside the coordination sphere of the metal atom (so-called off-metal dimerization). As a result, the second-order rate constant k_2 was determined to be 0.065 M^{-1} s^{-1} at 18°C (Fig. 5).

Unfortunately, the preliminary NMR study in toluene-d_8 of the evolution of complex **IIIa** during catalysis did not allow us to detect intermediates. The resonance of complex **IIIa** disappears immediately after the addition of DMAB to a solution of the catalyst indicating, most likely, fast (in the NMR timescale) transformations of the intermediates formed. After the end of catalysis, the ^{31}P NMR spectrum exhibits only two resonances attributed to the initial complex **IIIa** (doublet at δ_P = 40.4 ppm) and new unidentified complex with the signal at δ_P = 37.7 ppm.

Additional experiments showed that complex **IIIa** did not react with $Me_3N{\cdot}BH_3$; i.e., the acidic hydrogen atom is required for the initiation of the catalytic cycle. Recently the mechanism involving the assistance of the Cp* ligand in the transfer of hydrogen ions from the metal atom with transformation into the η^4-C_5Me_5H ligand was proposed for the catalytic

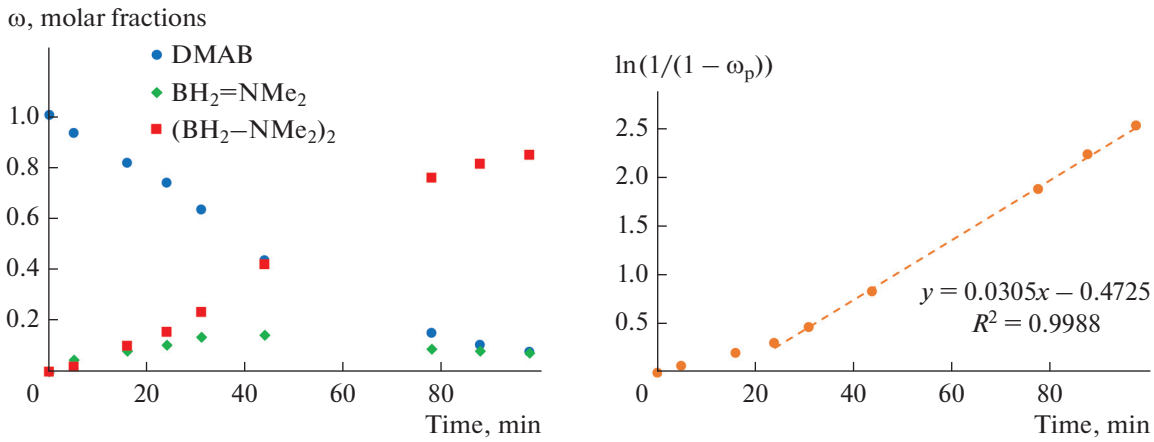
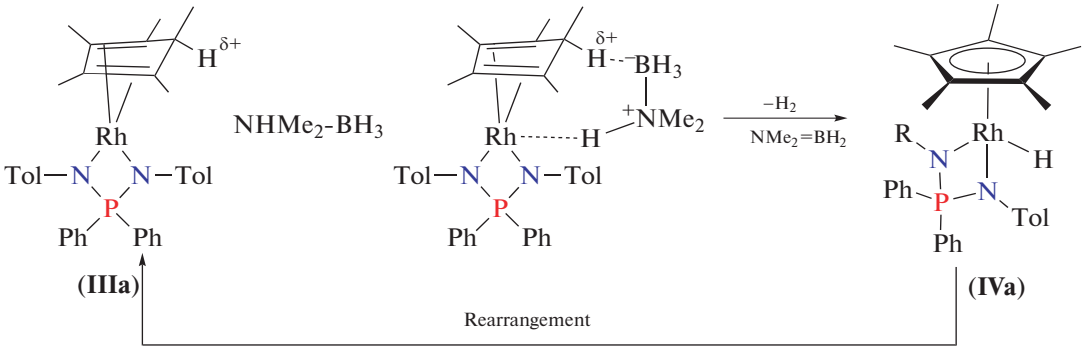


Fig. 5. Plots of changing the relative concentrations of the boron-containing reaction products (left) and the first-order kinetic curve with the calculation of the observed reaction rate constant (right). The same conditions as in Fig. 4.

dehydrogenation of DMAB by the bipyridyl Cp*Rh(III) complexes [20]. Probably, the proposed mechanism [20] is also realized for complexes **IIIa** and **IIIb**. At the first stage, DMAB is coordinated by the acidic NH proton to the nucleophilic rhodium(I) atom to form the dihydrogen bond B–H···H–C_{Cp^*} between the coordinated DMAB and proton of the η^4-C_5Me_5H ligand, and the subsequent proton transfer results in H_2 evolution and formation of the hydride complex [Cp*RhH(NPN)] (**IVa**, **IVb**) (Scheme 2). It is important to note that this mechanism is valid only for the endo-H isomer of complexes **IIIa** and **IIIb** apparently formed, by the intramolecular rearrangement of hydride intermediates **IVa** and **IVb**.



Scheme 2. Proposed isomerization of complex **IIIa** to **IVa** in the reaction with DMAB accompanied by the hydrogen atom transfer from Cp*H to the Rh atom and H_2 evolution.

In summary, the rhodium iminophosphonamide complexes studied in this work exhibit th e high activity in the catalytic dehydrogenation of the model substrate DMAB. The catalysts prepared in situ by the treatment of chloride complexes **Ia** and **Ib** with $NaHBEt_3$ and being, according to the NMR data, η^4-cyclopendiene complexes **IIIa** and **IIIb** exhibit the highest activity (by an order of magnitude higher than that of the described half-sandwich rhodium complexes). To elucidate details of the mechanism that would explain such a high activity of the rhodium iminophosphonamide complexes, additional studies including model NMR experiments and quantum-chemical calculations will be performed.

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CONFLICT OF INTEREST

The authors of this work declare no conflicts of interest.

REFERENCES

1. Colebatch, A.L. and Weller, A.S., *Chem.-Eur. J.*, 2019, vol. 25, p. 1379. https://doi.org/10.1002/chem.201804592
2. Staubitz, A., Robertson, A.P.M., and Manners, I., *Chem. Rev.*, 2010, vol. 110, p. 4079. https://doi.org/10.1021/cr100088b
3. Du, V.A., Jurca, T., Whittell, G.R., and Manners, I., *Dalton Trans.*, 2016, vol. 45, p. 1055. https://doi.org/10.1039/C5DT03324A
4. Resendiz-Lara, D.A., Stubbs, N.E., Arz, M.I., et al., *Chem. Commun.*, 2017, vol. 53, p. 11701.
5. Kumar, A., Daw, P., Milstein, D., et al., *Chem. Rev.*, 2022, vol. 122, p. 385. https://doi.org/10.1021/acs.chemrev.1c00412
6. Alig, L., Fritz, M., Schneider, S., et al., *Chem. Rev.*, 2019, vol. 119, p. 2681. https://doi.org/10.1021/acs.chemrev.8b00555
7. Glüer, A., Förster, M., Celinski, V.R., et al., *ACS Catal.*, 2015, vol. 5, p. 7214. https://doi.org/10.1021/acscatal.5b02406
8. Luconi, L., Osipova, E.S., Giambastiani, G., et al., *Organometallics*, 2018, vol. 37, p. 3142. https://doi.org/10.1021/acs.organomet.8b00488
9. Todisco., S., Luconi., L., Giambastiani., G., et al., *Inorg. Chem.*, 2017, vol. 56, p. 4296. https://doi.org/10.1021/acs.inorgchem.6b02673
10. Titova, E.M., Osipova, E.S., Pavlov, A.A., et al., *ACS Catal.*, 2017, vol. 7, p. 2325. https://doi.org/10.1021/acscatal.6b03207
11. Sewell, L.J., Huertos, M.A., Dickinson, M.E., et al., *Inorg. Chem.*, 2013, vol. 52, p. 4509. https://doi.org/10.1021/ic302804d
12. Johnson, H.C., Leitao, E.M., Whittell, G.R., et al., *J. Am. Chem. Soc.,* 2014, vol. 136, p. 9078. https://doi.org/10.1021/ja503335g
13. Douglas, T.M., Chaplin, A.B., Weller, A.S., et al., *J. Am. Chem. Soc.*, 2009, vol. 131, p. 15440. https://doi.org/10.1021/ja906070r
14. Kirkina, V.A., Osipova, E.S., Filippov, O.A., et al., *Mendeleev Commun.*, 2020, vol. 30, p. 276. https://doi.org/10.1016/j.mencom.2020.05.004
15. Brodie, C.N., Sotorrios, L., Boyd, T.M., et al., *ACS Catal.*, 2022, vol. 12, p. 13050. https://doi.org/10.1021/acscatal.2c03778
16. Brodie, C.N., Boyd, T.M., Sotorrios, L., et al., *J. Am. Chem. Soc.*, 2021, vol. 143, p. 21010. https://doi.org/10.1021/jacs.1c10888
17. White, C., Yates, A., Maitlis, P.M., et al., *Inorg. Synth.*, 1992, vol. 29, p. 228. https://doi.org/10.1002/9780470132609.ch53
18. Nekrasov, R.I., Peganova, T.A., Fedyanin, I.V., et al., *Inorg. Chem.*, 2022, vol. 61, p. 16081. https://doi.org/10.1021/acs.inorgchem.2c02478
19. Kruger, C.R. and Niederprum, H., *Inorg. Synth.*, 1966, vol. 8, p. 15.
20. Pal, S., Kusumoto, S., and Nozaki, K., *Organometallics*, 2018, vol. 37, p. 906. https://doi.org/10.1021/acs.organomet.7b00889
21. Sinopalnikova, I.S., Peganova, T.A., Belkova, N.V., et al., *Eur. J. Inorg. Chem.*, 2018, vol. 2018, p. 2285. https://doi.org/10.1002/ejic.20170134423
22. Pal, S., Iwasaki, T., and Nozaki, K., *Dalton Trans.*, 2021, vol. 50, p. 7938. https://doi.org/10.1039/D1DT01705E
23. Dallanegra, R., Robertson, A.P.M., Chaplin, A.B., et al., *Chem. Commun.*, 2011, vol. 47, p. 3763. https://doi.org/10.1039/C0CC05460G
24. Gulyaeva, E.S., Osipova, E.S., Kovalenko, S.A., et al., *Chem. Sci.*, 2024, vol. 15, p. 1409. https://doi.org/10.1039/D3SC05356C

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