Chelation versus Cyclometalation in a Cationic Dppn−Rh^{I} Complex − A Unique Rearrangement of Norbornadiene via C−H Activation of the Pyridazine Ring

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The tetradentate ligand 3,6-bis(2-pyridyl)pyridazine (dppn) was treated with cationic Rh^{I} precursors. The mononuclear complexes [Rh(dppn)(NBD)]BF_4 (**1**) and [Rh(dppn)(COD)]BF_4 (**5**) were obtained in quantitative yield when treating dppn with [Rh(NBD)$_2$]BF_4 or [Rh(COD)$_2$]BF_4 respectively. Treatment of **1** with a second equivalent of the metal precursor [Rh(NBD)(CH$_3$CN)$_2$]BF_4 led to the dinuclear complex [Rh$_2$(dppn-H)(NBD)(η^1-C$_7$H$_9$)(CH$_3$CN)$_2$](BF_4)$_2$ (**2**) [dppn-H = μ-C$_4$HN$_2$(C$_5$H$_4$N)$_2$-3,6], a mixed Rh^{I}–Rh^{III} complex. This complex arises from C–H activation of the pyridazine ring, followed by a unique rearrangement of the NBD ligand. Compound **2** was also obtained directly by treating dppn with 2 equiv. of [Rh(NBD)(CH$_3$CN)$_2$]BF_4. The complex [Rh$_2$(dppn-H)(NBD)(η^1-C$_7$H$_9$)(CH$_3$OH)$_2$(CH$_3$CN)](BF_4)$_2$ (**4**) was obtained by dissolving **2** in methanol. Full characterization of compounds **1**, **4** and **5** included an investigation by ^{1}H-^{15}N GHMBC NMR spectroscopy and single-crystal X-ray structures of **1** and **4**.

Introduction

Late transition metal systems with chelating nitrogen ligands are the subject of intense recent research due to their catalytic potential in processes such as the polymerization of olefins,[1] the selective C−H bond activation,[2] and the catalysis by monolayers.[3] The ease of C−H activation, when such ligands are employed, might depend on their inherently electron-rich nature. In particular, it has been shown that *ortho*-metalation of aromatic *N*-donor ligands by d^8-M^{I} complexes is strongly dependent on the basic properties of the metal precursor.[4] In addition, dinucleating ligands that can form homo- or heterodinuclear transition metal complexes with well-defined geometries are of considerable interest, considering the rapidly evolving area of dimetallic catalysts,[5] and supramolecular chemistry.[6] We thus decided to investigate the coordination chemistry of the tetradentate ligand 3,6-bis(2-pyridyl)pyridazine (dppn) towards cationic Rh^{I} precursors, especially in view of the fact that surprisingly little is known about its coordination behaviour and its reactivity with d^8-M^{I} metal precursors.[7]

In this paper we report the unexpected reactivity of this ligand towards cationic diene−Rh^{I} precursors (diene = norbornadiene and cyclooctadiene) giving rise to mono- and dinuclear complexes. Surprisingly, the dinuclear complex consists of an Rh^{I}−Rh^{III} complex arising from C−H activation of the pyridazine ligand, followed by a unique rearrangement of the norbornadiene ligand, rather than the expected *N*,*N*-coordinated bis(Rh^{I}) complexes. Full characterization of the resulting compounds included an investigation by ^{1}H-^{15}N GHMBC NMR spectroscopy and the single-crystal X-ray structures of two of them.

Results and Discussion

The ligand 3,6-bis(2-pyridyl)pyridazine (dppn) was synthesized in two steps in 45% overall yield. Lithiation of 2-bromopyridine with BuLi and subsequent reaction of the lithiated adduct with trimethyltin chloride yielded (2-pyridyl)trimethyltin in quantitative yield.[8] The second step consisted of a double Stille-type coupling between the organotin compound and 3,6-dichloropyridazine which was performed using Pd^0 or Pd^{II} catalyst precursors. The highest yield (45%) was obtained with 1 mol % of $PdCl(PPh_3)_2(CH_2Ph)$ as the catalyst.[9]

Upon addition of 1 equiv. of dppn to a stirred CH_2Cl_2 solution of [Rh(NBD)$_2$]BF_4 or [Rh(NBD)(CH$_3$CN)$_2$]BF_4, precipitation of a dark red solid took place within 30 min.

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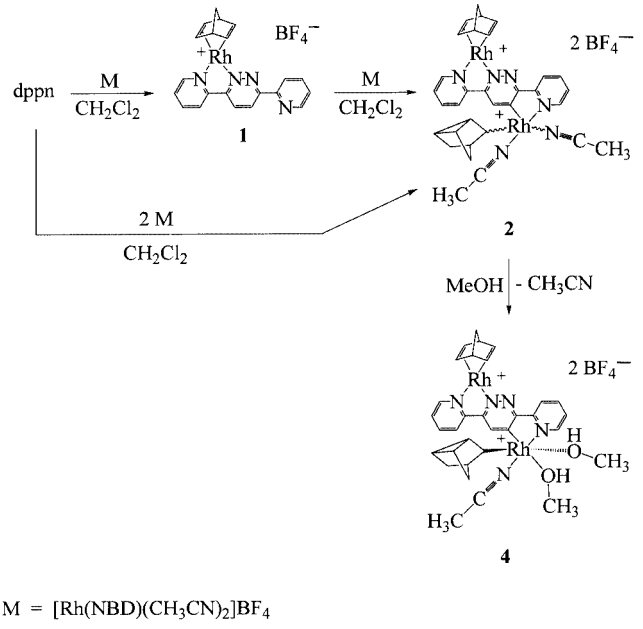
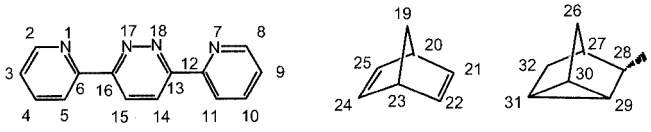
This compound was characterized as [Rh(dppn)(NBD)]BF_4 (**1**) (Scheme 1) using various NMR techniques. As expected, the ligand dppn gave rise to ten distinct signals in the ^{1}H NMR spectrum. Except for the routine NMR methods used for such organometallic compounds, we also performed a ^{1}H-^{15}N GHMBC experiment, a technique used for the characterization of bioorganic molecules,[10] but which has very rarely been applied to transition metal complexes.[11] The resulting spectrum clearly showed the four signals of the nitrogen atoms of dppn (Figure 1). The correlation provided their ^2J and ^3J couplings to the neighboring hydrogen atoms. Very clear shifts in the nitrogen spectrum were seen for N(1), N(17) and N(18) (for atom numbering see Scheme 2) and are given in Table 1. The noncoordinated pyridine moiety [N(7)] showed essentially the same shift as seen in the free ligand.[12] Furthermore, the two nitrogen atoms coordinated to the rhodium metal gave rise to coupling constants of $J_{N\text{-}Rh}$ = 20−30 Hz.



Scheme 1. Synthetic route to complexes **1**, **2** and **4**



Scheme 2. Numbering scheme used for the characterization of the compounds

Crystals of **1** suitable for an X-ray crystallographic analysis were grown by diffusion of diethyl ether into a concentrated solution of **1** in methanol and confirmed the structure. The crystal consists of discrete [Rh(dppn)(NBD)]$^+$ cations, BF_4^- counterions and methanol solvent molecules. An ORTEP view of the cationic complex with the atomic numbering scheme, together with selected bond lengths and angles, is shown in Figure 2. The Rh atom is in a square-

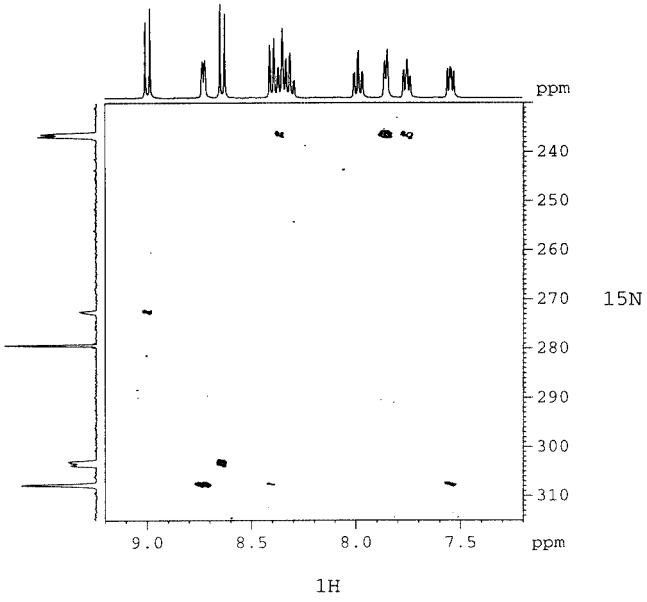


Figure 1. ^{1}H-^{15}N GHMBC NMR in CD_3NO_2 of complex **1**

planar arrangement with the two *cis*-nitrogen atoms of the dppn molecule acting as a bidentate chelating ligand through two neighboring pyridyl and pyridazinyl nitrogen atoms. As in complex **4** (see below), the N−Rh distance of the pyridazinyl is slightly shorter than the corresponding pyridyl N−Rh distance and concomitantly the Rh−olefin bond *trans* to it somewhat longer. The noncoordinating N atoms are mutually *trans* to each other with respect to the C(9)−C(10) (for atom numbering see Figure 2) axis, as previously observed in other crystallographically characterized mononuclear complexes of dppn.[7,13]

Treatment of **1** with a second equivalent of [Rh(NBD)-$(CH_3CN)_2$]BF_4 in CH_2Cl_2 led to the slow formation of a pink precipitate. The product was tentatively identified as the complex [Rh_2(dppn-H)(NBD)(η^1-C_7H_9)$(CH_3CN)_2$]-$(BF_4)_2$ (**2**) (Scheme 1) [dppn-H = μ-$C_4HN_2(C_5H_4N)_2$-3,6]. Characterization of **2** by NMR spectroscopy was hampered by its low solubility in noncoordinating, polar solvents. Despite this, the ^{1}H NMR spectrum in CD_2Cl_2 clearly showed that the dppn ligand was orthometalated on the pyridazine ring giving rise to only nine proton signals. Furthermore, two resonances at δ = 2.34 and 2.64 ppm were attributed to the two acetonitrile molecules bound to the Rh^{III} metal center.[14] The formulation of **2** was also supported by elemental analysis. When **2** was dissolved in the weakly coordinating solvent methanol, dissociation of one of the acetonitrile ligands (peak at δ = 2.34 ppm) was observed, leading most probably to a highly labile 14e-Rh^{III} complex. Slow addition of diethyl ether to a concentrated solution of **2** in methanol gave **4** as a deep red solid. Characterization of **4** by ^{1}H NMR in [D_4]methanol showed that indeed, both of the methanol molecules are highly labile and exchange rapidly with the deuterated solvent. The structure of the compound was elucidated by using various NMR techniques to assign all the protons and carbon atoms. Especially for complex **4**, the ^{1}H-^{15}N GHMBC

Table 1. Results of the ^{1}H-^{15}N GHMBC NMR experiment of dppn, **1**, **4** and **5** (for atom numbering see Scheme 2)

[a]	dppn[b]	**1**[c]	**4**[d]	**5**[c]
N(1)	306.9; ^{2}J with 2-H, ^{3}J with 3-H and 5-H	236.5; ^{2}J with 2-H, ^{3}J with 3-H and 5-H, $J^{N\text{-}Rh}$ = 19.7 Hz	238.3; ^{2}J with 2-H, ^{3}J with 3-H and 5-H, $J_{N\text{-}Rh}$ = 24.7 Hz	235.1; ^{2}J with 2-H, ^{3}J with 3-H and 5-H, $J_{N\text{-}Rh}$ = 26.0 Hz
N(7)	306.9; ^{2}J with 8-H, ^{3}J with 9-H and 11-H	307.6; ^{2}J with 8-H, ^{3}J with 9-H and 11-H	234.5; ^{2}J with 8-H, ^{3}J with 9-H and 11-H, $J_{N\text{-}Rh}$ = 42.4 Hz	307.7; ^{2}J with 8-H, ^{3}J with 9-H and 11-H
N(17)	388.0; ^{3}J with 15-H	303.2; ^{3}J with 15-H, $J_{N\text{-}Rh}$ = 24.1 Hz	283.2; ^{3}J with 15-H, $J_{N\text{-}Rh}$ = 40.2 Hz	300.2; ^{3}J with 15-H, $J_{N\text{-}Rh}$ = 20.5 Hz
N(18)	388.0; ^{3}J with 14-H	272.4; ^{3}J with 14-H		271.1; ^{3}J with 14-H
others			174.1; CH_3CN; ^{3}J with CH_3, $^{2}J_{N\text{-}Rh}$ = 45.9 Hz	

[a] Chemical shifts in ppm (referenced to liquid ammonia). [b] In $CDCl_3$. [c] In CD_3NO_2. [d] In CD_3OD.

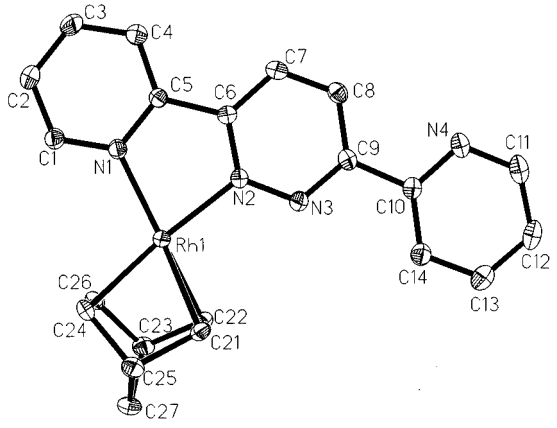


Figure 2. ORTEP drawing of a molecule of **1** (50% of probability); BF_4^-, solvent molecules and hydrogen atoms are omitted for clarity; selected bond lengths [A] and angles [°]: Rh(1)−N(1) 2.077(2), Rh(1)−N(2) 2.049(2), Rh(1)−C(21) 2.127(2), Rh(1)−C(22) 2.120(2), Rh(1)−C(24) 2.155(2), Rh(1)−C(26) 2.145(2); N(2)−Rh(1)−N(1) 78.91(8), N(2)−Rh(1)−C(22) 101.87(9), N(1)−Rh(1)−C(22) 156.99(9), N(2)−Rh(1)−C(21) 102.65(9), N(1)−Rh(1)−C(21) 164.63(9), C(22)−Rh(1)−C(21) 38.19(10), N(2)−Rh(1)−C(26) 159.45(9), N(1)−Rh(1)−C(26) 103.89(9), C(22)−Rh(1)−C(26) 67.52(10), C(21)−Rh(1)−C(26) 80.11(10), N(2)−Rh(1)−C(24) 161.69(9), N(1)−Rh(1)−C(24) 106.56(9), C(22)−Rh(1)−C(24) 80.01(10), C(21)−Rh(1)−C(24) 67.42(10), C(26)−Rh(1)−C(24) 37.53(10)

NMR experiment proved to be extremely informative (Table 1). As expected, the signal of one of the nitrogen atoms [N(18)] of the pyridazyl unit is not seen due to the lack of ^{2}J and ^{3}J coupling with any hydrogen atoms. In **4**, both pyridyl moieties are bound to the metal atom and show significant shifts of the signals of the nitrogen atoms [N(1) and N(7)] compared to those of the free ligand dppn. In addition, both nitrogen atoms [N(1) and N(7)] gave rise to coupling constants with the corresponding rhodium centers ($J_{N\text{-}Rh}$ = 24.7 and 42.4 Hz, respectively) as well as the coordinated pyridazyl nitrogen atom ($J_{N\text{-}Rh}$ = 40.2 Hz).[15] To unambiguously ascertain the exact structure of **4**, crystals suitable for X-ray crystallography were grown by slow diffusion of diethyl ether into a concentrated methanol/CH_2Cl_2 solution containing **4**. The ORTEP representation along with selected bond lengths and angles is shown in Figure 3. In complex **4**, the deprotonated ligand acts as a quadridentate ligand chelating the two metal atoms on opposite sides, one through one pyridyl and one pyridazinyl nitrogen atom, the other through one pyridyl nitrogen and one pyridazinyl carbon atom. The two metal centers differ in their geometry and their oxidation state, one being a square-planar Rh^{I} and the other an octahedral Rh^{III}. The part of the ligand with the square-planar metal atom shows nearly identical bond lengths and angles as seen in complex **1**. The octahedral metal atom is surrounded by the chelating C,N fragment of dppn, the 3-nortricyclyl unit, one acetonitrile and two methanol molecules. To the best of our knowledge, there are only two previous structural reports of methanol bonded to Rh^{III}, one involving a Cp^*Rh^{III} complex,[16] and the other one being $[RhCl_2(MeOH)(PCP)]$ [PCP = C_6H_3-2,6-$(CH_2PCy_2)_2$].[17] Interestingly, the two methanol molecules are *trans* to the two carbon fragments, whereas the acetonitrile molecule lies *trans* to the pyridine unit. The two methanol ligands show markedly different bond lengths to the metal atom: Rh(2)−O(2) is 2.202(3) Å, and Rh(2)−O(1) is 2.298(3) Å. This indicates that the latter is the additional sixth ligand with respect to the pentacoordinate complex **2**, whereas the methanol molecule *trans* to the pyridazyl moiety is the methanol ligand displacing the acetonitrile ligand of **2**. The lability of both methanol ligands is also reflected when comparing their metal−O bond lengths to the ones found in $[Cp^*Rh\{\eta^1(N7)\text{-}9\text{-}MH\}(CH_3OH)_2](OTf)_2\cdot CH_3OH$ (9-MH = 9-methylhypoxanthine).[16] In addition, the X-ray structure reveals that hydrogen bonding occurs between one of the coordinated methanol molecules and one of the fluorine atoms of tetrafluoroborate ($F_3BF\cdots HOCH_3$ 1.973 Å). Chelation on the

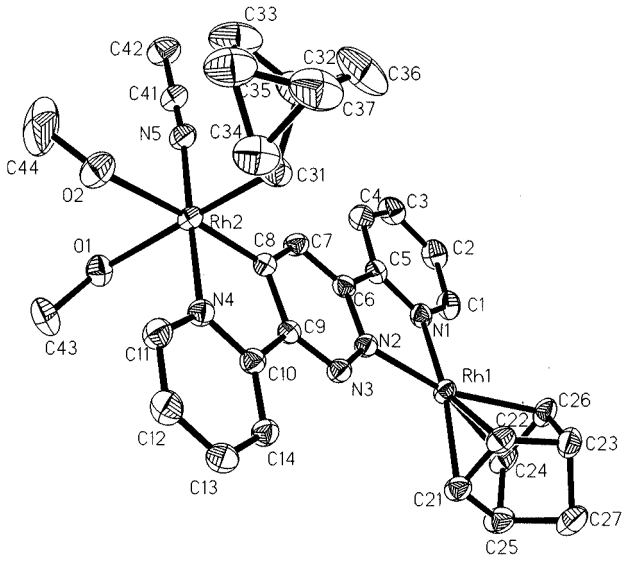
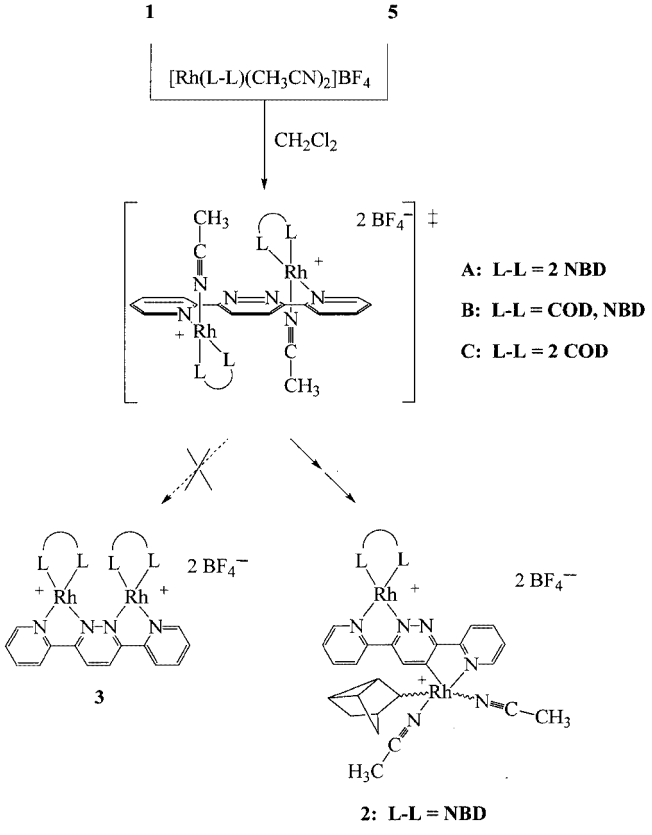


Figure 3. ORTEP drawing of a molecule of **4** (50% of probability); BF_4^-, solvent molecules and hydrogen atoms are omitted for clarity; selected bond lengths [Å] and angles [°]: Rh(1)−N(1) 2.073(3), Rh(1)−N(2) 2.047(3), Rh(1)−C(21) 2.124(4), Rh(1)−C(22) 2.114(4), Rh(1)−C(24) 2.144(4), Rh(1)−C(26) 2.132(4), Rh(2)−C(8) 1.953(4), Rh(2)−N(5) 2.010(3), Rh(2)−N(4) 2.027(3), Rh(2)−C(31) 2.054(4), Rh(2)−O(1) 2.298(3), Rh(2)−O(2) 2.202(3); N(2)−Rh(1)−N(1) 78.83(13), N(2)−Rh(1)−C(22) 101.40(15), N(1)−Rh(1)−C(22) 154.87(15), N(2)−Rh(1)−C(21) 103.82(14), N(1)−Rh(1)−C(21) 166.72(15), C(22)−Rh(1)−C(21) 38.07(17), N(2)−Rh(1)−C(26) 156.94(16), N(1)−Rh(1)−C(26) 102.71(14), C(22)−Rh(1)−C(26) 67.38(16), C(21)−Rh(1)−C(26) 80.05(16), N(2)−Rh(1)−C(24) 164.04(16), N(1)−Rh(1)−C(24) 106.79(15), C(22)−Rh(1)−C(24) 79.94(17), C(21)−Rh(1)−C(24) 67.34(16), C(26)−Rh(1)−C(24) 37.80(18), C(8)−Rh(2)−N(5) 92.58(15), C(8)−Rh(2)−N(4) 82.21(14), N(5)−Rh(2)−N(4) 173.82(13), C(8)−Rh(2)−C(31) 87.04(18), N(5)−Rh(2)−C(31) 96.10(16), N(4)−Rh(2)−C(31) 87.00(16), C(8)−Rh(2)−O(2) 175.96(14), N(5)−Rh(2)−O(2) 90.86(13), N(4)−Rh(2)−O(2) 94.22(13), C(31)−Rh(2)−O(2) 94.70(18), C(8)−Rh(2)−O(1) 94.29(13), N(5)−Rh(2)−O(1) 86.34(13), N(4)−Rh(2)−O(1) 90.70(12), C(31)−Rh(2)−O(1) 177.17(15), O(2)−Rh(2)−O(1) 83.82(12)

opposite side of the ligand gives rise to a relatively large separation between the two metal atoms (Rh···Rh 6.737 Å).

We thus clearly see that compounds **2** and **4** are the product of oxidative addition of the C−H bond on the pyridazine ring resulting in the formation of dinuclear Rh^{I}−Rh^{III} species. The C−H activation step is most probably followed by Rh−H addition to the double bond of the norbornadiene moiety and subsequent rearrangement of the norbonenyl molecule.[18] To the best of our knowledge, the rearrangement on a metal center of norbornadiene resulting in the formation of a 3-nortricyclyl ligand unit is unprecedented, although such rearrangements are thought to be involved in catalytic reactions such as the di- and trimerization of norbornadiene,[19] and catalytic amination reactions.[20] Complex **2** was also prepared directly by treating the ligand dppn with 2 equiv. of [Rh(NBD)$(CH_3CN)_2$]BF_4 in a CH_2Cl_2 solution (Scheme 1). To obtain a more detailed picture of this reaction, we monitored the transformation on a small scale in an NMR tube using deuterated dichloromethane. Although complex **1** is not very soluble in dichloromethane, the addition of 1 equiv. of [Rh(NBD)-$(CH_3CN)_2$]BF_4 to **1** gave a deep red solution. Recording the ^{1}H NMR spectrum after 10 min showed the formation of compound **A** (Scheme 3).[21] The formulation of this intermediate is supported by several characteristic peaks in the ^{1}H NMR spectrum. Firstly, the aromatic region shows 5 signals for the 10 hydrogen atoms of the ligand dppn indicating the presence of a symmetrical species. One of these signals (corresponding to 2 hydrogen atoms) is shifted downfield and is attributed to the α-hydrogen atoms on the two pyridyl moieties that are bound to the metal center. Furthermore, the signals of the NBD also indicate that both rhodium atoms are in an electronically equivalent situation. A peak at δ = 2.20 ppm for the methyl groups of the two acetonitrile ligands shows coordination of these molecules to the metal center {for [Rh(NBD)$(CH_3CN)_2$]BF_4 at δ = 2.30 ppm, the chemical shift of free CH_3CN is δ = 2.05 ppm}. After 30 min, the peaks of the product **2** can already be seen (ca. 10% by integration) and after 2 h, product **2** started to precipitate. During the transformation of **A** to **2**, the unknown dinuclear complex **3**, as shown in Scheme 3, was not observed. The X-ray structure of **1** shows that a complex such as **3** is not obtained most likely because of steric crowding of the two vicinal norbornadiene ligands. Furthermore, no hydride or norbornenyl were detected, indicating that the C−H activation step (or an earlier step) is probably rate-determining in the overall process.



Scheme 3. Reaction pathway of the mononuclear complexes **1** and **5** with a second equivalent of [Rh(diene)$(CH_3CN)_2$]BF_4

As expected, C−H activation did not take place when complex **1** in dichloromethane was treated with the relatively electron-poor complex $[Rh(NBD)_2]BF_4$. The reaction did also not take place in coordinating solvents such as acetonitrile, pyridine, acetone or methanol. Such coordinating solvents stabilize complexes of the type $[Rh(NBD)(solvent)_2]BF_4$ and retard binding to the pyridine moiety of dppn to give **A**. The unique rearrangement of NBD to the final 3-nortricyclyl unit seems to be a prerequisite in this reaction. To test this, we synthesized the analogous mononuclear cyclooctadiene complex $[Rh(dppn)(COD)]BF_4$ (**5**), which was fully characterized including by ^1H-^{15}N GHMBC NMR (Table 1). When **5** was treated with 1 equiv. of $[Rh(COD)(CH_3CN)_2]BF_4$ in deuterated dichloromethane, products arising from C−H activation were not observed, showing that if indeed C−H activation takes place, it is reversible and the resulting labile hydride does not insert into the double bond of the diene. Instead, the dinuclear complex **C**, analogous to **A**, was formed in this case (Scheme 3). On the other hand, when complex **5** was added to 1 equiv. of $[Rh(NBD)(CH_3CN)_2]BF_4$, we observed intermediate **B** before disappearance of the NBD signals and concomitant formation of the characteristic signals for 3-nortricyclyl were seen.[22] Interestingly, reaction of 2-phenylpyridine with 1 equiv. of $[Rh(NBD)(CH_3CN)_2]PF_6$ did not give any activation of the phenyl ring of this ligand. The unique reactivity of **1** might thus arise from the hindered rotation of the pyridazine ring as shown in structure **A** and the subsequently easier approach of the metal center towards the C−H bond.[23]

Summary

We have reported the reactivity of cationic diene−Rh^I complexes with the linear tetradentate ligand dppn. Clean formation of the mononuclear complexes **1** and **5** was observed when the corresponding precursors were treated with an equimolar amount of the ligand and the X-ray study of one of them (**1**) showed the expected chelation through two neighboring nitrogen atoms of dppn. Surprisingly, further reaction of **1** or **5** with $[Rh(NBD)(CH_3CN)_2]BF_4$ gave rise to C−H activation of the pyridazine ring of the ligand and a unique rearrangement of the norbornadiene yielding a 3-nortricyclyl ligand unit. Complete characterization includes the X-ray crystallographic study of complex **4**. Complexes **1**, **4** and **5** were also characterized by ^1H-^{15}N GHMBC NMR spectroscopy, a technique which proved extremely useful for the characterization of these complexes. Several control experiments showed that this reactivity is not only crucially dependent on the basicity of the metal precursor used, but that the presence of at least one metal precursor with coordinated NBD is a prerequisite. Furthermore, it seems to be unique to the ligand used, possibly by the influence of the *N*,*N*-coordinated metal center on the C−H activation process by the second metal center. Further work is underway to extend the chemistry of these dppn−Rh systems and to explore their catalytic potential.

Experimental Section

General Procedures: All experiments were carried out under purified nitrogen in a Vacuum Atmospheres glove box equipped with an MO 40−2 inert gas purifier. All solvents were reagent-grade or better. All nondeuterated solvents were refluxed in the presence of sodium benzophenone ketyl and distilled under argon. Deuterated solvents were used as received. All the solvents were degassed with argon and kept in the glove box over molecular sieves. Commercially available reagents were used as received. The complexes $[Rh(NBD)_2]BF_4$, $[Rh(NBD)(CH_3CN)_2]BF_4$, $[Rh(COD)_2]BF_4$ and $[Rh(COD)(CH_3CN)_2]BF_4$ [24] were prepared according to literature procedures. ^1H and ^{13}C (DEPT) 1D NMR spectra were recorded with a Bruker DPX-250 spectrometer. A Bruker DRX-400 spectrometer operating at 400.13 MHz (^1H), 100.61 MHz (^{13}C) or 40.54 MHz (^{15}N) was used for 2D spectra. The spectrometer was equipped with a 5-mm Bruker inverse multinuclear resonance probe with a single-axis (*z*) gradient coil. Measurements were carried out at a probe temperature of 25 °C using concentrations of ca. 20 mg/ml. 2D ^1H-^{13}C correlation spectra were acquired with 1 K points in F_2, 128−256 complex increments in F_1 and 4−8 scans per increment for GHMQC; 1 K−2 K points in F_2, 128−256 increments in F_1 and 8−16 scans for GHMBC experiments. 2D ^1H-^{15}N correlation spectra were measured using the Bruker standard microprogram GHMBC. The GHMBC spectra were collected with 2 K × 256 (512) data points and 96−120 scans for each increment using the spectral widths in F_1 and F_2 of ca. 8−9 ppm for proton and 100−300 ppm for nitrogen-15. The long-range delay was optimized for 50−60 ms. Apodization was done with a sine bell in both dimensions. All ^{15}N spectra were referenced to liquid ammonia. Abbreviations used in the description of NMR spectroscopic data are as follows: br., broad; s, singlet; d, doublet; t, triplet; m, multiplet. The atom numbering in Scheme 2 has been used for the characterization of the compounds. Elemental analyses were performed by H. Kolbe, Mikroanalytisches Laboratorium, 45470 Mülheim, Germany.

Synthesis of dppn: (a) Preparation of 2-$(CH_3)_3Sn(C_5H_4N)$: To a solution of BuLi (50.000 mmol) in diethyl ether (50.0 mL) at −78 °C was added dropwise a solution of 2-bromopyridine (7.90 g, 50.000 mmol) in diethyl ether (25.0 mL). The resulting solution was stirred at −78 °C for 2 h. $SnCl(CH_3)_3$ (9.95 g, 50.000 mmol), dissolved in THF (10.0 mL), was added dropwise and the resulting deep-red solution was warmed to room temperature overnight during which time a heavy precipitate formed. The precipitate was filtered off and the solution was concentrated in vacuo and distilled under reduced pressure (135 °C, ca. 10 Torr). Yield: 12.10 g, 100%. **(b) Preparation of dppn:** 2,6-dichloropyridazine (2.60 g, 17.450 mmol), $Sn(C_5H_4N)(CH_3)_3$ (10.60 g, 44.000 mmol) and $PdCl(Ph_3P)_2(CH_2Ph)$ (0.50 g, 0.661 mmol) were placed in a Schlenk tube containing xylenes (300.0 mL) and refluxed under argon for 24 h. The resulting brown solution was treated at 0 °C with a saturated solution of KF (210.0 mL) and diethyl ether (300.0 mL) was added. The slurry was stirred for 40 min and poured into H_2O (750.0 mL). The product was extracted with diethyl ether, dried ($MgSO_4$), filtered and concentrated in vacuo. Chromatography on deactivated silica (eluent: hexane/diethyl ether, 1:1) gave dppn as a golden-colored, crystalline material. Yield: 1.84 g, 45%. ^1H NMR ($CDCl_3$): δ = 7.41 (ddd, ^3J = 7.6, ^3J = 4.8, ^4J = 1.2 Hz, 2 H, 3,9-H), 7.91 (ddd, ^3J = 7.7, ^4J = 1.8 Hz, 2 H, 4,10-H), 8.70 (d, 2 H, 14,15-H), 8.76 (m, 4 H, 2,5,8,10-H) ppm. ^{13}C NMR ($CDCl_3$): δ = 121.92 (2 C, C-3,9), 125.53 (2 C, C-14,15), 125.77 (2 C, C-5,11), 138.10 (2 C, C-4,10), 150.52 (2 C, C-2,8), 154.29 (2 C, C-13,16), 159.03 (2 C, C-6,12) ppm. ^{15}N ($CDCl_3$): δ = 306.89 (s,

^{2}J with 2,8-H, ^{3}J with 3,5,9,11-H, 2 N, N-1,7), 387.98 (s, ^{3}J with 14,15-H, 2 N, N-17,18) ppm. MS (EI): m/z = 235 [M^{+}].

Preparation of [Rh(dppn)(NBD)]BF$_4$ (1): A solution of dppn (100.0 mg, 0.427 mmol) in CH_2Cl_2 (3.0 mL) was added to a solution of [Rh(NBD)$_2$]BF$_4$ (159.0 mg, 0.427 mmol) in CH_2Cl_2 (3.0 mL). Stirring the resulting red solution at room temperature led to the precipitation of a deep red solid. The suspension was stirred for another 3 h, the solid filtered, washed with diethyl ether (2 times 5.0 mL) and dried in vacuo. Yield: 220.0 mg, 100%. Crystals suitable for an X-ray analysis were grown by slow concentration of a concentrated solution of **1** in methanol. ^{1}H NMR (CD_3NO_2): δ = 1.61 (br. s, 2 H, 19-H), 4.19 (br. s, 2 H, 20,23-H), 4.77 (br. s, 4 H, 21,22,24,25-H), 7.55 (ddd, ^{3}J = 7.5 Hz and 4.8, ^{4}J = 0.9 Hz, 1 H, 9-H), 7.76 (ddd, ^{3}J = 7.4 Hz and 5.3, ^{4}J = 1.3 Hz, 1 H, 3-H), 7.87 (d, ^{3}J = 5.1 Hz, 1 H, 5-H), 8.00 (ddd, ^{3}J = 7.8, ^{4}J = 1.7 Hz, 1 H, 10-H), 8.32 (ddd, ^{3}J = 7.8, ^{4}J = 1.4 Hz, 1 H, 4-H), 8.36 (d, ^{3}J = 7.7 Hz, 1 H, 2-H), 8.40 (d, ^{3}J = 8.0 Hz, 1 H, 11-H), 8.64 (d, ^{3}J = 9.0 Hz, 1 H, 15-H), 8.73 (d, ^{3}J = 4.6 Hz, 1 H, 8-H), 9.00 (d, ^{3}J = 9.0 Hz, 1 H, 14-H) ppm. ^{13}C NMR (CD_3OD): δ = 52.16 (d, $^{3}J_{Rh,C}$ = 2.5 Hz), 63.55 (d, $^{2}J_{Rh,C}$ = 6.1 Hz), 66.50 (d, $^{1}J_{Rh,C}$ = 9.8 Hz), 121.84, 123.69, 126.20, 127.84, 128.27, 128.45, 137.82, 141.25, 150.05, 150.26, 151.16, 153.59, 159.92 ppm. ^{15}N NMR (CD_3NO_2): δ = 242.45 (d, ^{2}J with 2-H, ^{3}J with 3-H and 5-H, $^{1}J_{N,Rh}$ = 19.3 Hz, 1 N, N-1), 271.03 (d, ^{3}J with 14-H, $^{2}J_{N,Rh}$ = 10.6 Hz, 1 N, N-18), 309.21 (s, ^{3}J with 9-H and 11-H, 1 N, N-7, ^{2}J with 8-H), 312.04 (d, ^{3}J with 15-H, $^{1}J_{N,Rh}$ = 20.2 Hz, 1 N, N-17) ppm. $C_{21}H_{18}BF_4N_4Rh$ (516.13): calcd. C 48.87, H 3.52, N 10.86; found C 48.81, H 3.54, N 10.80.

In situ Characterization of A: A solution of [Rh(NBD)(CH$_3$CN)$_2$]BF$_4$ (12.5 mg, 0.034 mmol) in CD_2Cl_2 (0.5 mL) was added to a suspension of [Rh(dppn)(NBD)]BF$_4$ (17.6 mg, 0.034 mmol) in CD_2Cl_2 (0.5 mL). The resulting red solution was transferred to an NMR tube and the spectrum was measured after 10 min. ^{1}H NMR (CD_2Cl_2): δ = 1.43 (s, 4 H), 2.20 (br. s, 6 H), 3.99 (br. s, 4 H), 4.45 (br. s, 8 H), 7.68 (dt, 2 H), 8.18 (dd, 2 H), 8.30 (d, 2 H), 8.36 (d, 2 H), 9.18 (s, 2 H) ppm.

In situ Characterization of C: A solution of [Rh(COD)(CH$_3$CN)$_2$]BF$_4$ (15.0 mg, 0.039 mmol) in CD_2Cl_2 (0.5 mL) was added to a suspension of [Rh(dppn)(COD)]BF$_4$ (21.0 mg, 0.039 mmol) in CD_2Cl_2 (0.5 mL). The resulting deep red solution was transferred to an NMR tube and the spectrum was measured. ^{1}H NMR (CD_2Cl_2): δ = 2.07 (d, br, 4 H), 2.28 (s, 6 H), 2.49 (br. s, 4 H), 4.58 (br. s, 8 H), 7.73 (dt, 2 H), 8.17 (dd, 2 H), 8.37 (d, 2 H), 8.48 (br, 2 H), 9.18 (s, 2 H) ppm.

Preparation of [Rh$_2$(dppn-H)(NBD)(η^1-C$_7$H$_9$)(CH$_3$CN)$_2$](BF$_4$)$_2$ (2): A solution of [Rh(NBD)(CH$_3$CN)$_2$]BF$_4$ (37.4 mg, 0.103 mmol) in CH_2Cl_2 (3.0 mL) was added to a suspension of [Rh(dppn)(NBD)]BF$_4$ (53.0 mg, 0.103 mmol) in CH_2Cl_2 (3.0 mL). The resulting red solution was stirred overnight during which time a slow precipitation of a pink solid occurred. The solid was recovered, washed with diethyl ether and dried in vacuo. Yield: 67.0 mg, 74%. ^{1}H NMR (CD_2Cl_2): δ = 0.8−1.5 (several m, 7 H), 1.54 (s, 2 H), 1.71 (br. s, 1 H), 2.34 (s, 3 H), 2.51 (br. s, 1 H), 2.64 (s, 3 H), 4.09 (br. s, 2 H), 4.56 (br. s, 4 H), 7.52−7.68 (m, 3 H), 8.04 (dt, not well defined, 1 H), 8.15 (m, 1 H), 8.28 (dt, J = 7.7 Hz, 1 H and 1.5 Hz), 8.72 (m, 2 H), 8.89 (br. s, 1 H) ppm. $C_{32}H_{32}B_2F_8N_6Rh_2$ (880.10): calcd. C 43.67, H 3.67, N 9.55; found C 44.29, H 3.76, N 9.36.

Preparation of [Rh$_2$(dppn-H)(NBD)(η^1-C$_7$H$_9$)(CH$_3$OH)$_2$(CH$_3$CN)](BF$_4$)$_2$ (4): Complex **2** (80.0 mg, 0.091 mmol) was dissolved in methanol (3.0 mL) and stirred at room temperature for 1 h. Addition of diethyl ether to the resulting red solution led to the precipitation of a red solid that was filtered, washed with additional diethyl ether and dried in vacuo. Yield: 76.0 mg, 93%. Crystals suitable for X-ray crystallography were obtained by slow diffusion of diethyl ether into a concentrated methanol/CH_2Cl_2 solution and subsequent slow concentration. ^{1}H NMR (CD_3OD): δ = 0.82 (dd, ^{3}J = 11.5 Hz, 2 H, 26-H), 0.86 (br. s, 1 H, 27-H), 1.02 (d, J = ca. 9 Hz, 1 H, 32-H), 1.10 (br. s, 1 H, 30-H), 1.04 (s, 1 H, 29-H), 1.16 (d, J ca. 9 Hz, 1 H, 32-H), 1.32 (br. s, 1 H, 31-H), 1.60 (s, 2 H, 19-H), 2.58 (br. s, 1 H, 28-H), 2.75 (s, 3 H, CH_3CN), 4.14 (br. s, 2 H, 20,23-H), 4.69 (t, ^{3}J = 2.0 Hz, 4 H, 21,22,24,25-H), 7.73 (ddd, ^{3}J = 7.7 Hz and 5.3, ^{4}J = 1.1 Hz, 1 H, 3-H), 7.76 (ddd, ^{3}J = 6.0, ^{4}J = 1.2 Hz, 1 H, 9-H), 7.92 (d, ^{3}J = 5.2 Hz, 1 H, 2-H), 8.24 (ddd, ^{3}J = 7.8, ^{4}J = 1.4 Hz, 1 H, 10-H), 8.31 (ddd, ^{3}J = 7.6 Hz,^{4}J = 1.6 Hz, 1 H, 4-H), 8.32 (d, ^{3}J = 7.4 Hz, 1 H, 8-H), 8.71 (d, 5, ^{3}J = 8.2 Hz, 1 H), 8.73 (d, ^{3}J = 8.0 Hz, 1 H, 11-H), 8.82 (s, 1 H, 15-H) ppm. ^{13}C NMR (CD_3OD): δ = 3.41 (CH_3CN), 13.45 (C-27), 13.86 (C-29), 19.18 (C-30), 33.26 (C-26), 34.27 (C-32), 37.10 (C-31), 45.29 (d, C-28), 53.31 (d, J = 2.3 Hz, 2 C, C-20,23), 64.78 (d, J = 5.8 Hz, C-19), 67.24 (t, J = 9.0 Hz, 4 C, C-21,22,24,25), 123.41 (C-8), 125.29 (C-5), 125.62 (br, CH_3CN), 128.62 (C-9), 129.22 (C-3), 135.28 (C-15), 141.53 (C-9), 142.55 (C-4), 151.37 (2 C, C-2,11), 155.08 (C-6), 156.51 (C-13), 160.56 (C-12), 169.44 (C-16) ppm. ^{15}N NMR (CD_3OD): δ = 174.10 (^{3}J with CH_3CN, $^{1}J_{N,Rh}$ = 45.9 Hz, 1 N, CH_3CN), 234.51 (d, ^{2}J with 8-H, ^{3}J with 9-H and 11-H, $^{1}J_{N,Rh}$ = 42.4 Hz, 1 N, N-7), 238.32 (d, ^{2}J with 2-H, ^{3}J with 3-H and 5-H, $^{1}J_{N,Rh}$ = 24.7 Hz, 1 N, N-1), 283.20 (d, ^{3}J with 15-H, $^{1}J_{N,Rh}$ = 40.2 Hz, 1 N, N-17) ppm. $C_{32}H_{37}B_2F_8N_5O_2Rh_2$ (903.13): calcd. C 42.56, H 4.13, N 7.75; found C 42.85, H 4.15, N 7.98.

Preparation of [Rh(dppn)(COD)]BF$_4$ (5): A solution of dppn (79.1 mg, 0.338 mmol) in CH_2Cl_2 (3.0 mL) was added to a solution of [Rh(COD)$_2$]BF$_4$ (137.1 mg, 0.338 mmol) in CH_2Cl_2 (3.0 mL). The resulting solution was stirred at room temperature for 24 h. Some of the compound readily precipitated from the solution. Addition of diethyl ether led to complete precipitation of a green compound that was washed with diethyl ether and dried in vacuo. Yield: 174.0 mg, 97%. ^{1}H NMR (CD_3NO_2): δ = 2.29 (m, 4 H, CH_2 of COD), 2.63 (m, 4 H, CH_2 of COD), 4.92 (s, 4 H, 4 olefins COD), 7.54 (ddd, ^{3}J = 7.6, 4.8, ^{4}J = 1.2 Hz, 1 H, 9-H), 7.80 (ddd, ^{3}J = 7.4, 5.4, ^{4}J = 1.4 Hz, 1 H, 3-H), 7.97 (ddd, ^{3}J = 7.8, ^{4}J = 1.7 Hz, 1 H, 10-H), 8.05 (d, 5, ^{3}J = 5.3 Hz, 1 H), 8.31 (ddd, ^{3}J = 7.8, ^{4}J = 1.5 Hz, 1 H, 4-H), 8.38 (m, 2 H, 2,11-H), 8.64 (d, ^{3}J = 9.1 Hz, 1 H, 15-H), 8.75 (dd, ^{3}J = 4.8 Hz, 1 H, 8-H), 9.09 (d, ^{3}J = 9.1 Hz, 1 H, 14-H) ppm. ^{15}N NMR (CD_3NO_2): δ = 235.13 (d, ^{2}J with 2-H, ^{3}J with 3-H and 5-H, $^{1}J_{N,Rh}$ = 26.0 Hz, 1 N, N-1), 271.05 (s, ^{3}J with 14-H, 1 N, N-18), 300.24 (d, $^{1}J_{N,Rh}$ = 20.5 Hz, ^{3}J with 15-H, 1 N, N-17), 307.71 (s, ^{3}J with 9-H and 11-H, ^{2}J with 8-H, 1 N, N-7) ppm. $C_{22}H_{22}BF_4N_4Rh$ (532.17): calcd. C 49.65, H 4.17, N 10.53; found C 49.60, H 4.14, N 10.39.

X-ray Crystal Structure Determination of 1 and 4: Single crystals of **1** and **4** were mounted on a nylon loop and flash-frozen in a nitrogen stream at 120 K. Data were collected with a Nonius Kappa CCD diffractometer mounted on an FR590 generator equipped with a sealed tube with Mo-K_α radiation (λ = 0.71073 Å) and a graphite monochromator. The structures were solved using direct method with SHELXS-97 and refined by full-matrix least-squares technique with SHELXL-97 based on F^2.[25] CCDC-183245 (**1**), and -183246 (**4**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html or from the Cambridge Crystallographic Data Center, 12, Union Road, Cambridge CB2 1EZ, UK [Fax: (internat.) + 44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk].

Complex 1: $C_{21}H_{18}N_4Rh{\cdot}BF_4{\cdot}CH_3OH$, dark orange, plates, 0.10 × 0.10 × 0.05 mm, triclinic, $P\bar{1}$ (no. 2), a = 7.887(2), b = 11.904(2), c = 12.564(3) Å, α = 110.10(3), β = 99.17(3), γ = 98.63(3)° from 20° of data, V = 1066.6(4) Å^3, Z = 2, M_w = 548.16, $D_{calcd.}$ = 1.707 Mg/m^3, μ = 0.859 mm^{-1}. The final cycle of refinement based on F^2 gave an agreement factor R = 0.0336 for data with $I > 2\sigma(I)$ and R = 0.0437 for all data (5490 reflections) with a goodness-of-fit of 1.017. Idealized hydrogen atoms were placed and refined in riding mode.

Complex 4: $C_{32}H_{37}N_5Rh_2{\cdot}(BF_4)_2{\cdot}CH_2Cl_2$, red, 0.2 × 0.2 × 0.2 mm, triclinic, $P\bar{1}$, a = 12.114(2), b = 12.400(2), c = 15.136(3) Å, α = 67.58(3), β = 83.86(3), γ = 69.04(3)° from 20° of data, V = 1961.6(6) Å^3, Z = 2, M_w = 988.03, $D_{calcd.}$ = 1.673 Mg/m^3, μ = 1.053 mm^{-1}. The final cycle of refinement based on F^2 gave an agreement factor R = 0.0497 for data with $I > 2\sigma(I)$ and R = 0.0537 for all data (8833 reflections) with a goodness-of-fit of 1.055. Idealized hydrogen atoms were placed and refined in riding mode.

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