Dinuclear Pyridine-1-Imine-Bridged Rhodium(III) Complexes. Intramolecular Carbon-Hydrogen Bond Activation

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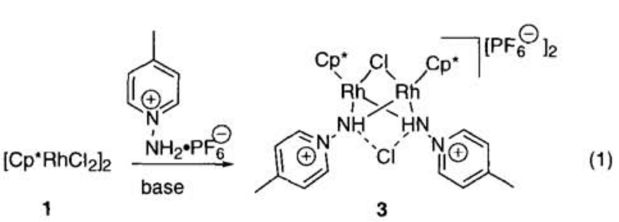
(Received August 24, 1998; CL-980650)

Novel dinuclear pyridine-1-imine Rh(III) complexes $[Cp^*Rh(\mu_2\text{-}Cl)\{\mu_2\text{-}NHNC_5H_4(4\text{-}Me)\}_2RhCp^*]Cl[PF_6]_2$ (**3**) and $[Cp^*Rh(\mu_2\text{-}Cl)\{\mu_2\text{-}NHNC_5H_3(2\text{-}CH_2)(6\text{-}Me)\}RhCl\text{-}Cp^*][PF_6]$ (**4**) were synthesized by the reaction of $[Cp^*RhCl_2]_2$ with $[NH_2NC_5H_4(4\text{-}Me)][PF_6]$ and $[NH_2\text{-}NC_5H_3(2,6\text{-}Me_2)][PF_6]$, respectively, in the presence of a base. The formation of **4** involves $C(sp^3)$-H bond activation at the benzylic position of a pyridine-1-imine ligand.

In the course of our continuous study on the reactivities of coordinated dinitrogen on transition metal complexes,[1] we have recently reported that the tungsten (1-pyridinio)imido complex $[WCl_2(CO)(PMe_2Ph)_2\{NNC_5H_2\text{-}(2,4,6\text{-}Me_3)\}][BF_4]$[2] exhibits higher reactivity with respect to N-N bond cleavage in comparison with other hydrazidium-type complexes ($M{\equiv}N\text{-}N^+R_3$) so far reported.[3] The finding that the N-N bond cleavage occurs in the presence of electron donors such as Cp_2Co[2] led us to investigate reactivities of other (1-pyridinio)imido ($M{\equiv}N\text{-}Py^+$) and pyridine-1-imine ($M{=}NH\text{-}Py^+$) complexes of late transition metals, as late transition metal complexes may not need the external addition of electrons in order to cleave the N-N bond. Late transition metal amido, imido and hydrazido complexes have been studied less extensively than those of early and middle transition metals in spite of their potentially rich chemistry.[4]

Treatment of $[Cp^*RhCl_2]_2$ (**1**; $Cp^* = \eta^5\text{-}C_5Me_5$) with two molar equiv of $[NH_2NC_5H_4(4\text{-}Me)][PF_6]$ (**2a**) in the presence of two molar equiv of NEt^iPr_2 in CH_2Cl_2 gave the dinuclear pyridine-1-imine-bridged rhodium complex $[Cp^*Rh(\mu_2\text{-}Cl)\{\mu_2\text{-}NHNC_5H_4(4\text{-}Me)\}_2RhCp^*]Cl[PF_6]_2$ (**3**) as an orange precipitate in 88% yield (eq. 1). The precipitate was essentially pure but could be recrystallized as large orange crystals of $\mathbf{3}{\bullet}CH_3CN$ from $CH_3CN\text{-}Et_2O$. Complex $\mathbf{3}{\bullet}CH_3CN$ was characterized spectroscopically[5] as well as by X-ray analysis.[6] When the reaction was performed at -78 °C using BuLi as the base, **3** was similarly formed in 73% yield. An ORTEP drawing (Figure 1) clearly confirms the dinuclear structure of $\mathbf{3}{\bullet}CH_3CN$, having two bridging nitrogen atoms and one bridging chlorine atom. The N-N bond lengths for **3** are 1.409(7) and 1.386(7) Å, respectively, and are in the range of N-N distances observed in the (1-pyridinio)imido complex $[WCl_2(CO)(PMe_2Ph)_2(NNC_5H_2Me_3)][OTf]$ (1.366(10) Å),[2] and hydrazidium complexes $[WCl(NNH_3)\text{-}(PMe_3)_4]Cl_2$ (1.396(20) Å),[3a] $[Cp^*MoMe_3(NNMe_3)][OTf]$ (1.426(5) Å)[3b] and $[Cp^*TaS(S^tBu)(NNMe_2{}^tBu)]$ (1.46(1) Å).[3c] The Rh(1)-Rh(2) distance (3.101(1) Å) indicates the absence of a metal-metal bond. The hydrogen atoms on N(1) and N(3) could be located in the Fourier map and are both hydrogen bonded to the non bridging chloro anion, Cl(2).[7] The ν_{NH} absorptions in the IR spectrum at 3249 and 3142 cm^{-1} are also indicative of the presence of hydrogen bonding. This type of hydrogen bonded ion pairs have been reported for rhodium and iridium complexes having amido- or hydrosulfido-bridges.[4c,8] In agreement with the symmetric molecular structure, the ^1H NMR spectrum of **3** shows just one set of signals attributable to the Cp* and pyridine-imine ligands.



(1)

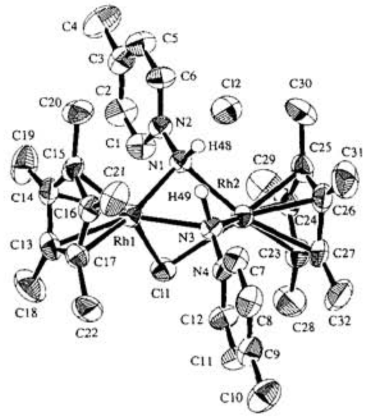
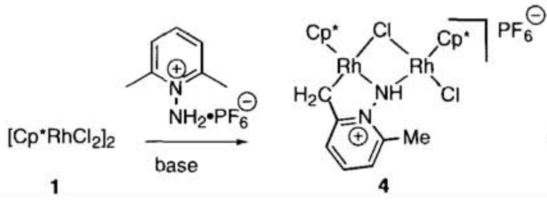


Figure 1. ORTEP drawing of **3**. The PF_6^- anions and the hydrogen atoms, except for the N-H hydrogens, are omitted. Selected bond distances (Å) and angles (deg): Rh(1)-Rh(2), 3.101(1); Rh(1)-N(1), 2.126(5); Rh(1)-N(3), 2.165(5); Rh(2)-N(1), 2.135(5); Rh(2)-N(3), 2.154(5); N(1)-N(2), 1.409(7); N(3)-N(4), 1.386(7); Rh(1)-N(1)-Rh(2), 93.4(2); Rh(1)-N(1)-N(2), 121.2(4); Rh(2)-N(1)-N(2), 124.5(4); Rh(1)-N(3)-Rh(2), 91.8(2); Rh(1)-N(3)-N(4), 120.2(4); Rh(2)-N(3)-N(4), 124.5(4).

In contrast, treatment of **1** with two molar equiv of $[NH_2NC_5H_3(2,6\text{-}Me_2)][PF_6]$ (**2b**) in the presence of two molar equiv of BuLi in THF gave the novel monocationic dinuclear rhodium complex $[Cp^*Rh(\mu_2\text{-}Cl)\{\mu_2\text{-}NHNC_5H_3(2\text{-}CH_2)(6\text{-}Me)\}RhClCp^*][PF_6]$ (**4**). Recrystallization from CH_2Cl_2-hexanes afforded red-brown crystals of **4** in 84% yield



(2)

(eq. 2). Use of NEt^{i}Pr$_2$ as the base instead of BuLi also led to the formation of **4** but in lower yield (35%). In order to establish the structure unambiguously an X-ray analysis was performed (Figure 2).[9] Complex **4** has a dinuclear structure having one nitrogen and one chlorine bridge. One of the rhodium atoms is further coordinated to a benzylic carbon atom of the pyridine ring. The Rh(1)-C(1) bond length at 2.10(1) Å is consistent with a Rh-C single bond. The N-N bond length is 1.42(1) Å and slightly longer than the N-N bond distances observed in **3**. The Rh(1)-Rh(2) distance (3.443(1) Å) precludes metal-metal bonding. The Rh(1)-Cl(1)-Rh(2)-N(1) entity is, unlike **3**, almost planar with a dihedral angle of 9.52° between the Rh(1)-Cl(1)-Rh(2) and Rh(1)-N(1)-Rh(2) planes.[10] In accordance with the molecular structure, the ^{1}H NMR spectrum showed two Cp* signals (δ 1.35 and δ 1.42), one pyridine methyl signal (δ 2.65) and three ring proton signals in the aromatic area.[11] The methylene hydrogens have significantly different chemical shifts (δ 2.99 and δ 4.61), and each of them showed a coupling to the rhodium nucleus (J_{HRh} = 2.0 and 3.0 Hz, respectively) and a coupling to each other (J_{HH} = 12.7 Hz). The ν_{NH} absorption in the IR spectrum was found at 3287 cm^{-1}, and the N-H signal was observed in the ^{1}H NMR spectrum at δ 5.78.

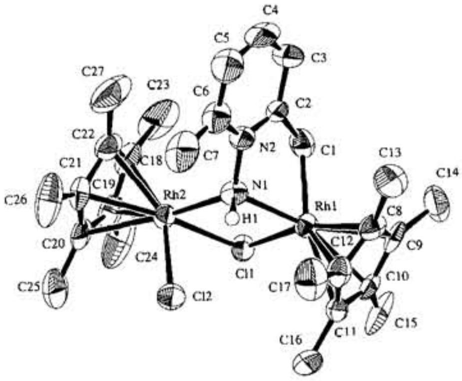


Figure 2. ORTEP drawing of **4**. The PF$_6^-$ anion and the hydrogen atoms, except for the N-H hydrogen, are omitted. Selected bond distances (Å) and angles (deg): Rh(1)-Rh(2), 3.443(1); Rh(1)-N(1), 2.105(8); Rh(1)-C(1), 2.10(1); Rh(2)-N(1), 2.199(8); N(1)-N(2), 1.42(1); C(1)-C(2), 1.46(1); Rh(1)-N(1)-Rh(2), 106.2(3); Rh(1)-N(1)-N(2), 109.7(6); N(1)-Rh(1)-C(1), 75.3(4).

Interestingly, the N-N bond is not cleaved in either complex **3** or **4** even though they contain two d^6 rhodium centers.[12] The fact that N-N bond cleavage does not occur may be ascribed to the reluctance of Rh(III) to be oxidized. This observation is in sharp contrast to the reaction of [Cp*IrCl$_2$]$_2$ with **2b** where the exclusive N-N bond cleavage was observed.[13]

The formation of **4** under ambient conditions is noteworthy. Intramolecular C-H bond activation of a ligating molecule is most commonly observed at the *ortho* position of an aromatic group (orthometallation).[14] On the other hand, activation of C(sp^3)-H bonds of *ortho* substituents has been studied much less intensively. Examples so far reported mainly concern the reactions of *ortho* substituted phosphine, isocyanide, and aryloxy ligands.[4b,15] We consider that the formation of a 36 electron dimeric species like complex **3** is unfavorable for further activation of the C-H bonds of the pyridine ring. In contrast, the sterically bulky NC$_5$H$_3$(2,6-Me$_2$) group is expected to allow the formation of a monomeric intermediate of the form [Cp*Rh{NNC$_5$H$_3$(2,6-Me$_2$)}]$^+$.[16] We presume that the C-H bond activation of one *ortho* CH$_3$-group of the pyridine ring proceeds on the Rh=N bond of the monomeric intermediate, which is followed by reaction with [Cp*RhCl$_2$]$_2$ to give **4**.

This work was supported by a Grant-in-Aid for Specially Promoted Research (No. 09102004) from the Ministry of Education, Science, Sports, and Culture of Japan. M. R. acknowledges scholarships from the Danish Research Councils and the Danish Research Academy.

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5 **3**•CH$_3$CN: ^{1}H NMR (CD$_3$CN): δ 1.16 (s, 30H, *Cp**), 2.47 (s, 6H, *Me*), 7.70 (br, 4H, *py*), 8.92 (br, 4H, *py*), 9.17 (br, 2H, N*H*). IR (KBr): 3249, 3141 (*NH*), 1642, 1509 (*py*) cm^{-1}. Anal. Found: C, 37.46; H, 4.44; N, 6.28%. Calcd. for C$_{34}$H$_{49}$Cl$_2$F$_{12}$N$_5$P$_2$Rh$_2$: C, 37.31; H, 4.51; N, 6.40%.

6 Crystallographic data for **3**•CH$_3$CN: C$_{34}$H$_{49}$Cl$_2$F$_{12}$N$_5$P$_2$Rh$_2$, M = 1094.44, orthorhombic, $P2_12_12_1$, a = 12.260(3) Å, b = 29.981(4) Å, c = 11.634(7) Å, V = 4276(2) Å^3, Z = 4, d_c = 1.700 gcm^{-1}, μ(Mo Kα) = 10.54 cm^{-1}, R = 0.039, R_w = 0.043, GOF = 2.41 for 4840 unique reflections with $I > 3\sigma(I)$. The hydrogen atoms coordinated to N(1) and N(3) could be found in the Fourier map.

7 Distances between hydrogen bonded atoms (Å); H(48)-Cl(2), 2.26; H(49)-Cl(2), 2.26.

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9 Crystallographic data for **4**: C$_{27}$H$_{39}$Cl$_2$F$_6$N$_2$PRh$_2$, M = 813.30, tetragonal, space group $I\bar{4}$, a = 18.352(2) Å, c = 19.018(3) Å, V = 6405(1) Å^3, Z = 8, d_c = 1.687 gcm^{-1}, μ(Mo Kα) = 13.00 cm^{-1}, R = 0.045, R_w = 0.029, GOF = 2.22 for 2947 unique reflections with $I > 3\sigma(I)$.

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11 **4**: ^{1}H NMR (CDCl$_3$): δ 1.35 (s, 15H, *Cp**), 1.42 (s, 15H, Cp*), 2.65 (s, 3H, *Me*), 2.99 (dd, *J* = 2.0, 12.7 Hz, 1H, C*H*H), 4.61 (dd, *J* = 3.0, 12.7 Hz, 1H, CH*H*), 5.78 (s, 1H, N*H*), 7.22 (d, *J* = 7.6 Hz, 1H, *py*), 7.59-7.69 (m, 2H, *py*). IR (KBr): 3287 (*NH*), 1611 and 1578 (*py*) cm^{-1}. Anal. Found: C, 39.82; H, 4.90; N, 3.79%. Calcd. for C$_{27}$H$_{39}$Cl$_2$F$_6$N$_2$PRh$_2$: C, 39.81; H, 4.83; N, 3.44%.

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16 Monomeric complexes [Cp*Ir≡NR] were obtained from [Cp*IrCl$_2$]$_2$ and LiNHR when the R group is C$_6$H$_3$(2,6-Me$_2$) or larger, see Ref. 4a.