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# Preparation and Structure of [RhCl(nbd)(dmap)] (nbd = bicyclo[2.2.1]hepta-2,5-diene; dmap = 4-(*N*,*N*-dimethylamino)pyridine)

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4-(*N*,*N*-Dimethylamino)pyridine (dmap) reacts with [{RhCl(nbd)}$_2$] to give [RhCl(nbd)(dmap)] (**1**), which was characterized by X-ray crystallography and NMR spectroscopy. The crystal structure and dynamic behavior of the molecule in solution are compared with those of [RhCl(nbd)-(PPh$_3$)] (**2**).

Rh(I)–diene complexes undergo facile substitution of the diene ligand with amine and phosphine ligands and are regarded as convenient precursors of various organorhodium complexes. Recently, several research groups have presented efficient polymerization of alkynes catalyzed by Rh(I) complexes with an nbd (bicyclo[2.2.1]hepta-2,5-diene) ligand in the presence of tertiary amines such as $NEt_3$ and dmap (4-(*N*,*N*-dimethylamino)pyridine).[1—18] The Rh–nbd complexes with the amine ligand have not been studied well, in spite of their importance in coordination chemistry and synthetic organic chemistry. In this paper, we report preparation of a Rh–nbd complex with dmap ligand and its structures in solid state and in solution.

The reaction of 4-(*N*,*N*-dimethylamino)pyridine (dmap) with [{RhCl(nbd)}$_2$] gives [RhCl(nbd)(dmap)] (**1**) in a high yield. A similar reaction of $PPh_3$ affords the known complex [RhCl(nbd)($PPh_3$)] (**2**) (Eq. 1).[19—21] Figure 1(a) shows the molecular structure of **1**, which contains nbd, Cl, and dmap ligands forming a square-planar coordination around the metal center. Rh–C bonds, 2.082(9)—2.137(8) Å, are without significant differences from each other, taking their esd's into considerations. The $PPh_3$ coordinated analogue **2** (Fig. 1(b)) contains more elongated Rh–C bonds at *trans* positions to $PPh_3$ (Rh–C1 2.210(3), Rh–C2 2.223(3)) than the others (Rh–C3 2.102(3), Rh–C4 2.108(3) Å). The results suggest a larger trans influence of $PPh_3$ than of Cl and probably than of dmap.

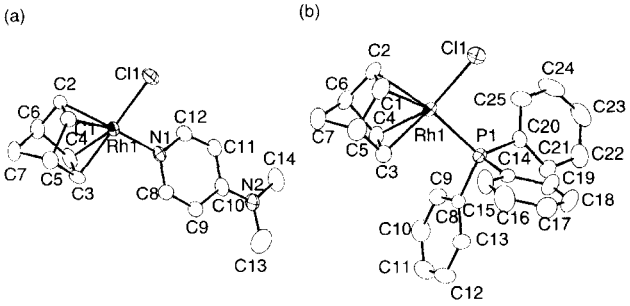
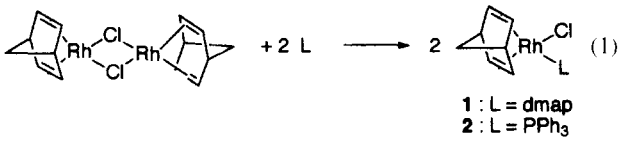



Fig. 1. (a) ORTEP drawing of [RhCl(nbd)(dmap)] (**1**). Selected bond distances (Å) and angles (deg): Rh(1)–Cl-(1) 2.364(2), Rh(1)–N(1) 2.106(7), Rh(1)–C(1) 2.104(8), Rh(1)–C(2) 2.137(8), Rh(1)–C(3) 2.082(9), Rh(1)–C(4) 2.102(8), Cl(1)–Rh(1)–N(1) 91.6(2). (b) ORTEP drawing of [RhCl(nbd)($PPh_3$)] (**2**). Selected bond distances (Å) and angles (deg): Rh(1)–Cl(1) 2.361(1), Rh(1)–P(1) 2.307(1), Rh(1)–C(1) 2.218(3), Rh(1)–C(2) 2.219(3), Rh-(1)–C(3) 2.103(4), Rh(1)–C(4) 2.103(4), Cl(1)–Rh(1)–P(1) 95.78(4).




The vinyl hydrogen signals of the $^1$H NMR spectum of **1** are observed at $\delta = 4.01$ and 3.60 at $-60$ °C. The signals due to hydrogens of two unequivalent olefinic groups are broadened on raising the temperature and undergo coalescence at $\delta = 3.80$ at 25 °C (11.8 mM in $CD_2Cl_2$) and at 10 °C (27.4 mM in $CD_2Cl_2$). Peak widths of the signals above $-30$ °C also increase with increase in the concentration of the complex. The apparent increase in the rate of exchange of the olefinic group with increasing in concentration of **1** suggests an associative mechanism. Previously Vrieze et al. reported that the $^1$H NMR signals of **2** above 50 °C also undergo an exchange whose rate is proportional to the concentration of the complex and proposed that this is attributed to bimolecular exchange of the ligand.[19—21] The large difference of the coalescence temperatures between **1** and **2** is ascribed not only to a smaller peak separation of the two vinyl hydrogens signals of **1** at low temperature than **2** but also to more facile dissociation of the dmap than of $PPh_3$. More facile exchange of the dmap ligand than of $PPh_3$ in this Rh–nbd system is due to less severe steric congestion of **1** than **2** and/or more labile Rh–dmap bond than the Rh–$PPh_3$ bond, which is stabilized by the π-acidic character of the phosphine ligand.

## Experimental

**General Procedure, Materials, and Measurement.** All the manipulations of the Rh complexes were carried out under nitrogen or argon using standard Schlenk techniques. The NMR spectra ($^1$H, $^{13}$C, and $^{31}$P) were recorded on a JEOL EX-400 spectrometer. $^{31}$P{$^1$H} NMR peak positions were referenced to external 85% $H_3PO_4$. [{RhCl(nbd)}$_2$] and [RhCl(nbd)($PPh_3$)] (**2**) were prepared according to the literature.[19—21]

Data of **2**. $^1$H NMR (400 MHz, at 25 °C in $CD_2Cl_2$) $\delta = 7.63$

(dd, 6H, *meta*, $J$ = 8, 10 Hz), 7.42 (m, 9H, *ortho*, *para*), 5.26 (s, 2H, =CH), 3.74 (s, 2H, CH), 3.03 (s, 2H, =CH), 1.38 (dd, 2H, $CH_2$, $J$ = 8, 16 Hz). $^{13}C\{^1H\}$ NMR (100 MHz, at −60 °C in $CD_2Cl_2$) $\delta$ = 134.0 ($J$ = 12 Hz), 130.8, 130.4, 130.1, 128.1 ($J$ = 12 Hz), 85.6 ($J$ = 12 Hz), 63.6 ($J$ = 8 Hz), 51.7 ($J$ = 12 Hz), 50.5 ($CH_2$). $^{31}P\{^1H\}$ NMR (160 MHz, at 25 °C in $C_6D_6$) $\delta$ = 36.0 (d, $J$(RhP) = 172 Hz).

**Preparation of 1.** To a THF (10 $cm^3$) solution of [{RhCl(nbd)}$_2$] (151.4 mg, 0.328 mmol) was added dmap (96.3 mg, 0.788 mmol) at room temperature. After stirring of the reaction mixture for 1 h, hexane (20 $cm^3$) was added slowly to cause separation of a yellow solid. This was collected by filtration, washed with hexane two times, and dried in vacuo. **1** was obtained as a yellow microcrystalline solid (230 mg, 92%). Mp 169.5—170.5 °C. Anal. Calcd for $C_{14}H_{18}N_2ClRh$: C, 47.68; H, 5.14; N, 7.94; Cl, 10.05%. Found: C, 47.50; H, 4.83; N, 7.93; Cl, 10.35%. $^1H$ NMR (400 MHz, at 25 °C in $CD_2Cl_2$) $\delta$ = 7.84 (d, 2H, *ortho*, $J$ = 6 Hz), 6.38 (d, 2H, *meta*, $J$ = 6 Hz), 3.80 (br, 4H, =CH), 3.79 (s, 2H, CH), 3.00 (s, 6H, $N(CH_3)_2$), 1.29 (s, 2H, $CH_2$). $^1H$ NMR (400 MHz, at −60 °C in $CD_2Cl_2$): $\delta$ = 7.72 (d, 2H,*ortho*, $J$ = 6 Hz), 6.32 (d, 2H, *meta*, $J$ = 6 Hz), 4.01 (s, 2H, =CH), 3.75 (s, 2H, CH), 3.60 (s, 2H, =CH), 2.97 (s, 6H, $N(CH_3)_2$), 1.24 (s, 2H, $CH_2$). $^{13}C\{^1H\}$ NMR (100 MHz, at −60 °C in $CD_2Cl_2$) $\delta$ = 153.7 (*C*–N(Me)$_2$), 148.0 (*ortho*), 105.7 (*meta*), 61.1 (*CH*), 56.1 (=*C*H), 56.0 (=*C*H), 51.1 (=*C*H), 51.0 (=*C*H), 49.5 ($CH_2$), 39.3 ($N(CH_3)_2$).

**X-Ray Crystallography.** Single crystals of **1** and **2** were obtained by recrystallization from THF/hexane and mounted in glass capillaries under argon. Data were collected at 23 °C on a Rigaku AFC-5R automated four-circle diffractometer equipped with monochromated Mo $K\alpha$ radiation ($\lambda$ = 0.71073 Å) and $\omega$–2$\theta$ scan method, and an empirical absorption correction ($\Psi$ scan) was applied. Calculations were carried out using a program package teXsan for Windows. The structures were solved by a direct method and subsequent Fourier technique. Atomic scattering factors were obtained from the literature.[22] Crystal data of **1**: $C_{14}H_{18}N_2ClRh$; $M_r$, 352.67; monoclinic; space group, $C2/c$ (No. 15); $a$ = 11.279(3); $b$ = 10.416(2); $c$ = 23.399(3) Å; $\beta$ = 92.50(2)°; $V$ = 2746.4(8) Å$^3$; $Z$ = 8; $\mu$(Mo $K\alpha$) = 1.418 mm$^{-1}$; $F$(000) = 1424; $D_{calcd}$ = 1.706 g cm$^{-3}$; Unique reflections ($2\theta \leq 55°$), 3320; Used reflections ($I \geq 3\sigma(I)$), 2569; No. of variables, 217; $R(F_o)$, 0.055; $R_w(F_o)$, 0.061. Crystal data of **2**: $C_{25}H_{23}ClRhP$; $M_r$, 492.79; triclinic; space group, $P\bar{1}$ (No. 2); $a$ = 10.543(3); $b$ = 11.475(2); $c$ = 10.301(2) Å; $\alpha$ = 102.82(2)°; $\beta$ = 115.54(2)°; $\gamma$ = 98.81(2)°; $V$ = 1051.7(6) Å$^3$; $Z$ = 2; $\mu$(Mo $K\alpha$) = 1.021 mm$^{-1}$; $F$(000) = 500; $D_{calcd}$ = 1.556 g cm$^{-3}$; Unique reflections ($2\theta \leq 55°$), 4836; Used reflections ($I \geq 3\sigma$(I)), 3905; No. of variables, 253; $R(F_o)$, 0.031; $R_w(F_o)$, 0.034. The crystallographic results including $F_o$–$F_c$ table are deposited as Document No. 73008 at the Office of the Editor of Bull. Chem. Soc. Jpn. Crystallographic data have been deposited at the CCDC, 12 Union Road, Cambridge CB21EZ, UK and copies can be obtained on request, free of charge, by quoting the publication citation and the deposition numbers 136135-136136.

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