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Note

Synthesis of tridentate 2,6-bis(imino)pyridyl aminechlorohydro ruthenium(II) complexes: The convenient use of amine hydrochlorides to generate metal-hydride

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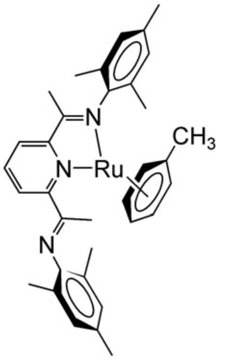
ABSTRACT

The reaction of low-valent ruthenium complexes with 2,6-bis(imino)pyridine ligand, [η^2-N_3]Ru(η^6-Ar) (**1**) or {[N_3]Ru}$_2$(μ-N_2) (**2**) with amine hydrochlorides generates six-coordinate chlorohydro ruthenium (II) complexes with amine ligands, [N_3]Ru(H)(Cl)(amine) (**4**). Either complex **1** or **2** activates amine hydrochlorides **3**, and the amines coordinate to the ruthenium center to give complex **4**. This is a convenient and useful synthetic approach to form ruthenium complexes with amine and hydride ligands using amine hydrochloride.

1. Introduction

Late transition metal complexes bearing bis(imino)pyridine ligands have drawn much attention recently due to their possible use in catalysis and in other chemical transformations [1–6]. Bis(imino)pyridyl transition metal complexes are effective catalysts for polymerization of ethylene [2–6], hydrosilylation [7,8], epoxidation [9], cyclopropanation [9], etc. Tridentate bis(imino)pyridine ligands form *mer* geometry, which provide spatial advantages for the interaction of transition metal centers with other ligands [2–11]. Ruthenium complexes with 2,6-bis(imino)pyridine ligands have been reported as well [9–12]. In particular, novel low-valent ruthenium complexes of the 2,6-bis(imino)pyridine ligands, [η^2-N_3]Ru(η^6-Ar) (**1**) and {[N_3]Ru}$_2$(μ-N_2) (**2**), where Ar = C_6H_6 or $C_6H_5(CH_3)$, and [N_3] = 2,6-(MesN=CMe)$_2C_5H_3N$, have been synthesized and characterized (Fig. 1) [11,12]. These low-valent Ru(0) complexes show interesting reactivities toward Si–Cl bond activation as a route to silyl and silylene complexes [12,13], and the coordination of other donating ligands (e.g. CO and PR_3) to generate a variety of [N_3]Ru(II) families [11,13].

Here, we describe the reaction of low-valent bis(imino)pyridyl ruthenium complexes with amine hydrochlorides to form [N_3]Ru(H)(Cl)(amine) (**4**). In particular, we use amine hydrochloride salts instead of using amines or ammonia gas to generate ruthenium complexes with amine and hydride ligands. The precursor amine hydrochloride salts are commercially available and easy to handle; therefore, this method is expected to be applicable for the generation of stable and potentially useful transition metal complexes with amine and hydride ligands [14,15]. Proposed formation mechanisms for these transformations are also discussed.



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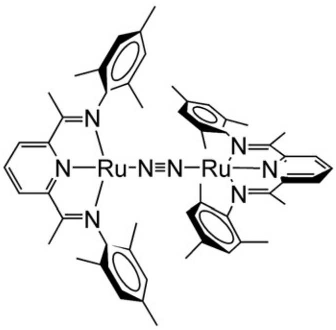

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Fig. 1. Low-valent ruthenium complexes of the 2,6-bis(imino)pyridine ligands, **1** and **2**.

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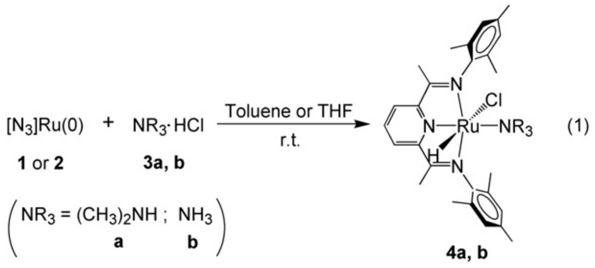
2. Results and discussion

Treatment of either [N_3]Ru(0) complex **1** or **2** with excess dimethylamine hydrochloride ($(CH_3)_2NH \cdot HCl$ (**3a**); about 14 equiv.) in toluene at room temperature leads to formation of [N_3]Ru(H)(Cl)($(CH_3)_2NH$) (**4a**) in one day (eq. (1)).



Complex **4a** has been isolated in 59% yield, as a dark green solid. The solid-state structure of **4a** was determined by a single-crystal X-ray diffraction study (Fig. 2 and Table 1), and exhibits a six-coordinate, pseudo-octahedral geometry with a *trans* arrangement of hydride and chloride ligands (H1–Ru1–Cl1 = 168.9(13)°). The dimethylamine ($(CH_3)_2NH$) ligand is *cis* to the chloride and hydride (H1–Ru1–N4 = 84.5(12)°, Cl1–Ru1–N4 = 85.31(8)°) and *trans* to the pyridine ligand (N2–Ru1–N4 = 176.13(10)°). The *trans* N1–Ru1–N3 bond angle is 156.13(10)°, which reflects a typical bis(imino)pyridyl complex and shows the constraints of the chelating ligand [9–12]. The mesityl ligands are oriented approximately perpendicular to the [N_3] ligand plane, and form a pocket surrounding the dimethylamine ligand. The ^{1}H NMR spectrum of **4a** in solution is consistent with the solid state structure, and exhibits four resonances determined as the imine methyls, two pairs of *o*-mesityl methyls, and *p*-mesityl methyls, consistent with mirror symmetry in the plane bisecting pyridine. A single ^{1}H NMR resonance for the ruthenium hydride (δ −19.72, singlet) indicates a *trans* hydride-chloride arrangement [11,12]. A single ^{1}H NMR resonance for inequivalent N–CH_3 groups is observed at room temperature (δ 2.25, doublet, $^3J_{HH} = 6.3$ Hz), which shows that the rotation of dimethylamine ligand around Ru–N bond is not hindered in solution on the NMR time scale.

Table 1
Crystallographic Data for [N_3]Ru(H)(Cl)($(CH_3)_2NH$), **4a**.

Formula	$C_{35}H_{51}N_4ClRu$
Formula weight	664.32
Crystal class	Triclinic
Space group	$P\bar{1}$ (#2)
Z	2
Cell constants	
a	8.2645(10) Å
b	13.5201(14) Å
c	16.513(2) Å
α	71.591(8)°
β	79.949(9)°
γ	81.082(9)°
V	1713.9(3) Å^3
μ	5.64 cm^{-1}
Crystal size, mm	0.42 × 0.12 × 0.08
D_{calc}	1.287 g/cm^3
F(000)	700
Radiation	Mo-K_α ($\lambda = 0.71069$ Å) Diffractometer: Rigaku Mercury CCD
Scan type	φ and ω rotations
Rotation width	0.5°
Exposure	30 s
Total number of images	824
2θ range	5.04–54.96°
Hkl collected	$-9 \le h \le 10$; $-17 \le k \le 17$; $-21 \le l \le 19$
No. reflections measured	19,144
No. unique reflections	7583 ($R_{int} = 0.0334$)
No. observed reflections	6711 ($F > 4\sigma$)
No. reflections used in refinement	7583
No. parameters [25]	402
Weighting scheme	$w = 1/[\sigma^2(F_o^2) + 0.0937P^2 + 0.6261P]$, where $P = (F_o^2 + 2F_c^2)/3$
R indices ($F > 4\sigma$)	$R_1 = 0.0512$, $wR_2 = 0.1352$
R indices (all data)	$R_1 = 0.0566$, $wR_2 = 0.1426$
GOF	1.041
Final Difference Peaks, e/Å^3	+2.428, −1.221

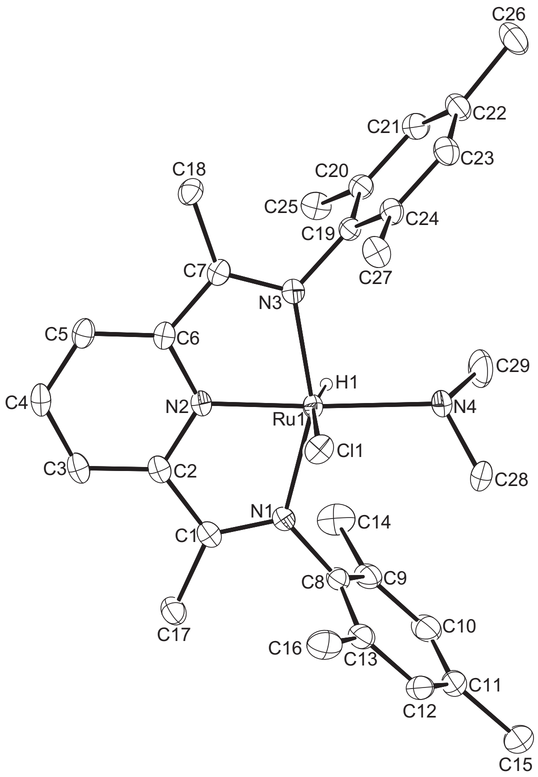
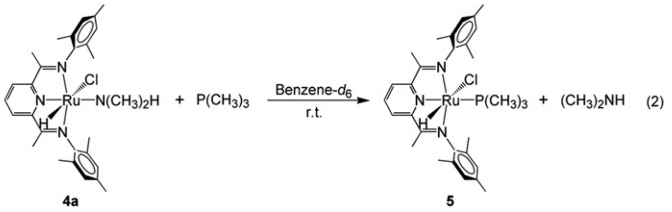


Fig. 2. ORTEP drawing of [N_3]Ru(H)(Cl)($(CH_3)_2NH$), **4a** with 30% probability thermal ellipsoids.

Treatment of either [N_3]Ru(0) complex **1** or **2** with excess ammonium chloride (NH_4Cl (**3b**); about 53 equiv.) in THF at room temperature leads to formation of [N_3]Ru(H)(Cl)(NH_3) (**4b**) in one day (eq. (1)). Complex **4b** was isolated in 45% yield, as a dark green solid. Although attempts to grow crystals for a single-crystal X-ray diffraction study were not successful, the structure of **4b** is most likely similar to that of **4a**: a six-coordinate, pseudo-octahedral geometry with a *trans* arrangement of hydride and chloride ligands, based on the ^{1}H NMR experimental results. A single resonance for the NH_3 ligand (δ 2.63) and a ruthenium hydride (δ −19.69) are observed.

Reaction of **4a** with excess $P(CH_3)_3$ (8 equiv.) in benzene-d_6 at room temperature leads to rapid displacement of dimethylamine and formation of Ru(II) phosphine complex, [N_3]Ru(H)(Cl)($P(CH_3)_3$) (**5**) [16]. Further reaction with additional $P(CH_3)_3$ to form probable Ru(0) complex such as the bis(phosphine) complex [N_3]Ru(PMe_3)$_2$ [16] and the dimethylamine hydrochloride salt **3a**, is not observed at room temperature. Complex **4a** is not able to reduce even in the presence of excess $P(CH_3)_3$.



Formation of ruthenium amine complexes **4a** and **4b** is most likely the result of ionic oxidative addition of hydrochloride (HCl) from amine hydrochlorides followed by the addition of amine to the ruthenium center [17]. Oxidative addition of HCl by the $[N_3]Ru(0)$ complexes can yield the intermediate structure **6**. Finally, coordination of amines to ruthenium can lead to formation of **4a** and **4b** (Scheme 1).

In conclusion, low-valent bis(imino)pyridyl ruthenium complexes show interesting reactivities toward the amine hydrochloride salts to generate hydrochloro ruthenium(II)-amine complexes, $[N_3]Ru(H)(Cl)(amine)$ (**4**). Either $[N_3]Ru(0)$ complexes $[\eta^2\text{-}N_3]Ru(\eta^6\text{-}Ar)$ (**1**) or $\{[N_3]Ru\}_2(\mu\text{-}N_2)$ (**2**) activates amine hydrochlorides **3**, and the amines coordinate to the ruthenium center to give complex **4**. The synthetic methods can be further applied to generate other transition metal-amine hydride complexes which are useful for catalysis.

3. Experimental

3.1. General methods

All manipulations were performed in Schlenk-type glassware on a dual-manifold Schlenk line or in a nitrogen-filled Vacuum Atmospheres glovebox [18]. All glassware was oven-dried prior to use. ^1H NMR spectra were obtained at 300, 360 and 500-MHz on Bruker DMX-300, AM-360, and AMX-500 FT NMR spectrometers, respectively. $^{31}P\{^1H\}$ NMR spectra were recorded with broadband ^1H decoupling at 121.5 MHz on Bruker DMX-300 spectrometers. All NMR spectra were recorded at 303 K unless stated otherwise. Chemical shifts are reported relative to tetramethylsilane for ^1H and external 85% H_3PO_4 for ^{31}P resonances.

3.2. Materials

Hydrocarbon solvents were dried over Na/K alloy-benzophenone. Benzene-d_6, toluene-d_8, cyclohexane-d_{12}, and tetrahydrofuran-d_8 were dried over Na/K alloy. Chloroform-*d* was dried over molecular sieves. C_2H_4 (Airco) was used as received. Triethylsilane (Aldrich) was dried over Na prior to use. Ruthenium complexes $[\eta^2\text{-}N_3]Ru(\eta^6\text{-}C_6H_5(CH_3))$ (**1**) [11], $\{[N_3]Ru\}_2(\mu\text{-}N_2)$ (**2**) [11], $P(CH_3)_3$ [19] were synthesized according to the literature procedures. Amine hydrochloride salts, **3a** and **3b** (Aldrich) were dried *in vacuo* prior to use.

3.3. Synthesis of $[N_3]Ru(H)(Cl)((CH_3)_2NH)$ (**4a**)

A toluene solution (5 mL) of $[\eta^2\text{-}N_3]Ru(\eta^6\text{-}C_6H_5(CH_3))$ (**1**) (31 mg, 0.053 mmol) and dimethylamine hydrochloride, **3a** (60 mg, 0.75 mmol) was stirred under nitrogen at 25 °C for 1 day. The reaction mixture was filtered under N_2 to filter out excess **3a** as a white solid, and then reduced in volume to approximately 0.5 mL *in vacuo*. The product was multiply recrystallized from pentane/toluene at room temperature, yielding 18 mg of dark green **4a** (59% yield). ^1H NMR of **4a** (benzene-d_6): 7.25 (d, $^3J_{HH}$ = 7.9 Hz, 2H, Py–H_m), 6.93 (t, $^3J_{HH}$ = 7.9 Hz, 1H, Py–H_p), 6.84 and 6.73 (s, each 2H, Mes–H_m), 3.98 (m, 1H, NH), 2.69, 2.14, 1.95, and 1.88 (s, each 6H, Mes–$CH_{3o,p}$, Im–CH_3), 2.25 (d, $^3J_{HH}$ = 6.3 Hz, 6H, N–CH_3), −19.72 (s, 1H, Ru–H).

3.4. Reaction of **4a** with $P(CH_3)_3$

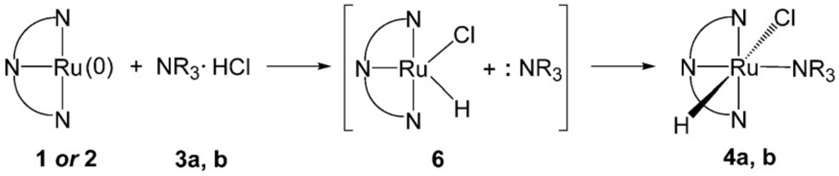
An NMR tube was loaded with a benzene-d_6 solution (0.3 mL) of **4a** (6 mg, 0.010 mmol), and the solution was degassed *in vacuo*. At −196 °C, $P(CH_3)_3$ (0.08 mmol, 8 equiv.) was added, and the NMR tube was sealed. The reaction mixture was then warmed to room temperature and the reaction was monitored via ^1H NMR spectroscopy. The color of the reaction mixture immediately changed from green to purple. After 5 min, all **4a** were consumed, and changed to $[N_3]Ru(H)(Cl)(P(CH_3)_3)$ (**5**) [16].

3.5. Synthesis of $[N_3]Ru(H)(Cl)(NH_3)$ (**4b**)

A THF solution (5 mL) of $[\eta^2\text{-}N_3]Ru(\eta^6\text{-}C_6H_5(CH_3))$ (**1**) (31 mg, 0.053 mmol) and ammonium chloride, **3b** (150 mg, 2.8 mmol) was stirred under nitrogen at 25 °C for 1 day. The reaction mixture was filtered under N_2 to filter out excess **3b** as a white solid, and then pumped out *in vacuo*. The product was multiply recrystallized from pentane/toluene at −78 °C, yielding 13 mg of green **4b** (45% yield). ^1H NMR (benzene-d_6): 7.28 (d, $^3J_{HH}$ = 7.5 Hz, 2H, Py–H_m), 6.95 (t, $^3J_{HH}$ = 7.5 Hz, 1H, Py–H_p), 6.83 and 6.74 (s, each 2H, Mes–H_m), 2.63 (s, 3H, NH_3), 2.64, 2.17, 1.96, and 1.82 (s, each 6H, Mes–$CH_{3o,p}$, Im–CH_3), −19.69 (s, 1H, Ru–H).

3.6. Single crystal X-ray diffraction analysis

Suitable X-ray quality crystals of **4a** were grown from benzene. Fig. 1 is an ORTEP [20] representation of the molecule with 30% probability thermal ellipsoids displayed. X-ray intensity data were collected on a Rigaku Mercury CCD area detector employing graphite-monochromated Mo-K_α radiation (λ = 0.71069 Å) at a temperature of 143 K. Preliminary indexing was performed from a series of twelve 0.5° rotation images with exposures of 30 s. Oscillation images were processed using CrystalClear [21], producing a listing of unaveraged F^2 and $\sigma(F^2)$ values, which were then passed to the CrystalStructure [22] program package for further processing and structure solution on a Dell Pentium III computer. The intensity data were corrected for Lorentz and polarization effects and for absorption using REQAB. The structure was solved by direct methods (SIR97) [23]. Refinement was by full-matrix least



Scheme 1. Proposed formation mechanism of complex **4**.

squares based on F^2 using SHELXL-97 [24]. All reflections were used during refinement (F^2's that were experimentally negative were replaced by $F^2 = 0$). Non-hydrogen atoms were refined anisotropically and hydrogen atoms were refined using a “riding” model, except hydride hydrogen atoms, which were refined isotropically.

Acknowledgments

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Appendix. Supplementary material

X-ray crystallographic data (in CIF format) and ^{1}H NMR spectra of purified samples associated with this article can be found in the online version at doi:10.1016/j.jorganchem.2010.12.015.

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[25] $R_1 = \sum||F_o| - |F_c||/\sum|F_o|$, w$R_2 = \{\sum w(F_o^2 - F_c^2)^2/\sum w(F_o^2)^2\}^{1/2}$, GOF $= \{\sum w(F_o^2 - F_c^2)2/(n - p)\}1/2$, where n = the number of reflections and p = the number of parameters refined.