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Note

Efficient transfer hydrogenation reaction Catalyzed by a dearomatized PN^3P ruthenium pincer complex under base-free Conditions

Li-Peng He [a,b], Tao Chen [a,b], Dong-Xu Xue [a,c], Mohamed Eddaoudi [a,c], Kuo-Wei Huang [a,b,*]

[a] Division of Chemicals and Life Sciences and Engineering, King Abdullah University of Science and Technology, Thuwal 23955-6900, Saudi Arabia
[b] KAUST Catalysis Center, King Abdullah University of Science and Technology, Thuwal 23955-6900, Saudi Arabia
[c] KAUST Advanced Membranes & Porous Materials Center, King Abdullah University of Science and Technology, Thuwal 23955-6900, Saudi Arabia

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ABSTRACT

A dearomatized complex [RuH(PN^3P)(CO)] (PN^3P=*N*, *N*′-bis(di-*tert*-butylphosphino)-2,6-diaminopyridine) (**3**) was prepared by reaction of the aromatic complex [RuH(Cl)(PN^3P)(CO)] (**2**) with *t*-BuOK in THF. Further treatment of **3** with formic acid led to the formation of a rearomatized complex (**4**). These new complexes were fully characterized and the molecular structure of complex **4** was further confirmed by X-ray crystallography. In complex **4**, a distorted square-pyramidal geometry around the ruthenium center was observed, with the CO ligand *trans* to the pyridinic nitrogen atom and the hydride located in the apical position. The dearomatized complex **3** displays efficient catalytic activity for hydrogen transfer of ketones in isopropanol.

1. Introduction

Pincer transition–metal complexes have recently attracted much attention due to their versatile reactivities to catalyze many organic transformations and to activate strong chemical bonds [1–5]. In particular, complexes with ligand derived from tridentate pyridine-based framework (L_1–Py–L_2) exhibit interesting reactivities [4]. This class of complexes share useful features as pincer compounds to allow their catalytic reactivity to be tuned by modifying the ancillary ligands, e.g. changing the donor atoms in the ligand backbone (L_1 and L_2: PR_2, NR_2, :CR_2, SR, S(=O)R, etc.) [6–16], and introducing heteroatoms as the linkers between the central pyridine and the donor groups [17–21]. Moreover, it has been demonstrated that unique bond activation reactions can be achieved through aromatization–dearomatization of the central pyridine ring [4,22].

Studies on the applications of pyridine-based PNP and PNN ruthenium complexes by Milstein and co-workers have revealed their effective reactivities for dehydrogenation of alcohols to ketones [23], dehydrogenative homocoupling of primary alcohols to esters [24], coupling of alcohols and amines to amides [25], N–H bond activation [26], light-induced splitting of water [27], etc. It is noted that these reactions proceed via the "metal-ligand cooperation" mechanism in which the reversible deprotonation of a pyridinyl methylene group takes place. In an effort to broaden the scope of this concept for the preparation of novel cooperative catalysts, we become interested in employing the NH spacer to replace the methylene groups. It is our intuition that the more acidic NH spacer may favor the dearomatization step and thus offer distinct reactivities. Herein, we report the preparation and reactivity of a new dearomatized ruthenium complex based on the PN^3P ligand and its application in transfer hydrogenation of ketones.

2. Results and Discussions

2.1. Synthesis and characterization

Reaction of the PN^3P ligand [18] with $RuHCl(PPh_3)_3(CO)$ in THF at 65 °C for 12 h afforded **2** as a pale yellow solid (Scheme 1). The appearance of a triplet at −26.11 ppm in the ^1H NMR spectrum indicates the existence of a hydride ligand. Treatment of complex **2** with one equivalent of *t*-BuOK in THF resulted in an immediate color change from orange to carmine. The ^1H and ^{31}P NMR analysis of the reaction mixture in benzene-d_6 revealed the full consumption of **2** and formation of a new complex (**3**). The ^1H NMR spectrum showed the disappearance of a broad N–H signal (2H) at 9.51 ppm

* Corresponding author. King Abdullah University of Science and Technology, Division of Chemicals and Life Sciences and Engineering, KAUST Catalysis Center, Thuwal 23955-6900, Saudi Arabia. Tel.: +966 28080328.
E-mail address: hkw@kaust.edu.sa (K.-W. Huang).

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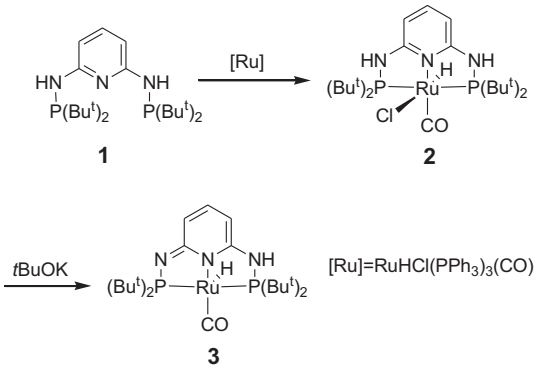
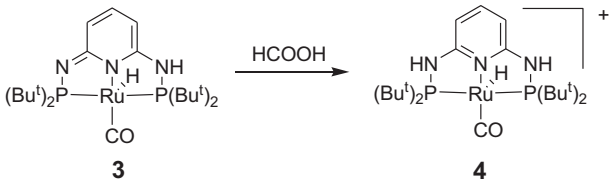


Scheme 1. Synthesis of dearomatized complex **3**.



Scheme 2. Rearomatization of complex **3**.

and the formation of a new N–H at 4.23 ppm (1H) as well as a set of sp^2 C–H signals at 5.17, 6.76, and 6.89 ppm, indicative of the dearomatization of the pyridine ring. The ^{31}P NMR spectrum confirmed the proposed structure with two doublets at 127.4 and 130.5 ppm. Rearomatization of complex **3** was examined by the reaction of 1.5 eq of formic acid with **3** freshly prepared from **2** (Scheme 2). A suitable crystal for the X-ray crystallographic analysis was obtained and the crystal data and structure refinements are summarized in Table 1. The molecular structure confirmed that the protonation of complex **3** was achieved. As shown in Fig. 1, a distorted square-pyramidal geometry around the ruthenium center was observed, with the CO ligand *trans* to the pyridine nitrogen atom and the hydride located in the apical position.

2.2. Transfer hydrogenation of ketones by ruthenium complexes

Ruthenium complexes have shown great potential to catalyze transfer hydrogenation reactions of ketones using 2-propanol (*i*-PrOH) as the hydrogen donor and solvent [28–30]. These reactions

Table 1
Crystal data and structure refinement for complex **4**.

Empirical formula	C46H87N6O6P4Ru2Cl
Formula weight	1181.69
Crystal system	Monoclinic
Space group	C2/c
Unit cell dimensions	a = 10.5118 (7) Å alpha = 90° b = 11.8403 (8) Å beta = 91.589 (2)° c = 44.641(3) Å gamma = 90°
Volume, Z	5554.1(6)Å^3, 4
ρcalc/mg mm^{-3}	1.413
μ/mm^{-1}	6.324
F(000)	2472
Crystal size/mm^3	0.36 × 0.24 × 0.18
2θ range for data collection	11.26–132.44°
Index ranges	$-12 \le h \le 9$, $-13 \le k \le 14$, $-51 \le l \le 52$
Reflections collected	20420
Independent reflections	4681[R(int) = 0.0354]
Data/restraints/parameters	4681/0/316
Goodness-of-fit on F^2	1.241
Final R indices [I > 2σ (I)]	$R1$ = 0.0333, wR2 = 0.0798
R indices (all data)	$R1$ = 0.0334, wR2 = 0.0798
Largest diff. peak/hole/e Å^{-3}	0.596/−0.636

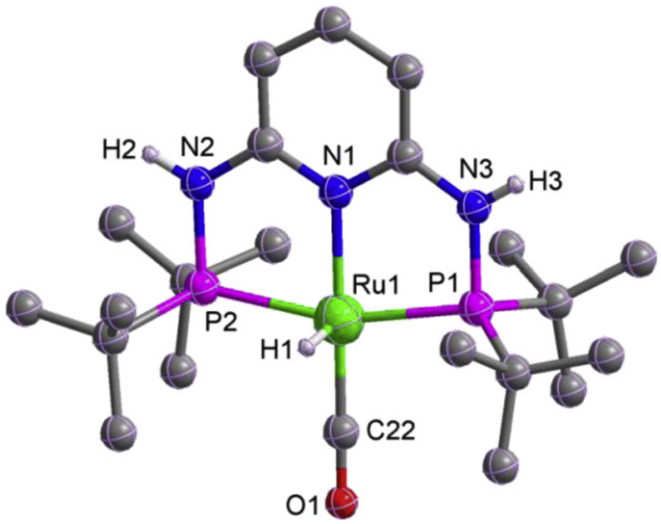


Fig. 1. Molecular structure of [RuH(PN^{3}P)(CO)]$^+$Cl$^-$·HCOOH (**4**·HCOOH) showing 50% thermal ellipsoids (C-bonded H atoms, HCOOH, and Cl$^-$ are omitted for clarity). Selected bond lengths (Å) and angles (°): Ru-N(1)=2.110(3), Ru-P(1)=2.319(8), Ru-P(2)=2.320(8), Ru- C(22)=1.848(4), N(2)-P(2)=1.706(3), N(3)-P(1)=1.701(3), N(1)-Ru-C(22)=178.69(13), P(1)-Ru- C(22)=98.92(10), P(2)-Ru-C(22)=98.85(10), N(1)-Ru-P(1)=81.07(7), N(1)-Ru-P(2)=81.18(7), P(1)-Ru-P(2)=162.21(3).

are particularly convenient for larger-scale synthesis, since it avoids the employment of high hydrogen pressure and hazardous reducing agents. Selected recent examples include the well-defined pincer-type N-heterocyclic carbene ruthenium complexes [31], tetradentate iminophosphorane-based ruthenium complexes [32], heterocyclic carbene ruthenium complexes [33,34], and unsymmetrical NNN ruthenium complexes [35]. These results prompted us to investigate the reactivities of our new PN^{3}P ruthenium complexes toward transfer hydrogenation (Table 2).

An initial test was carried at 82 °C using cyclohexanone as the model substrate. It was found that complex **2** was inactive for the reaction (entry 1), while full conversion to cyclohexanol was achieved within 16 h when complex **3** was employed (entry 2). Lowering the temperature to 40 °C still provided the reduction product in excellent yields, although increasing the reaction time was required (entry 3). Complex **3** showed high activity for the linear aliphatic ketones (entry 4), but low conversion was observed for 4,4-dimethyl-2-pentanone, presumably due to the bulkiness of the *tert*-butyl substituent (entry 5). Aromatic ketones can also be transfer hydrogenated effectively with the formation of a small amount of styrene byproducts (entry 6 and 7).

The results from entry **1** and **2** suggest that ruthenium hydride **3** is an active catalyst and the presence of the deprotonated N-arm/dearomatized pyridine ring is essential [22]. The transfer hydrogenation reaction could operate via a plausible mechanism similar to those of analogous PNN-Ru systems (Scheme 3) [31]. Complex **3** first reacts with *i*-PrOH to form hydridoruthenium alkoxide species **A** via proton transfer from O to N. β-hydride elimination to expel one acetone molecule occurs next to generate the dihydride species **B**. The ketone substrate can then insert into the Ru–H bond of **B** to afford a new hydridoruthenium alkoxide species **C**. Deprotonation of one of the NH arms by the alkoxide ligand of **C** affords the alcohol product and regenerates complex **3**. Noteworthy, the overall process does not involve any change in the oxidation state of the ruthenium center [22].

3. Conclusion

Ruthenium(II) complex **2** was prepared by reaction of the RuHCl(PPh$_3$)$_3$(CO) with *N*,*N*′-bis(di-*tert*-butylphosphino)-2,6-