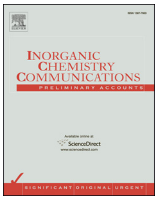
Inorganic Chemistry Communications 66 (2016) 15–18

Contents lists available at ScienceDirect

Inorganic Chemistry Communications

journal homepage: www.elsevier.com/locate/inoche



Short Communication

Synthesis, structures and catalytic activities of half-sandwich ruthenium complexes based on Schiff Base ligands

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ARTICLE INFO

Article history:
Received 28 December 2015
Received in revised form 23 January 2016
Accepted 1 February 2016
Available online 3 February 2016

Keywords:
Ruthenium
Complex
Structure
Nitroarene
Reduction

ABSTRACT

A series of half-sandwich ruthenium(II) complexes containing Schiff-base ligands [Ru(*p*-cymene)LCl] [HL = (E)-4-X-2-((phenylimino)methyl)phenol, X = H (2a); X = CH_3 (2b); X = Cl (2c) and X = Br (2d)] have been synthesized and fully characterized by ^1H and ^{13}C NMR spectra, elemental analyses and infrared spectrometry. Moreover, the molecular structures of ruthenium complexes 2b and 2c were confirmed by single-crystal X-ray diffraction methods. These half-sandwich ruthenium complexes are highly catalyzed hydrogenation of nitroarenes to aromatic anilines to proceed in the presence of sodium borohydride reducing agent in ethanol solvent. Notably, complex 2c was found to be a very efficient catalyst toward reduction of nitroarene compounds with wide functional group compatibility and substrate scope.

In the past decades, the half-sandwich ruthenium complexes have attracted considerable attention as active catalysts in the formation of C—C and C—heteroatom bond [1,2]; second building units for the assembly of metallomacrocycles [3,4] and anticancer drugs in clinic trials [5]. Syntheses and characterization of half-sandwich ruthenium complexes are important research fields in organometallic and inorganic chemistry. Within the past years, significant progress for half-sandwich ruthenium complexes' exceptional catalytic abilities has been made in organic transformation [6–10]. Schiff-base compound is an important class of ligands that can be easily obtained and modified to attain the desired steric bulkiness — or electronic properties [11]. Thus, it is an interesting issue to synthesize half-sandwich ruthenium complexes with Schiff-base ligands and explore their properties. Heterogeneous ruthenium-based catalysts as the potential candidate for the hydrogenation of nitroarenes have received more attention for their high activity [12]. However, the use of well-defined half-sandwich ruthenium complexes containing Schiff-base ligands as homogeneous catalysts for hydrogenation of nitroarenes is rare.

Herein, we have synthesized the half-sandwich ruthenium complexes containing Schiff-base ligands [HL = (E)-4-X-2-((phenylimino)methyl)phenol, X = H (2a); X = CH_3 (2b); X = Cl (2c) and X = Br (2d)] and explored their catalytic activities for reduction of nitroarenes to aromatic anilines. The half-sandwich ruthenium complexes catalyst allowed the hydrogenation of nitroarenes to aromatic anilines to proceed in the presence of sodium borohydride reducing agent with high yields in ethanol solvent. Moreover, the molecular structures of **2b** and **2c** were confirmed by single-crystal X-ray diffraction. The results indicate that the synthesized half-sandwich ruthenium complexes adopt classic "piano-stool" conformation with a six-membered metallocycle formed by coordination of the Schiff-base ligands to the metal centers.

The Schiff-base ligands (**1a**–**1d**) were obtained from the condensation of the corresponding salicyaldehyde and its derivatives with aniline, respectively, in moderate to good yields according to literature methods [13]. The dark red half-sandwich ruthenium complexes (**2a**–**2d**) were synthesized by the reaction of [Ru(*p*-Cymene)(*μ*-Cl)Cl]$_2$ with two equivalents of the Schiff-base ligands in the presence of K_2CO_3 in CH_3CN under reflux for 3 h according to Scheme 1. Complexes **2a**–**2d** were isolated as pure complexes by chromatography on silica gel using EtOAC and petroleum ether as eluent in yields of 80–90%. All complexes have been characterized by IR, NMR spectroscopy as well as elemental analyses. The half-sandwich ruthenium complexes are air and moisture stable, soluble in chlorohydrocarbon, alcohol and acetonitrile solvents.

X-ray crystallographic data has been analyzed for complexes **2b** and **2c**, both single crystals were obtained using slow diffusion of diethyl ether into a concentrated solution of the complexes in methanol solution. The crystallographic data for compounds **2b** and **2c** are summarized in Table S1, and selected bond lengths and angles are given in Table S3–5. The molecular structures of **2b** and **2c** are shown in Fig. 1 and Fig. 2.

Solutions were performed in a monoclinic P21/n (**2b**) and monoclinic P21/c (**2c**) space groups. As shown in Fig. 1 and Fig. 2, each Ru is surrounded by one chlorine atom, one nitrogen atom and one oxygen atom from the Schiff-base ligand and one of the *p*-cymene rings. Both the ruthenium centers have six-coordinate geometry expected for

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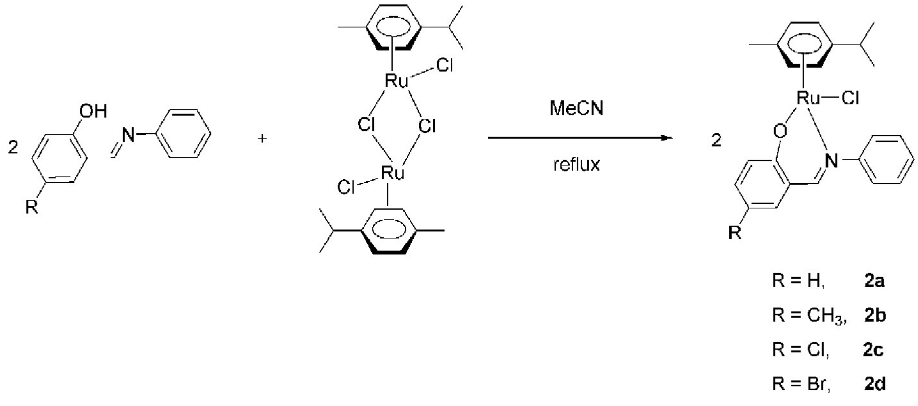


Scheme 1. Synthesis of half-sandwich ruthenium complexes with Schiff-base ligands (2a–2d).

pseudo-octahedral compounds assuming that the *p*-cymene ring serve as three-coordinated ligand, which is common for half-sandwich "piano stool" configuration [6,14–18]. The Ru—O distances (2.0586(12) Å in **2b** and 2.044(14) Å in **2c**) and Ru—N distances (2.0964(14) Å in **2b** and 2.070(16) Å in **2c**) are comparable to those of half-sandwich ruthenium complex containing [N,O] anionic bidentate ligands [19–24].

Catalytic reduction of nitroarene is possibly the most often used reaction to test the catalytic activity of transition metal complexes catalysts in aqueous solution. Aromatic anilines are important intermediates and precursors in the construction of pharmaceuticals, agrochemicals, pigments and dyes [25,26]. The catalytic performance of the half sandwich ruthenium complexes was evaluated in the reduction of 4-nitroanisole in the presence of $NaBH_4$ under homogeneous conditions. As shown in Table 1, the half-sandwich ruthenium complex **2c** was found to be very active toward the reduction of nitro compounds. Then, we chose **2c** as the best catalyst to test the influence of solvents, reaction temperature and catalysts loading on reaction yield (Table S1–3). The optimized results were obtained when nitroarene was allowed to react with 0.5 mol% complex **2c** at 30 °C in the presence of four equivalent of $NaBH_4$ in EtOH solvent.

With the optimal reaction conditions in hand, we started to expand the scope and efficiency of this methodology. As Table 2 demonstrates, moderate to good yields can be obtained for a range of substrates (Table 2). The reaction is tolerant of a range of aromatic functional groups including electron-donating and electron-withdrawing groups. It appeared that the steric hindrance of methyl on nitroarene had not an influence on the catalytic activities of the transformation from nitroarene to toluidine (Table 2, entries 6–8). The half-sandwich ruthenium system also promotes chemoselective nitro hydrogenation even in the presence of other reducible substituents. The reduction reaction of the nitro group in the presence of other functionality groups such as $-CH_2OH$, $-COMe$ and $-NHCOMe$ has also been performed (Table 2, entries 9–11). In the case of 4-nitroacetophenone, $-COMe$ groups are also reduced along with the reduction of the nitro group. Under the same reaction conditions, the $-NHCOMe$ groups remain totally unchanged. Under optimized conditions, the highly sterically hindered 2,6-dimethylnitrobenzen could be reduction in 95% yield (Table 2, entry 12).

In summary, we have synthesized and characterized a series of novel half-sandwich ruthenium complexes with Schiff-base ligands. A combination of spectroscopic studies and X-ray crystallographic confirmed the molecular structures of all half-sandwich ruthenium complexes. And these half-sandwich ruthenium complexes are highly catalyzed hydrogenation of aromatic nitro to aromatic anilines using sodium borohydride in ethanol solvent. The reaction offers wide functional group compatibility, broad substrate scope and provides aromatic anilines in good to excellent yields.

Acknowledgment

We acknowledge the financial support from the National Natural Science Foundation of China (Grant number 21102004), and the Project-sponsored by SRF for ROCS and Special and Excellent Research Fund of Anhui Normal University.

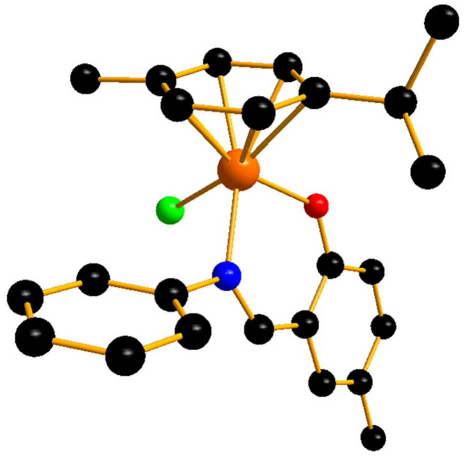


Fig. 1. Molecular structure of complex 2b. All hydrogen atoms are omitted for clarity.

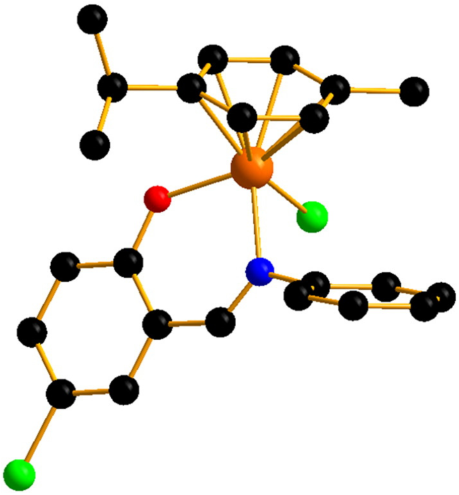
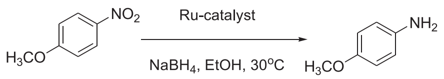


Fig. 2. Molecular structure of complex 2c. All hydrogen atoms are omitted for clarity.

Table 1
Screening of half-sandwich ruthenium complexes catalysts for p-nitroanisole reduction.[a]



Entry	Ru catalyst	Time (h)	Yield (%)[b]
1	$[Ru(p\text{-Cymene})(\mu\text{-Cl})Cl]_2$	25	30
2	2a	25	70
3	2b	25	75
4	2c	18	96
5	2d	18	90

[a] Reaction conditions: 0.3 mmol p-nitroanisole, 1.2 mmol sodium borohydride, (0.5 mol%) catalyst, EtOH, 30 °C.

[b] Isolated yield.

Appendix A. Supplementary material

Supplementary data associated with this article including experimental section, crystallographic data, catalytic data and NMR spectra can be found, in the online version, at http://dx.doi.org/10.1016/j.inoche.2016.02.001.

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(c) G. Suss-Fink, Arene ruthenium complexes as anticancer agents, Dalton Trans. 39 (2010) 1673–1688;
(d) M. Gras, B. Therrien, G. Suss-Fink, O. Zava, P.J. Dyson, Thiophenolato-bridged dinuclear arene ruthenium complexes: a new family of highly cytotoxic anticancer agents, Dalton Trans. 39 (2010) 10305–10313;
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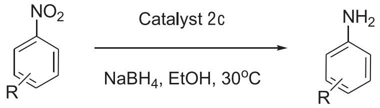
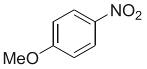
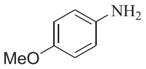
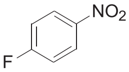
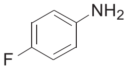
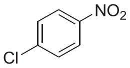
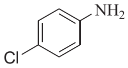
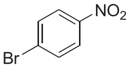
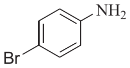
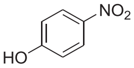
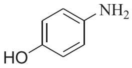
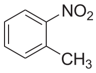
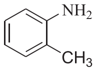
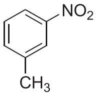
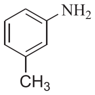
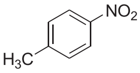
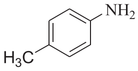
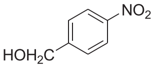
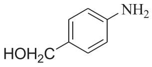
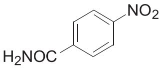
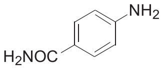
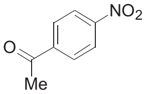
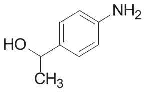
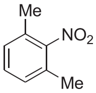
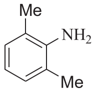
Table 2
Screening of substrates for nitroarene reduction catalyzed by ruthenium complex 2c.[a]



Entry	Substrate	Product	Time (h)	Yield (%)[b]
1			18	96
2			20	87
3			16	90
4			16	96
5			20	82
6			24	93
7			24	95
8			24	96
9			20	96
10			22	93
11			18	90
12			20	95

[a] Reaction conditions: 0.3 mmol nitroarene, 1.2 mmol sodium borohydride, catalyst **2c** (0.5 mol%), EtOH, 30 °C.

[b] Isolated yield.

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  (d) L. Zhang, Y.-J. Lin, Z.-H. Li, G.-X. Jin, Rational design of polynuclear organometallic assemblies from a simple heteromultifunctional ligand, J. Am. Chem. Soc. 137 (2015) 13670–13678.

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