# Synthesis and Structure of Novel ($\eta^1$:$\eta^6$-Aminoalkylarene)Ru$^{II}$ Complexes

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A series of mononuclear tethered complexes, $RuCl_2(\eta^1:\eta^6$-aminoalkylarene), in which the $\eta^6$-arene group and the ligated protic amine group are connected by suitable aliphatic carbon chains, were synthesized from $RuCl_2(\eta^6$-$PhCO_2C_2H_5)$(aminoalkylarene-$\kappa$-*N*) complexes via an intramolecular arene displacement reaction.

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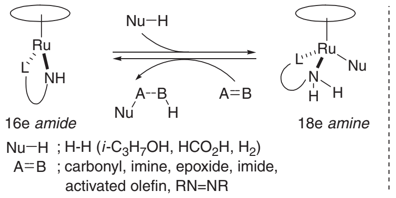
In recent years, much attention has been focused on the "metal–ligand bifunctional catalysis," established by Noyori and co-workers,[1] where both the metal and the ligand concertedly participate in bond-forming and -breaking processes, and a coordinatively saturated metal complex reacts with an unsaturated substrate directly without metal ligation. Much of our effort in this area has been devoted to the molecular design of half-sandwich type complexes, $(\eta^6$-$C_6R_6)Ru^{II}$ or $(\eta^5$-$C_5R_5)Ru^{II}$ with the characteristic Ru/NH bifunctionality, in which a 16-electron amide complex activates protic molecules to provide an 18-electron amine complex with a nucleophilic part as a ligand (Scheme 1).

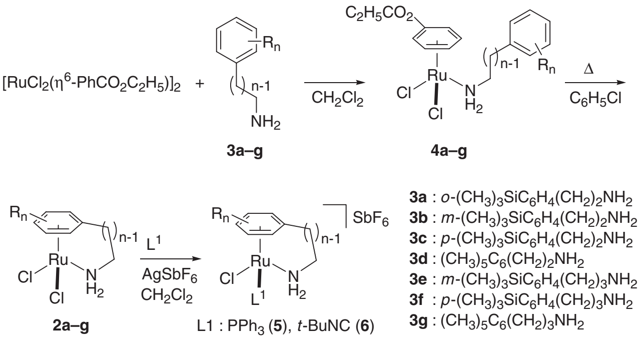


**Scheme 1.**

Not only have *sec*-alcohols,[2] formic acid,[3] and molecular dihydrogen[4] been found to serve as a hydrogen donor to provide amine hydride complexes, but also organic compounds with an acidic C–H bond[5] including nitroalkanes,[5a,5d] malonates,[5b,5c,5e] and various acidic compounds[5f] serve as a pronucleophile to give amine complexes with a Ru-bonded nucleophile. The interconversion between the amide and amine complexes facilitates catalytic chemo- and stereoselective reduction of ketones,[2a,2b,3,4a] imines,[3a] epoxides,[4b] and imides[4c] via a smooth transfer of the protic N*H* and hydridic Ru*H* to the polar functionality. In addition, stereoselective Henry[5a] and Michael-type reactions[5b–5f] are also accomplished by the amine complex, which possibly delivers the protic N*H* and Ru-bonded nucleophiles to aldehydes,[5a] activated olefins,[5b–5e] and azo compounds,[5f] regenerating amide complexes in an analogous manner.

In principle, half-sandwich type $(\eta^6$-$C_6R_6)Ru^{II}$ amide complexes have been prepared or generated in situ by the base-induced dehydrochlorination of the readily prepared amine chloride complexes **1**. A range of chelating protic amines ($L$–$NH_2$) such as N-sulfonylated 1,2-diamines,[1a] 2-aminoalcohols,[6] and benzylamine derivatives[7] can be used as excellent ligands of the bifunctional catalysts. These results prompted us to expand the conceptual Ru/NH bifunctionality by introducing new chelating protic amine ligands, in which the $\eta^6$-arene and the ligated amine groups are connected by suitable tethers such as **2** in Scheme 1. We disclose herein the synthesis and the structure of new tethered complexes, $RuCl_2(\eta^1:\eta^6$-aminoalkylarene), which have been conveniently prepared by the intramolecular arene displacement reaction.[8]

A reaction of dimeric $[RuCl_2(\eta^6$-$PhCO_2C_2H_5)]_2$[8a] in $CH_2Cl_2$ with 2-aminoethyl- or 3-aminopropylarenes (**3a**–**3g**) with an NH group was found to proceed smoothly in $CH_2Cl_2$ to give mononuclear $RuCl_2(\eta^6$-$PhCO_2C_2H_5)$(aminoalkylarene-$\kappa$-*N*) (**4a**–**4g**) (Scheme 2).



**Scheme 2.**

The resulting complexes **4a**–**4g** were subjected to thermal intramolecular arene displacement in chlorobenzene at 140 °C to produce $RuCl_2(\eta^1:\eta^6$-aminoalkylarene) (**2a**–**2g**) with concomitant elimination of ethyl benzoate. Precipitation by adding hexane to the reaction mixture led to the isolation of **2a**–**2g** as brownish yellow solids in 32–90% yields. Figure 1 illustrates the molecular structures of **2d** and **2g** determined by X-ray diffraction.[9]

The tethered moiety in **2** is surprisingly robust and tolerant of several reaction conditions in the presence of other 2e donor ligands including phosphines or isonitriles. For example, the reaction of **2** with excess $PPh_3$ in the presence of $AgSbF_6$ in refluxing $CH_2Cl_2$ or methanol yielded cationic $[RuCl(\eta^1:\eta^6$-aminoalkylarene)$(PPh_3)]^+$ complexes **5**.[10] Notably, the planar chiral complexes **2b** and **2e** afforded single diastereomers **5b** and **5e**

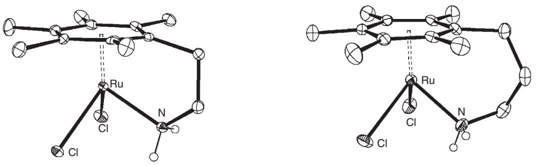


**Figure 1.** Molecular structures of **2d** (left) and **2g** (right). All hydrogens except on nitrogen are omitted for clarity.

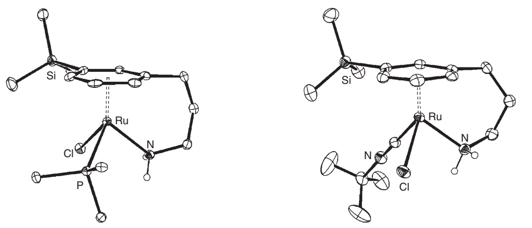


**Figure 2.** Molecular structures of *anti*-**5e** (left) and *syn*-**6e** (right). Ortho, meta, and para carbons on $PPh_3$ and all hydrogens except on nitrogen are omitted for clarity.

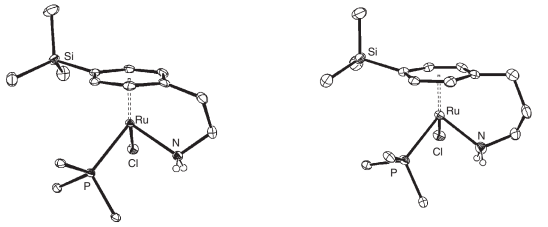


**Figure 3.** Molecular structures of **5c** (left) and **5f** (right). Ortho, meta, and para carbons on $PPh_3$ and all hydrogens except on nitrogen are omitted for clarity.

in reasonably high yields, as evidenced by $^{31}$P NMR analysis of the crude reaction mixtures. X-ray diffraction on a single crystal of **5e**[9] revealed that the silyl substituent and phosphine ligand adopt anti orientation with each other (Figure 2, left).

In sharp contrast, a 1:1 mixture of diastereomers of $[\mathrm{RuCl}(\eta^1{:}\eta^6\text{-aminoalkylarene})(\textit{tert}\text{-BuNC})]^+$ complexes **6** was obtained when *tert*-BuNC was used in place of $PPh_3$. Relative orientation of the silyl group and isonitrile ligand for the less soluble **6e** was unambiguously determined to be syn orientation by X-ray crystallographic analysis[9] (Figure 2, right). These results may suggest that steric congestion of incoming ligand is crucial for the high diastereoselectivity.[11]

Additionally, solid-state structural analysis indicated that the relatively short $C_2$ tether would impose the conformational constraints of the arene ligand. For example, the $C_2$ tethered complexes **2d** and **5c**[9] (Figure 3, left) consistently have the shortest Ru–C bond in the Ru–$C_{\mathrm{ipso}}$ (2.098 and 2.15 Å, respectively) and the longest one in the Ru–$C_{\mathrm{para}}$ (2.227 and 2.284 Å, respectively). In contrast, the $C_3$ tethered **2g** and **5d**[9] (Figure 3, right) show no salient feature in the difference of the Ru–C bond lengths (See Supporting Information).[13] Similar difference of the tethered structure has played a crucial role in the catalytic performance of triflylamide tethered arene–Ru complexes.[12]

In summary, we have developed an efficient method for the preparation of a series of tethered complexes $\mathrm{RuCl_2}(\eta^1{:}\eta^6\text{-aminoalkylarene})$. The tethered dichloride complexes were found to serve as convenient precursors for a variety of other tethered complexes. Their catalytic performance focusing on their Ru/NH bifunctionality will be reported in due course.

This paper is dedicated to Professor Ryoji Noyori on the occasion of his 70th birthday.

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8 The intramolecular arene displacement has been extensively used to prepare a variety of tethered Ru($\eta^6$-arene) complexes since the following two papers[8a,8b] were reported, but there had been no report that employs the protic amine group as an anchor when we initiated this research.[8c] Independently, a similar reaction was recently reported by Melchart et al.[8d] a) B. Therrien, T. R. Ward, M. Pilkington, C. Hoffmann, F. Gilardoni, J. Weber, *Organometallics* **1998**, *17*, 330. b) P. Smith, A. H. Wright, *J. Organomet. Chem.* **1998**, *559*, 141. c) M. Ito, H. Komatsu, T. Ikariya, 51st Symposium on Organometallic Chemistry, Tokyo, Japan, October, **2004**, Abstr. No. PA210. d) M. Melchart, A. Habtemariam, O. Novakova, S. A. Moggach, F. P. A. Fabbiani, S. Parsons, V. Brabec, P. J. Sadler, *Inorg. Chem.* **2007**, *46*, 8950.

9 Crystallographic data reported in this paper have been deposited with Cambridge Crystallographic Data Centre as supplementary publication Nos. CCDC-704734 (**2d**), -704735 (**2g**), -704736 (*anti*-**5e**), -704737 (*syn*-**6e**), -704738 (**5c**), and -704739 (**5f**). Copies of the data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html.

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