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Chemical Science

ARTICLE

Cite this: DOI: 10.1039/xoxxooooox

Received ooth January 2012, Accepted ooth January 2012

DOI: 10.1039/x0xx00000x

www.rsc.org/

2,2'-Bipyridyl Formation from 2-Arylpyridines through Bimetallic Diyttrium Intermediate

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An alkylyttrium complex supported by an N,N'-bis(2,6-diisopropylphenyl)ethylenediamido ligand, (ArNCH₂CH₂NAr)Y(CH₂SiMe₃)(THF)₂ (**1**, Ar = 2,6-^{*i*}Pr₂C₆H₃), activated an *ortho*-phenyl C—H bond of 2-phenylpyridine (**2a**) to form a (2-pyridylphenyl)yttrium complex (**3a**) containing a fivemembered metallacycle. Unique C(sp²)—C(sp²) coupling of 2-phenylpyridine proceeded through a bimetallic yttrium intermediate derived from a subsequent intramolecular shift of the yttrium center to an *ortho*-position of the pyridine ring in **3a** to yield a bimetallic yttrium complex (**4a**) bridged by two-electron reduced 6,6'-diphenyl-2,2'-bipyridyl. Aryl substituents at the *ortho*-position of the pyridine ring were a key for destabilizing the μ,κ^2 –(C,N)-pyridyldiyttrium intermediate prior to the C(sp²)—C(sp²) bond formation.

Introduction

Transition metal-catalyzed homo-coupling reactions of two arenes are an important category of C-C bond forming reactions to construct π -conjugated biaryl skeletons.^{1,2} For example, in the Ullmann coupling reaction, activation of aryl C-X bonds of heteroarenes with a low-valent metal species, such as Cu powder and Ni(cod)₂, produces the corresponding biaryl compounds. Although these reductive homo-coupling reactions are frequently used, the formation of salt-waste is inevitable and thus a more atom-economical method to synthesize biaryl skeletons is in high demand. The most direct protocol for $C(sp^2)-C(sp^2)$ bond formation is through C-H bond activation of aromatic compounds. To date, various transitionmetal complexes have been applied to such dehydrogenative biaryl coupling reactions.³ The most well-established mechanism for the biaryl $C(sp^2)-C(sp^2)$ bond formation mediated by the mononuclear species is reductive elimination of mononuclear di(aryl)metal species. However, some monoarylated metal species undergo biaryl $C(sp^2)-C(sp^2)$ coupling reactions. In this reaction, two mechanisms are proposed to be involved, i.e. disproportionation for producing a di(aryl)metal and low-valent metal species,⁴ and an associative C-C bond formation mediated by two metal centers.^{5,6} In the associative mechanism, species A is a bridged dimer through the π -coordination of the aryl moiety to another metal center before the formation of species **B** that contains a 3-centered-2electrons bridging aryl moiety (Figure 1). Subsequent C-C bond formation from species B produces the corresponding biaryl compound. Closely related chemistry is the Glaser diyne coupling reaction of terminal alkynes using a Cu-catalyst, whose mechanism involves a stepwise process through π coordination of the C=C bond to the different metal center and 3-centered-2-electrons C(sp)-bridging dinuclear intermediate before the C–C bond-forming step.⁷ Synthesis of the C=C π - coordination-bridged multimetallic species and mechanistic studies of the bimetallic aggregation-assisted C(sp)-C(sp) bond formation are feasible due to the strong coordination ability of the alkyne moiety to the metal center; however, corresponding studies of arylmetal species and the mechanism of associative biaryl $C(sp^2)-C(sp^2)$ bond formation have not been established due to the weaker π -aromatic coordination to the metal center compared with C=C π -coordination.

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Fig. 1 Aggregated monoarylated and monoalkynylated metal species. **A**: π -Coordination-bridged bimetallic species. **B**: 3-Centered-2-electrons Ph-bridged bimetallic species. **C**: Dianionic biphenyl-bridged bimetallic lanthanide complex. **D**: Dianionic diynebridged bimetallic lanthanide complex.

Rare-earth metal complexes containing a mono(aryl)- or mono(alkynyl)metal moiety, generated by C-H bond activation of arenes and terminal alkynes using an alkylmetal species, also mediate $C(sp^2)-C(sp^2)$ and C(sp)-C(sp) bond formation through the aggregation of two metal species. Because of the stability of the +3 oxidation state of the rareearth metal center, the C-C bond forming products, biaryl and diyne, were trapped in their dianionic form to give bimetallic complexes such as **C** and **D** as shown in Figure 1 reported by Fryzuk et al.,5,8,9 even though low-valent rare-earth metal complexes were recently accessible by the work of Evans et al..¹⁰ In our studies on C–H bond activation of heteroaromatic compounds by rare-earth metal and early transition metal complexes,¹¹ we found that σ -bond metathesis and subsequent 2,2'-bipyridyl formation of 2-arylpyridines proceeded upon treatment of an alkyl complex of (ethylenediamido)yttrium (1) with 2-arylpyridine (2). During this transformation, the C-H bond adjacent to the nitrogen atom of the pyridine ring was selectively functionalized. Mononuclear (2 pyridylphenyl)yttrium complex 3 was detected and isolated as an intermediate before producing dianionic 2,2'-bipyridylbridged dinuclear yttrium complexes 4 (Scheme 1). This is the first example for 2,2'-bipyridyl formation through the bimetallic aggregation pathway, even though dimerization of pyridine via C-H bond activation and insertion reactions was already reported by Teuben and Diaconescu, respectively.12 Catalytic 2,2'-bipyridyl formation via C-H bond activation was only addressed by heterogeneous Pd/C and Ru cluster catalysts.¹³ In addition, steric and electronic tuning of the pyridine derivatives led to the isolation of dinuclear bis(μ,κ^2 –(C,N)-pyridyl)diyttrium, mononuclear κ^2 –(C,N)pyridylyttrium, and 5-membered metallacycle complexes as possible intermediates in the C-C bond formation.



Scheme 1 Pyridylyttrium-mediated 2,2'-Bipyridyl Formation. [Y] = (ArNCH₂CH₂NAr)Y.

Results and Discussion

We first treated an alkvlvttrium complex $(ArNCH_2CH_2NAr)Y(CH_2SiMe_3)(THF)_2$ (1, Ar = 2.6- ${}^{i}Pr_{2}C_{6}H_{3}$ with 1 equiv of 2-phenylpyridine (2a) in benzene at The color of the solution changed room temperature. immediately from pale yellow to orange then to dark green, from which green-colored crystals of 4a were precipitated (eq 1). The green crystals were sparingly soluble in aromatic and The molecular structure of 4a was aliphatic solvents. determined by an X-ray diffraction study, and its ORTEP drawing is shown in Figure 2. During the reaction, 6,6'diphenyl-2,2'-bipyridyl was formed as a biaryl coupling product of 2-phenylpyridine. Two (ethylenediamido)yttrium moieties are bridged by the two-electron reduced 6,6'-diphenyl-2,2'-bipyridyl ligand. The nitrogen atoms in the 2,2'-bipyridyl moiety located on the opposite side, and the 2,2'-bipyridyl ligand coordinates to two yttrium atoms in an μ - η^4 : η^4 coodination mode. The bond length of Y1-N1 (2.344 Å) is shorter than the typical yttrium-nitrogen dative bonds (ca. 2.5 Å),¹⁵ but longer than those of Y1–N2 and Y1–N3 bonds (ca. 2.19 Å). The Y1–C2* bond (2.661 Å) is much longer than the vttrium-carbon covalent bond (ca. 2.45 Å).^{5b,15c} A C1-C1* bond (1.396 Å) at the central 2,2'-bipyridyl moiety is similar to that of two-electron reduced 2,2'-bipyridyl bound to two alkali metal centers with alternate planes (1.400 Å, rubidium).¹⁶





Fig. 2 Molecular structure of complex **4a** with 30% thermal ellipsoids. All hydrogen atoms and isopropyl groups are omitted for clarity. Selected bond lengths (Å) and angles (°): Y1–N1, 2.344(5); Y1–C1, 2.746(5); Y1–C1*, 2.857(5); Y1–C2*, 2.661(5); N1–C1, 1.424(6); C1–C2, 1.476(7); C1–C1*, 1.396(10); Y1–N2, 2.194(4); Y1–N3, 2.192(5); N1–Y1–C2*, 70.68(16); N2–Y1–N3, 80.78(17). Dihedral angle between N1–Y1–C2* and N1–C1–C1*–C2* planes, 109.6.

In addition to 2-phenylpyridine, 2-arylpyridines having methyl and methoxy groups at the *para*-position of the phenyl group were applicable to the 2,2'-bipyridyl formation. Complex **4b** was isolated in quantitative yield after treatment of **1** with 1 equiv of 2-(4-methylphenyl)pyridine (**2b**) at room temperature for 48 h. When 2-(4-methoxyphenyl)pyridine (**2c**) was used as the substrate, heating the reaction mixture at 50 °C for 68 h led to the formation of green crystals of **4c** in 36% yield. The low isolated yield of **4c** was attributed to decomposition during the C–C bond forming process. Because complexes **4b** and **4c** had poor solubility in aliphatic and aromatic solvents and low stability in coordinating solvents, characterization of **4b** and **4c** was based only on the X-ray diffraction study and combustion analyses.¹⁷

We next conducted a deuterium-labeling experiment. The addition of C_6D_5 derivative **2a**- d_5 to complex **1** in C_6H_6 resulted in the formation of the same green crystals together with a mixture of SiMe₄ and SiMe₄- d_1 , the former indicating the direct C-H bond activation of an *ortho*-pyridine ring by the alkylyttrium moiety, and the latter indicating that C-D bond activation of the *ortho*- C_6D_5 position by Y-CH₂SiMe₃ followed by an intramolecular shift of the yttrium atom to the *ortho*-pyridyl position before the C-C bond forming process (*vide infra*). These processes are consistent with subsequent oxidative quenching of the crystalline compound by CCl₄ to give a mixture of d_{8^-} , d_{9^-} , and d_{10} -6,6'-diphenyl-2,2'-bipyridyl

as evidenced by the intensity (69%-H) of the singlet signal due to *ortho*-position of the phenyl ring at $\delta_{\rm H}$ 8.18 (Scheme 2).



Scheme 2 Deuterium Labelling Experiment.

In addition, when 1 was reacted with 2a at room temperature in THF for 9 days to complete C—H bond activation, 5membered metallacyclic complex 3a was isolated in 98% yield. Complex 3a was stable and no further coupling reaction was detected in THF, but dissolution of 3a in C_6D_6 afforded the bimetallic compound 4a quantitatively, clearly indicating that the 5-membered metallacyclic complex 3a was a metastable species in benzene that could lead to a subsequent intramolecular shift of the yttrium center to *ortho*-position of the pyridine ring followed by C-C bond formation to afford 4a (Scheme 3).



Scheme 3 Stepwise Metallacycle and C—C Bond Formation.

When 2-arylpyridines 2c and 2d were treated with 1 in C_6D_6 at room temperature, C-H bond activation at the aryl ring proceeded to form five-membered metallacyclic complexes 3c and 3d (Scheme 4). By heating C_6D_6 solution of 3c at 50 °C, green microcrystals were precipitated from the reaction mixture, as observed in eq 1. In contrast, 3d was stable in C_6D_6 at 50 °C. We thus presumed that the C-C bond formation was affected by the electron-donating/-withdrawing substituents *meta* to the metallated carbon; THF coordination to yttrium for 3a and 3b was weaker than that of 3c and 3d in benzene, leading to easy dissociation of THF from yttrium of 3a and 3b and C-C bond formation to form 4a and 4b at room temperature.



Scheme 4 Effect of Substituents on the Aryl Ring of 2-arylpyridine for C-C Bond Formation Step.

In addition to isolation of stable five-membered metallacyclic complex 3d, reaction of 1 with benzo[h]quinolone at room temperature gave 3e in quantitative yield (eq 2). Complex 3e was isolated as microcrystals suitable for X-ray diffraction study. Although quality of the crystallographic data by X-ray diffraction study was insufficient, we determined the overall structure of 3e, in which a C-H bond of <math>benzo[h]quinolone proceeded to form five-membered metallacycle as shown in Supporting Information (Figure S1). Complex 3e was not converted to the C-C bond forming product similar to <math>4a-c, probably due to the low-flexibility of the benzo[h]quinolone scaffold.



In sharp contrast to the reaction of **1** with 2-arylpyridines 2a-2c, treatment of 1 with 1 equiv of pyridine (5a) or 4- or 3substituted pyridines (**5b-d**) afforded $bis(\mu,\kappa^2-(C,N)$ pyridyl)diyttrium complexes 6a-d as poor-soluble yellow microcrystals (Scheme 5). The ORTEP drawing of 6a is shown Figure 3. μ,κ^2 –(C,N)–Pyridyl ligands position at the bridging part of the bimetallic structure. The bond lengths of Y-N1 (2.328(4) Å) and Y*-C1 (2.560(5) Å) are longer than those found for mononuclear $\kappa(C,N)$ -pyridylyttrium complexes.^{17,18} Two yttrium atoms, two bridging carbons, and two nitrogen atoms of the bridging pyridine are located on the same plane. The ¹H NMR spectrum of **6a** displayed four resonances assignable to the bridging pyridine ring at δ_H 9.18 (3-py), 8.81 (6-py), 7.46 (4-py), and 6.80 (5-py). A significant downfield shift of the resonance at the 3-py position might be due to the proximity of the C-H bond to the metal fragment. When 3,5dimethylpyridine (5e) was used as the substrate, mononuclear yttrium complex **7e** was isolated in 97% yield. In the ¹³C NMR spectrum, a doublet signal was observed for the carbon atom attached to the yttrium center at $\delta_{\rm C}$ 219.6 (¹ $J_{\rm Y-C}$ = 35.2 Hz), which was in the typical range for mononuclear arylyttrium complexes.¹⁸ Even after heating the solution of complexes 6ad and 7e, which contained a 2-pyridylyttrium moiety in the molecular structure, C-C coupling products were not detected from the reaction mixture; decomposition of the complexes was observed, and no single species was isolated from the reaction mixture. 2-Trimethylsilylpyridine (5f) was also reacted with yttrium complex 1 to form (dimethylpyridylsilyl)methylyttrium complex 8f via $C(sp^3)$ —H bond activation reaction. In this case, an intramolecular shift of the yttrium center to form 2pyridylyttrium species or 6,6'-bis(trimethylsilyl)-2,2'-bipyridyl formation was not observed.



Scheme 5 Reactions of Alkylyttrium Complex **1** with Pyridine Derivatives.



Fig. 3 Molecular structure of complex 6a with 30% thermal ellipsoids. All hydrogen atoms are omitted for clarity. Selected Bond Lengths (Å): Y1–N1 2.328(4); Y1–C1 2.681(5); Y1–C1* 2.560(5); Y1–N2 2.216(4); Y1–N3 2.219(4); Y1–O1 2.422(3).

Based on our findings for the alkylyttrium-mediated C-H bond activation and C-C coupling reaction, we propose a mechanism for 2,2'-bipyridyl formation as shown in Scheme 6. First, alkylyttrium complex 1 cleaves a C-H bond at the orthoposition on the phenyl ring of 2a to produce five-membered metallacycle complex 3a. Complex 3a is isomerized to threemembered metallacycle intermediate E. Initial formation of the five-membered metallacycle prior to formation of the threemembered metallacycle, as the major pathway, was confirmed by the deuterium labeling experiment as shown in Scheme 2, where mono-deuterated $SiMe_4-d_1$ was generated and one H atom was incorporated into the phenyl ring. Direct formation of the intermediate E was plausible from complex 1 as the minor pathway, which was confirmed by the detection of SiMe₄ in the deuterium labelling experiment. Isomerization between three- and five-membered metallacycles was similarly reported by Diaconescu et al for rare-earth metal complexes. Although the trend of the isomerization is opposite to the report by

Diaconescu *et al.*, they mentioned that the pyridyl carbanion is more stable (2.8 kcal/mol) than the phenyl carbanion for the phenylpyridyl anion. We presume that the relative stabilities of the three- and five-membered metallacycle are significantly affected by the attached metal fragment.¹⁹ Substituent effect of the 2-arylpyridines for the C-C bond formation as shown in Scheme 4 indicates that the dissociation of the coordinating THF from the vttrium is a key for further isomerization.

Scheme 4 indicates that the dissociation of the coordinating THF from the yttrium is a key for further isomerization. Although the three-membered metallacycle intermediate **E** dimerized as a doubly $\mu,\kappa^2-(C,N)$ -bridged dinuclear structure, similar to diyttrium complexes **6a-d**, introduction of aryl groups at the *ortho*-position of the pyridine ring might destabilize the $\mu,\kappa-(C,N)$ -bridging mode of the pyridine moiety to afford **4a** through 3-centered-2-electrons aryl-bridged intermediate **F**.



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Scheme 6 Plausible Mechanism for the Reductive Dimerization of 2-Phenylpyridine.

Conclusions

We demonstrated that yttrium-mediated 2,2'-bipyridyl formation proceeded through bimetallic pyridylyttrium intermediate. Introduction of aryl substituents at the orthoposition of the pyridine ring destabilized the $\mu,\kappa^2-(C,N)$ -bridged intermediates to accelerate an associative bimetallic $C(sp^2)$ — $C(sp^2)$ bond formation. Further application of such bimetallic-mediated coupling reactions by not only rare-earth metal complexes but also early transition metal complexes is ongoing in our laboratory.

Acknowledgements

Y. S. acknowledges to the financial support by the JSPS Postdoctral Fellowship. H. N. expresses his special thanks for the financial support provided by the JSPS Research Fellowships for Young Scientists. H. T. acknowledges financial support by a Grant-in-Aid for Young Scientists (A) of The Ministry of Education, Culture, Sports, Science, and Technology, Japan. This work was supported by the Core Research for Evolutional Science and Technology (CREST) Program of the Japan Science and Technology Agency.

Notes and references

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[†] Electronic Supplementary Information (ESI) available: Experimental details for the synthesis and characterization of Y complexes, ¹H NMR spectrum of the deuterium labelling experiment, and crystal data for **3e** (CCDC 1409167), **4a** (CCDC 1048580), **4b** (CCDC 1048581), **4c**

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