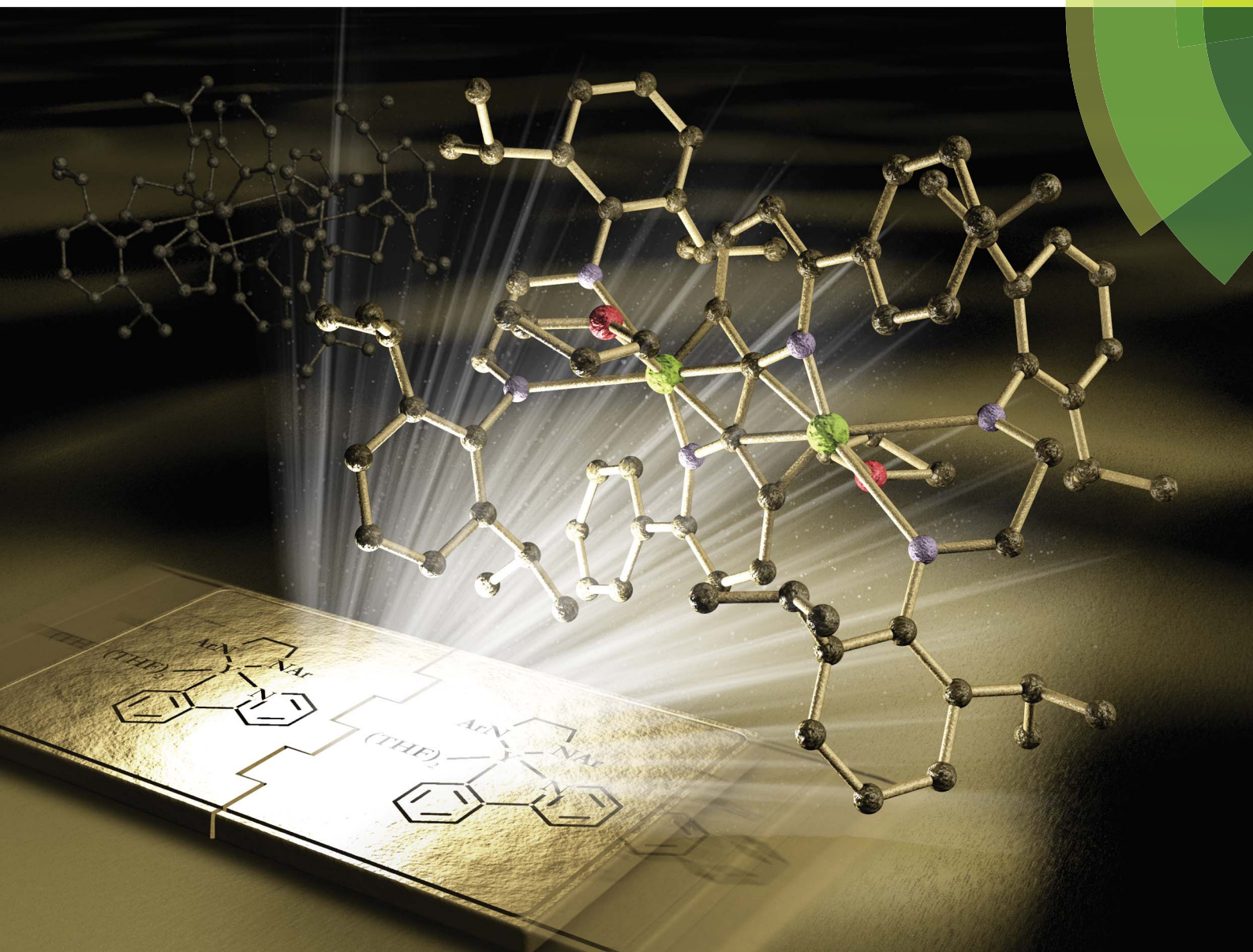


Chemical Science

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ISSN 2041-6539



EDGE ARTICLE

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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 five-membered metallacycle. Subsequently, a unique C(sp²)–C(sp²) coupling of 2-phenylpyridine proceeded through a bimetallic yttrium intermediate, derived from an 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 key in order to destabilize the μ,κ^2 -(C,N)-pyridyldiyttrium intermediate prior to the C(sp²)–C(sp²) bond formation.

Received 2nd May 2015
Accepted 17th July 2015

DOI: 10.1039/c5sc01599e

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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, the activation of aryl C–X bonds of heteroarenes with a low-valent metal species, such as Cu powder or 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 there is a demand for a more atom-economical method to synthesize biaryl skeletons. The most direct protocol for C(sp²)–C(sp²) bond formation is through C–H bond activation of aromatic compounds. To date, various transition metal complexes have been applied to such dehydrogenative biaryl coupling reactions.³ The most well-established mechanism for biaryl C(sp²)–C(sp²) bond formation mediated by a mononuclear species is reductive elimination of mononuclear di(aryl) metal species. However, some monoarylated metal species undergo biaryl C(sp²)–C(sp²) coupling reactions. In this reaction, two mechanisms are proposed to be involved, *i.e.* disproportionation to produce 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, a bridged dimer species **A** is first formed through π -coordination of the aryl moiety to another metal center, followed by the formation of species **B**, which contains a 3-centered-2-electron bridging aryl moiety (Fig. 1). Subsequent C–C bond formation from species **B** produces the corresponding biaryl compound. A closely related reaction is the Glaser diyne coupling reaction of terminal alkynes using a Cu catalyst, the mechanism of which involves a stepwise process through π -coordination of the C \equiv C bond to a different metal center and a 3-centered-2-electron C(sp)-bridging dinuclear intermediate before the C–C bond-forming step.⁷ Synthesis of the C \equiv 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 coordinating ability of the alkyne moiety to the metal center; however, corresponding studies of arylmetal species and the mechanism of associative biaryl C(sp²)–C(sp²) bond formation have not been established due to the weaker

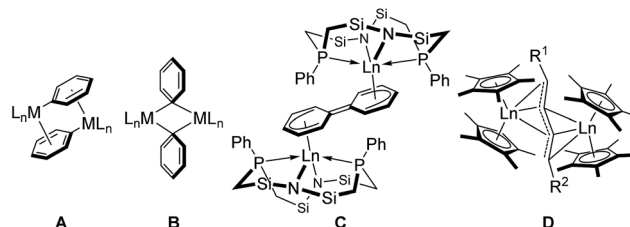


Fig. 1 Aggregated monoarylated and monoalkynylated metal species. A: π -coordination-bridged bimetallic species. B: 3-centered-2-electron Ph-bridged bimetallic species. C: dianionic biphenyl-bridged bimetallic lanthanide complex. D: dianionic diyne-bridged bimetallic lanthanide complex.

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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** (CCDC 1048582), **6a** (CCDC 1048583), **6c** (CCDC 1048584) and **6d** (CCDC 1048585). For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c5sc01599e

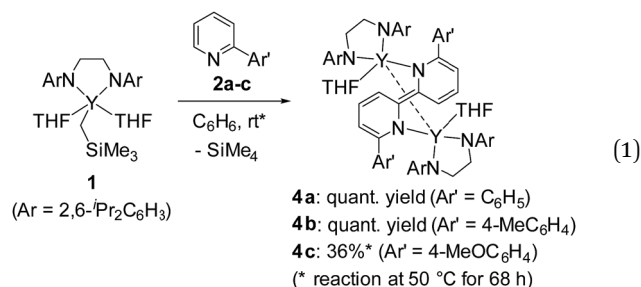
π -aromatic coordination to the metal center compared with $C\equiv C$ π -coordination.

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 rare-earth metal center, C–C bond formation products, biaryls and diynes, have been trapped in their dianionic form to give bimetallic complexes such as **C** and **D** as reported by Fryzuk *et al.* (Fig. 1),^{5,8,9} even though access to low-valent rare-earth metal complexes has been reported by Evans *et al.*¹⁰ In our studies on the 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 from 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 in the formation of dianionic 2,2'-bipyridyl-bridged dinuclear yttrium complex **4** (Scheme 1). This is the first example of 2,2'-bipyridyl formation through bimetallic aggregation, even though dimerization of pyridine *via* C–H bond activation and insertion reactions has previously been reported by Teuben and Diaconescu, respectively.¹² Catalytic 2,2'-bipyridyl formation *via* C–H bond activation has only been achieved using 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)-pyridyl yttrium, and 5-membered metal-lacycle complexes as possible intermediates in the C–C bond formation.

Results and discussion

We first treated an alkyl yttrium complex ($ArNCH_2CH_2NAr$) $Y(CH_2SiMe_3)(THF)_2$ (**1**, $Ar = 2,6\text{-}i\text{-Pr}_2C_6H_3$)¹⁴ with 1 equiv. of 2-phenylpyridine (**2a**) in benzene at room temperature. The color of the solution changed immediately from pale yellow to orange and then to dark green, and green-colored crystals of **4a** were precipitated (eqn (1)). The green crystals were sparingly soluble in aromatic and aliphatic solvents. The molecular structure of **4a** was determined by X-ray diffraction studies, and its ORTEP drawing is shown in Fig. 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 are located on opposite sides, and the 2,2'-bipyridyl ligand coordinates to the two yttrium atoms in a μ - η^4 : η^4 -coordination mode. The bond length of Y1–N1 (2.344 Å) is shorter than the typical yttrium–nitrogen dative bond (*ca.* 2.5 Å),¹⁵ but longer than the Y1–N2 and Y1–N3 bonds (*ca.* 2.19 Å). The Y1–C2* bond (2.661 Å) is much longer than the yttrium–carbon covalent bond (*ca.* 2.45 Å).^{5b,15c} The C1–C1* bond (1.396 Å) of the central 2,2'-bipyridyl moiety is similar in length to the analogous bond in two-electron reduced 2,2'-bipyridyl bound to two alkali metal centers with alternate planes (1.400 Å, rubidium).¹⁶



In addition to 2-phenylpyridine, 2-arylpyridines with 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

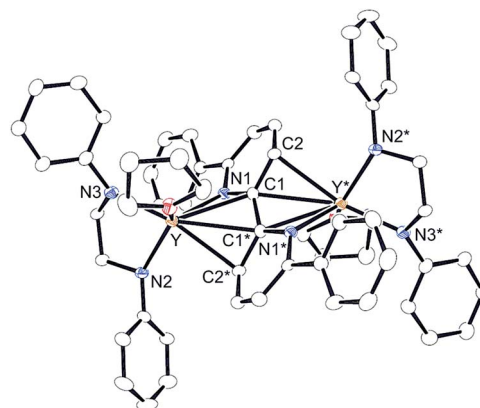
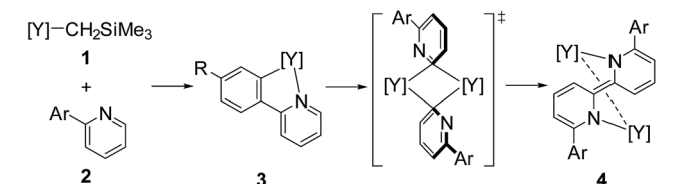


Fig. 2 Molecular structure of complex **4a** with 30% thermal ellipsoids. All hydrogen atoms and isopropyl groups are omitted for clarity. Selected bond lengths (Å) and angles (°): Y1–N1, 2.344(5); Y1–C1, 2.746(5); Y1–C1*, 2.857(5); Y1–C2*, 2.661(5); N1–C1, 1.424(6); C1–C2, 1.476(7); C1–C1*, 1.396(10);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



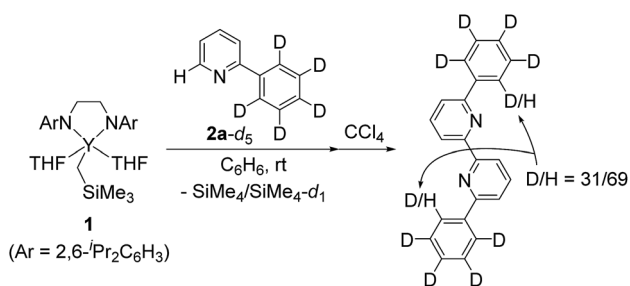
Scheme 1 Pyridyl yttrium-mediated 2,2'-bipyridyl formation. [Y] = ($ArNCH_2CH_2NAr$)Y.

poor solubility in aliphatic and aromatic solvents and low stability in coordinating solvents, characterization of **4b** and **4c** was based only on X-ray diffraction studies and combustion analyses.¹⁷

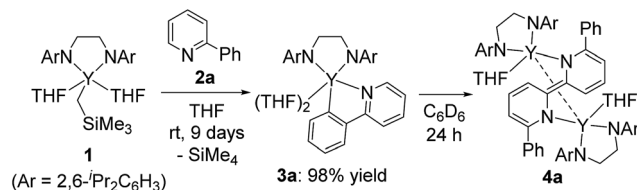
We next conducted a deuterium labelling experiment. The addition of C₆D₅ derivative **2a-d₅** to complex **1** in C₆H₆ resulted in the formation of the same green crystals together with a mixture of SiMe₄ and SiMe₄-d₁, the former indicating direct C–H bond activation at the *ortho*-position of the pyridine ring by the alkylttrium moiety, and the latter indicating C–D bond activation of the *ortho*-C₆D₅ position by Y–CH₂SiMe₃ followed by an intramolecular shift of the yttrium atom to the *ortho*-position of the pyridyl 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 d₈-, d₉-, and d₁₀-6,6'-diphenyl-2,2'-bipyridyl, as evidenced by the intensity (69%-H) of the singlet signal corresponding to the *ortho*-position of the phenyl ring at δ_H 8.18 (Scheme 2).

In addition, when **1** was reacted with **2a** at room temperature in THF for 9 days to allow complete C–H bond activation, 5-membered 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 C₆D₆ afforded the bimetallic compound **4a** quantitatively. This clearly indicated that the 5-membered metallacyclic complex **3a** is a metastable species in benzene that could lead to a subsequent intramolecular shift of the yttrium center to the *ortho*-position of the pyridine ring, followed by C–C bond formation to afford **4a** (Scheme 3).

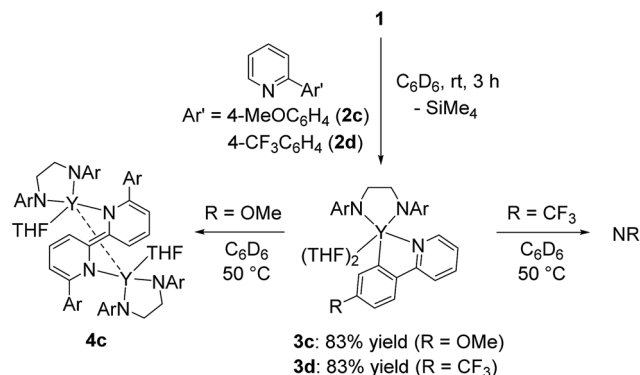
When 2-arylpyridines **2c** and **2d** were treated with **1** in C₆D₆ at room temperature, C–H bond activation of the aryl ring proceeded to form five-membered metallacyclic complexes **3c** and **3d** (Scheme 4). On heating the C₆D₆ solution of **3c** at 50 °C, green microcrystals were precipitated from the reaction mixture, as determined by eqn (1). In contrast, **3d** was stable in C₆D₆ at 50 °C. We thus presumed that the C–C bond formation was affected by electron-donating/-withdrawing substituents *meta* to the metallated carbon; THF coordination to yttrium for **3a** and **3b** was weaker than that for **3c** and **3d** in benzene, leading to easy dissociation of THF from yttrium for **3a** and **3b** and C–C bond formation to form **4a** and **4b** at room temperature.



Scheme 2 Deuterium labelling experiment.

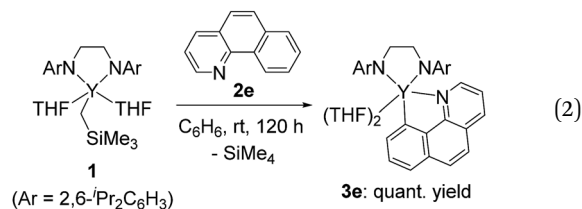


Scheme 3 Stepwise metallacycle and C–C bond formation.

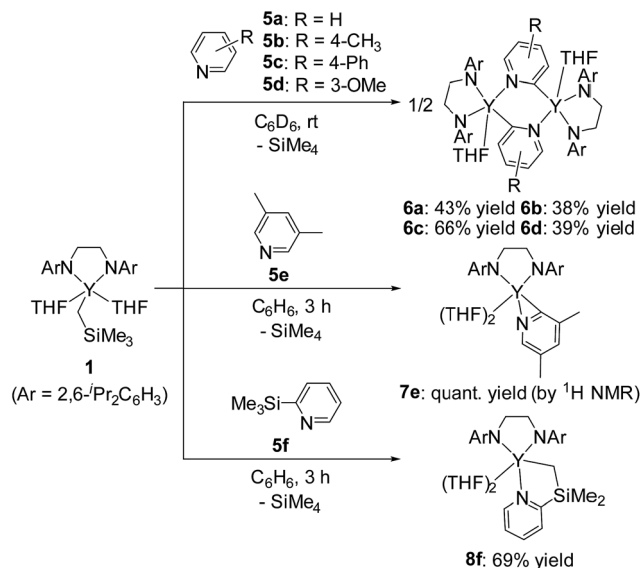


Scheme 4 Effect of substituents on the aryl ring of 2-arylpyridine on the C–C bond formation step.

In addition to the isolation of stable five-membered metallacyclic complex **3d**, the reaction of **1** with benzo[*h*]quinolone at room temperature gave **3e** in quantitative yield (eqn (2)). Complex **3e** was isolated as microcrystals suitable for X-ray diffraction studies. Although the quality of the crystallographic data from the X-ray diffraction studies was insufficient, we determined the overall structure of **3e**, in which a C–H bond of benzo[*h*]quinolone was activated to form a five-membered metallacycle as shown in the ESI (Fig. S1†). Complex **3e** was not converted to the C–C bond formation product analogous to **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 3-substituted pyridines (**5b–d**) afforded bis(μ,κ²-(C,N)-pyridyl) diyttrium complexes **6a–d** as poorly soluble yellow microcrystals (Scheme 5). The ORTEP drawing of **6a** is shown in Fig. 3. The μ,κ²-(C,N)-pyridyl ligand is positioned 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 κ(C,N)-pyridylttrium complexes.^{17,18} Two yttrium atoms, two bridging carbons, and the two nitrogen atoms of the bridging



Scheme 5 Reactions of alkylttrium complex **1** with pyridine derivatives.

pyridines are located in the same plane. The ^1H NMR spectrum of **6a** displays four resonances corresponding 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 3,5-dimethylpyridine (**5e**) was used as the substrate, mononuclear yttrium complex **7e** was isolated in 97% yield. In the ^{13}C NMR spectrum, a doublet signal was observed for the carbon atom attached to the yttrium center at δ_{C} 219.6 ($^1J_{\text{Y-C}} = 35.2$ Hz), which is in the typical range for mononuclear arylttrium complexes.¹⁸ Even after heating solutions of complexes **6a–d** and **7e**, which contained a 2-pyridylttrium moiety in the molecular structure, C–C coupling products were not detected in 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)methylttrium complex **8f** via $\text{C}(\text{sp}^3)\text{--H}$ bond activation. In this case, an intramolecular shift of the yttrium center to form 2-pyridylttrium species or 6,6'-bis(trimethylsilyl)-2,2'-bipyridyl formation was not observed.

Based on our findings for the alkylttrium-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, alkylttrium complex **1** cleaves a C–H bond at the *ortho*-position on the phenyl ring of **2a** to produce five-membered metallacycle complex **3a**. Complex **3a** is isomerized to three-membered metallacycle intermediate **E**. Initial formation of the five-membered metallacycle prior to formation of the three-membered metallacycle, as the major pathway, was confirmed by the deuterium labelling experiment as shown in Scheme 2, where mono-deuterated $\text{SiMe}_4\text{-}d_1$ was generated and one H atom was incorporated into the phenyl ring. Direct formation of the intermediate **E** from complex **1** was plausible as a minor pathway, and this was confirmed by the detection of SiMe_4 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 isomerization trend is opposite to the report by Diaconescu *et al.*, they mentioned that the pyridyl carbanion is more stable ($2.8 \text{ kcal mol}^{-1}$) than the phenyl carbanion for the phenylpyridyl anion. We presume that the relative stabilities of the three- and five-membered metallacycles are significantly affected by the attached metal fragment.¹⁹ The effect of substituents of the 2-arylpyridines on the C–C bond formation as shown in Scheme 4 indicates that the dissociation of the coordinating THF from the yttrium is key for further isomerization. Although the three-membered metallacycle intermediate **E** dimerized as a doubly $\mu, \kappa^2\text{-(C,N)}$ -bridged dinuclear structure, similar to diyttrium complexes **6a–d**, introduction of aryl groups at the *ortho*-position of the pyridine ring might destabilize the $\mu, \kappa\text{-(C,N)}$ -bridging mode of the pyridine moiety to afford **4a** through 3-centered-2-electron aryl-bridged intermediate **F**.

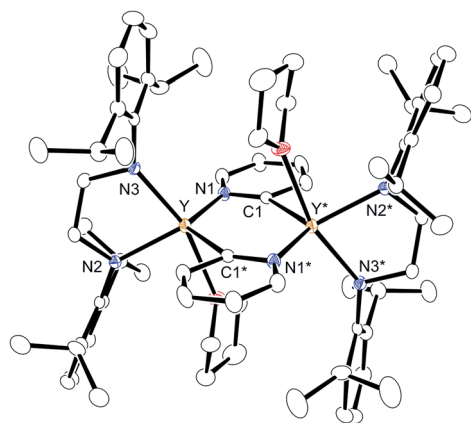
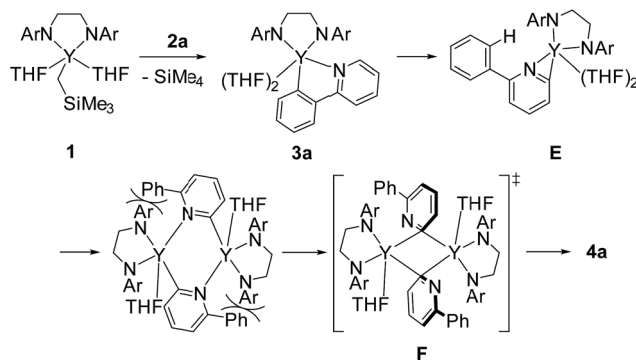


Fig. 3 Molecular structure of complex **6a** with 30% thermal ellipsoids. All hydrogen atoms are omitted for clarity. Selected bond lengths (Å): Y1–N1, 2.328(4); Y1–C1, 2.681(5); Y1–C1*, 2.560(5); Y1–N2, 2.216(4); Y1–N3, 2.219(4); Y2–O1, 2.422(3).



Scheme 6 Plausible mechanism for the reductive dimerization of 2-phenylpyridine.

Conclusions

We demonstrated that yttrium-mediated 2,2'-bipyridyl formation proceeded through a bimetallic pyridylttrium intermediate. Introduction of aryl substituents at the *ortho*-position of the pyridine ring destabilized the μ, κ^2 -(C,N)-bridged intermediate to accelerate associative bimetallic C(sp²)-C(sp²) bond formation. Further application of such bimetallic-mediated coupling reactions with not only rare-earth metal complexes but also early transition metal complexes is ongoing in our laboratory.

Acknowledgements

Y. S. acknowledges the financial support from the JSPS Postdoctoral 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 from 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.

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