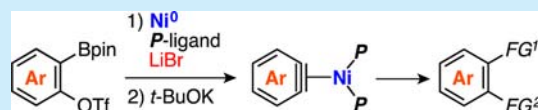


Preparation of Aryne–Nickel Complexes from *ortho*-Borylaryl TriflatesYuto Sumida,<sup>†</sup> Tomoe Sumida,<sup>†</sup> Daisuke Hashizume,<sup>‡</sup> and Takamitsu Hosoya<sup>\*,†,§</sup><sup>†</sup>Chemical Biology Team, Division of Bio-Function Dynamics Imaging, RIKEN Center for Life Science Technologies, 6-7-3 Minatojima-minamimachi, Chuo-ku, Kobe 650-0047, Japan<sup>‡</sup>Materials Characterization Support Unit, Supramolecular Chemistry Division, RIKEN Center for Emergent Matter Science, 2-1 Hirosawa, Wako, Saitama 351-0198, Japan<sup>§</sup>Laboratory of Chemical Bioscience, Institute of Biomaterials and Bioengineering, Tokyo Medical and Dental University 2-3-10 Kanda-Surugadai, Chiyoda-ku, Tokyo 101-0062, Japan

## S Supporting Information

**ABSTRACT:** A facile method for preparing diverse aryne–nickel complexes from readily synthesized *ortho*-borylaryl triflates is described. Exploratory synthetic applications, including the synthesis of 1,2-difunctionalized arenes, based on the nucleophilic character of the aryne–nickel complexes are also demonstrated.



Arynes are highly reactive species widely used as synthetic intermediates for the construction of diverse aromatic compounds.<sup>1</sup> While arynes are too reactive to be isolated, aryne–metal complexes, which are generally prepared by the complexation of arynes with a transition metal, are often isolable as mononuclear or cluster complexes (Figure 1).<sup>2–6</sup> The reactivity

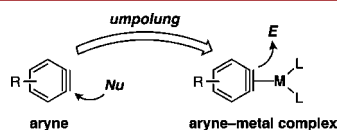


Figure 1. Aryne and aryne–metal complex.

of arynes and aryne–metal complexes contrast starkly; the former are electrophilic, while the latter are nucleophilic. Nevertheless, the synthetic application of aryne–metal complexes with “umpolung” reactivity of the arynes is largely limited, which stands in stark contrast to uncomplexed aryne with an enormous number of synthetic applications.<sup>1,8,9</sup> One possible reason for the paucity of applications is the lack of a general method for preparing aryne–metal complexes, in particular, for those bearing functional groups. Here we report a facile method for preparing aryne–nickel (Ni) complexes from *ortho*-borylaryl triflates, which we previously developed as aryne precursors.<sup>8</sup>

Aryne–metal complexes have been studied for more than half a century.<sup>2</sup> A number of aryne–metal complexes involving early or late transition metals have been prepared, and their unique reactivities have been surveyed.<sup>2–6</sup> The involvement of aryne–metal complexes as intermediates in transition-metal-catalyzed reactions with aryne has also been suggested, albeit the aryne–metal complexes were not isolated in these cases.<sup>10,11</sup> In particular, Bennett and co-workers reported a series of pioneering works on the chemistry of aryne–Ni complexes.<sup>4</sup> They showed that aryne–Ni complexes could be prepared via the oxidative

addition of *ortho*-borylaryl bromide to low-valent nickel, followed by intramolecular transmetalation, enabling the mild complexation of aryne with d<sup>10</sup> transition metals (Figure 2A).<sup>4d</sup>

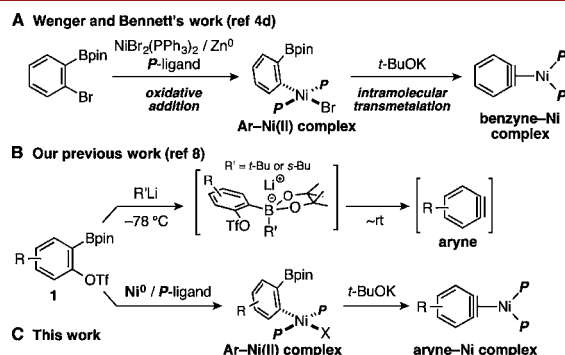


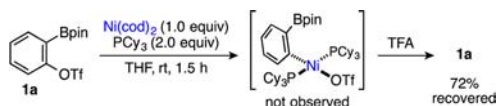
Figure 2. Proposed strategy.

During the course of our studies on aryne chemistry,<sup>8,9</sup> we recently found that *ortho*-borylaryl triflates **1** serve as efficient precursors of aryne (Figure 2B).<sup>8</sup> A diverse range of **1** were easily synthesized from the corresponding phenols by a simple two-step protocol: iridium-catalyzed direct *ortho*-borylation of phenols,<sup>12</sup> followed by triflylation. We presumed that **1** would also serve as good precursors for a broad range of aryne–Ni complexes (Figure 2C);<sup>11</sup> however, our initial attempt to achieve the oxidative addition of *ortho*-borylphenyl triflate **1a** to Ni(0) was unsuccessful (Scheme 1). Treatment of **1a** with Ni(cod)<sub>2</sub> and PCy<sub>3</sub> did not afford the desired aryl–Ni triflate complex, and most of **1a** was recovered after protonation with trifluoroacetic acid (TFA). We

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## Scheme 1. An Initial Attempt



assumed that the oxidative addition process was problematic due to the instability of the cationic divalent-nickel complex.<sup>13</sup>

After extensive screening of reaction conditions,<sup>14</sup> we found that the addition of an equimolar amount of lithium bromide afforded the desired aryl–Ni(II)Br complex  $[\text{NiBr}(2\text{-BpinC}_6\text{H}_4)(\text{PCy}_3)_2]$  (**2a-PCy<sub>3</sub>**) in excellent yield (Figure 3A), which was identical to the spectroscopic data reported previously.<sup>4d</sup> The addition of lithium bromide must have accelerated the oxidative addition step and served to stabilize the aryl–Ni(II) complex.<sup>15</sup> Conversely, attempts to prepare **2a-PCy<sub>3</sub>** from 2-trimethylsilylphenyl triflate,<sup>16</sup> a popular benzyne precursor, under similar procedures were unsuccessful, probably due to sluggish oxidative addition.<sup>14</sup> With an aim to prepare stable aryne–Ni complexes, we exchanged the ligand of the aryl–Ni(II)Br complex from PCy<sub>3</sub> with a bulky bidentate ligand, bis(dicyclohexylphosphino)ethane (DCPE).<sup>17</sup> Thus, similar to the reported procedure,<sup>4d</sup> treatment of **2a-PCy<sub>3</sub>** with DCPE smoothly afforded the ligand-exchanged complex  $[\text{NiBr}(2\text{-BpinC}_6\text{H}_4)\text{dcpe}]$  (**2a-dcpe**), which was treated with potassium *tert*-butoxide to give the benzyne–Ni complex  $[\text{Ni}(\eta^2\text{-benzyne-dcpe})]$  (**3a-dcpe**).<sup>4a,d</sup>

This simple three-step procedure made various aryne–Ni complexes easily accessible (Figure 3).<sup>14</sup> For example, the 2,3-naphthalene–Ni complex **3b-dcpe**,<sup>4b</sup> 4-methylbenzyne–Ni complex **3c-dcpe**, and 4-methoxybenzyne–Ni complex **3d-dcpe** were prepared from the corresponding *ortho*-borylaryl

triflates **1b–d** with high efficiencies. This method was also applicable to the preparation of aryne–Ni complexes bearing an electron-deficient group, such as 4-methoxycarbonylbenzyne–Ni complex **3e-dcpe** and 4-trifluoromethylbenzyne–Ni complex **3f-dcpe**, easily widening the scope of available complexes compared with the conventional methods. The structures of some aryne–Ni complexes were confirmed by X-ray crystal structure analysis,<sup>14</sup> showing an  $\eta^2$ -coordination of the aryne triple bond to the Ni atom being in an almost trigonal planar rearrangement similar to the reported benzyne–Ni(dcpe) complex **3a-dcpe**.<sup>4a</sup> Interestingly, the distance of C1–C2 (1.368(2) Å) of  $[\text{Ni}(\eta^2\text{-2,3-naphthalene})\text{dcpe}]$  (**3b-dcpe**) is slightly shorter than other aromatic C–C bonds (C2–C3 = 1.374(2) Å, C1–C10 = 1.375(2) Å) (Figure 4). This is probably due to the long  $\pi$ -

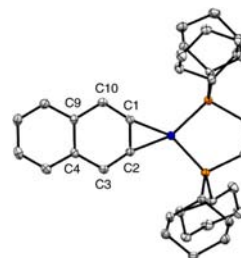


Figure 4. X-ray structure of **3b-dcpe**. Displacement ellipsoids show 50% probability levels; hydrogen atoms are omitted for clarity.

conjugated system of the naphthalene structure, because larger differences are usually observed in monocyclic aryne–Ni(dcpe) complexes such as **3a-dcpe**,<sup>4a</sup> **3d-dcpe**, and **3f-dcpe**.<sup>14</sup>

The same procedure was unavailable for the synthesis of dcpe-coordinated aryne–Ni complexes from 3-substituted *ortho*-

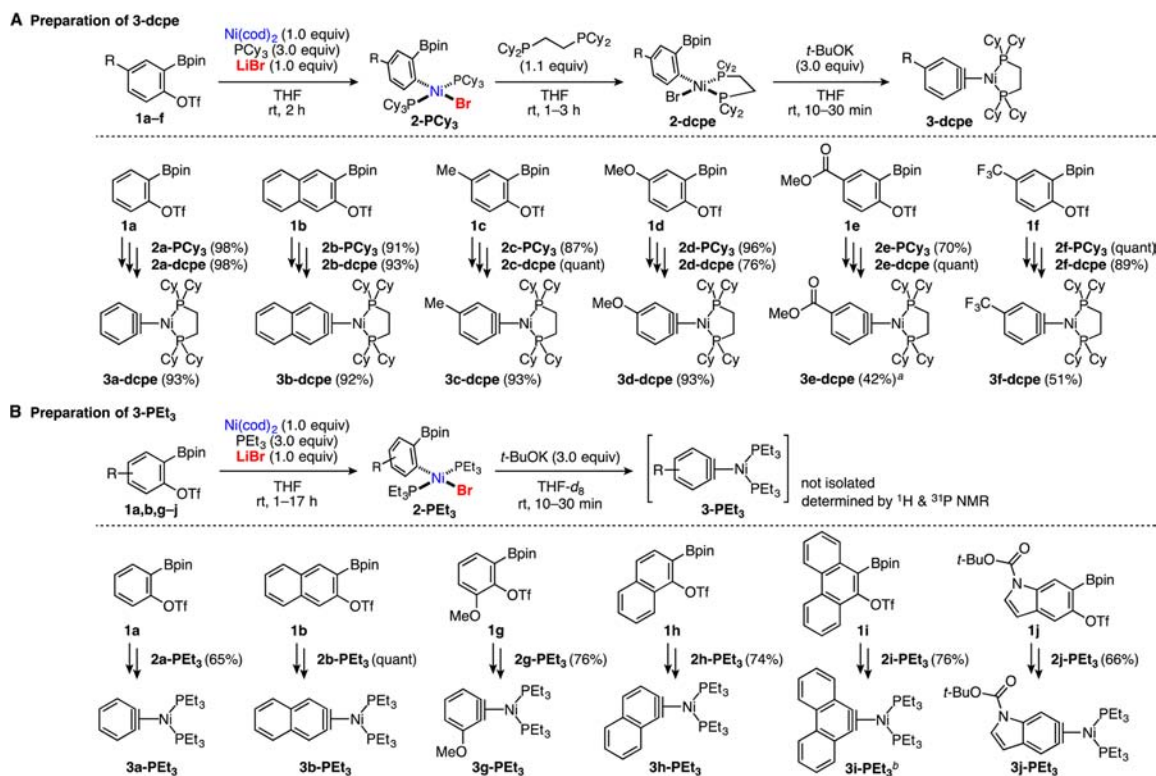
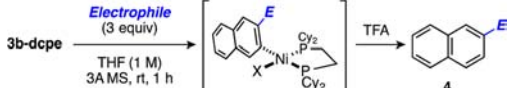


Figure 3. Preparation of various aryne–nickel complexes coordinated with dcpe (A) and PEt<sub>3</sub> (B). <sup>a</sup> The reaction was performed at 0 °C. <sup>b</sup> The reaction was performed for 6.5 h.

borylaryl triflates **1**, such as **1g–i**, probably because oxidative addition of bulky substrates to Ni(0) with PCy<sub>3</sub> was very slow. Fortunately, the oxidative addition of these bulky substrates proceeded smoothly by using triethylphosphine (PEt<sub>3</sub>) instead of PCy<sub>3</sub> to give the corresponding adducts **2g–i-PEt<sub>3</sub>**, which expanded the scope of accessible aryne–Ni complexes, including **3g–i-PEt<sub>3</sub>** (Figure 3B). Furthermore, the 5,6-indolyne–Ni complex **3j-PEt<sub>3</sub>** was prepared in a similar manner from **1j**, of which oxidative addition using PCy<sub>3</sub> was sluggish. Because the PEt<sub>3</sub>-coordinated aryne–Ni complexes **3-PEt<sub>3</sub>** could not be transformed to DCPE-coordinated complexes and also they were less stable than **3-dcpe**, we handled them as a THF-*d*<sub>8</sub> solution. Their structures were determined based on <sup>1</sup>H and <sup>31</sup>P NMR analyses, in which a single product, except PEt<sub>3</sub>, was observed, indicating that the formation of aryne–Ni(PEt<sub>3</sub>)<sub>2</sub> complexes proceeded almost exclusively.<sup>14</sup>

With various aryne–Ni complexes in hand, we explored their synthetic applicability. Previous reports indicated that aryne–metal complexes have a nucleophilic character, unlike uncomplexed arynes, which have an electrophilic nature. For example, the reaction of aryne–Ni complexes with electrophiles, such as iodomethane, alkynes, and carbon dioxide, was shown to proceed promptly.<sup>4,6</sup> We revisited the reactivity of aryne–Ni complexes with various electrophiles using the 2,3-naphthalene–Ni complex **3b-dcpe** (Table 1). Similar to the reported case for **3a-dcpe**,<sup>4d</sup>

Table 1. Reactions of **3b-dcpe** with Various Electrophiles



entry	electrophile	product	yield (%) <sup>a</sup>
1	Me–I	<b>4a</b>	77 <sup>b,c</sup> (89) <sup>d</sup>
2		<b>4b</b>	68 (58) <sup>d</sup>
3 <sup>e</sup>		<b>4c</b>	18 <sup>b</sup>
4		<b>4d</b>	81 (72) <sup>d</sup>
5	Ac–Cl	<b>4e</b>	41
6 <sup>f</sup>	Ac–Br	<b>4e</b>	59
7 <sup>e</sup>		<b>4f</b>	43

<sup>a</sup>Isolated yields, unless otherwise noted. <sup>b</sup>Yield determined by <sup>1</sup>H NMR analysis. <sup>c</sup>The reaction was performed using 5 equiv of iodomethane. <sup>d</sup>Yields based on neat conditions are shown in parentheses. <sup>e</sup>The reaction was performed using 10 equiv of electrophile in THF (0.2 M). <sup>f</sup>CH<sub>2</sub>Cl<sub>2</sub> was used as a solvent instead of THF.

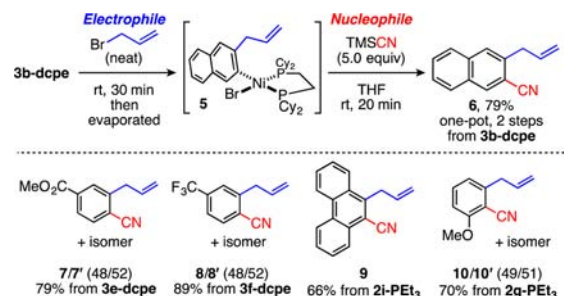
treatment of **3b-dcpe** with excess amounts of iodomethane and subsequent protonation with TFA afforded 2-methylnaphthalene (**4a**) (entry 1). The reactions with allyl, 3,3-dimethylallyl, and propargyl bromides also took place to afford the corresponding alkylated products **4b–d** (entries 2–4).<sup>18</sup> Since NMR monitoring of the methylation and alkylation reactions showed almost quantitative formation of the corresponding alkynaphthyl–Ni complexes (Figures S2 and S3), the yield of the products must have decreased during the protonation step (entries 1 and 2). Reactions with acetyl chloride or bromide afforded 2-acetylnaphthalene (**4e**) in moderate yields (entries 5 and 6). We also found that an  $\alpha,\beta$ -unsaturated ester participated as an electrophile in the reaction with **3b-dcpe** to afford the formal 1,4-adduct **4f** (entry 7). Although we have not succeeded in obtaining an X-ray structure of the presumed intermediate, the heteronickelacycle,<sup>19</sup> its in situ formation was suggested by <sup>1</sup>H and <sup>31</sup>P NMR analyses (Figures

S5 and S6).<sup>14</sup> Unexpectedly, benzyl bromide, which usually serves as a good electrophile, did not react with **3b-dcpe**. Iodobenzene was also an inert substrate for this reaction.

We found that methylation of the 4-methoxybenzyne–Ni complex **3d-dcpe** with iodomethane proceeded faster than for the 4-trifluoromethylbenzyne–Ni complex **3f-dcpe** (Figure S7).<sup>14</sup> We also observed faster decomposition of **3d-dcpe** in C<sub>6</sub>D<sub>6</sub> than **3f-dcpe** by <sup>1</sup>H NMR analysis (Figures S10 and S11).<sup>14</sup> These results indicated that the electron-rich aryne-coordinated Ni complex is more reactive than the electron-deficient complex, as contrasted with uncomplexed aryne species.<sup>9d</sup>

The intermediary aryl–Ni(II) complexes formed from the reaction of aryne–Ni complexes with an electrophile were available for functionalizations other than protonation. For example, treatment of crude alkylated Ni complex **5**, prepared from the reaction of **3b-dcpe** with neat allyl bromide followed by removal of the remaining allyl bromide under reduced pressure, with trimethylsilyl cyanide<sup>20</sup> afforded 3-allyl-2-naphthonitrile (**6**) in high yield (Scheme 2). This one-pot double functionalization

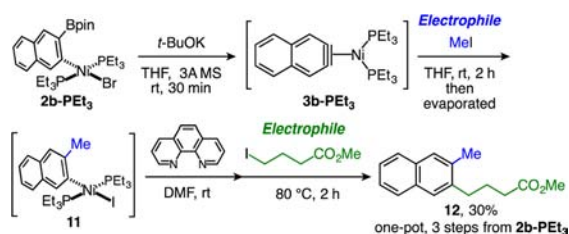
Scheme 2. Double Functionalization of Aryne–Ni Complexes



procedure was applicable to other substrates, such as the electron-deficient 4-substituted aryne–Ni complexes **3e-dcpe** and **3f-dcpe**, which afforded **7/7'** and **8/8'**, respectively, without significant regioselectivity. Similarly, the PEt<sub>3</sub>-bound 9,10-phenanthryne–Ni complex **3i-PEt<sub>3</sub>**, prepared in situ from **2i-PEt<sub>3</sub>**, also participated in this transformation to afford 10-allylphenanthrene-9-carbonitrile (**9**). Interestingly, the reaction of 3-methoxy substrate **3g-PEt<sub>3</sub>** afforded a regioisomeric mixture of **10** and **10'** in a ratio of 49:51, which was in stark contrast to the reactions of 3-methoxybenzyne with nucleophiles, where high regioselectivity is usually observed.<sup>21</sup>

Furthermore, exchanging the ligand of an intermediary aryl–Ni complex from phosphine to a bipyridyl-type ligand, such as 1,10-phenanthroline (Phen), dramatically altered the reactivity;<sup>22</sup> treatment of the methylated product **11**, prepared in situ from **3b-PEt<sub>3</sub>** and methyl iodide, with Phen, followed by heating with another electrophile, such as methyl 4-iodobutanoate, afforded 2,3-dialkylated naphthalene **12** (Scheme 3).

Scheme 3. Double Alkylation of **3b-PEt<sub>3</sub>**





In summary, we have shown that *ortho*-borylaryl triflates serve as aryne precursors, as well as precursors of aryne–Ni complexes. Several exploratory studies have revealed the potential ability of aryne–Ni complexes as synthetic intermediates, which would be used differently compared with noncoordinated aryne species. Further synthetic applications are currently underway in our group.

## ■ ASSOCIATED CONTENT

### ■ Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.orglett.6b02831.

Experimental procedures and characterization for new compounds including copies of NMR spectra (PDF)

X-ray data for **2d-PCy<sub>3</sub>** (CCDC 1438693) (CIF)

X-ray data for **2e-PCy<sub>3</sub>** (CCDC 1438698) (CIF)

X-ray data for **2f-dcpe** (CCDC 1438694) (CIF)

X-ray data for **3b-dcpe** (CCDC 1438692) (CIF)

X-ray data for **3d-dcpe** (CCDC 1438696) (CIF)

X-ray data for **3f-dcpe** (CCDC 1438695) (CIF)

X-ray data for **2g-PET<sub>3</sub>** (CCDC 1438690) (CIF)

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### Notes

The authors declare no competing financial interest.

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(18) Generation of the 2-allyl-3-naphthyl–Ni complex was confirmed by the deuteration experiment using TFA-d<sub>1</sub> (99.5%D) which afforded **4b-d** (98%D). See Supporting Information.

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