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Synthesis, crystal structure and reactivity of η^2–thiophyne Ni complexes

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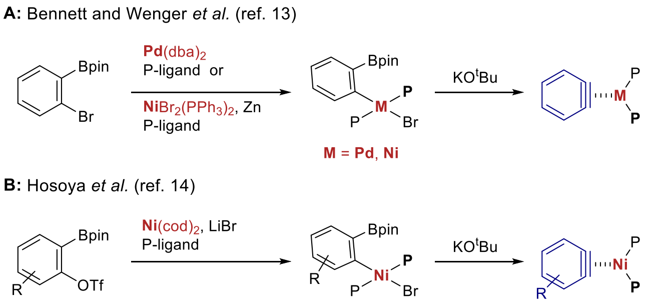
The first synthesis and crystal structures of five-membered ring aryne complexes, Ni(dcpe)(η^2-thiophyne) and Ni(dcpe)(η^2-benzo[*b*]thiophyne), are described. The aryne fragments retain considerable aromatic character and the two coordinated carbon atoms exhibit distinct reactivity due to the asymmetric nature.

Arynes are highly reactive, transient molecules that are widely adopted as useful synthetic intermediates for the construction of elaborate aromatic frameworks.[1] Arynes are formally generated by removing two adjacent substituents from the parent aromatic molecules, and best described to have a strained C–C triple bond in the ring systems.[2] In sharp contrast to the fact that various six-membered arynes are readily accessible, it is obviously a challenging task to handle smaller ring size arynes due to the severe ring strains.[3] Historically, a five-membered ring aryne, 2,3-didehydrobenzofuran,[4] was first postulated half a century in advance of the threshold of benzyne chemistry[5,6] to rationalize the *cine*-substitution with ethoxide. However, its intermediacy has been questioned because such *cine*-substitution reactions can proceed *via* non-aryne mechanisms.[7] Diels-Alder adducts and cycloadducts are also known to be obtained without aryne intermediates, so that isolation of these adducts has provided ambiguous evidences for the actuality of five-membered arynes. Flash vacuum thermolysis of the parent carboxylic anhydrides has been emerged as the first experimental evidence for the generation of five-membered arynes.[8] Such harsh conditions are not sufficient for practical use in organic synthesis, and little achievements have been made in the chemistry of five-membered arynes to date.[9,10]

Although arynes are fragile species which cannot be isolated in the free states, a number of aryne-metal complexes have been synthesized and characterized, providing convincing evidence for the triple bond character of the aryne fragments.[11,12] Among the reported synthetic protocols, an intramolecular transmetallation strategy where *ortho*-metalated boronic esters are readily converted into the corresponding aryne complexes by a simple base treatment is highly practical. The strategy was first developed by Bennett and Wenger for the synthesis of benzyne complexes of nickel and palladium (Scheme 1A).[13] Recently, Hosoya and co-workers adopted the method to achieve the preparation of various benzyne complexes from *ortho*-borylated aryl triflates (Scheme 1B).[14]



Scheme 1 Synthesis of benzyne complexes via intramolecular transmetallation.

We envisaged that five-membered arynes would be isolable upon coordinating to an appropriate transition metal, and we herein report the first isolation and crystal structure of five-membered aryne complexes Ni(dcpe)(η^2-thiophyne) and Ni(dcpe)(η^2-benzo[*b*]thiophyne).[15,16] Preliminary study on the reactivity of the thiophyne fragments is also demonstrated.

At the outset, the synthesis of precursors for Ni-aryne complexes was carried out (Scheme 2). A Ni(II) complex **2a** was synthesized by oxidative addition of the corresponding boronic ester **1a** onto Ni(cod)$_2$ in the presence of a bidentate phosphine

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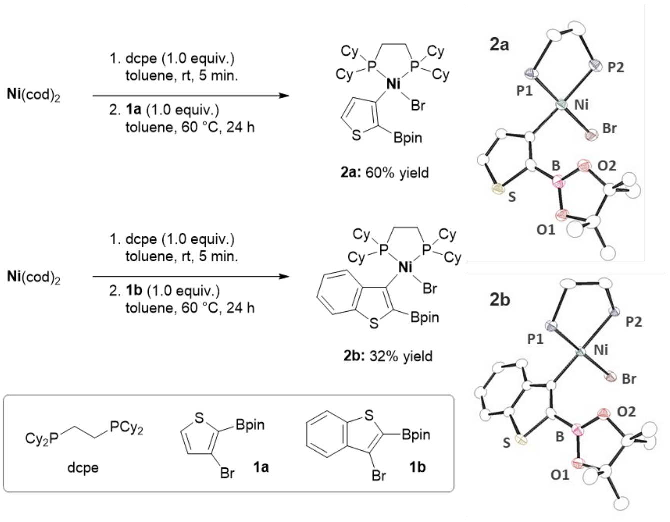
ligand 1,2-bis(dicyclohexylphosphino)ethane (dcpe). A benzo[*b*]thiophene analogue **2b** was prepared from a boronic ester **1b** in the same procedure. The structures of **2a** and **2b** were confirmed by X-ray diffraction measurements.



Scheme 2 Preparation of complexes **2a** and **2b**. Molecular structures are drawn with 50% thermal ellipsoid. Hydrogen atoms and cyclohexyl groups are omitted for clarity.

Other phosphine ligands such as PPh$_3$, PCy$_3$, and 1,2-bis(diphenylphosphino)ethane (dppe) afforded complicated mixtures and the isolation of desired complexes was unsuccessful. We also examined the synthesis of analogous Pd complexes from Pd$_2$(dba)$_3$ or CpPd(π-allyl); however, no clean complexation was observed.

The precursors were then treated with KO^{t}Bu in THF-d_8 and the reactions were monitored by ^{31}P NMR measurement. Two doublet peaks characteristic of the complex **2a** (62.1 and 68.5 ppm; J_{pp} = 25.9 Hz) were instantaneously replaced by a set of doublet peaks (81.6 and 85.8 ppm; J_{pp} = 7.3 Hz), which could be assigned to the corresponding η^2-thiophyne Ni complex (Figure 1, left). A similar result was obtained with the complex **2b**; immediate replacement of original peaks (58.7 and 61.9 ppm; J_{pp} = 27.5 Hz) by doublet peaks (81.6 and 85.8 ppm; J_{pp} = 8.1 Hz) was observed (Figure 1, right). These species were further reacted with an excess amount of trifluoroacetic acid (TFA) to give thiophene and benzo[*b*]thiophene, respectively, along with Ni(dcpe)(OCOCF$_3$)$_2$, supporting the formation of aryne complexes.[17]

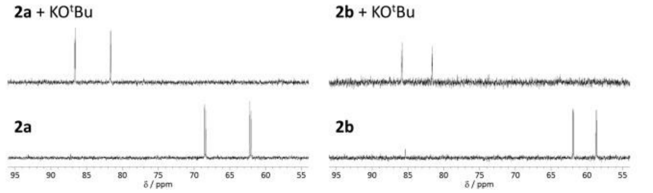
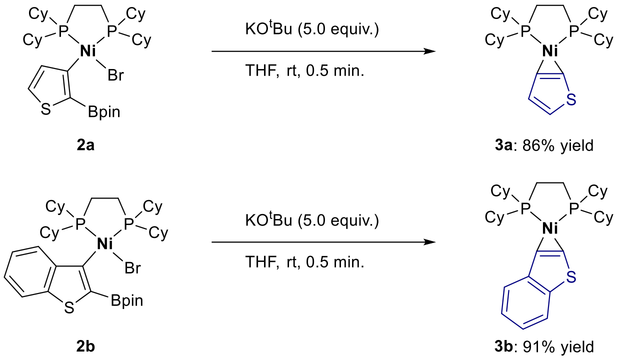


Fig. 1 ^{31}P{^{1}H} NMR spectra for the reaction of complex **2a** (left) and **2b** (right) with KO^{t}Bu in THF-d_8.

The generated complexes were successfully isolated in good yields (Scheme 3), and the structures were confirmed by X-ray crystallography to be monomeric η^2-aryne complexes **3a** and **3b** (Figure 2). In their ^{13}C NMR spectra, the carbon atoms directly bonded to nickel resonance around 150 ppm (149.6 and 156.6 ppm for **3a**, 152.6 and 154.9 ppm for **3b**) as double doublets signals. This sufficiently evident that these complexes retain their monomeric structure in the solution state as well.



Scheme 3 Preparation of complexes **3a** and **3b**.

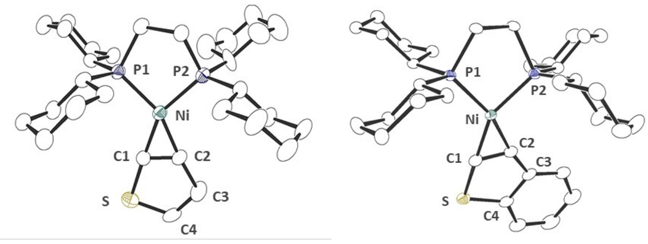


Fig. 2 Molecular structure of **3a** (left) and **3b** (right) with 50% thermal ellipsoid. Hydrogen atoms are omitted for clarity and only major orientation of the disordered groups is shown for **3a**.

The complex **3a** decomposed with a half-life of approximately 60 hours in C$_6$D$_6$; however, fate of the thiophyne fragment was unestablished. In sharp contrast, the benzo-fused analog **3b** remained unchanged at least for 4 days at ambient temperature. Higher temperature was required to trigger the complete decomposition (60 °C, 24 hours).[17] This peculiar stability might be rationalized by the presence of an extra benzene ring which provides steric barrier and the extended π-conjugation.

Selected geometric parameters of the complexes **3a**, **3b**, and Ni(dcpe)(η^2-benzyne)[18] are listed in Table 1. Because **3b** has two independent molecules in the unit sell, the parameters are inscribed separately for each structure (part 1 and 2). The complexes **3** exhibit small dihedral angles between P1–Ni–P2 and C1–Ni–C2 planes, and sum of the bond angles around the Ni atom is close to 360 degrees in their solid state. These structural features indicate that both **3a** and **3b** have the trigonal planer geometry where the midpoint of the coordinated triple bond occupies one coordination site as similar to the reported Ni-aryne complexes.[13,14,18] The C1–C2 bond length of the complex **3a** is considerably elongated from the "free" 2,3-thiophyne and is rather close to the value of thiophene C–C double bond (Figure 3). This is consistent with

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the idea that the thiophyne fragment retains delocalized aromatic nature; thus, **3a** possesses thieno-nickelacyclopropene character as a major resonance contributor. A smiler trend was observed in the complex **3b**, whose aryne fragment bears structural resemblance to benzo[*b*]thiophene.

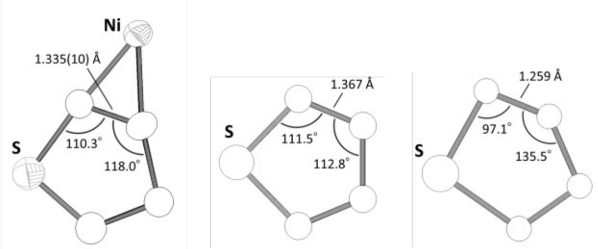
Table 1 Selected bond lengths [Å] and angles [deg.] of **3a**, **3b**, and Ni(dcpe)(η^2-benzyne)

	3a	**3b** (part 1)	**3b** (part 2)	Ni(dcpe) (η^2-benzyne)
Ni–C1	1.851(8)	1.903(5)	1.860(4)	1.870(4)
Ni–C2	1.849(9)	1.843(5)	1.888(4)	1.868(4)
Ni–P1	2.137(2)	2.156(2)	2.142(1)	2.140(1)
Ni–P2	2.153(2)	2.131(1)	2.148(1)	2.152(1)
C1–C2	1.335(10)	1.335(7)	1.329(6)	1.332(6)
P1-Ni-P2	91.62(9)	91.41(5)	91.15(5)	91.8(1)
C1-Ni-C2	42.3(3)	41.7(2)	41.5(2)	41.7(2)
S-C1-C2	110.3[a]	110.8(4)	113.5(3)	
C1-C2-C3	118.0[a]	116.9(4)	114.2(4)	
θ[b]	4.07	9.08	10.84	
ϕ[c]	359.93	358.97	360.02	360.0

[a] Average of two disordered groups without considering the errors.

[b] Dihedral angle between the P1-Ni-P2 and C1-Ni-C2 planes.

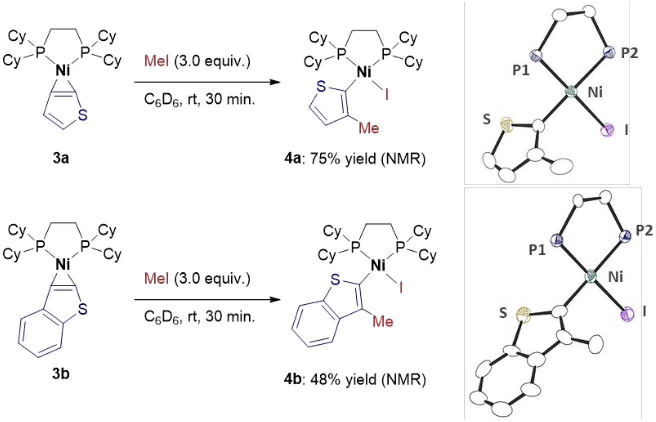
[c] The sum of the bond angles around the Ni atom.



3a thiophene 2,3-thiophyne

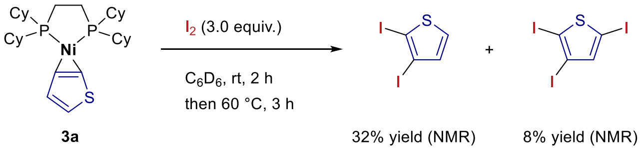
Fig. 3 Comparison of selected bond lengths and angles: crystal structure of **3a** (left, angles are average of two disordered groups); optimized structures of thiophene (middle) and 2,3-thiophyne (right) by DFT calculation (B3LYP/6-31G(d)). Hydrogen atoms are omitted for clarity.

We further investigated the reactivity of the Ni-aryne complexes. Methylation of the thiophyne fragment of **3a** with iodomethane resulted in the formation of a Ni(II) complex **4a** (Scheme 4). The methyl group was installed predominantly at the C2 position (refer to Fig. 2 for the atom labeling), whereas Ni-benzyne complexes were reported to react with electrophiles non-selectively to give almost 1:1 mixture of regioisomers.[14] This is probably because the cleavage of stable Ni–C1 (2-thienyl) bond was kinetically unfavorable. Reaction of complex **3b** with iodomethane was also examined, and the corresponding C2-methylated complex **4b** was afforded in 48% yield. In contrast, no clean transformation was observed when complexes **3** were reacted with alkyl bromides or allyl halides.



Scheme 4 Reaction of complexes **3a** and **3b** with MeI. Molecular structures are drawn with 50% thermal ellipsoid. Hydrogen atoms and cyclohexyl groups are omitted for clarity.

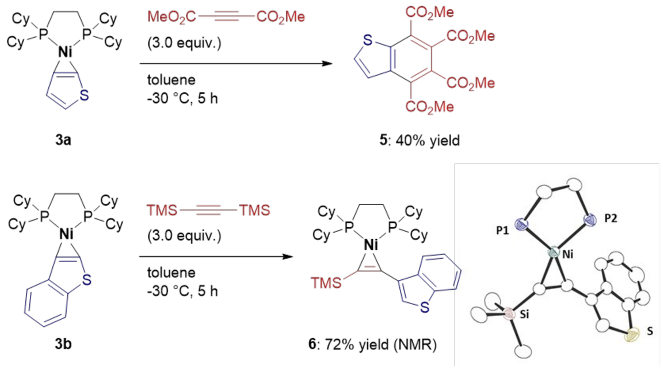
When complex **3a** was treated with an excess amount of I_2, both of the Ni–C bonds reacted to give 2,3-diiodothiophene along with a small amount of 2,3,5-triiodothiophene (Scheme 5).



Scheme 5 Reaction of complexes **3a** with iodine.

Bennett reported that the aryne moiety of Ni(dcpe)(η^2-benzyne) can be replaced by diphenylacetylene to give the corresponding alkyne-coordinated complex.[18] We carried out relevant experiments using complexes **3a** and **3b**; however, such a ligand exchange was not observed even with the use of an excess amount of the alkyne. Additionally, no significant amount of Diels-Alder adducts was detected when the complexes **3** were heated or treated with an oxidant such as cerium ammonium nitrate or a ferrocenium salt in the presence of cyclopentadiene or furan derivatives. These results indicate the reluctance of η^2-thiophyne fragment to dissociate from the Ni center.

On the other hand, **3a** smoothly reacted with dimethyl acetylenedicarboxylate to give a benzo[*b*]thiophene derivative **5** which was formed probably through two-fold alkyne insertion and subsequent reductive elimination.[19] Interestingly, reaction of **3b** with bis(trimethylsilyl)acetylene resulted in the formation of an alkyne-coordinated complex **6** as a single isomer. While the mechanistic detail remains unclear, X-ray diffraction analysis unambiguously revealed the connectivity of the alkynyl moiety at β position of the thiophene ring (Scheme 6).



Scheme 6 Reaction of complexes **3a** and **3b** with alkynes. Molecular structures are drawn with 50% thermal ellipsoid. Hydrogen atoms and cyclohexyl groups are omitted for clarity.

In summary, we achieved the synthesis of Ni η^2-thiophyne complexes as the first example of metal complexes bearing a five-membered aryne. The structures were successfully determined by single-crystal X-ray diffraction measurements[20] and their structural resemblance to the related benzyne-metal complexes were disclosed. Two carbon atoms in the thiophyne moiety exhibited distinct reactivity reflecting the asymmetric nature of the aryne moiety. These results represent the convincing evidence for the actuality of five-membered heteroarynes and their potential utility in synthesizing complex heteroaromatics.

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Conflicts of interest

The authors declare no competing financial interest.

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