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Indenyl-functionalised triethylborane adduct of *N*-heterocyclic carbene: stepwise coordination of indenyl and NHC ligands toward molybdenum fragment†Daichi Takaki,<sup>a</sup> Tetsuya Okayama,<sup>a</sup> Hiroshi Shuto,<sup>a</sup> Sawako Matsumoto,<sup>a</sup> Yoshitaka Yamaguchi<sup>\*a</sup> and Shinya Matsumoto<sup>b</sup>

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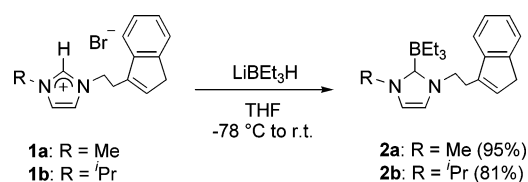
Indenyl-functionalised  $\text{BEt}_3$ -adduct NHCs were prepared by the reaction of imidazolium pro-ligands with  $\text{LiBEt}_3\text{H}$ . This compound was converted into the indenyl-coordinate molybdenum complex dangling the  $\text{NHC}\cdot\text{BEt}_3$  moiety as a substituent. The stepwise coordination of NHC afforded a chelate-type mononuclear complex as well as a bimetallic complex.

*N*-Heterocyclic carbenes (NHCs) are now fully established as an important class of ligands for homogeneous catalysts, because NHCs provide an electron-rich metal centre with a robust metal–ligand bond.<sup>1</sup> Although new catalytic applications have been extensively reported, only a small number of synthetic methods for NHC complexes have been reported.<sup>2</sup> The most straightforward method might be the direct complexation of the free NHC, either isolated or generated *in situ*, produced by deprotonation of the corresponding salt. However manipulation of a free NHC was often difficult due to their highly reactive nature toward air and moisture. Recently the employment of NHC adducts as “protected” forms of the free NHC, such as NHC-alcohol,<sup>3</sup> -chloroform,<sup>4</sup> -amine,<sup>5</sup> -carbon dioxide,<sup>6</sup> -pentafluorobenzene,<sup>7</sup> or -triethylborane,<sup>8</sup> attracted much attention for the synthesis of NHC complexes. These NHC adducts act as effective precursors for the preparation of NHC complexes, whereas these adducts reported so far are limited for simple monodentate NHC ligands. The most promising procedure for the preparation of the NHC complex is transmetalation of the NHC from a silver NHC complex. Furthermore, this procedure is applicable to the preparation of novel NHC complexes containing bis-NHCs and hybrid-type NHCs such as phosphine- or pyridine-functionalised NHCs.<sup>9</sup>

Recently, anionic tethered NHCs have attracted much attention because of their ability to stabilise a wide range of metal complexes

through the chelating coordination mode.<sup>10</sup> Especially, in recent years, the NHCs bearing indenyl, fluorenyl, or cyclopentadienyl moiety as an anionic tether have received increased interest.<sup>11–16</sup> These ligands established the unique mononuclear complexes, in which the ligand acted as a chelating coordination mode. Contrary to the utilisation of these ligands to a chelating mode for a mononuclear complex, a bimetallic complex constructed by these ligands as a bridging mode is extremely rare.<sup>11c</sup> Danopoulos and co-workers investigated the employment of silver NHC complexes bearing a dangling indene in order to make a bimetallic complex and thus they prepared the bimetallic complex by the thermal reaction of Rh-NHC complex bearing a dangling indene with an alkoxide complex by means of MeOH-elimination reaction.<sup>17</sup> However their synthetic procedure was not satisfying because of a low yield of the desired complex. Thus, the utilisation of this type of ligands to build up a bimetallic complex effectively will open access to a new bimetallic complex expecting as a synactic catalyst. Therefore we examined an application of our method,<sup>8</sup> *i.e.*, the utilisation of  $\text{NHC}\cdot\text{BEt}_3$ , to indenyl-functionalised NHC. In this communication we describe (i) the synthesis of indenyl-functionalised  $\text{BEt}_3$ -adduct NHC, (ii) the synthesis of the indenyl-coordinate molybdenum complex dangling the  $\text{NHC}\cdot\text{BEt}_3$  unit, and (iii) stepwise coordination of NHC affording a mononuclear chelate-type complex as well as a bimetallic complex.

Indenyl-functionalised imidazolium pro-ligands were successfully obtained in good yields by a modification of the previously reported method,<sup>11a</sup> *i.e.*, treating  $\beta$ -bromoethylindene with methyl- or isopropylimidazoles without solvent for *ca.* 48 h (see ESI†). A treatment of imidazolium pro-ligand **1a** with one equivalent of  $\text{LiBEt}_3\text{H}$  in THF at  $-78^\circ\text{C}$  gave a homogeneous reaction mixture from which a yellow oil **2a** was isolated in 95% yield (Scheme 1). In case of **1b**, similar reaction took place to give a yellow solid **2b** (81%).  $^1\text{H}$ ,  $^{13}\text{C}$ , and  $^{11}\text{B}$  NMR spectra ensured the formation



Scheme 1

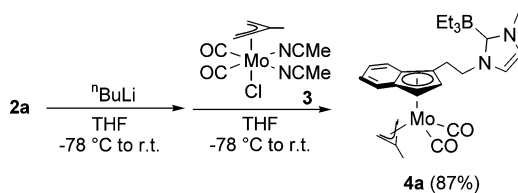
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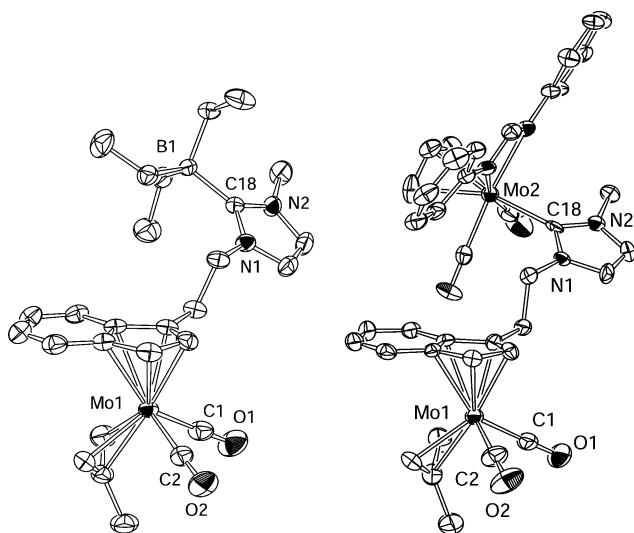
† Electronic supplementary information (ESI) available. CCDC reference numbers 792228–792230. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c0dt01641a

of  $\text{BEt}_3$ -adduct NHC compounds bearing ethylindene moiety as a substituent. In the  $^1\text{H}$  NMR spectra of **2**, the signal of the imidazolium proton in **1** (10.26 ppm for **1a** and 10.43 ppm for **1b**) disappeared and the acidic proton of indene was still observed (3.35 ppm for **2a** and 3.36 ppm for **2b**). The  $^{13}\text{C}$  NMR spectra showed the broad signals assignable to the carbene carbon at 175.9 ppm for **2a** and at 174.3 ppm for **2b**, respectively. A signal due to  $\text{BEt}_3$  was observed at  $-11.5$  ppm for **2a** and at  $-11.3$  ppm for **2b**, respectively, in  $^{11}\text{B}$  NMR. These chemical shifts ( $^{13}\text{C}$  and  $^{11}\text{B}$  NMR) are consistent with those of the reported NHC- $\text{BEt}_3$  compounds.<sup>8a</sup>

Next we examined the derivation of the “indenyl” complex of molybdenum. Molybdenum complex **3** was treated with a lithiated indenyl-NHC compound, which was prepared by the reaction of **2a** with  $n\text{-BuLi}$  *in situ*, in THF at  $-78^\circ\text{C}$ . After being allowed to warm to room temperature, the reaction mixture was worked up to yield the indenyl complex of molybdenum **4a** (87%) as a yellow solid (Scheme 2), which was characterised by EA, IR,  $^1\text{H}$ ,  $^{13}\text{C}$ ,  $^{11}\text{B}$  NMR, and X-ray analysis.<sup>‡</sup> In the IR spectrum, complex **4a** showed two CO stretching bands at 1950 and  $1856\text{ cm}^{-1}$ . The signals due to the NHC- $\text{BEt}_3$  moiety were observed at 176.6 ppm for carbene carbon in  $^{13}\text{C}$  NMR and at  $-10.9$  ppm for  $\text{BEt}_3$  boron in  $^{11}\text{B}$  NMR. The structure of **4a** obtained by X-ray analysis is shown in Fig. 1 (left) and is consistent with the spectroscopic data. The B–C(carbene) bond distance is  $1.660(4)\text{ \AA}$  and is similar to that of the reported NHC- $\text{BEt}_3$  compounds.<sup>8a</sup> During the preparation of **4a**, NHC- $\text{BEt}_3$  moiety was intact for a base such as  $n\text{-BuLi}$  and this result clearly demonstrated that the NHC- $\text{BEt}_3$  moiety was tolerant toward a strong base.

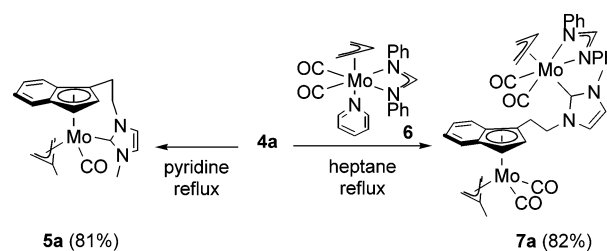


Scheme 2



**Fig. 1** ORTEP drawings of complexes **4a** (left) and **7a** (right) (30% probability of thermal ellipsoids). All hydrogen atoms are omitted for clarity.

In order to elucidate the coordination ability of the dangling NHC protected by  $\text{BEt}_3$ , we examined the conversion of **4a** into the chelating indenyl-NHC complex **5a**. On refluxing complex **4a** in toluene for *ca.* 24 h, only a small amount of the desired complex **5a** was formed. Next, the thermal reaction of **4a** in pyridine instead of toluene was examined expecting the acceleration of the B–C bond cleavage by the formation of the Lewis base adduct of  $\text{BEt}_3$ . Refluxing the yellow solution of **4a** in pyridine for 4 h afforded a homogeneous red solution from which the chelate-type complex **5a** was isolated in 81% yield (Scheme 3). In the IR spectrum, complex **5a** showed the CO stretching bands at 1794 and  $1773\text{ cm}^{-1}$ , which have a lower frequency than those of the starting complex **4a**. In  $^{13}\text{C}$  NMR spectrum of **5a**, signals assignable to carbene and carbonyl carbons were observed at 201.0 and 260.6 ppm, respectively. The X-ray analysis of **5a** also proved the formation of the chelating indenyl-NHC complex of molybdenum (see ESI†).



Scheme 3

Next, we examined the preparation of a bimetallic complex by the coordination of NHC to the other metal fragment. The reaction of complex **4a** with molybdenum complex **6**,<sup>8b,18</sup> which has a labile pyridine ligand, under the heptane-refluxing conditions successfully afforded the bimetallic complex **7a** in 82% yield as a yellow solid. Complex **7a** was characterised by the spectroscopic measurements as well as by the X-ray diffraction analysis.<sup>‡</sup> The structure of **7a** is shown in Fig. 1 (right). The indenyl molybdenum fragment adopts normal piano stool geometry and shows similar structural features as the parent complex **4a**. The other molybdenum fragment shows pseudo-octahedral geometry around the metal centre and is basically similar to that of the amidinato-NHC complex of molybdenum.<sup>8b</sup> The IR spectrum of **7a** showed four CO stretching bands at 1949, 1914, 1874, and  $1822\text{ cm}^{-1}$ . The two bands ( $1949$  and  $1874\text{ cm}^{-1}$ ) were assignable to those of the indenyl molybdenum fragment. The other two bands ( $1914$  and  $1822\text{ cm}^{-1}$ ) were due to those of the NHC molybdenum fragment. In  $^{13}\text{C}$  NMR, the four carbonyl carbons were observed; the carbonyl carbons of the indenyl molybdenum fragment were seen at 240.4 and 241.4 ppm and those of the NHC molybdenum fragment at 229.4 and 229.7 ppm.

In conclusion, the indenyl-functionalised  $\text{BEt}_3$ -adduct NHC was successfully prepared and subsequently converted to the indenyl anion bearing the NHC- $\text{BEt}_3$  moiety as a simple substituent. We therefore demonstrated the stepwise coordination of the indenyl and NHC ligands to the same metal as well as the other one. Our results indicate that the protection of NHC by  $\text{BEt}_3$  can effectively control the coordination ability of the NHC ligand to a metal. This concept might be compared to the methodology of “protecting groups” in synthetic organic chemistry and thus could represent a reliable procedure for the preparation of hybrid-type NHC complexes. Further investigations on the preparation

of hetero-bimetallic complexes and their applications to catalytic reactions are now in progress.

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## Notes and references

† Crystal data for **4a**, **5a**, and **7a**. **4a**:  $C_{27}H_{37}BMoN_2O_2$ ,  $M = 528.35$ , monoclinic,  $a = 6.8287(15)$ ,  $b = 26.711(5)$ ,  $c = 14.680(3)$  Å,  $\beta = 97.025(5)^\circ$ ,  $U = 2657.6(9)$  Å<sup>3</sup>, space group  $P2_1/c$  (no. 14),  $Z = 4$ ,  $D_c = 1.320$  g cm<sup>-3</sup>,  $F(000) = 1104.00$ ,  $T = 296(1)$  K,  $\mu(\text{Cu-K}\alpha) = 42.118$  cm<sup>-1</sup>, 22903 reflections measured, 4646 independent ( $R_{\text{int}} = 0.055$ ). The final refinement converged to  $R_1 = 0.0393$  for  $I > 2.0\sigma(I)$ ,  $wR_2 = 0.1130$  for all data. **5a**:  $C_{30}H_{32}MoN_2O_4$ ,  $M = 402.35$ , monoclinic,  $a = 8.7708(11)$ ,  $b = 16.5056(17)$ ,  $c = 12.1411(13)$  Å,  $\beta = 91.388(10)^\circ$ ,  $U = 1757.1(3)$  Å<sup>3</sup>, space group  $P2_1/c$  (no. 14),  $Z = 4$ ,  $D_c = 1.521$  g cm<sup>-3</sup>,  $F(000) = 824.00$ ,  $T = 296(1)$  K,  $\mu(\text{Cu-K}\alpha) = 61.458$  cm<sup>-1</sup>, 13487 reflections measured, 3066 independent ( $R_{\text{int}} = 0.073$ ). The final refinement converged to  $R_1 = 0.0334$  for  $I > 2.0\sigma(I)$ ,  $wR_2 = 0.0832$  for all data. **7a**:  $C_{39}H_{38}Mo_2N_4O_4$ ,  $M = 818.63$ , monoclinic,  $a = 7.411(2)$ ,  $b = 38.544(8)$ ,  $c = 3.169(3)$  Å,  $\beta = 76.26(2)^\circ$ ,  $U = 3654.0(15)$  Å<sup>3</sup>, space group  $P2_1/a$  (no. 14),  $Z = 4$ ,  $D_c = 1.488$  g cm<sup>-3</sup>,  $F(000) = 1664.00$ ,  $T = 296(1)$  K,  $\mu(\text{Cu-K}\alpha) = 59.673$  cm<sup>-1</sup>, 29621 reflections measured, 6121 independent ( $R_{\text{int}} = 0.111$ ). The final refinement converged to  $R_1 = 0.0594$  for  $I > 2.0\sigma(I)$ ,  $wR_2 = 0.1043$  for all data.

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