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The reaction of amidinato(pyridine) complexes of molybdenum and tungsten with triethylborane adduct of *N*-heterocyclic carbene (NHC · BEt$_3$): Investigation on the reactivity of NHC · BEt$_3$ as carbene precursor toward transition metal complexes

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Abstract

The reaction of triethylborane adduct of *N*-heterocyclic carbene, NHC · BEt$_3$, (NHC = I^{i}Pr = 1,3-diisopropylimidazol-2-ylidene (I^{i}Pr · BEt$_3$; **1a**), NHC = IMes = 1,3-dimesitylimidazol-2-ylidene (IMes · BEt$_3$; **1b**)), which was prepared by the reaction of the corresponding imidazolium salt with one equivalent of LiBEt$_3$H, with amidinato(pyridine) complex, [M(η^3-allyl){η^2-(NPh)$_2$CH}(CO)$_2$(NC$_5$H$_5$)] (M = Mo; **2-Mo** M = W; **2-W**), was investigated. The reaction of compound **1** with complex **2** under toluene-reflux conditions resulted in the formation of carbene complex [M(η^3-allyl){η^2-(NPh)$_2$CH}(CO)$_2$(NHC)] (M = Mo, NHC = I^{i}Pr; **3a-Mo**, M = Mo, NHC = IMes; **3b-Mo**, M = W, NHC = I^{i}Pr; **3a-W**, M = W, NHC = IMes; **3b-W**). These complexes were characterized spectroscopically as well as by X-ray analyses. Complex **3a-Mo** was formed in various solvents such as 1,2-dimethoxyethane (DME), 1,2-dichloroethane, and acetonitrile under refluxing conditions for 3 h. In toluene, **3a-Mo** was obtained in a good yield by heating at 70 °C for only 20 min. Employment of NHC · BEt$_3$ (**1**) was found to afford convenient route for the introduction of the carbene ligand to the transition metal complexes.
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Keywords: *N*-heterocyclic carbene; Triethylborane adduct; Amidinato(pyridine) complex; Molybdenum; Tungsten

1. Introduction

Since the successful isolation of *N*-heterocyclic carbenes (NHCs) by Arduengo and his co-workers in 1991 [1,2], NHCs derived from imidazolium salts have been widely used as ancillary ligands for not only transition metals but also for main group elements [3]. The utilization of free NHCs, either isolated or generated in situ, produced by the deprotonation of the corresponding salts is the most common method for the syntheses of their complexes. However, manipulation of the free carbene is often difficult due to their highly reactive nature toward air and moisture. Recently, the employment of NHCs adducts as protected forms attracted much attention for the syntheses of metal complexes bearing these ligands. Grubbs and co-workers [4], Herrmann and co-workers [5] independently reported the utilization of alcohol or chloroform adducts of NHC as a carbene source. Lin et al. [6] reported that silver(I) complexes of NHC, which are prepared by the treatment of imidazolium salt with Ag$_2$O, are able to transfer their NHC ligands to other metal complexes [7]. Since the Lin's report, the use of Ag(I) complexes of NHC is becoming popular method for synthesis of NHC complex, in particular, in the field of the late transition metals [8,9].

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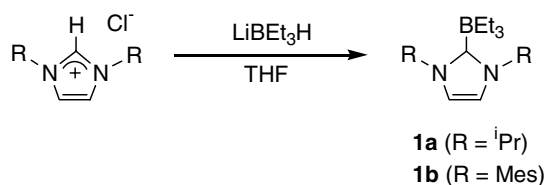
Scheme 1.

We have recently reported one-pot synthesis of tri-ethylborane adduct of NHC, NHC · BEt$_3$ (**1**), (NHC = I^{i}Pr = 1,3-diisopropylimidazol-2-ylidene (I^{i}Pr · BEt$_3$; **1a**), NHC = IMes = 1,3-dimesitylimidazol-2-ylidene (IMes · BEt$_3$; **1b**)), which was obtained by the reaction of the imi-dazolium salt with LiBEt$_3$H (Scheme 1) [10]. It was found that these compounds acted as a carbene transfer reagent for a transition metal complex as well as for a main group element. We also compared the behavior of BEt$_3$-adduct toward Mo(CO)$_6$ with those of BH$_3$- and BF$_3$-adducts with a view of carbene transfer reagents. The results clearly showed that NHC · BEt$_3$ (**1**) effectively acted as a carbene precursor for the metal complex.

In order to establish the availability of NHC · BEt$_3$ (**1**) as a carbene precursor, we investigated the reaction of **1** with amidinato(pyridine) complexes of molybdenum and tungsten, [M(η^3-allyl){η^2-(NPh)$_2$CH}(CO)$_2$(NC$_5$H$_5$)] (M = Mo; **2-Mo**, W; **2-W**), under various reaction conditions. In this paper we wish to report the reactivity of NHC · BEt$_3$ (**1**) in view of a carbene transfer reagent.

2. Results and discussion

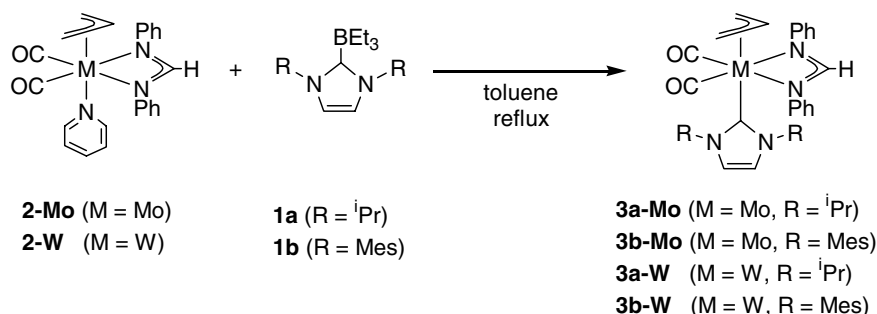### 2.1. Synthesis and characterization of amidinato(N-heterocyclic carbene) complexes 3

We have recently reported the preparation of novel amidinato(pyridine) complexes of molybdenum and tungsten, [M(η^3-allyl){η^2-(NPh)$_2$CH}(CO)$_2$(NC$_5$H$_5$)] (M = Mo; **2-Mo**, W; **2-W**), whose pyridine ligand showed the labile nature [11]. In the reaction of complex **2** with various Lewis bases such as phosphine and phos-phite, pyridine ligand is found to be easily substituted by

Lewis base under mild conditions, i.e., at ambient tem-perature, to afford the substituted product. It has been recognized that the NHC plays a role parallel to triva-lent phosphorus compound in organometallic chemis-try. Thus, the reaction of complex **2** with NHC · BEt$_3$ (**1**) was examined. Whereas substitution reaction did not take place at room temperature, clean substitution reaction took place under thermal conditions to give amidinato(NHC) complex **3** (Scheme 2).
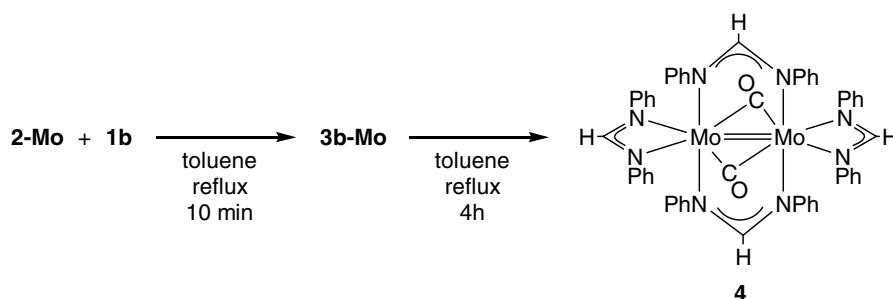
On treatment of molybdenum complex **2-Mo** with **1a** in toluene under refluxing conditions for 3 h, carbene complex **3a-Mo** was obtained as a yellow solid in 92% yield. In a case of tungsten complex **2-W**, a similar reac-tion took place to give a yellow solid **3a-W** in 92% yield. In the reaction with IMes · BEt$_3$ (**1b**), tungsten-IMes complex **3b-W** was isolated in a moderate yield (71%), whereas the corresponding molybdenum complex **3b-Mo** was not obtained under the same conditions. In the reaction of **2-Mo** with **1b**, an initial yellow solution of the reaction mixture gradually changed to an orange solution and after several hours black precipitates were formed. By heating for the short time (10 min), carbene complex **3b-Mo** was obtained, although the yield of which was low (14%). One of by-products isolated was found to be dinuclear Mo complex **4** (Scheme 3), as was characterized by X-ray analysis [12].

In order to identify the dissociated triethylborane, the reaction mixture of **1a** with **2-Mo** was subjected to the ^{11}B NMR measurement. In ^{11}B NMR, broad singlet was observed at 2.9 ppm, which is assignable to pyridine adduct of triethylborane [13]. We next examined the reaction of **1a** with **2-Mo** in the presence of excess amount of Lewis base such as pyridine, NEt$_3$, and PPh$_3$, hoping that these bases may accelerate the B–C bond cleavage of compound **1** by the formation of Lewis base adduct of BEt$_3$. However, there was no effect in any case. The reaction of **1a** with **2-Mo** under photo-irradi-ation conditions decomposed **2-Mo** remaining **1a** intact. These results suggested that the thermal conditions are necessary to produce the free carbene by the cleavage of B–C bond in **1**.

The spectroscopic data of carbene complexes **3a-Mo**, **3b-Mo**, **3a-W**, and **3b-W** are summarized in Table 1. In IR spectra, complex **3a-Mo** showed two CO stretching

2-Mo (M = Mo) **1a** (R = ^{i}Pr) 　**3a-Mo** (M = Mo, R = ^{i}Pr)
2-W (M = W)　 **1b** (R = Mes)　　**3b-Mo** (M = Mo, R = Mes)
　　　　　　　　　　　　　　　　　3a-W (M = W, R = ^{i}Pr)
　　　　　　　　　　　　　　　　　3b-W (M = W, R = Mes)

Scheme 2.

Scheme 3.

Table 1
Spectroscopic data

Complex	IR[a] v_{CO} (cm^{-1})	^{1}H NMR δ (ppm)	^{13}C{^{1}H} NMR δ (ppm)
3a-Mo	1913 1829	(in C$_7$D$_8$, at 20 °C): 0.9 (br, ^{i}Pr-CH$_3$), 1.79 (d, $J = 10.6$ Hz, 2H, allyl CH$_2$), 4.0 (m, 1H, allyl-CH), 4.22 (d, $J = 6.6$ Hz, 2H, allyl-CH$_2$), 4.71 (sept, $J = 6.6$ Hz, 2H, ^{i}Pr-CH), 6.30 (s, 2H, CH=CH), 6.9–7.1(m, 10H, Ph), 8.39 (s, 1H, amidinato-CH) (in C$_7$D$_8$, at 80 °C): 0.90 (d, $J = 6.6$ Hz, 12H, ^{i}Pr-CH$_3$), 1.77 (d, $J = 9.9$ Hz, 2H, allyl-CH$_2$), 4.1(m, 1H, allyl-CH), 4.16 (d, $J = 7.3$ Hz, 2H, allyl-CH$_2$), 4.72 (sept, $J = 6.6$ Hz, 2H, ^{i}Pr–CH), 6.42 (s, 2H, CH=CH), 6.8–7.1 (m, 10H, Ph), 8.41(s, 1H, amidinato-CH) (in C$_7$D$_8$, at −60 °C): 0.33 (d, $J = 6.6$ Hz, 6H, ^{i}Pr–CH$_3$), 1.40 (d, $J = 6.6$ Hz, 6H, ^{i}Pr–CH$_3$), 1.84 (d, $J = 10.6$ Hz, 2H, allyl-CH$_2$), 4.0 (m, 1H, allyl-CH), 4.33 (d, $J = 6.6$ Hz, 2H, allyl-CH$_2$), 4.74 (sept, $J = 6.6$ Hz, 2H, ^{i}Pr–CH), 6.02 (s, 2H, CH=CH), 6.9–7.2 (m, 10H, Ph), 8.36 (s, 1H, amidinato-CH)	(in CDCl$_3$, at 55 °C): 23.7 (^{i}Pr-CH$_3$), 52.3 (^{i}Pr-CH), 60.6 (allyl-CH$_2$), 86.1 (allyl-CH), 117.4 (CH=CH), 117.8, 121.1, 129.1, 147.4 (Ph), 153.9 (amidinato-CH), 189.4 (NCN), 228.6 (CO)
3b-Mo	1906 1811	(in C$_6$D$_6$, at 25 °C): 1.47 (d, $J = 10.6$ Hz, 2H, allyl-CH$_2$), 2.01 (s, 12H, CH$_3$), 2.08 (s, 6H, CH$_3$), 3.46 (tt, $J = 10.6$, 6.6 Hz, 1H, allyl-CH), 3.90 (d, $J = 6.6$ Hz, 2H, allyl-CH$_2$), 5.99 (s, 2H, CH=CH), 6.5–7.0 (m, 14H, Ph), 8.57 (s, 1H, amidinato-CH)	(in C$_6$D$_6$, at 25 °C): 18.4 (CH$_3$), 21.4 (CH$_3$), 30.4 (allyl- CH$_2$), 63.0 (allyl-CH), 118.2, 120.7, 124.7, 128.7, 129.4, 135.7, 137.7, 138.5, 146.5 (CH=CH and Ph), 153.5 (amidinato-CH), 192.7 (NCN), 228.1 (CO)
3a-W	1904 1818	(in CDCl$_3$, at 30 °C): 1.0 (br, ^{i}Pr-CH$_3$), 1.92 (d, $J = 9.9$ Hz, 2H, allyl-CH$_2$), 3.21 (tt, $J = 9.9$, 6.6 Hz, 1H, allyl-CH), 4.19 (d, $J = 6.6$ Hz, 2H, allyl-CH$_2$), 4.64 (sept, $J = 6.6$ Hz, 2H, ^{i}Pr–CH), 6.94 (s, 2H, CH=CH), 6.9–7.4 (m, 10H, Ph), 9.40 (s, 1H, amidinato-CH) (in C$_7$D$_8$, at 80 °C): 0.88 (d, $J = 6.6$ Hz, 12H, ^{i}Pr–CH$_3$), 2.01 (d, $J = 10.6$ Hz, 2H, allyl-CH$_2$), 3.17 (tt, $J = 10.6$, 5.9 Hz, 1H, allyl-CH), 4.16 (d, $J = 5.9$ Hz, 2H, allyl-CH$_2$), 4.72 (sept, $J = 6.6$ Hz, 2H, ^{i}Pr–CH), 6.39 (s, 2H, CH=CH), 6.8–7.1 (m, 10H, Ph), 8.99 (s, 1H, amidinato-CH) (in CDCl$_3$, at −40 °C): 0.42 (d, $J = 6.6$ Hz, 6H, ^{i}Pr–CH$_3$), 1.52 (d, $J = 6.6$ Hz, 6H, ^{i}Pr–CH$_3$), 1.88 (d, $J = 9.9$ Hz, 2H, allyl-CH$_2$), 3.15 (tt, $J = 9.9$, 6.6 Hz, 1H, allyl-CH), 4.21 (d, $J = 6.6$ Hz, 2H, allyl-CH$_2$), 4.53 (sept, $J = 6.6$ Hz, 2H, ^{i}Pr–CH), 6.93 (s, 2H, CH=CH), 6.9–7.3 (m, 10H, Ph), 9.44 (s, 1H, amidinato-CH)	(in CDCl$_3$, at 55 °C): 23.3 (^{i}Pr–CH$_3$), 52.6 (^{i}Pr–CH), 53.1 (allyl-CH$_2$), 80.3 (allyl-CH), 117.4 (CH=CH), 117.8, 121.6, 129.1, 146.2 (Ph), 154.3 (amidinato-CH), 191.4 (NCN), 220.7 (CO)
3b-W	1897 1798	(in CDCl$_3$ at 55 °C): 1.45 (d, $J = 9.9$ Hz, 2H, allyl-CH$_2$), 1.98 (s, 12H, CH$_3$), 2.19 (s, 6H, CH$_3$), 2.52 (tt, $J = 9.9$, 6.6 Hz, 1H, allyl-CH), 3.69 (d, $J = 6.6$ Hz, 2H, allyl-CH$_2$), 6.5–7.2 (m, 16H, CH=CH and Ph), 9.38 (s, 1H, amidinato-CH)	(in CDCl$_3$ at 55 °C): 18.2 (CH$_3$), 21.2 (CH$_3$), 56.1 (allyl-CH$_2$), 77.2 (allyl-CH), 117.7, 120.8, 125.1, 128.3, 129.1, 130.0, 135.6, 138.5, 144.8 (CH=CH and Ph), 153.5 (amidinato-CH), 192.8 (NCN), 220.0 (CO)

[a] KBr.

bands at 1913 and 1829 cm^{-1}, which was slightly higher frequency than those for mesityl analogue **3b-Mo** (1906, 1811 cm^{-1}). Similar tendency was observed in tungsten complexes **3a-W** and **3b-W**. The CO stretching bands

for these NHC complexes showed lower frequency than those for the corresponding PEt$_3$ complexes (1921, 1836 cm^{-1} for Mo complex [14] and 1912, 1820 cm^{-1} for W complex [11]). This observation is in good

agreement with the previous studies that the NHC ligand acts as a greater electron donor to the metal fragment than phosphine ligand [3].

The ambient-temperature ^{1}H NMR spectrum of **3a-Mo** showed symmetrical allylic signals at 1.79 (*anti*-CH$_2$), 4.0 (central proton) and 4.22 (*syn*-CH$_2$) ppm. Amidinato-CH proton was detected at 8.39 ppm as singlet. The septet signal due to isopropyl methine protons of the carbene ligand was observed at 4.71 ppm with a coupling constant of 6.6 Hz, whereas the broad signal assignable to isopropyl methyl protons were observed at 0.90 ppm. At higher temperature (80 °C), the isopropyl methyl protons were observed as a sharp doublet at 0.90 ppm with $J = 6.6$ Hz. The low-temperature ^{1}H NMR spectrum (at −60 °C) showed two sets of doublets at 0.33 and 1.40 ppm ($J = 6.6$ Hz) with each 6H integration. Little change was observed for other signals in variable-temperature ^{1}H NMR. These results suggest that the free rotation of isopropyl group around C–N bond is restricted at room temperature. The ^{13}C NMR spectrum of **3a-Mo** at 55 °C also suggested that the complex **3a-Mo** has a symmetrical geometry around molybdenum; allylic carbons were appeared at 60.6 (terminal carbon) and 86.1 (central carbon) ppm and the singlet due to two CO carbons was observed at 228.6 ppm. The carbene carbon was observed at 189.4 ppm. This finding is within a region of normal tendency for a series of these sorts of carbene complexes [3]. These NMR data showed that the carbene ligand of complex **3a-Mo** was located in the *trans* position to the allyl ligand in solution. Tungsten complex **3a-W** showed similar NMR data. Mesityl analogues, **3b-Mo** and **3b-W**, were similarly characterized by NMR spectroscopies (Table 1).

The NHC complexes were characterized by X-ray diffraction studies. The ORTEP drawings of molybdenum complexes **3a-Mo** and **3b-Mo** are displayed in Figs. 1 and 2, respectively. Tungsten complexes have a similar structure to the corresponding molybdenum complexes.
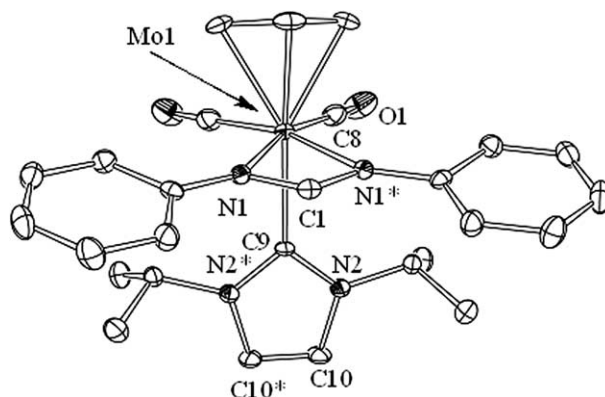

Fig. 1. ORTEP drawing of **3a-Mo** with thermal ellipsoids drawn at the 30% probability level. Hydrogen atoms are omitted for clarity.
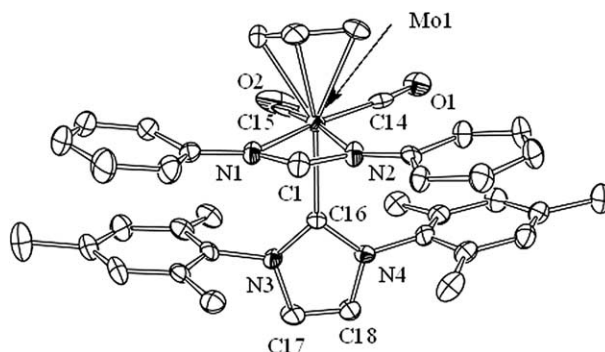

Fig. 2. ORTEP drawing of **3b-Mo** with thermal ellipsoids drawn at the 30% probability level. Hydrogen atoms are omitted for clarity.

Selected bond distances and angles of all complexes are listed in Tables 2 and 3.

These complexes show pseudo-octahedral geometry around the metal center. The amidinato ligand is located coplanar with two CO ligands, and the carbene ligand is positioned *trans* to the η^3-allyl ligand. The open face of the allyl ligand is directed toward two carbonyl ligands,

Table 2
Selected bond distances (Å) and angles (°) for I^{i}Pr-complexes **3a-Mo** and **3a-W**

		3a-Mo		3a-W
Carbene	Mo(1)–C(9)	2.276(4)	W(1)–C(9)	2.22(2)
	N(2)–C(9)	1.359(5)	N(2)–C(9)	1.36(1)
	N(2)–C(10)	1.395(6)	N(2)–C(10)	1.38(1)
	C(10)–C(10*)	1.336(10)	C(10)–C(10*)	1.32(2)
CO	Mo(1)–C(8)	1.952(5)	W(1)–C(8)	1.95(1)
	O(1)–C(8)	1.152(6)	O(1)–C(8)	1.17(1)
Amidinato	Mo(1)–N(1)	2.276(4)	W(1)–N(1)	2.266(8)
	N(1)–C(1)	1.314(5)	N(1)–C(1)	1.33(1)
Carbene	Mo(1)–C(9)–N(2)	127.9(3)	W(1)–C(9)–N(2)	129.7(6)
	N(2)–C(9)–N(2*)	104.2(5)	N(2)–C(9)–N(2*)	100(1)
CO	Mo(1)–C(8)–O(1)	178.3(5)	W(1)–C(8)–O(1)	178(1)
Amidinato	Mo(1)–N(1)–C(1)	93.3(3)	W(1)–N(1)–C(1)	94.2(6)
	N(1)–Mo(1)–N(1*)	58.3(2)	N(1)–W(1)–N(1*)	58.7(4)
	N(1)–C(1)–N(1*)	115.1(6)	N(1)–C(1)–N(1*)	112(1)

Table 3
Selected bond distances (Å) and angles (°) for IMes-complexes **3b-Mo** and **3b-W**

	3b-Mo		**3b-W**	
Carbene	Mo(1)–C(16)	2.285(9)	W(1)–C(16)	2.28(1)
	N(3)–C(16)	1.36(1)	N(3)–C(16)	1.37(1)
	N(3)–C(17)	1.41(1)	N(3)–C(17)	1.38(1)
	N(4)–C(16)	1.38(1)	N(4)–C(16)	1.34(1)
	N(4)–C(18)	1.38(1)	N(4)–C(18)	1.39(1)
	C(17)–C(18)	1.32(2)	C(17)–C(18)	1.29(1)
CO	Mo(1)–C(14)	1.93(1)	W(1)–C(14)	1.93(1)
	Mo(1)–C(15)	1.94(1)	W(1)–C(15)	1.93(1)
	O(1)–C(14)	1.16(1)	O(1)–C(14)	1.15(1)
	O(2)–C(15)	1.18(2)	O(2)–C(15)	1.19(1)
Amidinato	Mo(1)–N(1)	2.293(8)	W(1)–N(1)	2.30(1)
	Mo(1)–N(2)	2.216(8)	W(1)–N(2)	2.24(1)
	N(1)–C(1)	1.33(1)	N(1)–C(1)	1.29(1)
	N(2)–C(1)	1.36(1)	N(2)–C(1)	1.34(1)
Carbene	Mo(1)–C(16)–N(3)	130.9(6)	W(1)–C(16)–N(3)	130.5(7)
	Mo(1)–C(16)–N(4)	127.2(6)	W(1)–C(16)–N(4)	127.3(8)
	N(3)–C(16)–N(4)	101.9(7)	N(3)–C(16)–N(4)	102.1(8)
CO	Mo(1)–C(14)–O(1)	175.6(9)	W(1)–C(14)–O(1)	172.9(9)
	Mo(1)–C(15)–O(2)	170(1)	W(1)–C(15)–O(2)	170(1)
Amidinato	Mo(1)–N(1)–C(1)	93.2(6)	W(1)–N(1)–C(1)	93.8(7)
	Mo(1)–N(2)–C(1)	96.0(5)	W(1)–N(2)–C(1)	95.0(7)
	N(1)–Mo(1)–N(2)	59.1(3)	N(1)–W(1)–N(2)	57.7(3)
	N(1)–C(1)–N(2)	111.6(9)	N(1)–C(1)–N(2)	113(1)

which has been known to be a favorable orientation for a series of $[M(\eta^3\text{-allyl})(CO)_2]$ (M = Mo, W) complexes [15]. The geometry of these complexes revealed by X-ray analyses coincides with the solution-state geometry observed by the ^1H and ^{13}C NMR spectra.

The Mo–C(NHC) bond distances are 2.276(4) Å for **3a-Mo** and 2.285(9) Å for **3b-Mo**. These Mo–C bond distances were in good agreement with the Mo–C(NHC) bond distances reported so far; the reported Mo–C distances are in the range from 2.152(5) to 2.35(1) Å [3,16,17]. In tungsten complexes, the W–C(NHC) bond distances are 2.22(2) Å for **3a-W** and 2.28(1) for **3b-W**, which are similar to those of corresponding molybdenum complexes. This result might have come from the similar covalent radii of the metals (M; 1.29 Å, W; 1.30 Å) [18]. Although comparison of the CO stretching frequency supports that NHC ligand possesses more electron donating ability than PEt_3, no evidence was observed by X-ray analyses.

2.2. Investigation of the reactivity of NHC · BEt₃ (1) as a carbene precursor toward amidinato(pyridine) complex 2 under various conditions

As mentioned above, it is found that NHC · BEt₃ (**1**) can act as a carbene precursor to the transition metals under toluene-refluxing conditions. We were interested in the reaction conditions such as solvents and temperature with a view to find the availability of **1** as a carbene transfer reagent. In this respect we examined the reac-

tion of **1a** with **2-Mo** under various conditions. For this investigation, toluene, 1,2-dimethoxyethane (DME), THF, 1,2-dichloroethane, and acetonitrile were selected as reaction media. The results and reaction conditions are summarized in Table 4.

In a toluene solution, refluxing conditions brought about the clean reaction to give carbene complex **3a-Mo** in a good yield (92%). At 70 °C for 3 h, complex **3a-Mo** was isolated in a good yield (93%). Furthermore, the isolated yield of 87% for **3a-Mo** was obtained by the reaction even for only 20 min. At 60 °C, the yield decreased to be 62%. Considerable amount of impurities was formed at 50 °C. One of impurities was considered to be an imidazolium salt formed by the decomposition of compound **1a**. The ^1H NMR spectrum showed characteristically low-field resonance at 10.24 ppm assignable to the CH-acidic proton of the imidazolium salt. In addition, complex

Table 4
Yield of **3a-Mo** by the reaction of **2-Mo** with **1a** under various conditions[a]

Solvent (b.p.)	Reflux	70 °C	60 °C	50 °C
Toluene (110 °C)	92%	93%	62%	21%
DME (85 °C)	90%	83%	50%	–[c]
1,2-Dichloroethane (84 °C)	80%	48%	–[c]	–[c]
Acetonitrile (82 °C)	61%	–[b]	–[c]	–[c]

[a] Isolated yield. Reaction conditions; **2-Mo/1a** = 1:1, reaction time = 3 h.
[b] Considerable amount of impurities was formed, whereas a little amount of **3a-Mo** was also formed.
[c] Not examined.

3a-Mo was isolated in 21% yield. In a case of tungsten complex in toluene, refluxing conditions resulted in clean formation of complex **3a-W** in 92% yield. At 70 °C, **3a-W** was isolated in 76% yield after prolonged reaction time (10 h).

In a DME solution, complex **3a-Mo** was obtained in a good yield (90%) under refluxing conditions. Complex **3a-Mo** was also formed in 83% yield at 70 °C, whereas at 60 °C the yield of **3a-Mo** decreased in 50%. On the other hand, it was found that THF was not favorable solvent for this reaction, because considerable amounts of by-products derived from HNC unit were formed.

In a case of 1,2-dichloroethane as a chlorinated solvent, refluxing conditions afforded the clean formation of complex **3a-Mo** in 80% yield. However, lower reaction temperature (70 °C) resulted in the decrease of the yield (48%). Acetonitrile was also available in the formation of carbene complex **3a-Mo**, which was isolated in moderate yield (61%).

3. Concluding remarks

NHC · BEt$_3$ (**1**), which is prepared by the reaction of an imidazolium salt with LiBEt$_3$H, has following features; stable toward air and moisture, high solubility toward various organic solvents, and available as a carbene transfer reagent for not only transition metals but also for main group elements. In this paper, we investigated the reaction of NHC · BEt$_3$ (**1**) with amidinato(pyridine) complexes of molybdenum and tungsten (**2**). Under thermal conditions, compound **1** worked as carbene precursor to the metal fragment to afford amidinato(NHC) complex (**3**). Furthermore, this reaction proceeded in various organic solvents such as toluene (aromatic hydrocarbon), DME (ethereal), 1,2-dichloroethane (chlorinated hydrocarbon), and acetonitrile under refluxing conditions. Concerning the thermal conditions, it was necessary to heat at 60 °C or above. Compared with the previously reported alcohol or chloroform adducts of NHC, required reaction conditions for NHC · BEt$_3$ (**1**) as a carbene source is quite similar allowing satisfactorily mild conditions to produce the metal–carbene complexes. Employment of NHC · BEt$_3$ (**1**) is thus proved to be quite useful in the introduction of the carbene ligand to a wide range of transition metal systems. A further investigation of the application to various *N*-heterocyclic carbene systems is now in progress.

4. Experimental

4.1. General procedures

All manipulations involving air- and moisture-sensitive organometallic compounds were carried out under an atmosphere of dry argon or nitrogen, which was purified by SICAPENT (Merck Co., Inc.), by using a standard Schlenk tube or high vacuum techniques. All solvents were distilled over appropriate drying agents prior to use. All reagents employed in this research were commercially available and used without further purification. I^{i}Pr · BEt$_3$ (**1a**) [10], IMes · BEt$_3$ (**1b**) [10], and [M(η^3-allyl){η^2-(NC$_6$H$_5$)$_2$CH}(CO)$_2$(NC$_5$H$_5$)] (M = Mo; **2-Mo**, W; **2-W**) [11] were prepared according to the literature methods.

IR spectra were recorded on a HORIBA FT-730 spectrometer. ^{1}H, ^{13}C{^{1}H} and ^{11}B{^{1}H} NMR spectra were recorded on a JEOL EX-270 spectrometer at ambient temperature, unless otherwise mentioned. ^{1}H and ^{13}C{^{1}H} NMR chemical shifts were recorded in ppm relative to internal Me$_4$Si. ^{11}B{^{1}H} NMR chemical shifts were recorded in ppm relative to external BF$_3$ · OEt$_2$. All coupling constants were recorded in Hz. Elemental analyses were performed on a Perkin–Elmer 240C.

4.2. Preparation of [Mo(η^3-allyl){η^2-(NC$_6$H$_5$)$_2$CH}-(CO)$_2$(I^{i}Pr)] (3a-Mo)

Compound **1a** (38 mg, 0.15 mmol), **2-Mo** (57 mg, 0.12 mmol), and toluene (5 mL) were put in a Schlenk tube. The reaction mixture was refluxed for 3 h, and then the solvent was removed under reduced pressure. The residual solid was washed with hexane (3 × 5 mL), and then dried in vacuo to give **3a-Mo** as a yellow powder (62 mg, 0.11 mmol, 92%). *Anal*. Calc. for C$_{27}$H$_{32}$MoN$_4$O$_2$: C, 60.00; H, 5.97; N, 10.37. Found: C, 60.18; H, 6.04; N, 10.27%.

4.3. Preparation of [Mo(η^3-allyl){η^2-(NC$_6$H$_5$)$_2$CH}-(CO)$_2$(IMes)] (3b-Mo)

Compound **1b** (100 mg, 0.25 mmol), **2-Mo** (107 mg, 0.23 mmol), and toluene (10 mL) were put in a Schlenk tube. The reaction mixture was refluxed for 10 min, and then the solvent was removed under reduced pressure. The residual material was recrystallized from toluene/hexane to give yellow crystals of **3b-Mo** (22 mg, 0.032 mmol, 14%). *Anal*. Calc. for C$_{39}$H$_{40}$MoN$_4$O$_2$: C, 67.62; H, 5.82; N, 8.09. Found: C, 67.53; H, 5.83; N, 8.06%.

4.4. Preparation of [W(η^3-allyl){η^2-(NC$_6$H$_5$)$_2$CH}-(CO)$_2$(I^{i}Pr)] (3a-W)

Complex **3a-W** was prepared from **1a** (35 mg, 0.14 mmol), **2-W** (72 mg, 0.13 mmol), and toluene (10 mL) in the same manner as that for **3a-Mo**. Complex **3a-W** was isolated as a yellow powder (76 mg, 0.12 mmol, 92%). *Anal*. Calc. for C$_{27}$H$_{32}$N$_4$O$_2$W: C, 51.60; H, 5.13; N, 8.92. Found: C, 51.35; H, 4.90; N, 8.81%.

4.5. Preparation of [W(η^3-allyl){η^2-(NC$_6$H$_5$)$_2$CH}-(CO)$_2$(IMes)] (3b-W)

Compound **1b** (44 mg, 0.11 mmol), **2-W** (51 mg, 0.092 mmol), and toluene (5 mL) were put in a Schlenk tube. The reaction mixture was refluxed for 30 min, and then the solvent was removed under reduced pressure. The residual solid was washed with hexane (3 × 5 mL), and then dried in vacuo to give **3b-W** as a yellow powder (51 mg, 0.065 mmol, 71%). *Anal*. Calc. for C$_{39}$H$_{40}$N$_4$O$_2$W: C, 60.01; H, 5.16; N, 7.18. Found: C, 59.88; H, 5.17; N, 7.14%.

4.6. General manipulations for the reaction of 1a with 2-Mo under various conditions

Complex **2-Mo** (40–50 mg, ca. 0.1 mmol), one equivalent of I^{i}Pr · BEt$_3$(**1a**) and appropriate solvent (5 mL) were put in a Schlenk tube. The reaction mixture was heated for 3h, and then the solvent was removed under reduced pressure. The residual solid was washed with methanol (3 × 5 mL), and then dried in vacuo to give **3a-Mo**. Spectroscopically pure **3a-Mo** was obtained as a yellow solid. The results are summarized in Table 4.

4.7. Experimental procedure for X-ray crystallography

Suitable single crystals were obtained by recrystallization from CH$_2$Cl$_2$ (**3a-Mo**, **3a-W**), or from toluene–hexane (**3b-Mo**, **3b-W**), in a refrigerator and are individually mounted on glass fibers. Diffraction measurements of **3a-Mo**, **3b-Mo**, **3a-W** and **3b-W** were made on a Rigaku AFC-7R automated four-circle diffractometer by using graphite-monochromated Mo Kα radiation ($\lambda = 0.71069$ Å). The data collections were carried out at -50 ± 2 °C using the ω–2θ scan technique to a maximum 2θ value of 60.0° for all crystals. Cell constants and an orientation matrix for data collection were determined from 25 reflections with 2θ angles in the range 20.01–24.58° for **3a-Mo**, 29.19–29.83° for **3b-Mo**, and 29.67–31.37° for **3b-W** and from 18 reflections with 2θ angles in the range 20.68–26.29° for **3a-W**. Three standard reflections were monitored at every 150 measurements. In the reduction of data, Lorentz and polarization corrections and as empirical absorption correction (Ψ scan) were made.

Crystallographic data and the results of measurements are summarized in Table 5. The structures were solved by direct methods (SIR 92) [19] for **3a-Mo** and **3a-W** or heavy-atom Patterson methods (DIRDIF94 PATTY) [20] for **3b-Mo** and **3b-W**, and expanded using Fourier techniques [21]. Least-squares refinements were carried out using SHELXL-97 [22] for **3b-Mo**. All of the non-hydrogen atoms were refined anisotropically. Hydrogen atoms for **3a-Mo** were located from difference Fourier maps and refined atomic coordinates. The isotropic thermal parameters of those hydrogen atoms were fixed at about 1.2 times that of the preceding

Table 5
Summary of crystal data for complexes **3a-Mo**, **3b-Mo**, **3a-W** and **3b-W**

	3a-Mo	3b-Mo	3a-W	3b-W
Emprical formula	C$_{27}$H$_{32}$MoN$_4$O$_2$	C$_{39}$H$_{40}$MoN$_4$O$_2$	C$_{27}$H$_{32}$ N$_4$O$_2$W	C$_{39}$H$_{40}$N$_4$O$_2$W
Formula weight	540.52	692.71	628.43	780.62
Crystal color, habit	Yellow, plate	Yellow, plate	Yellow, needle	Yellow, plate
Crystal size (mm)	0.25 × 0.15 × 0.05	0.38 × 0.20 × 0.10	0.15 × 0.08 × 0.05	0.25 × 0.13 × 0.08
Crystal system	Orthorhombic	Monoclinic	Orthorhombic	Monoclinic
Space group	*Pnma* (no. 62)	*P*2$_1$/*c* (no. 14)	*Pnma* (no. 62)	*P*2$_1$/*c* (no. 14)
Lattice parameters				
a (Å)	12.958(5)	9.008(7)	12.93(2)	8.97(6)
b (Å)	20.76(1)	15.133(10)	20.770(8)	15.10(10)
c (Å)	9.44(4)	25.46(1)	9.43(1)	25.01(8)
α (°)	90	90	90	90
β (°)	90	97.73(6)	90	96.8(5)
γ (°)	90	90	90	90
V (Å^3)	2538(11)	3439(3)	2530(5)	3364(33)
Z	4	4	4	4
D_c (g cm^{-3})	1.414	1.338	1.649	1.541
F_{000}	1120.00	1440.00	1248.00	1568.00
μ (Mo Kα) (cm^{-1})	5.47	4.20	46.01	34.78
Reflections measured	4170	10938	4178	10938
Independent reflections (R_{int})	3795 (0.170)	9986 (0.339)	3804 (0.000)	9979 (0.053)
Number of variables	209	421	160	415
Reflection/parameter ratio	14.46	11.19	14.26	14.33
Residuals: R; R_W	0.119; 0.142	0.262; 0.429	0.116; 0.140	0.093; 0.099
Residuals: R_1	0.056	0.113	0.060	0.054
Number of reflections to calculated R_1	1960 ($I > 2.0\sigma(I)$)	4711 ($I > 2.0\sigma(I)$)	2044 ($I > 2.0\sigma(I)$)	3596 ($I > 2.0\sigma(I)$)
Goodness-of-fit indicator	1.22	1.38	1.44	1.27
$\delta\rho_{max, min}$ (e Å^{-3})	1.57, −1.89	6.89, −8.85	1.52, −7.51	4.04, −3.71

carbon atom. In **3a-W**, hydrogen atoms except H1, H7 and H17 were introduced at the ideal positions. Hydrogen atoms, H1, H7, and H17, were located from difference Fourier maps and not refined. In complexes **3b-Mo** and **3b-W**, hydrogen atoms were introduced at the ideal positions. The methyl hydrogen atoms in **3b-Mo** were refined by using riding models (SHELXL-97) and the rest of hydrogen atoms were fixed at the calculated positions. However the methyl hydrogen atoms in **3b-W** were not able to be refined by using riding models, maybe due to poor crystallinity of it. The crystallinity of the yellow crystals of complex **3b-Mo** was also so poor that high quality intensity data were not obtained. All calculations were performed on an SGI Indy computer using the TEXSAN crystallographic software package of the Molecular Structure Corporation [23].

Appendix A. Supplementary data

ORTEP drawings of tungsten complexes (**3a-W** and **3b-W**) and dinuclear molybdenum complex (**4**) with the atom-numbering scheme have been deposited at the editorial office. Atomic coordinates, thermal parameters, and bond lengths and distances in CIF format have been deposited at the Cambridge Crystallographic Data Center, 12 Union Road, Cambridge CB2 1EZ, UK, fax: +44 1223 336 033, e-mail: deposit@ccdc.cam.ac.uk and copies can be obtained on request, free of charge, by quoting the publication citation and the deposition numbers 277022–277026. Supplementary data associated with this article can be found, in the on-line verison, at doi:10.1016/j.jorganchem.2005.07.015.

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