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# Twisted coordination mode of bis(*N*-heterocyclic carbene) ligands in octahedral geometry of group 6 transition metal complexes: Synthesis, structure, and reactivity

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#### ABSTRACT

On treatment of bis(imidazolium) salts bound by *o*-xylylene, propylene, and ethylene linkers with two moles of LiBEt<sub>3</sub>H, the corresponding BEt<sub>3</sub>-adducts of bis-NHCs, (Et<sub>3</sub>B-ImR)<sub>2</sub>E (Im = imidazole; R = Me, <sup>i</sup>Pr; E = *o*-xylylene, propylene, ethylene) (**2**), were obtained. Reaction of [Mo(CO)<sub>6</sub>] with compound **2** afforded the carbene complex, [Mo(CO)<sub>4</sub>(bis-NHC)] (**3-Mo**), in a good yield. Tungsten and chromium analogs of **3-Mo** were obtained from [M(CO)<sub>4</sub>( $\eta^4$ -norbornadiene)] (M = W, Cr). The X-ray analyses and NMR measurements of these complexes revealed that the bis-NHC ligand adopts a twisted conformation in an octahedral geometry and thus complexes **3** showed a *C*<sub>2</sub>-symmetric structure. In a reaction of **3-Mo** with trimethylphosphite, a CO/P(OMe)<sub>3</sub> substitution reaction took place to give *fac*-[Mo(CO)<sub>3</sub>(bis-NHC)](**9**(OMe)<sub>3</sub>)] (**4-Mo**). The formation of the *fac*-form was found to be caused by a strong electron donor ability of the NHC ligand. The electronic features of the bis-NHC ligand were investigated by X-ray analysis, CO stretching frequency, and cyclic voltammetry of the complex **3-Mo**. Furthermore, we estimated the donor ability of the bis-NHC ligand by comparing with those of 2,2'-bipyridine and 1,2-bis(diphenyl-phosphino)ethane. Density functional calculations (B3LYP/DGDZVP) showed that the *C*<sub>2</sub>-symmetric structure of *o*-xylylene-bridged **3-Mo** having *N*-methyl azole rings was more stable than a *C*<sub>5</sub>-symmetric structure by  $\Delta G = 6.69$  kcal mol<sup>-1</sup>.

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#### 1. Introduction

*N*-Heterocyclic carbenes (NHCs) are now fully established as an important class of ligands for organometallic chemistry, because NHCs enhance the electron density at the metal center with a robust metal–ligand bond. In particular, NHCs emerged as versatile ligands in late transition metal chemistry, proving their high potential in homogeneous catalysis [1]. The use of polydentate ligands containing NHC(s) allowed the preparation of new complexes whose stability is entropically improved by the chelate effect [2]. Most of these polydentate NHCs reported so far are bidentate NHC ligands and there are numerous studies on their late transition metal complexes of Rh, Ir, Ni, Pd, and so on [3,4].

The systematic study on the chelated bis-NHC complexes of late transition metals revealed that the structural properties of coordinated bis-NHC ligands depend on the length and rigidity of the linker unit [3b]. In this study,  $(CH_2)_n$  chains (n = 1-4) were used as the aliphatic linkers to connect two azole rings. For short linkers (n = 1, 2), the NHC ligand tends to prefer a conformation with the azole

rings in (or close to) the *xy* plane, while long linkers (n = 3, 4) allow the azole rings to align more closely with the *z*-axis (perpendicular to the *xy* plane). On the basis of many studies on the coordination chemistry of bis-NHC ligands binding to late transition metals, it has been demonstrated that the orientation of the azole rings adopts either the in-plane conformation (**A-1** in Chart 1) or perpendicular orientation (**A-2** in Chart 1). That is, these complexes have a  $C_{s}$ -symmetric structure.

On the other hand, introducing a rigid chiral linker as a binder of two azole rings in bidentate NHCs effectively led to chiral  $C_2$ -symmetric complexes. A novel family of axially chiral metal complexes with bidentate NHCs such as 1,1'-binaphthyl-2,2'-diamine (BI-NAM) or H<sub>8</sub>-BINAM framework has been developed by Shi and co-workers [5]. They also reported chiral bidentate NHC ligands with biphenyl framework [6]. Their systematic studies on chiral bidentate NHC complexes of Rh, Ir, and Pd revealed that these complexes operate as excellent catalysts for asymmetric organic transformations.

Compared with numerous reports on bis-NHC complexes of late transition metals, only a limited number of reports has been published on bis-NHC complexes of group 6 transition metals. In most of them, the methylene group was the linker of the bidentate



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Chart 1. Coordination modes of bis-NHC ligand.

ligand [7]. Hahn and co-workers reported the preparation of the molybdenum complex coordinated by a propylene-bridged bidentate NHC and revealed that the complex adopts the twisted conformation of two azole rings, i.e., the  $C_2$ -symmetric coordination mode in an octahedral geometry (**B** in Chart 1) [8]. However, to our best of knowledge, there is no systematic study on the coordination modes of bis-NHC ligands in group 6 transition metals.

We have recently reported the preparation of chiral *o*-xylylenebridged bis-NHC ligands, derived from chiral 1,4-diol,1,2-bis-(1hydroxypropyl)benzene, and their molybdenum complexes. The report revealed that these molybdenum complexes show the chiral  $C_2$ -symmetric structure in an octahedral geometry [9]. In this paper, we describe the results of the systematic investigation on the synthesis, structure, and reactivity of group 6 transition metal complexes having chelated bidentate NHC with *o*-xylylene, propylene, and ethylene linkers.

In the preparation of NHC complexes, the use of free NHCs, either isolated or generated *in situ* by the deprotonation of the corresponding salts, is one of the most common methods. However, manipulation of free NHCs is often difficult due to their highly reactive nature toward air and moisture. Therefore employing NHC adducts as protected forms of free NHC attracted much attention for the preparation of NHC complexes [10]. The most promising procedure for the preparation of the NHC complex to such late transition metals as Rh, Ir, Pd, and so on [11]. We have already reported the preparation of the efficient NHC transfer reagent, the BEt<sub>3</sub>-adduct of NHC [12]. In this paper, we also report the preparation of the Synthesis of bis-NHC complexes of group 6 transition metals.

#### 2. Experimental

#### 2.1. 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. 1,2-Bis(imidazolylmethyl)benzene [4c], **1a** [4c], **1d** [13], **2a** [12a], [W(CO)<sub>4</sub>( $\eta^4$ -C<sub>7</sub>H<sub>8</sub>)] [14], [Cr(CO)<sub>4</sub>( $\eta^4$ -C<sub>7</sub>H<sub>8</sub>)] [15], [Mo(CO)<sub>4</sub> (bpy)] [16], and [Mo(CO)<sub>4</sub>(dppe)] [17] were prepared according to literature methods.

IR spectra were recorded on a HORIBA FT-730 spectrometer. <sup>1</sup>H, <sup>13</sup>C{<sup>1</sup>H}, <sup>31</sup>P{<sup>1</sup>H} and <sup>11</sup>B{<sup>1</sup>H} NMR spectra were recorded on a JEOL EX-270 spectrometer at ambient temperature, unless otherwise mentioned. <sup>95</sup>Mo NMR spectra were recorded on a JEOL ECA-600 spectrometer. <sup>1</sup>H and <sup>13</sup>C{<sup>1</sup>H} NMR chemical shifts were recorded in ppm relative to internal Me<sub>4</sub>Si. <sup>31</sup>P{<sup>1</sup>H}, <sup>11</sup>B{<sup>1</sup>H}, and <sup>95</sup>Mo NMR chemical shifts were recorded in ppm relative to internal Me<sub>4</sub>Si. <sup>31</sup>P{<sup>1</sup>H}, <sup>11</sup>B{<sup>1</sup>H}, and <sup>95</sup>Mo NMR chemical shifts were recorded in ppm relative to external H<sub>3</sub>PO<sub>4</sub>, BF<sub>3</sub>·OEt<sub>2</sub>, and Na<sub>2</sub>MoO<sub>4</sub>, respectively. All coupling constants were recorded in Hz. Cyclic voltammograms were recorded on HECS 317S, 321, and 326 in CH<sub>3</sub>CN containing 0.1 M Bu<sub>4</sub>NBF<sub>4</sub> as a supporting electrolyte by using a conventional three-electrode system, platinum ( $\Phi$  = 1.6 mm, working electrode), platinum wire (counter electrode), and Ag/AgCl (reference electrode) at 100 mV/ s scan rate. Potentials are given *vs.* Fc/Fc<sup>+</sup>. Elemental analyses were performed on a Perkin Elmer 240C.

#### 2.2. Preparation of bis(imidazolium) salts 1

#### 2.2.1. Preparation of 1b

1,2-Bis(imidazolylmethyl)benzene (215 mg, 0.90 mmol), DME (15 mL), and 2-iodopropane (2.0 mL, 3.4 g, 20.0 mmol) were put in a Schlenk tube. The reaction mixture was refluxed for 8 h, and then the volatiles were removed under reduced pressure. The residual solid was washed with hexane ( $3 \times 5$  mL) and dried in vacuo to yield **1b** as a white solid (446 mg, 0.77 mmol, 86%). *Anal.* Calc. for C<sub>20</sub>H<sub>28</sub>I<sub>2</sub>N<sub>4</sub>: C, 41.54; H, 4.88; N, 9.69. Found: C, 41.31; H, 4.97; N, 9.58%. <sup>1</sup>H NMR (in CDCl<sub>3</sub>)  $\delta$  1.65 (d, J = 6.6 Hz, 12H, <sup>i</sup>Pr-CH<sub>3</sub>), 4.81 (sept, J = 6.6 Hz, 2H, <sup>i</sup>Pr-CH), 6.11 (s, 4H, -CH<sub>2</sub>-), 7.25-7.29 (m, 2H, Ph), 7.42-7.46 (m, 2H, Ph), 7.45 (s, 2H, CH=CH), 7.71 (s, 2H, CH=CH), 10.00 (s, 2H, NCHN). <sup>13</sup>C{<sup>1</sup>H} NMR (in CDCl<sub>3</sub>)  $\delta$  23.1 (<sup>i</sup>Pr-CH<sub>3</sub>), 51.0, 53.8 (<sup>i</sup>Pr-CH, -CH<sub>2</sub>-), 120.4, 123.0, 129.9, 130.2, 131.8, 134.7 (CH=CH, Ph, NCHN).

#### 2.2.2. Preparation of 1c

1,3-Dibromopropane (1743 mg, 0.88 mL, 8.63 mmol), 1-methylimidazole (2.0 mL, 2.0 g, 24.4 mmol) and ethanol (15 mL) were put in a Schlenk tube. The reaction mixture was refluxed for 10 h, and then the volatiles were removed under reduced pressure. The residual solid was washed with toluene ( $4 \times 10$  mL) and dried in vacuo to yield **1c** as a white solid (2798 mg, 7.64 mmol, 89%). *Anal.* Calc. for C<sub>11</sub>H<sub>18</sub>Br<sub>2</sub>N<sub>4</sub>: C, 36.09; H, 4.96; N, 15.30. Found: C, 36.00; H, 5.07; N, 15.28%. <sup>1</sup>H NMR (in DMSO-d<sub>6</sub>)  $\delta$  2.40 (quint, *J* = 7.3 Hz, 2H, -CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>-), 3.86 (s, 6H, CH<sub>3</sub>), 4.25 (t, *J* = 7.3 Hz, 4H, -CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>-), 7.31 (s, 2H, CH=CH), 7.80 (s, 2H, CH=CH), 9.24 (s, 2H, NCHN). <sup>13</sup>C{<sup>1</sup>H} NMR (in DMSO-d<sub>6</sub>)  $\delta$  29.5 (-CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>-), 35.8 (CH<sub>3</sub>), 45.6 (-CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>-), 121.9 (CH=CH), 123.4 (CH=CH), 136.6 (NCHN).

#### 2.3. Preparation of BEt<sub>3</sub>-adducts of bis-NHC compounds 2

#### 2.3.1. Preparation of 2b

Compound **1b** (155 mg, 0.27 mmol) was put in a Schlenk tube, which was attached to a high-vacuum line. THF (ca. 10 mL) was added by a trap-to-trap-transfer technique at -78 °C. At this temperature, LiBEt<sub>3</sub>H (0.54 mL of its 1.0 M THF solution, 0.54 mmol) was added by syringe. Then the reaction mixture was allowed to warm to room temperature. After being stirred for 16 h at room temperature, the volatiles were removed under reduced pressure. The residual solid was washed with distilled water (3 × 10 mL)

and dried in vacuo to yield **2b** as a white solid (133 mg, 0.26 mmol, 96%). *Anal.* Calc. for  $C_{32}H_{56}B_2N_4$ : C, 74.13; H, 10.89; N, 10.81. Found: C, 73.94; H, 11.39; N, 10.78%. <sup>1</sup>H NMR (in CDCl<sub>3</sub>)  $\delta$  0.47 (quint, *J* = 7.3 Hz, 12H, BCH<sub>2</sub>CH<sub>3</sub>), 0.61 (t, *J* = 7.3 Hz, 18H, BCH<sub>2</sub>CH<sub>3</sub>), 1.43 (d, *J* = 7.3 Hz, 12H, <sup>i</sup>Pr-CH<sub>3</sub>), 5.44 (s, 4H, -CH<sub>2</sub>-), 5.50 (sept, *J* = 7.3 Hz, 2H, <sup>i</sup>Pr-CH), 6.60 (d, *J* = 2.0 Hz, 2H, CH=CH), 6.91 (dd, *J* = 5.3, 3.3 Hz, 2H, Ph), 6.98 (d, *J* = 2.0 Hz, 2H, CH=CH), 7.29 (dd, *J* = 5.3, 3.3 Hz, 2H, Ph). <sup>13</sup>C{<sup>1</sup>H} NMR (in CDCl<sub>3</sub>)  $\delta$  11.5 (BCH<sub>2</sub>CH<sub>3</sub>), 14.5 (br, BCH<sub>2</sub>CH<sub>3</sub>), 23.8 (<sup>i</sup>Pr-CH<sub>3</sub>), 49.0, 50.3 (<sup>i</sup>Pr-CH, -CH<sub>2</sub>-), 116.2 (CH=CH), 120.9 (CH=CH), 128.0, 128.2, 134.3 (Ph), 175.6 (br, NCN). <sup>11</sup>B{<sup>1</sup>H} NMR (in CDCl<sub>3</sub>)  $\delta$  -12.2 (BEt<sub>3</sub>).

#### 2.3.2. Preparation of 2c

This compound was prepared form **1c** (545 mg, 1.49 mmol) and LiBEt<sub>3</sub>H (3.00 mL of its 1.0 M THF solution, 3.00 mmol) using THF (ca. 15 mL) as a solvent in the same manner as that for **2b**. Compound **2c** was isolated as a white solid (560 mg, 1.40 mmol, 94%). *Anal.* Calc. for C<sub>23</sub>H<sub>46</sub>B<sub>2</sub>N<sub>4</sub>: C, 69.02; H, 11.58; N, 14.00. Found: C, 68.53; H, 11.63; N, 14.03%. <sup>1</sup>H NMR (in CDCl<sub>3</sub>)  $\delta$  0.44 (quint, *J* = 7.3 Hz, 12H, BCH<sub>2</sub>CH<sub>3</sub>), 0.63 (t, *J* = 7.3 Hz, 18H, BCH<sub>2</sub>CH<sub>3</sub>), 2.25 (m, 2H, -CH<sub>2</sub>-), 3.85 (s, 6H, CH<sub>3</sub>), 4.30 (t, *J* = 7.9 Hz, 4H, -CH<sub>2</sub>-), 6.74 (d, *J* = 2.0 Hz, 2H, CH=CH), 6.76 (d, *J* = 2.0 Hz, 2H, CH=CH). <sup>13</sup>C{<sup>1</sup>H} NMR (in CDCl<sub>3</sub>)  $\delta$  11.4 (BCH<sub>2</sub>CH<sub>3</sub>), 14.1 (br, BCH<sub>2</sub>CH<sub>3</sub>), 37.9, 46.2, 68.1 (CH<sub>3</sub>, -CH<sub>2</sub>-), 119.5 (CH=CH), 122.4 (CH=CH), 175.9 (br, NCN). <sup>11</sup>B{<sup>1</sup>H} NMR(in CDCl<sub>3</sub>)  $\delta$  -12.5 (BEt<sub>3</sub>).

#### 2.3.3. Preparation of 2d

This compound was prepared from **1d** (200 mg, 0.57 mmol) and LiBEt<sub>3</sub>H (1.15 mL of its 1.0 M THF solution, 1.15 mmol) using THF (ca. 10 mL) as a solvent in the same manner as that for **2b**. Compound **2d** was isolated as a white solid (210 mg, 0.54 mmol, 96%). *Anal.* Calc. for C<sub>22</sub>H<sub>44</sub>B<sub>2</sub>N<sub>4</sub>: C, 68.41; H, 11.48; N, 14.51. Found: C, 68.15; H, 11.95; N, 14.50%. <sup>1</sup>H NMR (in CDCl<sub>3</sub>)  $\delta$  0.50 (quint, *J* = 6.6 Hz, 12H, BCH<sub>2</sub>CH<sub>3</sub>), 0.67 (t, *J* = 6.6 Hz, 18H, BCH<sub>2</sub>CH<sub>3</sub>), 3.88(s, 6H, CH<sub>3</sub>), 4.59 (s, 4H, -CH<sub>2</sub>-), 6.71 (d, *J* = 2.0 Hz, 2H, CH=CH), 6.73 (d, *J* = 2.0 Hz, 2H, CH=CH). <sup>13</sup>C{<sup>1</sup>H} NMR (in CDCl<sub>3</sub>)  $\delta$  11.5 (BCH<sub>2</sub>CH<sub>3</sub>), 14.5 (br, BCH<sub>2</sub>CH<sub>3</sub>), 38.0 (CH<sub>3</sub>), 49.7 (-CH<sub>2</sub>-), 120.4 (CH=CH), 122.4 (CH=CH), 176.5 (br, NCN). <sup>11</sup>B{<sup>1</sup>H} NMR(in CDCl<sub>3</sub>)  $\delta$  -12.5 (BEt<sub>3</sub>).

#### 2.4. Preparation of [M(CO)<sub>4</sub>(bis-NHC)] complexes 3

#### 2.4.1. Preparation of **3a-Mo**

Mo(CO)<sub>6</sub> (91 mg, 0.34 mmol), 2a (162 mg, 0.35 mmol), and heptane (10 mL) were put in a Schlenk tube. After being refluxed for 6 h, the volatiles were removed under reduced pressure. The residual solid was washed with hexane  $(3 \times 10 \text{ mL})$  and dried in vacuo to give **3a-Mo** as a yellow solid (138 mg, 0.29 mmol, 85%). Anal. Calc. for C<sub>20</sub>H<sub>18</sub>MoN<sub>4</sub>O<sub>4</sub>: C, 50.64; H, 3.83; N, 11.81. Found: C, 50.51; H, 3.87; N, 11.87%. IR (KBr) v<sub>CO</sub> 1999, 1896, 1847, and 1788 cm<sup>-1</sup>. <sup>1</sup>H NMR (in DMSO-d<sub>6</sub>)  $\delta$  3.96 (s, 6H, CH<sub>3</sub>), 4.71 (d, J = 13.9 Hz, 2H,  $-CH_2-$ ), 5.42 (d, J = 13.9 Hz, 2H,  $-CH_2-$ ), 6.90 (d, *I* = 1.3 Hz, 2H, CH=CH), 7.29 (d, *I* = 1.3 Hz, 2H, CH=CH), 7.34 (dd, I = 5.3, 3.3 Hz, 2H, Ph), 7.48 (dd, I = 5.3, 3.3 Hz, 2H, Ph).  ${}^{13}C{}^{1}H{}$ NMR (in DMSO-d<sub>6</sub>, at 60 °C) δ 51.5 (-CH<sub>2</sub>-), 120.1, 124.1, 128.2, 131.1, 136.3 (CH=CH, Ph), 191.5 (NCN), 210.3 (CO), 218.8 (CO). Methyl carbons on the imidazole rings were not able to detect due to an overlap with solvent signals. <sup>95</sup>Mo NMR (in DMSO-d<sub>6</sub>)  $\delta - 1657 (W_{1/2} = 6 \text{ Hz}).$ 

#### 2.4.2. Preparation of 3b-Mo

This compound was prepared from  $Mo(CO)_6$  (42 mg, 0.16 mmol) and **2b** (85 mg, 0.16 mmol) using heptane (5 mL) as a solvent in the same manner as that for **3a-Mo**. Complex **3b-Mo** was isolated as a yellow solid (70 mg, 0.13 mmol, 81%). *Anal.* Calc. for  $C_{24}H_{26}MoN_4O_4$ : C, 54.34; H, 4.94; N, 10.56. Found: C, 54.45; H,

4.71; N, 10.82%. IR (KBr)  $v_{CO}$  1998, 1877, 1849, 1802 cm<sup>-1</sup>. <sup>1</sup>H NMR (in CDCl<sub>3</sub>)  $\delta$  1.40 (d, J = 6.6 Hz, 6H, <sup>i</sup>Pr–CH<sub>3</sub>), 1.52 (d, J = 6.6 Hz, 6H, <sup>i</sup>Pr–CH<sub>3</sub>), 4.45 (d, J = 14.5 Hz, 2H,  $-CH_2-$ ), 5.74 (d, J = 14.5 Hz, 2H,  $-CH_2-$ ), 5.96 (sept, J = 6.6 Hz, 2H, <sup>i</sup>Pr–CH), 6.67 (d, J = 2.0 Hz, 2H, CH=CH), 6.96 (d, J = 2.0 Hz, 2H, CH=CH), 7.3 (m, 4H, Ph). <sup>13</sup>C{<sup>1</sup>H} NMR (in CDCl<sub>3</sub>)  $\delta$  22.7 (<sup>i</sup>Pr–CH<sub>3</sub>), 23.8 (<sup>i</sup>Pr–CH<sub>3</sub>), 51.1, 52.3 (<sup>i</sup>Pr–CH,  $-CH_2-$ ), 119.2, 121.6, 128.4, 131.3, 136.7 (CH=CH, Ph), 189.6 (NCN), 210.4 (CO), 218.5 (CO). <sup>95</sup>Mo NMR (in DMSO-d<sub>6</sub>)  $\delta$  –1637 ( $W_{1/2} = 6$  Hz).

#### 2.4.3. Preparation of 3c-Mo

This compound was prepared from Mo(CO)<sub>6</sub> (85 mg, 0.32 mmol) and **2c** (129 mg, 0.32 mmol) using heptane (10 mL) as a solvent in the same manner as that for **3a-Mo**. Complex **3c-Mo** was isolated as a yellow solid (113 mg, 0.27 mmol, 84%). Anal. Calc. for C<sub>15</sub>H<sub>16</sub>MoN<sub>4</sub>O<sub>4</sub>: C, 43.70; H, 3.91; N, 13.59. Found: C, 43.38; H, 4.16; N, 13.53%. IR (KBr)  $v_{CO}$  1993, 1879, 1844, 1792 cm<sup>-1</sup>. <sup>1</sup>H NMR (in acetone-d<sub>6</sub>)  $\delta$  1.81 (quint, *J* = 4.6 Hz, 2H, -CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>-), 3.96 (t, *J* = 4.6 Hz, 4H, -CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>-), 4.06 (s, 6H, CH<sub>3</sub>), 7.22 (d, *J* = 1.3 Hz, 2H, CH=CH), 7.32 (d, *J* = 1.3 Hz, 2H, CH=CH). <sup>13</sup>C{<sup>1</sup>H} NMR (in acetone-d<sub>6</sub>)  $\delta$  35.0, 40.4, 46.0 (-CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>-, -CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>-, CH<sub>3</sub>), 121.1 (CH=CH), 124.8 (CH=CH), 191.7 (NCN), 211.4 (CO), 220.3 (CO). <sup>95</sup>Mo NMR (in DMSO-d<sub>6</sub>)  $\delta$  -1649 ( $W_{1/2}$  = 7 Hz).

#### 2.4.4. Preparation of 3d-Mo

This compound was prepared from Mo(CO)<sub>6</sub> (47 mg, 0.18 mmol) and **2d** (70 mg, 0.18 mmol) using heptane (10 mL) as a solvent in the same manner as that for **3a-Mo**. Complex **3d-Mo** was isolated as a yellow solid (50 mg, 0.13 mmol, 72%). *Anal.* Calc. for C<sub>14</sub>H<sub>14</sub>MoN<sub>4</sub>O<sub>4</sub>: C, 42.22; H, 3.54; N, 14.07. Found: C, 42.05; H, 3.67; N, 14.02%. IR (KBr)  $\nu_{CO}$  1991, 1874, 1844, 1804 cm<sup>-1</sup>. <sup>1</sup>H NMR (in DMSO-d<sub>6</sub>)  $\delta$  3.80 (s, 6H, CH<sub>3</sub>), 4.62 (s, 4H, -CH<sub>2</sub>CH<sub>2</sub>-), 7.26 (s, 2H, CH=CH), 7.29 (s, 2H, CH=CH). <sup>13</sup>C{<sup>1</sup>H} NMR (in CD<sub>3</sub>CN)  $\delta$  40.2 (CH<sub>3</sub>), 50.5 (-CH<sub>2</sub>CH<sub>2</sub>-), 122.8 (CH=CH), 123.7 (CH=CH), 191.7 (NCN), 212.2 (CO), 220.6 (CO).

#### 2.4.5. Preparation of 3a-W

This compound was prepared from  $[W(CO)_4(\eta^4-nbd)]$  (71 mg, 0.18 mmol) and **2a** (88 mg, 0.19 mmol) using heptane (5 mL) as a solvent in the same manner as that for **3a-Mo**. Complex **3a-W** was isolated as a yellow solid (45 mg, 0.08 mmol, 44%). IR (KBr)  $v_{CO}$  1994, 1885, 1839, 1780 cm<sup>-1</sup>. <sup>1</sup>H NMR (in DMSO-d<sub>6</sub>)  $\delta$  3.30 (s, 6H, CH<sub>3</sub>), 4.72 (d, *J* = 13.8 Hz, 2H, -CH<sub>2</sub>-), 5.34 (d, *J* = 13.8 Hz, 2H, -CH<sub>2</sub>-), 6.90 (d, *J* = 2.0 Hz, 2H, CH=CH), 7.31 (d, *J* = 2.0 Hz, 2H, CH=CH), 7.34 (dd, *J* = 5.3, 3.3 Hz, 2H, Ph), 7.47 (dd, *J* = 5.3, 3.3 Hz, 2H, Ph). <sup>13</sup>C{<sup>1</sup>H} NMR (in DMSO-d<sub>6</sub>)  $\delta$  52.2 (-CH<sub>2</sub>-), 120.3, 124.4, 128.5, 131.3, 136.4 (CH=CH, Ph), 183.7 (NCN), 203.7 (CO), 210.7 (CO). Methyl carbons on the NHC rings were not able to be detected due to an overlap with solvent signals. Correct elemental analysis data of this complex could not be obtained, though satisfactory spectroscopic data were obtained.

#### 2.4.6. Preparation of **3a-Cr**

This compound was prepared from  $[Cr(CO)_4(\eta^4-nbd)]$  (59 mg, 0.23 mmol) and **2a** (116 mg, 0.25 mmol) using heptane (10 mL) as a solvent in the same manner as that for **3a-Mo**. Complex **3a-Cr** was isolated as a yellow solid (55 mg, 0.13 mmol, 57%). IR (KBr)  $v_{CO}$  1986, 1926, 1845, 1791 cm<sup>-1</sup>. <sup>1</sup>H NMR (in DMSO-d<sub>6</sub>)  $\delta$  3.99 (s, 6H, CH<sub>3</sub>), 4.70 (d, J = 13.8 Hz, 2H,  $-CH_2-$ ), 5.18 (d, J = 2.0 Hz, 2H, CH=CH), 7.31 (dd, J = 5.3, 3.3 Hz, 2H, Ph), 7.44 (m, 2H, Ph). <sup>13</sup>C{<sup>1</sup>H} NMR (in DMSO-d<sub>6</sub>)  $\delta$  51.1 ( $-CH_2-$ ), 121.1, 125.0, 128.3, 131.0, 136.6 (CH=CH, Ph), 196.4 (NCN), 222.8 (CO), 228.1 (CO). Methyl carbons on the NHC rings were not able to be detected due to an overlap with solvent signals. Correct elemental

analysis data of this complex could not be obtained due to highly hygroscopic nature, though satisfactory spectroscopic data were obtained.

#### 2.5. Preparation of [Mo(CO)<sub>3</sub>(bis-NHC)(phosphite)] complexes 4-Mo

#### 2.5.1. Preparation of 4a-Mo

**3a-Mo** (55 mg, 0.12 mmol), trimethylphosphite (30 µL, 32 mg, 0.26 mmol), and toluene (5 mL) were put in a Schlenk tube. After being refluxed for 3 h, the volatiles were removed under reduced pressure. The residual solid was washed with hexane ( $3 \times 5$  mL) and dried in vacuo to give **4a-Mo** as a white solid (40 mg, 0.070 mmol, 58%). IR (KBr)  $v_{CO}$  1913, 1806, 1765 cm<sup>-1</sup>. <sup>1</sup>H NMR (in DMSO-d<sub>6</sub>)  $\delta$  3.33 (d, J = 10.6 Hz, 9H, P(OCH<sub>3</sub>)<sub>3</sub>), 3.92 (s, 3H, CH<sub>3</sub>), 4.03 (s, 3H, CH<sub>3</sub>), 4.44 (d, J = 14.5 Hz, <sup>1</sup>H, -CH<sub>2</sub>–), 4.58 (d, J = 13.8 Hz, <sup>1</sup>H, -CH<sub>2</sub>–), 5.54 (d, J = 14.5 Hz, <sup>1</sup>H, -CH<sub>2</sub>–), 5.65 (d, J = 13.8 Hz, <sup>1</sup>H, -CH<sub>2</sub>–), 6.8–7.6 (m, 8H, CH=CH, Ph). <sup>31</sup>P{<sup>1</sup>H} NMR (in CDCl<sub>3</sub>)  $\delta$  167.9 (P(OCH<sub>3</sub>)<sub>3</sub>). <sup>13</sup>C{<sup>1</sup>H} NMR data of this complex were not obtained due to its low solubility and correct elemental analysis data of this complex were not able to be obtained.

#### 2.5.2. Preparation of 4b-Mo

This compound was prepared from **3b-Mo** (50 mg, 0.094 mmol) and trimethylphosphite (15  $\mu$ L, 16 mg, 0.13 mmol) using toluene (10 mL) as a solvent in the same manner as that for **4a-Mo**. Complex **4b-Mo** was isolated as a yellow solid (30 mg, 0.048 mmol, 51%). *Anal*. Calc. for C<sub>26</sub>H<sub>35</sub>MoN<sub>4</sub>O<sub>6</sub>P: C, 49.85; H, 5.63; N, 8.94. Found: C, 50.03; H, 5.41; N, 8.56%. IR (KBr)  $\nu_{CO}$  1917, 1814, 1775 cm<sup>-1</sup>. <sup>1</sup>H NMR (in CDCl<sub>3</sub>)  $\delta$  1.36 (d, *J* = 6.6 Hz, 3H, <sup>i</sup>Pr–Me), 1.42 (d, *J* = 6.6 Hz, 3H, <sup>i</sup>Pr–Me), 1.50 (d, *J* = 6.6 Hz, 6H, <sup>i</sup>Pr–Me), 3.43 (d, *J* = 10.6 Hz, 9H, P(OCH<sub>3</sub>)<sub>3</sub>), 4.29 (d, *J* = 14.5 Hz, <sup>1</sup>H, -CH<sub>2</sub>–), 4.38 (d, *J* = 14.5 Hz, <sup>1</sup>H, -CH<sub>2</sub>–), 5.75 (sept, *J* = 6.6 Hz, <sup>1</sup>H, <sup>i</sup>Pr–CH), 5.86 (d, *J* = 14.5 Hz, <sup>1</sup>H, -CH<sub>2</sub>–), 5.87 (d, *J* = 14.5 Hz, <sup>1</sup>H, -CH<sub>2</sub>–), 6.32 (sept, *J* = 6.6 Hz, <sup>1</sup>H, <sup>1</sup>NMR (in CDCl<sub>3</sub>)  $\delta$  23.4, 23.6, 25.0 (<sup>i</sup>Pr–CH<sub>3</sub>), 50.4 (d, *J* = 2.2 Hz, P(OCH<sub>3</sub>)<sub>3</sub>), 52.3, 52.5, 52.8, 53.1 (<sup>i</sup>Pr–CH, -CH<sub>2</sub>–), 117.7, 118.0, 120.0, 120.3 (CH=CH), 128.5, 130.7, 131.1, 137.5, 137.7 (Ph), 195.7 (d, *J* = 13.4 Hz, NCN), 196.7 (d,

| Table I |
|---------|
|---------|

| Summary of cryst | al data for com | pounds 2b, 3a-Mo | , 3b-Mo, 4 | 4b-Mo and 4c-Mo. |
|------------------|-----------------|------------------|------------|------------------|
|------------------|-----------------|------------------|------------|------------------|

*J* = 15.7 Hz, NCN), 219.2 (d, *J* = 59.2 Hz, CO), 220.5 (d, *J* = 12.3 Hz, CO), 221.1 (d, *J* = 13.4 Hz, CO). <sup>31</sup>P{<sup>1</sup>H} NMR (in CDCl<sub>3</sub>)  $\delta$  168.8 (P(OCH<sub>3</sub>)<sub>3</sub>).

#### 2.5.3. Preparation of 4c-Mo

This compound was prepared from **3c-Mo** (52 mg, 0.13 mmol) and trimethylphosphite (22 µL, 23 mg, 0.19 mmol) using toluene (10 mL) as a solvent in the same manner as that for 4a-Mo. Complex **4c-Mo** was isolated as a white solid (63 mg, 0.12 mmol, 92%). Anal. Calc. for C<sub>17</sub>H<sub>25</sub>MoN<sub>4</sub>O<sub>6</sub>P: C, 40.17; H, 4.96; N, 11.02. Found: C, 40.11; H, 5.04; N, 10.95%. IR (KBr) v<sub>CO</sub> 1900, 1797, 1752 cm<sup>-1</sup>. <sup>1</sup>H NMR (in acetone-d<sub>6</sub>)  $\delta$  1.73 (m, 2H, -CH<sub>2</sub>CH<sub>2</sub>-H<sub>2</sub>-), 3.34 (d, J = 10.6 Hz, 9H, P(OCH<sub>3</sub>)<sub>3</sub>), 3.58 (m, 4H, -CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>-), 4.03 (s, 3H, CH<sub>3</sub>), 4.14 (s, 3H, CH<sub>3</sub>), 7.11 (d, J = 1.3 Hz, 1H, CH=CH), 7.15 (d, J = 1.3 Hz, 1H, CH=CH), 7.19 (d, J = 1.3 Hz, 1H, CH=CH), 7.26 (d, J = 1.3 Hz, 1H, CH=CH). <sup>13</sup>C{<sup>1</sup>H} NMR (in DMSO-d<sub>6</sub>)  $\delta$ 34.3, 44.6, 45.1, 50.7, 50.9 (-CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>-, CH<sub>3</sub>), 50.0 (d, *J* = 2.2 Hz, P(OCH<sub>3</sub>)<sub>3</sub>), 120.1, 120.6, 123.7, 123.9 (CH=CH), 194.1 (d, J = 16.2 Hz, NCN), 194.4 (d, J = 12.9 Hz, NCN), 220.9 (d, J = 57.6 Hz, CO), 221.8 (d, J = 11.7 Hz, CO), 222.4 (d, J = 14.0 Hz, CO).  ${}^{31}P{}^{1}H{}$  NMR (in CDCl<sub>3</sub>)  $\delta$  170.9 (P(OCH<sub>3</sub>)<sub>3</sub>).

#### 2.6. Experimental procedure for X-ray crystallography

Suitable single crystals were obtained by recrystallization from hexane (**2b**), from CH<sub>3</sub>CN (**3a-Mo**), from toluene–hexane (**3b-Mo**), or from CH<sub>2</sub>Cl<sub>2</sub> (**4b-Mo**, **4c-Mo**), in a refrigerator and are individually mounted on glass fibers. Diffraction measurements of all compounds were made on a Rigaku AFC-7R automated four-circle diffractometer by using graphite-monochromated Mo K<sub> $\alpha$ </sub> radiation ( $\lambda = 0.71069$ ). The data collections were carried out at  $-50 \pm 2 \,^{\circ}$ C using the  $\omega - 2\theta$  scan technique to a maximum  $2\theta$  value of 55.0° for all crystals. Cell constants and an orientation matrix for data collection were determined from 25 reflections with  $2\theta$  angles in the range 22.39–25.01° for **2b**, 29.75–29.96° for **3a-Mo**, 29.58–29.99° for **3b-Mo**, 26.92–29.72° for **4b-Mo**, and 29.58–29.98° for **4c-Mo**. Three standard reflections were monitored at every 150

|  | 2b  | За-Мо   | 3b-Mo   | 4b-Mo   | 4c-Mo   |
|--|---|---|---|---|---|
| Empirical formula                                | C <sub>32</sub> H <sub>56</sub> B <sub>2</sub> N <sub>4</sub> | C <sub>20</sub> H <sub>18</sub> MoN <sub>4</sub> O <sub>4</sub> | C <sub>24</sub> H <sub>26</sub> MoN <sub>4</sub> O <sub>4</sub> | C <sub>26</sub> H <sub>35</sub> MoN <sub>4</sub> O <sub>6</sub> P | C <sub>17</sub> H <sub>25</sub> MoN <sub>4</sub> O <sub>6</sub> P |
| Formula weight                                   | 518.44  | 4/4.33  | 530.43  | 626.50  | 508.32  |
| Crystal color, habit                             | colorless, plate  | yellow, plate   | yellow, needle  | colorless, plate  | yellow, needle  |
| Crystal size/mm                                  | $0.25 \times 0.20 \times 0.13$                                | $0.50 \times 0.25 \times 0.08$                                  | $0.58 \times 0.10 \times 0.10$                                  | $0.25 \times 0.25 \times 0.08$                                    | $0.25 \times 0.13 \times 0.13$                                    |
| Crystal system                                   | monoclinic  | monoclinic  | monoclinic  | monoclinic  | monoclinic  |
| Space group                                      | $P2_1/c$ (No. 14)   | $P2_1/c$ (No. 14)   | $C_2/c$ (No. 15)  | $P2_1/c$ (No. 14)   | $P2_1/n$ (No. 14)   |
| Lattice parameters                               |   |   |   |   | 0.000/=)  |
| a (A)  | 18.129(9)   | 13.900(5)   | 16.590(9)   | 14.32(1)  | 9.633(7)  |
| b (A)  | 13.20(2)  | 9.108(4)  | 12.579(7)   | 12.49(2)  | 14.182(9)   |
| <i>c</i> (A)                                     | 14.472(9)   | 16.917(4)   | 12.574(9)   | 16.642(8)   | 15.50(2)  |
| $\beta$ (°)                                      | 106.89(4)   | 109.52(2)   | 114.94(4)   | 92.79(5)  | 96.52(7)  |
| V (A <sup>3</sup> )                              | 3314(5)   | 2018(2)   | 2379(3)   | 2974(3)   | 2104(3)   |
| Z  | 4   | 4   | 4   | 4   | 4   |
| $D_{\rm c} ({\rm g}{\rm cm}^{-3})$               | 1.039   | 1.561   | 1.481   | 1.399   | 1.605   |
| F(000)   | 1144.00   | 960.00  | 1088.00   | 1296.00   | 1040.00   |
| $\mu$ (Mo K $\alpha$ ) (cm <sup>-1</sup> )       | 0.597   | 6.825   | 5.876   | 5.377   | 7.394   |
| Index ranges                                     | $-23 \leqslant h \leqslant 22$                                | $0 \leqslant h \leqslant 18$                                    | $0 \leqslant h \leqslant 21$                                    | $-18 \leqslant h \leqslant 0$                                     | $0 \leqslant h \leqslant 12$                                      |
|  | $0 \leqslant k \leqslant 17$                                  | $-11\leqslant k\leqslant 0$                                     | $0 \leqslant k \leqslant 16$                                    | $0 \leqslant k \leqslant 16$                                      | $-18\leqslant k\leqslant 18$                                      |
|  | $0 \leqslant l \leqslant 18$                                  | $-21\leqslant l\leqslant 20$                                    | $-16 \leqslant l \leqslant 14$                                  | $-21 \leqslant l \leqslant 21$                                    | $-20 \leqslant l \leqslant 20$                                    |
| Reflections measured                             | 7931  | 4811  | 2832  | 7073  | 10018   |
| Independent reflections $(R_{int})$              | 7627 (0.0787)   | 4625 (0.0323)   | 2742 (0.0361)   | 6808 (0.0624)   | 4839 (0.1116)   |
| No. variables                                    | 399   | 280   | 163   | 378   | 287   |
| Reflection/parameter ratio                       | 19.12   | 16.52   | 16.82   | 18.01   | 16.86   |
| Residuals: R; R <sub>W</sub>                     | 0.2350; 0.1723  | 0.0397; 0.0898  | 0.0400; 0.0968  | 0.1260; 0.1834  | 0.0952; 0.1883  |
| Residuals: $R_1 [I > 2\sigma](I)$ ]              | 0.0703  | 0.0299  | 0.0333  | 0.0632  | 0.0579  |
| Goodness-of-fit (GOF) on $F^2$                   | 1.079   | 1.039   | 1.026   | 1.051   | 0.896   |
| $\delta  ho_{ m max,\ min}$ (e Å <sup>-3</sup> ) | 1.30, -1.22   | 0.62, -1.29   | 0.45, -1.18   | 1.68, -1.98   | 2.09, -2.44   |

measurements. The data were corrected for Lorentz and polarization effects.

Crystallographic data and the results of measurements are summarized in Table 1. The structures were solved by direct methods (SIR 92) [18] for **2b** and **4b-Mo** or by direct methods (SIR 97) [19] for **3a-Mo**, **3b-Mo**, and **4c-Mo** and expanded using Fourier techniques. The non-hydrogen atoms were refined anisotropically. Hydrogen atoms were introduced at the ideal positions and refined by using the riding model. All calculations were performed using the CrystalStructure [20,21] crystallographic software package.

#### 2.7. DFT calculations

Density functional theory (DFT) [22] calculations were performed with the hybrid Becke's three-parameter exchange functional [23] and the Lee–Yang–Parr nonlocal correlation functional [24] (B3LYP) implemented in the GAUSSIANO3 program package [25]. Double-zeta valence plus polarization (DGDZVP) basis set [26] was used on all atoms. All geometries were optimized without constraints, and vibrational frequencies were computed.

#### 3. Results and discussion

#### 3.1. Preparation of BEt<sub>3</sub>-adducts of bis-NHC compounds

We have already reported the preparation of the triethylboraneadduct of bis-NHC **2a**, which was prepared by the reaction of the corresponding bis(imidazolium) salt **1a** with two moles of LiBEt<sub>3</sub>H [12a]. In this study, we examined the preparation of the isopropyl analog of **2a** and propylene- and ethylene-bridged BEt<sub>3</sub>-adducts of bis-NHCs, **2c** and **2d** (Scheme 1).

The treatment of bis(imidazolium) salt 1b with two moles of Li-BEt<sub>3</sub>H at -78 °C afforded a homogeneous reaction mixture, from which a white solid of 2b was isolated in 96% yield. In cases of 1c and 1d, the propylene- and ethylene-bridged analogs of 1a, a similar reaction took place to give white solids of 2c and 2d in good yields. Elemental analyses and <sup>1</sup>H, <sup>13</sup>C{<sup>1</sup>H}, and <sup>11</sup>B{<sup>1</sup>H} NMR spectra indicated the formation of BEt<sub>3</sub>-adducts of bis-NHCs (2b-2d). In the <sup>1</sup>H NMR spectrum of **2b**, the signal of imidazolium proton atoms observed at 10.00 ppm for 1b disappeared and the signals of triethylborane proton atoms were observed at 0.47 and 0.61 ppm as quartet and triplet, respectively. The  ${}^{13}C{}^{1}H$  NMR spectrum showed the broad signal assignable to the carbene carbon atoms at 175.6 ppm. The broadening may be caused by the influence of the binding boron. A signal of the boron atom of the BEt<sub>3</sub> group was observed at -12.2 ppm in the <sup>11</sup>B{<sup>1</sup>H} NMR. These spectroscopic data are consistent with those of 2a [12a]. Compounds 2c and 2d also showed similar spectroscopic features to those of compounds 2a and 2b. The structure of 2b obtained by the X-ray analysis is shown in Fig. 1 and is consistent with the spectroscopic data. The B-C(carbene) bond lengths are 1.677(6) and 1.662(6) Å and similar to that of reported BEt<sub>3</sub>·NHC compounds [12a].



**Fig. 1.** ORTEP drawing of compound **2b** (30% probability of thermal ellipsoids). All hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (deg): B1–C1 = 1.677(6), B2–C15 = 1.662(6), C2–C3 = 1.330(5), C16–C17 = 1.329(5), N1–C1–N2 = 103.6(3), N1–C1–B1 = 131.9(3), N2–C1–B1 = 124.4(3), N3–C15–N4 = 102.1(3), N3–C15–B2 = 131.6(3), N4–C15–B2 = 126.2(3).

### 3.2. Synthesis and structures of [M(CO)<sub>4</sub>(bis-NHC)] complexes of group 6 transition metals

We have recently reported that the BEt<sub>3</sub>-adduct of monodentate NHC can act as an efficient NHC transfer reagent to molybdenum and tungsten complexes [12]. In this study we investigated the NHC transfer ability of the BEt<sub>3</sub>-adducts of bis-NHCs 2 toward group 6 transition metals. We first examined the reaction of [Mo(CO)<sub>6</sub>] with 2a under toluene-refluxing conditions, which referred to the reaction conditions for the preparation of [Mo (CO)<sub>5</sub>NHC] [12a]. The desired bis-NHC complex of molybdenum **3a** was obtained as a mixture containing  $[Mo(CO)_3(\eta^6-toluene)]$ as a by-product. After screening the reaction conditions, we found that heptane was a suitable solvent. On treatment of  $[Mo(CO)_6]$ with 2a in heptane under refluxing conditions, a substitution reaction cleanly took place to give the bis-NHC complex of molybdenum 3a-Mo as a yellow solid in 83% yield. Complex 3b-Mo as well as the propyrene- and ethylene-bridged homologs 3c-Mo and **3d-Mo** were also obtained in good yields by the same procedure as that for **3a-Mo** (Scheme 2). In cases of tungsten and chromium complexes, by refluxing  $[M(CO)_6]$  (M = W, Cr) with **2a**, desired complexes were obtained in low yields. In these cases, norbornadiene (nbd) complexes formulated as  $[M(CO)_4(\eta^4-nbd)]$ (M = W, Cr) were used as starting materials and thus the bis-NHC complexes 3a-W and 3a-Cr were obtained (Scheme 3).

The structures of *o*-xylylene-bridged bis-NHC complexes **3a-Mo** and **3b-Mo** were determined by the X-ray analyses. The ORTEP drawings of **3a-Mo** and **3b-Mo** are shown in Fig. 2. The selected bond lengths and angles for **3a-Mo** and **3b-Mo** are listed in Table 2. Complexes **3a-Mo** and **3b-Mo** have a pseudo-octahedral geometry around the central metal and show *C*<sub>2</sub>-symmetric structures in which the bis-NHC ligand coordinates in a twisted



Scheme 1. Preparation of BEt<sub>3</sub>-adducts of bis-NHCs.



**3b-Mo**: E = *o*-xylylene, R = <sup>i</sup>Pr (y.81%) **3c-Mo**: E = propylene, R = Me (y. 84%) **3d-Mo**: E = ethylene, R = Me (y. 72%)

Scheme 2. Preparation of bis-NHC complexes of molybdenum.





conformation. It was reported that, in cases of late transition metal complexes such as Rh [3a] and Pd [4c,4h,4p], *o*-xylylene-bridged bis-NHC ligands adopt a  $C_s$ -symmetric coordination mode in these complexes. The  $C_2$ -symmetric coordination mode in complex **3** might come from flexibility of the linker unit, which prevents the steric repulsion between the carbene ligand and the apical ligands in an octahedral geometry. The bond lengths of Mo–C(carbene) (2.305(3) and 2.293(3) Å for **3a-Mo** and 2.290(3) Å for **3b-Mo**) are similar to those of zero-valent Mo–NHC complexes [7,8,27]. Bite angles defined by C(carbene)–Mo–C(carbene) are 94.2(1)° for **3a-Mo** and 94.6(1)° for **3b-Mo**, which are quite larger than those

of the methylene-bridged bis-NHC complex of tungsten  $(79.2(2)^{\circ} \text{ and } 80.6(3)^{\circ})$  [7b], and slightly larger than those of late transition metal complexes (83.2–92.2°) reported by Crabtree and co-workers [3b].

In IR spectra of complexes **3a-Mo** and **3b-Mo**, both complexes showed four stretching bands at 1999, 1896, 1847, and 1788 cm<sup>-1</sup> for **3a-Mo** and 1998, 1877, 1849, and 1802 cm<sup>-1</sup> for **3b-Mo**. These observations indicate that the bis-NHC ligand coordinates in the *cis* position [28]. In <sup>13</sup>C{<sup>1</sup>H} NMR spectra, signals assignable to the carbene carbon atoms were observed at 191.5 ppm for **3a-Mo** and 189.6 ppm for **3b-Mo**. In the case of **3a-Mo**, the signals due to the carbonyl carbon atoms were observed at 210.3 and 218.8 ppm with almost equivalent intensities. Similar spectroscopic data were obtained in complexes **3b-Mo**, **3a-W**, and **3a-Cr**. These observations clearly demonstrate that the bis-NHC ligands in these complexes coordinate to the metals in the twisted mode to form the *C*<sub>2</sub>-symmetric structure in a solution state.

Suitable crystals of propylene- and ethylene-bridged bis-NHC complexes, **3c-Mo** and **3d-Mo**, were not obtained and thus we could not confirm the structures of these complexes in a solid state. However spectroscopic data of these complexes indicated that these complexes adopt the  $C_2$ -symmetric structure in a solution. In <sup>13</sup>C{<sup>1</sup>H} NMR spectra, two signals with almost equivalent intensities were observed in the region of the carbonyl carbon atoms; 211.4 and 220.3 ppm for **3c-Mo** and 212.2 and 220.6 ppm for **3d-Mo** as in the case of complexes **3a-Mo** and **3b-Mo**. Therefore the bis-NHC ligand in those complexes most probably adopts a twisted conformation in a solid state.

## 3.3. Reactivity of [Mo(CO)<sub>4</sub>(bidentate ligand)] toward phosphorus donors under thermal conditions

We were interested in the estimation of steric and/or electronic properties of the bis-NHC ligand in molybdenum complexes, comparing with other bidentate ligands such as 2,2'-bipyridine (bpy) and 1,2-bis(diphenylphosphino)ethane (dppe), by the reactivity with the phosphorous compound. We examined the reaction of  $[Mo(CO)_4(bis-NHC)]$  (3) with trimethylphosphite (P(OMe)<sub>3</sub>) (Scheme 4).

On treating complex **3a-Mo** with  $P(OMe)_3$  under toluene-refluxing conditions, a  $CO/P(OMe)_3$  substitution reaction took place to give complex **4a-Mo** as a white solid in 58% yield. Complex **4b-Mo** was also obtained by the reaction of complex **3b-Mo** with  $P(OMe)_3$  under the same conditions. Spectroscopic measurements and X-ray analysis (vide infra) revealed that complexes **4a-Mo** and **4b-Mo** show a facial geometry around the metal center. In



Fig. 2. ORTEP drawings of complexes 3a-Mo (left) and 3b-Mo (right) (30% probability of thermal ellipsoids). All hydrogen atoms are omitted for clarity.

| Table 2  |    |
|--|----|
| Selected bond lengths (Å) and angles (°) for complexes <b>3a-Mo</b> , <b>3b-Mo</b> , <b>4b-Mo</b> , and <b>4c-Mo</b> | D. |

| 3a-Mo      |          | 3b-Mo       |          | 4b-Mo      |          | 4c-Mo      |          |
|------------|----------|-------------|----------|------------|----------|------------|----------|
| Mo1-C1     | 2.044(3) | Mo1-C1      | 2.035(4) | Mo1-P1     | 2.468(3) | Mo1-P1     | 2.487(3) |
| Mo1-C2     | 1.968(3) | Mo1-C2      | 1.976(3) | Mo1-C1     | 1.962(6) | Mo1-C1     | 1.967(5) |
| Mo1-C3     | 1.969(3) | Mo1-Mo1-C3  | 2.290(3) | Mo1-C2     | 1.942(7) | Mo1-C2     | 1.969(6) |
| Mo1-C4     | 2.036(3) | 01-C1       | 1.140(4) | Mo1-C3     | 1.972(6) | Mo1-C3     | 1.970(5) |
| Mo1-C5     | 2.294(2) | 02-C2       | 1.157(4) | Mo1-C4     | 2.312(6) | Mo1-C4     | 2.331(5) |
| Mo1-C17    | 2.306(2) |             |          | Mo1-C18    | 2.304(6) | Mo1-C11    | 2.321(5) |
| 01-C1      | 1.141(3) |             |          | C1-01      | 1.169(8) | C1-01      | 1.166(6) |
| 02-C2      | 1.161(3) |             |          | C2-02      | 1.182(8) | C2-02      | 1.169(7) |
| 03-C3      | 1.156(3) |             |          | C3-03      | 1.157(8) | C3-03      | 1.162(7) |
| 04-C4      | 1.141(4) |             |          |            |          |            |          |
| C1-Mo1-C2  | 88.9(1)  | C1-Mo1-C2'  | 93.4(1)  | P1-Mo1-C1  | 100.8(2) | P1-Mo1-C1  | 92.9(1)  |
| C1-Mo1-C3  | 87.0(1)  | C1-Mo1-C2   | 88.0(1)  | P1-Mo1-C2  | 85.9(2)  | P1-Mo1-C2  | 88.9(2)  |
| C1-Mo1-C4  | 173.6(1) | C1-Mo-C1'   | 178.1(1) | P1-Mo1-C3  | 171.9(2) | P1-Mo1-C3  | 177.8(2) |
| C1-Mo1-C5  | 91.1(1)  | C1-Mo1-C3   | 87.4(1)  | P1-Mo1-C4  | 85.3(1)  | P1-Mo1-C4  | 90.1(2)  |
| C1-Mo1-C17 | 93.4(1)  | C1-Mo1-C3'  | 91.3(1)  | P1-Mo1-C18 | 94.3(1)  | P1-Mo1-C11 | 91.4(1)  |
| C2-Mo1-C4  | 88.3(1)  | C2'-Mo1-C1' | 88.0(1)  | C1-Mo1-C3  | 85.0(3)  | C1-Mo1-C3  | 85.0(2)  |
| C3-Mo1-C4  | 86.9(1)  | C2-Mo1-C1'  | 93.4(1)  | C2-Mo1-C3  | 89.2(3)  | C2-Mo1-C3  | 90.2(2)  |
| C4-Mo1-C5  | 91.5(1)  | C1'-Mo1-C3  | 91.3(1)  | C3-Mo1-C4  | 88.6(3)  | C3-M01-C4  | 92.0(2)  |
| C4-Mo1-C17 | 92.4(1)  | C1'-Mo1-C3' | 87.4(1)  | C3-Mo1-C18 | 91.4(3)  | C3-Mo1-C11 | 89.1(2)  |
| C5-Mo1-C17 | 94.2(1)  | C3-Mo1-C3'  | 94.6(1)  | C4-Mo1-C18 | 94.1(2)  | C4-Mo1-C11 | 95.1(2)  |



Scheme 4. Reaction of [Mo(CO)<sub>4</sub>(bis-NHC)] with P(OMe)<sub>3</sub>.

the IR spectra, three CO stretching bands were observed at 1913, 1806, and  $1765 \text{ cm}^{-1}$  for **4a-Mo** and at 1917, 1814, and 1775 cm<sup>-1</sup> for **4b-Mo**. In <sup>31</sup>P{<sup>1</sup>H} NMR, the singlet signal in the region of the coordinated P(OMe)<sub>3</sub> was observed at 167.9 ppm for **4a-Mo** and 168.8 ppm for **4b-Mo**. Although the <sup>13</sup>C{<sup>1</sup>H} NMR spectrum of 4a-Mo was not obtained due to its low solubility, substantial data of **4b-Mo** was obtained. The <sup>13</sup>C{<sup>1</sup>H} NMR spectrum of 4b-Mo showed two doublets due to the carbene carbon atoms with similar coupling constants ( $\delta$  = 195.7 (d), <sup>2</sup>J<sub>PC</sub> = 13.4 Hz, and  $\delta$  = 196.7 (d), <sup>2</sup>J<sub>PC</sub> = 15.7 Hz). This result indicates that the phosphorus ligand locates in the cis position toward the NHC ligands. In the region of the carbonyl carbon atoms, three doublet signals were observed; two doublet showed small coupling constants ( ${}^{2}J_{PC}$  = 12.3 and 13.4 Hz) and one showed a relatively large coupling constant  $(^{2}J_{PC} = 59.2 \text{ Hz})$ . This coupling pattern is indicative for a *fac* arrangement of the CO ligands. The CO ligand with the large coupling constant is located trans to the P(OMe)<sub>3</sub> ligand. We also examined the reaction of complex 3c-Mo having propylene-bridged bis-NHC with  $P(OMe)_3$  and thus fac- $[Mo(CO)_3(bis-NHC){P(OMe)_3}]$  (4c-Mo) was obtained. The <sup>13</sup>C{<sup>1</sup>H} NMR spectrum of **4c-Mo** in the region of carbene and carbonyl carbon atoms showed similar patterns to those of 4b-Mo. Furthermore, X-ray analysis revealed that the structure of **4c-Mo** shows a *fac*-form in an octahedral geometry.

The ORTEP drawings of complexes **4b-Mo** and **4c-Mo** are shown in Fig. 3. The selected bond lengths and angles are listed in Table 2. These complexes show slightly distorted *fac*-form in an octahedral geometry and a twisted configuration of the bis-NHC ligand. The Mo–P bond lengths are 2.468(3) Å for **4b-Mo** and 2.487(3) Å for **4c-Mo**. These lengths are normal Mo–P dative bond lengths which fall in the range 2.40–2.57 Å of previously reported complexes [29]. The Mo–C(carbene) bond lengths (2.312(6) and 2.304(6) Å for **4b**-Mo and 2.311(5) and 2.321(5) Å for 4c-Mo) are similar to those of parent bis-NHC complexes of molybdenum (3a-Mo, 3b-Mo). Bite angles of C(carbene)-Mo-C(carbene) are 94.1(2)° for 4b-Mo and 95.1(2)° for **4c-Mo**, which are guite similar to those of parent complexes **3a-Mo** and **3b-Mo**. In complex **4b-Mo**, steric repulsion between the phosphorus ligand and the isopropyl substituent on the imidazole ring was observed. Angles of P1-Mo1-C18  $(94.3(1)^{\circ})$  and P1-Mo1-C1  $(100.8(2)^{\circ})$  are larger than those of P1-Mo1-C4 (85.3(1)°) and P1-Mo1-C2 (85.9(2)°) and thus the angle of P1-Mo1-C3 (171.9(2)°), which is slightly distorted from an ideal octahedral geometry, is smaller than that of the corresponding angle in **4c-Mo** (177.8(2)°).

The reactivity of tetracarbonyl complexes of molybdenum bearing a bidentate ligand such as bpy or dppe with phosphorus compounds has been reported [30,31]. In the reaction of  $[Mo(CO)_4]$ (bpy)] with various phosphorus compounds (PR<sub>3</sub>) under thermal conditions, a CO/PR<sub>3</sub> substitution reaction cleanly took place to give fac-[Mo(CO)<sub>3</sub>(bpy)(PR<sub>3</sub>)]. On the other hand, in the case of [Mo (CO)<sub>4</sub>(dppe)], the geometrical isomers, i.e., fac- and mer-[Mo (CO)<sub>3</sub>(dppe)(PR<sub>3</sub>)], have been obtained. The different reactivity between bpy and dppe might have come from the difference of the  $\pi$ -acceptability of the bidentate ligands [28,32]. Bpy, which is a weaker  $\pi$ -acceptor ligand than dppe, may produce only *fac* isomer, whereas the phosphorus ligand which has greater  $\pi$ -acceptor strength might have formed both fac and mer isomers. In the case of [Mo(CO)<sub>4</sub>(bis-NHC)], the fac isomer was obtained. Although the steric influence of the bidentate ligands can not be ruled out, these results may indicate that the electronic feature of bis-NHC ligand is similar to that of a nitrogen donor, bpy, rather than a phosphorus donor, dppe.

## 3.4. Electronic and steric properties of [Mo(CO)<sub>4</sub>(bidentate ligand)]: experimental and theoretical investigations

In order to obtain further information about electronic and steric properties of the bis-NHC ligand, we investigated (i) bond lengths of Mo–CO in complexes **3a-Mo** and **3b-Mo** in detail, (ii) the comparison of CO stretching frequencies of a series of [Mo (CO)<sub>4</sub>(bid)] (bid = bis-NHC, bpy, dppe), (iii) oxidation potentials



Fig. 3. ORTEP drawings of complexes 4b-Mo (left) and 4c-Mo (right) (30% probability of thermal ellipsoids). All hydrogen atoms are omitted for clarity.

| Table 3  |  |
|--|--|
| IR spectra ( $v_{CO}/cm^{-1}$ ) of complex <b>3-Mo</b> , | $[Mo(CO)_4(bpy)]$ and $[Mo(CO)_4(dppe)]$ . |

|                      | 3a-Mo | 3b-Mo | 3c-Mo | 3d-Mo | [Mo(CO) <sub>4</sub> (bpy)] | [Mo(CO) <sub>4</sub> (dppe)] |
|----------------------|-------|-------|-------|-------|-----------------------------|------------------------------|
| Found <sup>a</sup>   | 1999  | 1998  | 1991  | 1993  | 2009                        | 2017                         |
|                      | 1896  | 1877  | 1874  | 1879  | 1918                        | 1922                         |
|                      | 1847  | 1849  | 1844  | 1844  | 1869                        | 1894                         |
|                      | 1788  | 1802  | 1804  | 1792  | 1814                        | 1877                         |
| Average <sup>b</sup> | 1883  | 1882  | 1877  | 1878  | 1903                        | 1928                         |

<sup>a</sup> Experimental data (KBr disk).

<sup>b</sup> The mean value of four CO stretching frequencies.

of [Mo(CO)<sub>4</sub>(bid)] by cyclic voltammograms, and (iv)  $^{95}$ Mo NMR spectroscopy of the bis-NHC complex **3-Mo**. The DFT calculations were also carried out from a viewpoint of the relative stability between  $C_2$ -symmetric and  $C_s$ -symmetric structures for **3a-Mo**.

#### 3.4.1. Structural features in bond lengths of Mo-CO

The strong donor ability of the carbene ligands is clearly illustrated by the different Mo–CO bond lengths of the carbonyl ligands that are *cis* and *trans* to the NHC ligands. Hahn and co-workers have reported that the Mo–C(carbonyl) bond length in the *trans* position of the NHC ligand is shorter than that in the *cis* position of the NHC ligand [8]. Similar tendencies were observed in complexes **3a-Mo** and **3b-Mo** (Table 2). The Mo–C(carbonyl) bond lengths in the *trans* position to the NHC ligand (1.968(3), 1.968(3) Å for **3a-Mo** and 1.976(3) Å for **3b-Mo**) are shorter than those in the *cis* position (2.035(3), 2.043(3) Å for **3a-Mo** and 2.035(4) Å for **3b-Mo**). Furthermore, the C–O bond lengths of the CO ligand *trans* to the NHC ligand (1.158(4), 1.161(3) Å for **3a-Mo** and 1.157(4) Å for **3b-Mo**) are somewhat longer than those of *cis* (1.140(4), 1.141(3) Å for **3a-Mo** and 1.140(4) Å for **3b-Mo**).

#### 3.4.2. CO stretching frequency in IR spectra

Comparison of the IR stretching frequency of the CO ligand is one of the reliable methods to estimate the electron donor ability of NHC ligands [33]. The IR data of complexes **3-Mo** were compared with those of  $[Mo(CO)_4(bid)]$  (bid = bpy, dppe). The data are summarized in Table 3. In a series of complexes **3-Mo**, there are a little influence of the electron donor ability of NHC ligands concerning the substituent on the nitrogen atom or the linker binding two imidazole rings. On the other hand, the mean value of  $v_{CO}$ 

#### Table 4

Cyclic voltammetric data of **2a**, **2c**, **3a-Mo**, **3c-Mo**, and  $[Mo(CO)_4(bid)]$  (bid = bpy, dppe) in CH<sub>3</sub>CN (vs. Fc/Fc<sup>+</sup>).

| npound                                  | $E_{\rm pa1}/V$                | $E_{\rm pa2}/V$                      | $E_{\rm pa3}/V$              | $E_{\rm pa4}/V$ |
|---|--------------------------------|--------------------------------------|------------------------------|-----------------|
|   |                                | 0.43                                 | 0.70                         |                 |
|   |                                | 0.42                                 | 0.70                         |                 |
| Мо                                      | -0.07                          | 0.44                                 | 0.73                         | 1.09            |
| Мо                                      | -0.15                          | 0.47                                 | 0.71                         | 0.95            |
| (CO) <sub>4</sub> (bpy)]                | 0.19                           | 0.72                                 |                              |                 |
| (CO) <sub>4</sub> (dppe)]               | 0.55                           |                                      |                              |                 |
| Mo<br>Mo<br>(CO)₄(bpy)]<br>(CO)₄(dppe)] | -0.07<br>-0.15<br>0.19<br>0.55 | 0.43<br>0.42<br>0.44<br>0.47<br>0.72 | 0.70<br>0.70<br>0.73<br>0.71 | 1.09<br>0.95    |

for **3a-Mo** (1883 cm<sup>-1</sup>) was 20 and 45 cm<sup>-1</sup> lower in frequency than those of [Mo(CO)<sub>4</sub>(bpy)] and [Mo(CO)<sub>4</sub>(dppe)], respectively. These results clearly demonstrate that bis-NHC ligand shows stronger electron donor ability and weaker  $\pi$ -acceptor than bpy or dppe.<sup>1</sup>

#### 3.4.3. Cyclic voltammograms of molybdenum complexes

In order to investigate electronic properties of the central metal, the cyclic voltammograms (CVs) of molybdenum complexes were measured in CH<sub>3</sub>CN. The results are listed in Table 4. The CV of **3a-Mo** showed irreversible oxidation waves at the potentials of -0.07, 0.44, 0.73, and 1.09 V vs. Fc/Fc<sup>+</sup>. The oxidation potentials of 0.44 and 0.73 V were similar to those of the BEt<sub>3</sub>-adducts of NHC **2a** and thus these waves were assigned to the oxidation caused by the NHC ligand [34]. The oxidation wave at -0.07 V

<sup>&</sup>lt;sup>1</sup> The bis-NHC ligand shows a stronger electron donor ability than bpy or dppe. This tendency was supported by the DFT calculations (B3LYP/DGDZVP) of **3a-Mo**, [Mo(CO)4(bpy)], and [Mo(CO)4(dppe)]. See the Supplementary material.



**Fig. 4.** Optimized structures of the twisted bis-NHC complex (*C*<sub>2</sub>-symmetric structure) (left) and the parallel bis-NHC complex (*C*<sub>s</sub>-symmetric structure) (right) calculated by B3LYP/DGDZVP. All hydrogen atoms are omitted for clarity.

was corresponded to the one-electron oxidation of the molybdenum center of **3a-Mo**. The one-electron oxidation wave of **3c-Mo**, the propylene-bridged analog of **3a-Mo**, showed slightly lower potential of -0.15 V than that of **3a-Mo**. The CVs of [Mo(CO)<sub>4</sub>(bid)] (bid =

bpy, dppe) in CH<sub>3</sub>CN were measured under the same conditions. These complexes showed one-electron oxidation wave at 0.19 V for [Mo(CO)<sub>4</sub>(bpy)] and 0.55 V for [Mo(CO)<sub>4</sub>(dppe)] vs. Fc/Fc<sup>+</sup>. Based on the one-electron oxidation potentials in those complexes, it was conceivable that  $\pi$ -acceptability of the ligands in molybdenum complexes increases in order of NHC < bpy < dppe. In other words, the electron density accumulated at the Mo center increases in the reverse order. This tendency is in good agreement with that observed in the CO stretching frequencies of molybdenum complexes (Table 3).

On scanning between -0.45 and 0.15 V in a CH<sub>3</sub>CN solution, carbene complex **3a-Mo** showed a quasi-reversible redox wave ( $E_{pa} = -0.07$  V,  $E_{pc} = -0.16$  V). On the other hand, bpy and dppe complexes showed an irreversible oxidation wave under the same conditions. Similar results have been already reported by Morse and Ackermann, independently [35]. In their reports, the irreversible wave shows the formation of seven-coordinate complexes by coordination of a solvent (CH<sub>3</sub>CN) in the oxidized state. Therefore, we considered that, in complex **3a-Mo**, the strong donor ability of the bis-NHC ligand stabilizes the oxidized molybdenum center by preventing the solvent molecule from coordination to the metal. Furthermore, from a steric point of view, the NHC ligand might give a significant influence on the stability of the oxidized form.

### 3.4.4. <sup>95</sup>Mo NMR spectroscopy of molybdenum complexes

In order to estimate the electronic feature at the Mo center, <sup>95</sup>Mo NMR measurements of molybdenum complexes, **3a-Mo**, 3b-Mo, and 3c-Mo, were undertaken. These complexes showed similar chemical shifts; -1657 ppm for **3a-Mo**, -1637 ppm for 3b-Mo, and -1649 ppm for 3c-Mo. These results suggested that the substituent on the nitrogen atom or the linker group of the bis-NHC ligand have a little influence on the chemical shift in <sup>95</sup>Mo NMR. We compared the <sup>95</sup>Mo chemical shift of **3-Mo** with those of  $[Mo(CO)_4(bid)]$  (bid = bpy, dppe). It has been reported that the resonances of  $[Mo(CO)_4(bpy)]$  and  $[Mo(CO)_4(dppe)]$  are observed at -1190 ppm and -1782 ppm, respectively [35b,36]. The <sup>95</sup>Mo shielding increases in the order [Mo(CO)<sub>4</sub>(bpy)] < **3-Mo** < [Mo(CO)<sub>4</sub>(dppe)], whereas this fact did not reflect the tendency observed in the IR and CV spectra (vide supra). Therefore it might be difficult to discuss the electronic feature at the Mo center of a bis-NHC complex comparing with bpy or dppe complexes by <sup>95</sup>Mo NMR spectroscopy, because of difference of the coordinating atoms (C, N, and P) to the metal.

#### 3.5. Conformations of bis-NHC ligand in octahedral geometry

As mentioned above, we revealed that the bis-NHC ligand bearing the hydrocarbon linker such as *o*-xylylene, propylene, or ethylene showed the twisted conformation in an octahedral geometry of group 6 transition metal complexes. This result is reverse tendency to the late transition metal complexes, in which the orientation of the azole rings adopts a perpendicular orientation ( $C_s$ -symmetric structure in Chart 1). To investigate the possibility of the formation of a  $C_s$ -symmetric structure in an octahedral geometry, we applied the DFT calculations to both isomers of molybdenum complexes bearing the *o*-xylylene-bridged bis-NHC ligand. The results of the optimized structures are shown in Fig. 4.

In the  $C_2$ -symmetric structure, the calculated  $C^{ap}$ -Mo- $C^{ap}$  angle (179.77°), in which C<sup>ap</sup> denotes the carbonyl carbon atom in the apical position, is somewhat larger than the experimental value (173.6(1)°) observed by X-ray analysis of **3a-Mo**. On the other hand, in the C<sub>s</sub>-symmetric structure, the C<sup>ap</sup>-Mo-C<sup>ap</sup> angle was calculated to be 160.32°, which is highly distorted from an ideal octahedral geometry. In the case of the  $C_2$ -symmetric geometry, two methyl groups on the imidazole rings directed toward the open space between apical and equatorial CO ligands and thus this conformation adopts an ideal octahedral geometry. In the C<sub>s</sub>-symmetric structure, two methyl groups and two methylene groups are oriented to the CO ligands in the apical positions and thus there is the steric repulsion between the CO ligands and these groups attached on the NHC ligand in this conformation. The Gibbs energy difference between these two isomers is estimated to be 6.69 kcal mol<sup>-1</sup> by the DFT calculations. The C<sub>2</sub>-symmetric structure is found to be more stable than the  $C_s$ -symmetric one in an octahedral geometry.

#### 4. Conclusion

The BEt<sub>3</sub>-adducts of bis-NHCs **2**, prepared by the reaction of imidazolium pro-ligand with two moles of LiBEt<sub>3</sub>H, were used efficiently to prepare bis-NHC complexes of group 6 transition metals. The systematic preparations of bis-NHC complexes bearing *o*-xylylene, propylene, and ethylene linkers were achieved using this method. These complexes are found to possess the  $C_2$ -symmetric structure in an octahedral geometry. This conformation of the bis-NHC ligand in the group 6 transition metal complexes is remarkably different from those in late transition metal complexes. This tendency observed in group 6 transition between the bis-NHC ligand and the CO ligands coordinating in the apical positions.

We also investigated the electron donor ability of bis-NHC comparing with a nitrogen donor, bpy, and with a phosphorus donor, dppe. The strong donor ability of NHCs was revealed by X-ray analysis, CO stretching frequency, and cyclic voltammetry of molybdenum complexes, [Mo(CO)<sub>4</sub>(bis-NHC)] (**3-Mo**), as well as by the reaction of **3-Mo** with P(OMe)<sub>3</sub> to give *fac*-form of molybdenum complexes (**4-Mo**).

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#### **Appendix A. Supplementary material**

CCDC 812230–812234; contain the supplementary crystallographic data for complexes **2b**, **3a-Mo**, **3b-Mo**, **4b-Mo**, and **4c-Mo**. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/ data\_request/cif. Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/ j.ica.2012.04.027.

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