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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 $LiBEt_3H$, the corresponding BEt_3-adducts of bis-NHCs, $(Et_3B{\cdot}ImR)_2E$ (Im = imidazole; R = Me, ^{i}Pr; E = *o*-xylylene, propylene, ethylene) (**2**), were obtained. Reaction of $[Mo(CO)_6]$ with compound **2** afforded the carbene complex, $[Mo(CO)_4(\text{bis-NHC})]$ (**3-Mo**), in a good yield. Tungsten and chromium analogs of **3-Mo** were obtained from $[M(CO)_4(\eta^4\text{-norbornadiene})]$ (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_2-symmmetric structure. In a reaction of **3-Mo** with trimethylphosphite, a $CO/P(OMe)_3$ substitution reaction took place to give *fac*-$[Mo(CO)_3(\text{bis-NHC})\{P(OMe)_3\}]$ (**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(diphenylphosphino)ethane. Density functional calculations (B3LYP/DGDZVP) showed that the C_2-symmetric structure of *o*-xylylene-bridged **3-Mo** having *N*-methyl azole rings was more stable than a C_s-symmetric structure by $\Delta G = 6.69$ kcal mol^{-1}.

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 (BINAM) or H_8-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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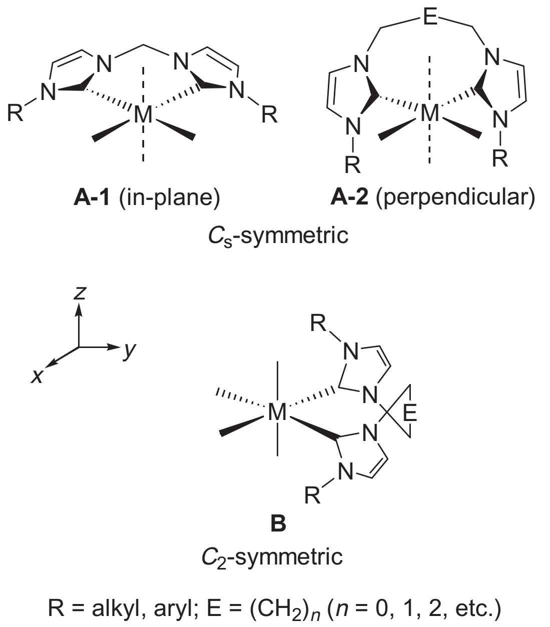

Chart 1. Coordination modes of bis-NHC ligand.

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*-xylylene-bridged bis-NHC ligands, derived from chiral 1,4-diol,1,2-bis-(1-hydroxypropyl)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 is transmetalation of NHC from a silver 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_3-adduct of NHC [12]. In this paper, we also report the preparation of the BEt_3-adducts of bis-NHCs and their application for 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], $[W(CO)_4(\eta^4\text{-}C_7H_8)]$ [14], $[Cr(CO)_4(\eta^4\text{-}C_7H_8)]$ [15], $[Mo(CO)_4(bpy)]$ [16], and $[Mo(CO)_4(dppe)]$ [17] were prepared according to literature methods.

IR spectra were recorded on a HORIBA FT-730 spectrometer. ^1H, $^{13}C\{^1H\}$, $^{31}P\{^1H\}$ and $^{11}B\{^1H\}$ NMR spectra were recorded on a JEOL EX-270 spectrometer at ambient temperature, unless otherwise mentioned. ^{95}Mo NMR spectra were recorded on a JEOL ECA-600 spectrometer. ^1H and $^{13}C\{^1H\}$ NMR chemical shifts were recorded in ppm relative to internal Me_4Si. $^{31}P\{^1H\}$, $^{11}B\{^1H\}$, and ^{95}Mo NMR chemical shifts were recorded in ppm relative to external H_3PO_4, $BF_3{\cdot}OEt_2$, and Na_2MoO_4, respectively. All coupling constants were recorded in Hz. Cyclic voltammograms were recorded on HECS 317S, 321, and 326 in CH_3CN containing 0.1 M Bu_4NBF_4 as a supporting electrolyte by using a conventional three-electrode system, platinum (Φ = 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^+. 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 × 5 mL) and dried in vacuo to yield **1b** as a white solid (446 mg, 0.77 mmol, 86%). *Anal*. Calc. for $C_{20}H_{28}I_2N_4$: C, 41.54; H, 4.88; N, 9.69. Found: C, 41.31; H, 4.97; N, 9.58%. ^1H NMR (in $CDCl_3$) δ 1.65 (d, J = 6.6 Hz, 12H, $^iPr\text{–}CH_3$), 4.81 (sept, J = 6.6 Hz, 2H, $^iPr\text{–}CH$), 6.11 (s, 4H, $\text{–}CH_2\text{–}$), 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). $^{13}C\{^1H\}$ NMR (in $CDCl_3$) δ 23.1 ($^iPr\text{–}CH_3$), 51.0, 53.8 ($^iPr\text{–}CH$, $\text{–}CH_2\text{–}$), 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 × 10 mL) and dried in vacuo to yield **1c** as a white solid (2798 mg, 7.64 mmol, 89%). *Anal*. Calc. for $C_{11}H_{18}Br_2N_4$: C, 36.09; H, 4.96; N, 15.30. Found: C, 36.00; H, 5.07; N, 15.28%. ^1H NMR (in DMSO-d_6) δ 2.40 (quint, J = 7.3 Hz, 2H, $\text{–}CH_2CH_2CH_2\text{–}$), 3.86 (s, 6H, CH_3), 4.25 (t, J = 7.3 Hz, 4H, $\text{–}CH_2CH_2CH_2\text{–}$), 7.31 (s, 2H, CH=CH), 7.80 (s, 2H, CH=CH), 9.24 (s, 2H, NCHN). $^{13}C\{^1H\}$ NMR (in DMSO-d_6) δ 29.5 ($\text{–}CH_2CH_2CH_2\text{–}$), 35.8 ($CH_3$), 45.6 ($\text{–}CH_2CH_2CH_2\text{–}$), 121.9 (CH=CH), 123.4 (CH=CH), 136.6 (NCHN).

2.3. Preparation of BEt_3-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, $LiBEt_3H$ (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)