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Synthesis and characterization five-coordinate molybdenum compounds bearing bi- or tridentate substituted pyrrole ligands: molecular structures of

$\{\text{Mo}(\text{NC}_6\text{H}_3\text{Pr}_2^i\text{-2,6})_2\text{R}[\text{NC}_4\text{H}_3(\text{CH}_2\text{NMe}_2)\text{-2}]\}$ and
 $\{\text{Mo}(\text{NC}_6\text{H}_3\text{Pr}_2^i\text{-2,6})_2\text{Cl}[\text{NC}_4\text{H}_2(\text{CH}_2\text{NMe}_2)_2\text{-2,5}]\}$, where R = Cl, Me, Bu

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Abstract

Reacting $[\text{Mo}(\text{NC}_6\text{H}_3\text{Pr}_2^i\text{-2,6})_2\text{Cl}_2(\text{dme})]$ with 1 equiv. of $\text{Li}[\text{NC}_4\text{H}_3(\text{CH}_2\text{NMe}_2)\text{-2}]$ in diethyl ether at -78°C yields a red crystalline solid of $\{\text{Mo}(\text{NC}_6\text{H}_3\text{Pr}_2^i\text{-2,6})_2\text{Cl}[\text{NC}_4\text{H}_3(\text{CH}_2\text{NMe}_2)\text{-2}]\}$ **1** in 86% yield. Alkylation of **1** with RLi in diethyl ether generates $\{\text{Mo}(\text{NC}_6\text{H}_3\text{Pr}_2^i\text{-2,6})_2\text{R}[\text{NC}_4\text{H}_3(\text{CH}_2\text{NMe}_2)\text{-2}]\}$ (**2a**, R = Me; **2b**, R = Bu) in high yield. Similarly, reacting $[\text{Mo}(\text{NC}_6\text{H}_3\text{Pr}_2^i\text{-2,6})_2\text{Cl}_2(\text{dme})]$ with 1 equiv. of $\text{Li}[\text{NC}_4\text{H}_2(\text{CH}_2\text{NMe}_2)_2\text{-2,5}]$ in diethyl ether at -78°C affords dark red crystals of $\{\text{Mo}(\text{NC}_6\text{H}_3\text{Pr}_2^i\text{-2,6})_2\text{Cl}[\text{NC}_4\text{H}_2(\text{CH}_2\text{NMe}_2)_2\text{-2,5}]\}$ **3** in 92% yield, in which one NMe₂ unit of the pyrrole ligand of **3** coordinates to molybdenum whilst the other one dangles outside the coordination sphere. Variable-temperature ¹H NMR study of **3** reveals fluxional behavior of the two NMe₂ units of the pyrrole ligand. The activation energy of the fluxionality has been determined as $\Delta G^\ddagger = 10.5 \text{ kcal mol}^{-1}$. Compounds **1**, **2a**, **2b** and **3** have been characterized by NMR spectroscopy and X-ray crystallography. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Pyrrole; Five coordinate; Molybdenum compounds; Bidentate; Tridentate

1. Introduction

Transition metal imido complexes have been widely studied because of their applications in the mechanistic study of the Haber ammonia synthesis [1], the reduction of nitrile [2], and the ammoxidation of propylene [3]. The reactivity of metal imido complexes depends on metals and their oxidation state, auxiliary ligands, and the nature of the substituents on nitrogen [4]. In addition, d⁰ bis-imido metal complexes (RN=)₂M(VI) (M =

Mo, W) have been treated as isolobal of biscyclopentadienyl metal complexes, Cp₂M(IV) (M = Ti, Zr) [5]. We are interested in finding new bis-imido molybdenum complexes bearing bi- or tridentate auxiliary ligands, which may provide new metal complexes with unusual properties due to the steric and electronic effects. 2-(Dimethylaminomethyl)pyrrole and 2,5-bis-(dimethylaminomethyl)pyrrole [6] had been synthesized in the late 1940s, however, very limited compounds bearing these types of ligands had been synthesized [7].

Metals involved in this series of chemistry, such as d⁰ early transition metals [8] and Group 13 elements [9], have been reported. We report herein the synthesis and structural characterization of bis-imido molybdenum complexes bearing the bi- or tridentate substituted

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pyrrole ligands along with their alkylation reactions and the results of dynamic studies by variable-temperature ^1H NMR.

2. Results and discussion

2.1. Synthesis and characterization

The reactions of this study are summarized in Scheme 1. Reacting $[\text{Mo}(\text{NC}_6\text{H}_3\text{Pr}_2\text{-2,6})_2\text{Cl}_2(\text{dme})]$ [10] with 1 equiv. of $\text{Li}[\text{NC}_4\text{H}_3(\text{CH}_2\text{NMe}_2)\text{-2}]$ in diethyl ether at -78°C affords a red crystalline solid of $\text{Mo}(\text{NC}_6\text{H}_3\text{Pr}_2\text{-2,6})_2\text{Cl}[\text{NC}_4\text{H}_3(\text{CH}_2\text{NMe}_2)\text{-2}]$ (**1**), which can be isolated in 86% yield. Alternatively, compound **1** can be prepared directly from $[\text{Mo}(\text{NC}_6\text{H}_3\text{Pr}_2\text{-2,6})_2\text{Cl}_2(\text{dme})]$ in 81% yield by treating it with 1 equiv. of $[\text{HNC}_4\text{H}_3(\text{CH}_2\text{NMe}_2)\text{-2}]$ in diethyl ether at room temperature. The ^1H NMR spectrum of compound **1** in CDCl_3 has one singlet resonance at 2.95 ppm for NMe_2 and one singlet resonance at 4.22 ppm for CH_2N , which are downfield shifting while comparing with that of free ligand, $[\text{HNC}_4\text{H}_3(\text{CH}_2\text{NMe}_2)\text{-2}]$, indicating the high oxidation state of molybdenum depletes electrons density from the substituted pyrrole ligand. The two phenylimido groups exhibit equivalent magnetic environment as evidenced by the observation of one isopropyl methine hydrogen resonance at 3.40 ppm.

Alkylation of **1** with RLi in diethyl ether at -78°C generates $\{\text{Mo}(\text{NC}_6\text{H}_3\text{Pr}_2\text{-2,6})_2\text{R}[\text{NC}_4\text{H}_3(\text{CH}_2\text{NMe}_2)\text{-2}]\}$ (**2a**, $\text{R} = \text{Me}$; **2b**, $\text{R} = \text{Bu}$) in high yield (81 and 88%). The ^1H NMR spectrum of **2a** reveals a singlet at 1.14 ppm for the Mo –methyl group with J_{CH} coupling

constant at ca. 126 Hz, showing no α -agostic interaction between molybdenum and methyl C–H bonds in solution [11]. The ^1H NMR spectrum of Mo –Bu of **2b** shows more complicated chemical shifts than the methyl group of **2a**, in which three resonances are observed at 1.89, 1.25 and 0.85 ppm with integration of 4H, 2H and 3H, respectively. Homonuclear decoupling and ^1H – ^{13}C 2-D NMR spectra of **2b** in CDCl_3 show that the α and β protons of the butyl group are coupled together and appear as a broad single band at 1.8 ppm while γ and δ protons appear at 1.25 and 0.85 ppm, respectively. It is worth noting that to our knowledge, compound **2b** is the first isolated bis-imido molybdenum compound containing a butyl ligand. The common alkylating reagents used in the literature usually lack either β -hydrogen or co-planar conformation of Mo –C–H such as methyl, neopentyl, silyl, or metallocyclopentane etc. [11,12].

Similarly, reacting $[\text{Mo}(\text{NC}_6\text{H}_3\text{Pr}_2\text{-2,6})_2\text{Cl}_2(\text{dme})]$ with 1 equiv. of $\text{Li}[\text{NC}_4\text{H}_2(\text{CH}_2\text{NMe}_2)_2\text{-2,5}]$ in diethyl ether at -78°C affords dark red crystals of $\{\text{Mo}(\text{NC}_6\text{H}_3\text{Pr}_2\text{-2,6})_2\text{Cl}[\text{NC}_4\text{H}_2(\text{CH}_2\text{NMe}_2)_2\text{-2,5}]\}$ (**3**), which was isolated in 92% yield. ^1H NMR spectrum of compound **3** in CDCl_3 at room temperature shows only one resonance for NMe_2 units indicating the two NMe_2 units of $[\text{NC}_4\text{H}_2(\text{CH}_2\text{NMe}_2)_2\text{-2,5}]$ ligand are either fast exchanging at room temperature in solution or magnetically equivalent. Variable-temperature ^1H NMR spectra of compound **3** in CDCl_3 using 600 MHz NMR were taken in order to resolve the ambiguity and the region of the NMe_2 resonances are depicted in Fig. 1.

Two resonances of the NMe_2 of the pyrrole ligand at 2.58 and 1.90 ppm were observed at 213 K with broad-

Scheme 1. (i) $\text{Li}[\text{NC}_4\text{H}_3(\text{CH}_2\text{NMe}_2)\text{-2}]$, Et_2O , -78°C or $[\text{HNC}_4\text{H}_3(\text{CH}_2\text{NMe}_2)\text{-2}]$, Et_2O , 0°C ; (ii) RLi , Et_2O , -78°C ; (iii) $\text{Li}[\text{NC}_4\text{H}_2(\text{CH}_2\text{NMe}_2)_2\text{-2,5}]$, Et_2O , -78°C .

Fig. 1. The variable-temperature ^1H NMR spectra of compound **3** in CDCl_3 at 600 MHz NMR spectrometer. The range of δ 2.8–1.7 is drawn showing the resonance of NMe_2 of pyrrole. The impurity is marked with asterisks.

ening as the temperature raised, and coalescence was observed at ca. 253 K. A single resonance at 2.38 ppm was obtained while the temperature of the NMR sample was raised to room temperature. The activation energy, $\Delta G^\ddagger$, for fluxionality calculated using the chemical shift differences of the proton resonances in the slow limit, is estimated at ca. $10.5 \text{ kcal mol}^{-1}$.

2.2. Solid state structure determination

2.2.1. Molecular structure of $\{\text{Mo}(\text{NC}_6\text{H}_3\text{Pr}_2^i-2,6)_2\text{Cl}[\text{NC}_4\text{H}_3(\text{CH}_2\text{NMe}_2)_2-2]\}$ (**1**)

Deep red crystals of **1** suitable for structure determination were grown from a saturated diethyl ether solution at -20°C . Data collection and selected bond distances and angles are shown in Tables 1 and 2, respectively. An ORTEP drawing of compound **1** is depicted in Fig. 2. The coordination geometry of **1** is best described as a distorted trigonal bipyramidal with one NMe_2 and one imido taking axial positions [$\text{N}(2)\text{--Mo--N}(3)$ at $152.34(7)^\circ$] with the other imido ligand, chloride and pyrrole in the equatorial plane [the sum of angles of $\text{Cl--Mo--N}(4)$, $\text{N}(4)\text{--Mo--N}(1)$, and $\text{Cl--Mo--N}(1)$ is ca. 354°]. The deviation of the axial position from the linear $\text{N}(2)\text{--Mo--N}(3)$ bond may result from the constrained bond angle of $[\text{NC}_4\text{H}_3(\text{CH}_2\text{NMe}_2)_2-2]$. The two imido ligands are substantially different and characterized as linear and bent imido with the bond angles of $\text{Mo--N}(3)\text{--C}(8)$ and $\text{Mo--N}(4)\text{--C}(20)$ being at $175.13(14)$ and $147.55(14)^\circ$, respectively. However, the two bond distances of $\text{Mo--N}(3)$ and $\text{Mo--N}(4)$ fall at the same range and similar results have also been observed in the literature as shown in Table 3. Two aspects can be attributed to the phenomena: (i) The two imido ligands are magnetically equivalent in the NMR time scale, the different Mo--N--C angles indicating the Mo--N bonds are best described as 2.5 [16]. (ii) The phenyl ring of equatorial imido bends toward the axial imido ligand, which can be rationalized as the steric interaction of lone pair electrons on the nitrogen with the dimethylamino part of the pyrrole ligand.

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2.2.2. Molecular structures of $\{\text{Mo}(\text{NC}_6\text{H}_3\text{Pr}_2^i-2,6)_2\text{Me}[\text{NC}_4\text{H}_3(\text{CH}_2\text{NMe}_2)_2-2]\}$ (**2a**) and $\{\text{Mo}(\text{NC}_6\text{H}_3\text{Pr}_2^i-2,6)_2\text{Bu}[\text{NC}_4\text{H}_3(\text{CH}_2\text{NMe}_2)_2-2]\}$ (**2b**)

Crystals of **2a** and **2b** are both obtained from saturated diethyl ether solution at -20°C . Data collection and selected bond distances and angles are shown in Tables 1 and 2, and ORTEP drawings of compounds **2a** and **2b** are depicted in Figs. 3 and 4, respectively. The molecular structures of **2a** and **2b** are both similar to that of **1** and can be described as distorted trigonal bipyramidal with the bond angles of axial ligands at $151.8(2)$ and $156.18(12)^\circ$ for **2a** and **2b**, respectively. Note the sum of the equatorial angles of **2a** (353.5°) and **2b** (353.9°) are close to 360° and the bond distances for Mo to imido ligands are in the same range as for **1**. The bond distance for Mo–alkyl, i.e. $\text{Mo--C}(32)$ $2.219(6)$ Å for compound **2a** and $\text{Mo--C}(32)$ $2.169(3)$ Å for compound **2b**, are in the short end when compared with other bond distances of Mo–alkyl [12].

2.2.3. Molecular structure of $\{\text{Mo}(\text{NC}_6\text{H}_3\text{Pr}_2^i-2,6)_2\text{Cl}[\text{NC}_4\text{H}_2(\text{CH}_2\text{NMe}_2)_2-2,5]\}$ (**3**)

Deep red crystals are obtained from saturated diethyl ether solution of compound **3** at -20°C . Crystal data collections are summarized in Table 1 and selected bond distances and angles are listed in Table 2. An ORTEP drawing of compound **3** is shown in Fig. 5. Comparing the solid state structures of compounds **1** and **3**, the bond distances and angles related to the molybdenum center are quite similar. Compound **3** can be described as a distorted trigonal bipyramid with pyrrole, chloride, and phenylimido ligand taking the trigonal plane positions. The other phenylimido and one of the two NMe_2 of the pyrrole ligand occupied the axial positions with a bond angle of $156.03(7)^\circ$, while the other NMe_2 of the pyrrole ligand dangles outside the coordinating sphere.

3. Experimental

All the reactions were performed using standard Schlenk techniques in an atmosphere of high purity nitrogen or in a glove box. Ethyl ether and heptane were dried over Na/benzophenone ketyl and distilled before use. Methylene chloride was dried over P₂O₅ and distilled prior to use. [Mo(NC₆H₃Prⁱ₂-2,6)₂Cl₂(dme)₂] [10], 2-(dimethylaminomethyl) pyrrole [6], 2,5-bis-(dimethylaminomethyl)pyrrole [6], and lithium salt of substituted pyrrole ligand [8] were prepared according to published literatures. CDCl₃ was degassed by freeze-and-thaw method and dried over 4 Å molecular sieves. ¹H and ¹³C NMR spectra were collected on a Bruker AC200 or Varian 600 instrument. Elemental analysis was performed on Perkin–Elmer CHN-2400.

3.1. Synthesis

3.1.1. {Mo(NC₆H₃Prⁱ₂-2,6)₂Cl[NC₄H₃(CH₂NMe₂)-2]} (1)

3.1.1.1. Method A. A 100 ml Schlenk flask was charged with 30 ml of diethyl ether and Mo(NC₆H₃Prⁱ₂-2,6)₂Cl₂(dme) (1.50 g, 2.5 mmol) and cooled to –78

°C. To this diethyl ether solution, [LiNC₄H₃-(CH₂NMe₂)-2] (0.32 g, 2.5 mmol) in 10 ml diethyl ether was added dropwise. The reaction mixture was warmed to room temperature after the addition was completed and stirred for 14 h. The resulting lithium chloride was removed via filtration and the dark red filtrate was concentrated and cooled to –20 °C to yield dark red crystals. Yield 1.28 g (86%). ¹H NMR (CDCl₃): δ 7.08 (s, 6H, aryl), 6.63 (m, 1H, pyrrole), 6.08 (m, 2H, pyrrole), 4.22 (s, 2H, CH₂N), 3.40 (sept, 4H, CHMe₂), 2.95 (s, 6H, NMe₂), 1.03 (m, 24H, CHMe₂). ¹³C NMR (CDCl₃): δ 152.4 (s), 145.4 (s), 136.9 (s), 131.3 (d, J_{CH} = 183 Hz), 128.2 (d, J_{CH} = 160 Hz), 122.4 (d, J_{CH} = 155 Hz), 110.2 (d, J_{CH} = 163 Hz), 104.3 (d, J_{CH} = 168 Hz), 63.5 (t, J_{CH} = 138 Hz), 49.1 (q, J_{CH} = 138 Hz), 28.3 (d, 128 Hz), 23.8 (q, J_{CH} = 126 Hz), 23.3 (q, J_{CH} = 126 Hz). *Anal.* Found: C, 61.21, H, 7.36, N, 9.26. Calc. for C₃₁H₄₅ClMoN₄: C, 61.53; H, 7.50; N, 9.26%.

3.1.1.2. Method B. A 100 ml Schlenk flask charged with Mo(NC₆H₃Prⁱ₂-2,6)₂Cl₂(dme) (1.5 g, 2.5 mmol) and [HNC₄H₃(CH₂NMe₂)-2] (0.31 g, 2.5 mmol) was added with 20 ml diethyl ether and stirred for 15 h. The resulting dark red solution was dried under vacuum

Table 1
Crystallographic data for compounds **1**, **2a**, **2b**, and **3**

	1	2a	2b	3
Empirical formula	C ₃₁ H ₄₅ ClMoN ₄	C ₃₂ H ₄₈ MoN ₄	C ₃₅ H ₅₄ MoN ₄	C ₃₄ H ₅₂ ClMoN ₅
Formula weight	605.10	584.68	626.76	662.20
Temperature (K)	150(1)	150(1)	150(1)	150(1)
Wavelength (Å)	0.71073	0.71073	0.71073	0.71073
Crystal system	monoclinic	monoclinic	monoclinic	monoclinic
Space group	P2 ₁ /n	P2 ₁ /n	P2 ₁ /c	P2 ₁ /n
<i>a</i> (Å)	10.7802(2)	10.8697(1)	17.7090(2)	11.5402(1)
<i>b</i> (Å)	16.8418(2)	16.7999(1)	10.8807(1)	16.8018(2)
<i>c</i> (Å)	17.1131(3)	17.0008(2)	17.8066(1)	17.9836(1)
β (°)	98.550(1)	97.203(1)	97.776(1)	90.416(1)
<i>V</i> (Å ³)	3072.49(9)	3080.01(5)	3399.54(5)	3486.86(5)
<i>Z</i>	4	4	4	4
<i>D</i> _{calc} (Mg m ^{–3})	1.308	1.261	1.225	1.261
Absorption coefficient (mm ^{–1})	0.539	0.451	0.414	0.482
<i>F</i> (000)	1272	1240	1336	1400
Crystal size (mm)	0.30 × 0.20 × 0.18	0.20 × 0.17 × 0.15	0.40 × 0.10 × 0.03	0.30 × 0.20 × 0.20
θ Range for data collection (°)	1.71–27.50	1.71–27.50	1.16–27.50	1.66–27.50
Reflections collected	16 316	17 539	20 109	21 322
Independent reflections	6759 [<i>R</i> _{int} = 0.0294]	6861 [<i>R</i> _{int} = 0.0544]	7643 [<i>R</i> _{int} = 0.0623]	7872 [<i>R</i> _{int} = 0.0299]
No. of observed reflections [<i>I</i> > 2σ(<i>I</i>)]	5845	4838	5835	6721
Max/min transmission	0.8944 and 0.8019	0.9280 and 0.7336	0.9280 and 0.7758	0.8621 and 0.7781
Data/restraints/parameters	6759/0/335	6859/0/335	7642/0/361	7871/0/398
Goodness-of-fit on <i>F</i> ²	1.073	1.148	1.136	1.039
Final <i>R</i> indices [<i>I</i> > 2σ(<i>I</i>)]	<i>R</i> ₁ = 0.0330 <i>wR</i> ₂ = 0.0653	<i>R</i> ₁ = 0.0794 <i>wR</i> ₂ = 0.1526	<i>R</i> ₁ = 0.0595 <i>wR</i> ₂ = 0.1119	<i>R</i> ₁ = 0.0318 <i>R</i> ₂ = 0.0671
<i>R</i> indices (all data)	<i>R</i> ₁ = 0.0444 <i>wR</i> ₂ = 0.0690	<i>R</i> ₁ = 0.1271 <i>wR</i> ₂ = 0.1706	<i>R</i> ₁ = 0.0931 <i>wR</i> ₂ = 0.1276	<i>R</i> ₁ = 0.0442 <i>wR</i> ₂ = 0.0715
Largest difference peak and hole (e Å ^{–3})	0.381 and –0.363	1.509 and –0.814	1.267 and –0.664	0.320 and –0.369

Table 2
Selected bond distances (Å) and angles (°) for compounds **1**, **2a**, **2b**, and **3**

Compound 1					
Mo–N(3)	1.762(2)	Mo–N(4)	1.766(2)		
Mo–N(1)	2.066(2)	Mo–Cl	2.3911(6)		
N(3)–Mo–N(4)	108.36(8)	N(3)–Mo–N(1)	92.17(7)	N(4)–Mo–N(1)	103.89(7)
N(3)–Mo–N(2)	152.34(7)	N(4)–Mo–N(2)	98.21(7)	N(1)–Mo–N(2)	73.67(6)
N(3)–Mo–Cl	96.54(6)	N(4)–Mo–Cl	107.96(6)	N(1)–Mo–Cl	142.23(5)
N(2)–Mo–Cl	82.10(5)	C(8)–N(3)–Mo	175.13(14)	C(20)–N(4)–Mo	147.55(14)
Compound 2a					
Mo–N(2)	1.745(4)	Mo–N(1)	1.759(4)	Mo–C(32)	2.219(6)
Mo–N(4)	2.376(5)	Mo–N(3)	2.070(5)		
N(2)–Mo–N(1)	109.3(2)	N(2)–Mo–N(3)	93.9(2)	N(1)–Mo–N(3)	107.8(2)
N(2)–Mo–C(32)	95.0(2)	N(1)–Mo–C(32)	105.5(2)	N(3)–Mo–C(32)	140.2(2)
N(2)–Mo–N(4)	151.8(2)	N(1)–Mo–N(4)	98.6(2)	N(3)–Mo–N(4)	73.0(2)
C(32)–Mo–N(4)	81.2(2)	C(1)–N(1)–Mo	148.6(4)	C(13)–N(2)–Mo	177.4(4)
Compound 2b					
Mo–N(2)	1.761(3)	Mo–N(1)	1.775(3)	Mo–C(32)	2.169(3)
Mo–N(4)	2.403(3)	Mo–N(3)	2.078(3)		
N(2)–Mo–N(1)	110.71(13)	N(2)–Mo–N(3)	96.00(13)	N(1)–Mo–N(3)	111.97(12)
N(2)–Mo–C(32)	90.29(14)	N(1)–Mo–C(32)	109.94(14)	N(3)–Mo–C(32)	131.94(13)
N(2)–Mo–N(4)	156.18(12)	N(1)–Mo–N(4)	93.07(12)	N(3)–Mo–N(4)	72.86(11)
C(32)–Mo–N(4)	82.55(12)	C(1)–N(1)–Mo	156.4(3)	C(13)–N(2)–Mo	174.9(2)
Compound 3					
Mo–N(5)	1.757(2)	Mo–N(4)	1.762(2)	Mo–N(1)	2.362(2)
Mo–Cl	2.3834(5)	Mo–N(2)	2.079(2)		
N(5)–Mo–N(4)	110.39(7)	N(5)–Mo–N(2)	104.36(7)	N(4)–Mo–N(2)	97.71(6)
N(5)–Mo–N(1)	93.56(6)	N(4)–Mo–N(1)	156.03(7)	N(2)–Mo–N(1)	74.40(6)
N(5)–Mo–Cl	105.84(5)	N(4)–Mo–Cl	92.17(5)	N(2)–Mo–Cl	142.47(4)
N(1)–Mo–Cl	81.97(4)	C(11)–N(4)–Mo	173.13(13)	C(23)–N(5)–Mo	158.03(13)

and recrystallized from diethyl ether to afford the desired product. Yield: 1.23 g (81%).

3.1.2. $\{Mo(NC_6H_3Pr^i-2,6)_2Me[NC_4H_3(CH_2NMe_2)-2]\}$ (**2a**)

A 50 ml Schlenk flask was charged with 20 ml of diethyl ether and **1** (1.00 g, 1.7 mmol) and cooled to -78°C . To the solution, MeLi (1.2 ml, 1.4 M in diethyl ether, 1.7 mmol) was added via syringe and stirred for 12 h after slowly warming up to room temperature. The mixture was filtered to removed lithium salt and the filtrate was concentrated and cooled to -20°C to afford deep red crystals, among which a very small amount of unidentified impurity was observed. Yield: 0.78 g (81%). ^1H NMR (CDCl_3): δ 7.10 (s, 6H, aryl), 6.82 (m, 1H, pyrrole), 6.14 (m, 2H, pyrrole), 4.16 (s, 2H, CH_2N), 3.53 (sept, 4H, CHMe_2), 2.84 (s, 6H, NMe_2), 1.14 (s, 3H, $\text{Mo}-\text{CH}_3$), 1.09 (m, 24H, CHMe_2). ^{13}C NMR (CDCl_3): δ 152.0 (s), 144.5 (s), 136.7 (s), 131.7 (d, $J_{\text{CH}} = 183$ Hz), 126.2 (d, $J_{\text{CH}} = 160$ Hz), 122.3 (d, $J_{\text{CH}} = 158$ Hz), 109.4 (d, $J_{\text{CH}} = 167$ Hz), 103.4 (d, $J_{\text{CH}} = 167$ Hz), 64.2 (t, $J_{\text{CH}} = 138$ Hz), 49.2 (t, $J_{\text{CH}} = 138$ Hz), 28.1 (d, 129 Hz), 24.1 (q, $J_{\text{CH}} = 126$ Hz), 23.9 (q, $J_{\text{CH}} = 126$ Hz), 23.2 (q, $J_{\text{CH}} = 126$ Hz).

3.1.3. $\{Mo(NC_6H_3Pr^i-2,6)_2Bu[NC_4H_3(CH_2NMe_2)-2]\}$ (**2b**)

A similar procedure had been applied as for **2a**. **1** (1.50 g, 2.5 mmol) and BuLi (1.0 ml, 2.5 M, 2.5 mmol) were used. Yield: 1.36 g (88%). ^1H NMR (CDCl_3): δ 7.05 (s, 6H, aryl), 6.79 (s, 1H, pyrroate), 6.08 (m, 2H, pyrroate), 4.03 (s, 2H, CH_2N), 3.56 (m, 4H, CHMe_2),

Fig. 2. The ORTEP plot of compound **1**. Thermal ellipsoids are drawn at 50% probability and hydrogen atoms are omitted for clarity.

Table 3

The comparison of bond distance and angle of five coordinate bis(2,6-diisopropylphenyl)imido complexes

Complex	Mo–N–C bond angle and Mo–N bond distance (°; Å)	Reference
Mo(NC ₆ H ₃ Pr ⁱ ₂ -2,6) ₂ -(CH ₂ SiMe ₃)-(Py-2-CMe ₂ O)	172.95, 1.769; 152.52, 1.753	[13]
[Mo(NC ₆ H ₃ Pr ⁱ ₂ -2,6) ₂ -Me(μ-OMe)] ₂	177.44, 1.756; 153.67, 1.757	[13]
Mo(NC ₆ H ₃ Pr ⁱ ₂ -2,6) ₂ -Me ₂ (PMe ₂ Ph)	175.93, 1.759; 151.90, 1.760	[11b]
Mo(NC ₆ H ₃ Pr ⁱ ₂ -2,6) ₂ -[Py(OCPh ₂ CH ₂) ₂ -2,6]	164.78, 1.760; 144.79, 1.771	[14]
Mo(NC ₆ H ₃ Pr ⁱ ₂ -2,6) ₂ -Cl[-C(Me) ₂ COOBu ^t]	158.58, 1.730; 157.66, 1.754	[15]
Mo(NC ₆ H ₃ Pr ⁱ ₂ -2,6) ₂ -Cl[CH(NMe ₂)COOEt]	171.10, 1.745; 160.95, 1.753	[15]
Compound 1	175.13, 1.762; 147.55, 1.766	This work
Compound 2a	177.4, 1.75; 148.6, 1.759	This work
Compound 2b	174.9, 1.761; 156.4, 1.775	This work
Compound 3	173.13, 1.762; 158.03, 1.757	This work

Fig. 3. The ORTEP plot of compound **2a**. Thermal ellipsoids are drawn at 50% probability and hydrogen atoms are omitted for clarity.

2.77 (s, 6H, NMe₂), 1.89 (s, br, 4H, Mo–CH₂CH₂–C₂H₅), 1.25 (m, 2H, Mo–CH₂CH₂CH₂CH₃), 1.01 (m, 24H, CHMe₂), 0.85 (m, 3H, Mo–CH₂CH₂CH₂CH₃). ¹³C NMR (CDCl₃): δ 151.6 (s), 144.6 (s), 136.8 (s), 132.2 (d, *J*_{CH} = 183 Hz), 126.1 (d, *J*_{CH} = 160 Hz), 122.4 (d, *J*_{CH} = 153 Hz), 109.3 (d, *J*_{CH} = 162 Hz), 103.4 (d, *J*_{CH} = 167 Hz), 64.3 (t, *J*_{CH} = 138 Hz), 52.4 (t, *J*_{CH} = 123 Hz), 49.4 (q, *J*_{CH} = 138 Hz), 37.8 (t, *J*_{CH} = 126 Hz), 29.1 (t, 123 Hz), 28.0 (d, *J*_{CH} = 128 Hz), 23.8 (q, *J*_{CH} = 126 Hz), 23.5 (q, *J*_{CH} = 126 Hz), 13.5 (q, *J*_{CH} = 124 Hz).

3.1.4. {Mo(NC₆H₃Prⁱ₂-2,6)₂Cl}[NC₄H₂(CH₂NMe₂)₂-2,5]} (3)

A procedure analogous to that utilized for **1** was employed. Mo(NC₆H₃Prⁱ₂-2,6)₂Cl₂(dme) (1.00 g, 1.65 mmol) and [LiNC₄H₂(CH₂NMe₂)₂-2,5] (0.31 g, 1.65 mmol) were used. Yield: 1.01 g (92%). ¹H NMR (CDCl₃): δ 7.07 (s, 6H, aryl), 6.05 (s, 2H, pyrrole), 3.61 (m, br, 8H, CH₂N and CHMe₂), 2.38 (s, br, 12H, NMe₂), 1.02 (s, br, 24H, CHMe₂). ¹³C NMR (CDCl₃): δ 153.1 (s), 145.5 (s), 139.4 (s), 128.2 (d, *J*_{CH} = 160 Hz), 122.4 (d, *J*_{CH} = 157 Hz), 106.8 (d, *J*_{CH} = 169 Hz), 61.7 (t, *J*_{CH} = 135 Hz), 47.4 (q, *J*_{CH} = 137 Hz), 28.2 (d, *J*_{CH} = 130 Hz), 24.2 (q, *J*_{CH} = 127 Hz), 23.4 (q, *J*_{CH} = 125 Hz), 15.2 (q, *J*_{CH} = 126 Hz).

Fig. 4. The ORTEP plot of compound **2b**. Thermal ellipsoids are drawn at 50% probability and hydrogen atoms are omitted for clarity.

Fig. 5. The ORTEP plot of compound **3**. Thermal ellipsoids are drawn at 50% probability and hydrogen atoms are omitted for clarity.

3.2. X-ray structure determination of compounds **1**, **2a**, **2b**, and **3**

The same procedures have been taken for the structural determination of compounds **1**, **2a**, **2b**, and **3**. The crystals were mounted on glass fibers using epoxy resin and transferred to a goniostat and cooled to 150 K under liquid nitrogen vapor. Data were collected on a Bruker SMART CCD diffractometer with graphite-monochromated Mo K α radiation. An empirical absorption was applied and based on the symmetry-equivalent reflections using the SADABS program. Using SHELXTL program on PC computer made the structure analysis. Structures were solved using the direct method and refined by full-matrix least-squares on F^2 values. Largest residual electron density for compounds **2a** and **2b**, which are very closed to Mo atom, should result from the noise peak. The high R_1 value of **2a** (0.0794) may result from the crystal quality. Non-hydrogen atoms were refined anisotropically. Hydrogen atoms were fixed at calculated positions and refined using a riding mode. The structure of compound **3** was disorder and the site occupancy of N3, C9, C10, N3', C9' and C10' have been processed with 0.50. The crystal data are summarized in Table 1.

4. Supplementary material

Crystallographic data for compounds **1**, **2a**, **2b**, and **3** are available from the authors on request.

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