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Diverse reactivity of stereoisomers containing quadruply bonded dimolybdenum with oxygen: formation of $[{Mo(\eta-N,N'-diisopropylbenzamidinato)oxo}_2(\mu-acetato)_2(\mu-oxo)]$

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Abstract

The reaction of quadruply bonded dimolybdenum complex, $[Mo_2(\mu-OAc)_4]$ (1), with lithiated amidinato, Li[(NⁱPr)₂CR] (R = ^{*i*}Bu; **2a**, Me; **2b**, Ph; **2c**), was investigated. The reaction of **1** with **2a** afforded the dark-red solid, whereas the product was so highly unstable that the product was not able to be characterized. In the case of acetamidinato **2b**, lantern-type mixed-ligand quadruply bonded dimolybdenum complex, $[Mo_2(\mu-OAc){\mu-(NⁱPr)_2CMe}_3]$ (3), was obtained as a yellow solid. In the reaction with benzamidinato **2c**, symmetrical lantern-type dimolybdenum complex, $[Mo_2(\mu-OAc)_2 {\mu-(NⁱPr)_2CPh}_2]$ (4), was isolated as a yellow solid. In the latter reaction, intermediary red compound (5), which is considered to be stereoisomer of **4** possessing non-lantern-type skeleton, was formed. However, isolation of **5** as a single component was not successful due to isomerization to **4**. Complex **5** readily reacted with dry oxygen to give dimolybdenum(V) complex, $[{Mo(\eta-(NⁱPr)_2CPh)oxo}_2 (\mu-OAc)_2(\mu-oxo)]$ (6), as a red solid. These complexes were characterized spectroscopically as well as, in some cases, by X-ray analyses. © 2005 Elsevier B.V. All rights reserved.

Keywords: Molybdenum complexes; Amidinato ligands; Dinuclear complexes; Mo-Mo bond; Oxo complexes

1. Introduction

Amidinato is one of the most important ancillary ligands in the coordination chemistry because it acts not only as a chelating mode but also as a bridging one [1]. The remarkable ability of an amidinato ligand, in particular of a formamidinato ligand formulated as $[(NR')_2CH]^-$, to construct the bridging mode of coordination may be useful to build up the dinuclear complexes containing the metal-metal multiple bonds [2].

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There have been a lot of excellent studies on the quadruply bonded dimolybdenum complexes, which are often named as lantern-type complexes from a viewpoint of their shapes. Recently, extensive attention has been focused on the formation of the linearly ordered multinuclear transition-metal complexes by assembling the metals along the lines with the metal-metal multiple bonds [3]. However, there are few examples of the investigation on the direct reactivity toward the quadruply bonded Mo₂ core in perpendicular directions [4].

The recent study on amidinato complexes has revealed that the steric repulsion between substituents on the amidinato ligand governs the coordination mode of the ligand: an amidinato ligand bearing sterically bulky substituents is likely to act as a chelating ligand

(Chart 1) [5]. Thus we are interested in the introduction of sterically hindered amidinato ligands onto the Mo₂ core for the purpose of producing new non-lantern-type Mo₂ complexes. Herein, we report that the reaction of [Mo₂(μ -OAc)₄] (1) with a series of Li[(NⁱPr)₂CR] (R = 'Bu; **2a**, Me; **2b**, Ph; **2c**) resulted in the formation of new mixed-ligand lantern-type dimolybdenum complexes. In the course of this study, we found the formation of non-lantern-type complex of dimolybdenum, the reactivity of which is also described.

2. Experimental

2.1. General procedures

All manipulations involving air- and moisture-sensitive compounds were carried out under an atmosphere of dry argon, 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. $[Mo_2(\mu-OAc)_4]$ (1) [6] and Li(amidinato) (**2a**, **2b**, and **2c**) [5b,7] were prepared according to the literature methods. Other reagents employed in this research were used without further purification.

¹H, ¹³C{¹H}, and ³¹P{¹H} NMR spectra were recorded on a JEOL EX-270 spectrometer at ambient temperature unless otherwise mentioned. ¹H and ¹³C{¹H} NMR chemical shifts were reported in ppm relative to internal Me₄Si. ³¹P{¹H} NMR chemical shifts were recorded in ppm relative to external 85% H₃PO₄. All coupling constants were recorded in Hz. Splitting patterns are indicated as s, singlet; d, doublet; t, triplet; sept, septet; m, multiplet; and br, broad signal. Elemental analyses were performed by a Perkin–Elmer 240C.

2.2. Preparation of $[Mo_2(\mu - OAc) \{\mu - (N^t Pr)_2 CMe\}_3]$ (3)

 $[Mo_2(\mu-OAc)_4]$ (1) (76 mg, 0.18 mmol) and Li- $[(N'Pr)_2CMe]$ (2b) (87 mg, 0.59 mmol) were put into 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 and the reaction mixture was allowed to be warmed to room temperature. The mixture



Chart 1. Coordination modes of amidinato ligand.

was then stirred overnight to give a brown solution. After removing the volatiles under reduced pressure, the residual solid was extracted with pentane. The solvent was evaporated off under high vacuum and spectroscopically pure 3 was obtained as a greenish yellow solid (111 mg, 0.16 mmol, 89%). Anal. Calc. for C₂₆H₅₄Mo₂₋ N₆O₂: C, 46.29; H, 8.07; N, 12.46. Found: C, 46.18; H, 8.08; N, 12.39. ¹H NMR (δ , in C₆D₆): 0.87 (d, J = 6.4Hz, 12H, i Pr–CH₃), 1.04 (d, J = 6.4 Hz, 12H, i Pr– CH_3), 1.42 (d, J = 6.9 Hz, 12H, ^{*i*}Pr- CH_3), 2.35 (s, 6H, amidinato-CCH₃), 2.42 (s, 3H, amidinato- or acetate- CCH_3), 2.49 (s, 3H, amidinato- or acetate- CCH_3), 3.80 (sept, J = 6.9 Hz, 2H, ^{*i*}Pr-CH), 4.23 (sept, J = 6.4Hz, 4H, ^{*i*}Pr–CH). ¹³C{¹H} NMR (δ , in C₆D₆): 16.0 (amidinato-CCH₃), 21.3 (amidinato- or acetate-CCH₃), 23.8 (ⁱPr-CH₃), 24.2 (amidinato- or acetate-CCH₃), 25.1 (¹Pr-CH₃), 25.2 (¹Pr-CH₃), 50.4 (¹Pr-CH), 51.6 (^{*i*}Pr-CH), 161.7, 162.9, 175.6 (amidinato and acetate central carbons).

2.3. Preparation of $[Mo_2(\mu - OAc)_2 \{\mu - (N^tPr)_2 CPh\}_2]$ (4)

 $[Mo_2(\mu-OAc)_4]$ (1) (289 mg, 0.68 mmol) and Li[(- $N'Pr)_2CPh$] (2c) (301 mg, 1.43 mmol) were put into a Schlenk tube, which was attached to a high-vacuum line. THF (ca. 15 mL) was added by a trap-to-trap-transfer technique at -78 °C and the reaction mixture was allowed to be warmed to room temperature. The mixture was then refluxed overnight to give a vellow solution. After removing the volatiles under reduced pressure, the residual solid was extracted with pentane. The solvent was evaporated off under high vacuum, and spectroscopically pure 4 was obtained as a yellow solid (452 mg, 0.63 mmol, 93%). Anal. Calc. for C₃₀H₄₄Mo₂₋ N₄O₄: C, 50.28; H, 6.19; N, 7.82. Found: C, 50.10; H, 6.20; N, 7.81. ¹H NMR (δ , in C₆D₆): 0.93 (d, J = 6.6 Hz, 24H, $Pr-CH_3$, 2.59 (s, 6H, acetate-CH₃), 4.02 (sept, J = 6.6 Hz, 4H, ^{*i*}Pr-CH), 7.12–7.39 (m, 10H, Ph). (δ , in CDCl₃): 0.68(d, J = 6.6 Hz, 24H, ^{*i*}Pr-CH₃), 2.56 (s, 6H, acetate– CH_3), 3.77 (sept, J = 6.6 Hz, 4H, ^{*i*}Pr–CH), 7.36–7.52 (m, 10H, Ph). ¹³C{¹H} NMR (δ , in C_6D_6): 23.7 (acetate-CCH₃), 26.3 (^{*i*}Pr-CH₃), 51.7 (¹Pr-CH), 127.8, 128.4, 129.4, 138.5 (Ph), 166.9, 177.1 (amidinato and acetate central carbons).

2.4. Formation of $[Mo_2(\mu - OAc)_2 \{\eta - (N^i Pr)_2 CPh\}_2]$ (5)

[Mo₂(μ -OAc)₄] (1) (268 mg, 0.63 mmol) and Li-[(N'Pr)₂CPh] (**2c**) (271 mg, 1.29 mmol) were put into a Schlenk tube, which was attached to a high-vacuum line. THF (ca. 15 mL) was added by a trap-to-trap-transfer technique at -78 °C and the reaction mixture was allowed to be warmed to room temperature. After several hours, the volatiles were removed under reduced pressure. The residual red solid was subjected to ¹H NMR

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measurement. ¹H NMR (δ , in C₆D₆): 0.97 (d, J = 6.3 Hz, 12H, ^{*i*}Pr–CH₃), 1.57 (d, J = 6.3 Hz, 12H, ^{*i*}Pr–CH₃), 2.63 (s, 6H, acetate–CH₃), 3.75 (sept, J = 6.3 Hz, 4H, ^{*i*}Pr–CH), 6.77–7.05 (m, 10H, Ph). Complex **5** was not able to be isolated due to its tendency to isomerize to **4**.

2.5. Preparation of $[\{Mo(\eta - (N^iPr)_2CPh)(oxo)\}_2(\mu - OAc)_2(\mu - oxo)]$ (6)

 $[Mo_2(\mu-OAc)_4]$ (1) (111 mg, 0.26 mmol) and Li- $[(N'Pr)_2CPh]$ (2c) (134 mg, 0.64 mmol) were put into 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 and the reaction mixture was allowed to be warmed to -30 °C. The reaction mixture was again cooled to -78 °C, and then oxygen (1 atm), which had been purified by SICAPENT, was introduced. After being allowed to be warmed to room temperature, the volatiles were removed under reduced pressure. The residual liver solid was extracted with hexane. The fractional recrystallization gave the title complex 6 (65 mg, 0.085 mmol, 33%) as a red crystal and 4 (60 mg, 0.084 mmol, 32%) as a yellow crystal. Anal. Calc. for C₃₀H₄₄Mo₂N₄O₇: C, 47.13; H, 5.80; N, 7.33. Found: C, 47.25; H, 5.71; N, 7.30. ¹H NMR (δ, in C_6D_6 : 1.38 (d, J = 6.6 Hz, 6H, ^{*i*}Pr-CH₃), 1.41 (d, J = 6.6 Hz, 6H, ^{*i*}Pr-CH₃), 1.69 (d, J = 6.6 Hz, 6H, ^{*i*}Pr- CH_3), 1.71 (s, 3H, acetato- CH_3), 1.71 (d, J = 6.6 Hz, 6H, i Pr-CH₃), 1.73 (s, 3H, acetate-CH₃), 3.85 (sept, J = 6.6 Hz, 2H, ^{*i*}Pr-CH), 3.98 (sept, J = 6.6 Hz, 2H, ^{*i*}Pr–CH), 7.03-7.28 (m, 10H, Ph). (δ , in CDCl₃): 1.15 (d, J = 6.6 Hz, 6H, ^{*i*}Pr-CH₃), 1.16 (d, J = 6.6 Hz, 6H, 1 Pr-CH₃), 1.40 (d, J = 6.6 Hz, 6H, 1 Pr-CH₃), 1.49 (d, J = 6.6 Hz, 6H, ^{*i*}Pr-CH₃), 1.69 (s, 3H, acetato-CH₃), 2.36 (s, 3H, acetate- CH_3), 3.69 (sept, J = 6.6 Hz, 2H, ^{*i*}Pr-CH), 3.88 (sept, J = 6.6 Hz, 2H, ^{*i*}Pr-CH), 7.26-7.49 (m, 10H, Ph). ${}^{13}C{}^{1}H$ NMR (δ , in C₆D₆): 23.1, 23.4, 23.5, 24.0, 24.5 (ⁱPr-CH₃ or acetato-CH₃), 50.9, 51.2 (^{*i*}Pr-*C*H), 126.7, 128.6, 128.9, 129.6, 131.7 (Ph), 180.9, 181.0 (OCO), 199.9 (s, NCN).

2.6. Experimental procedure for X-ray crystallography

Suitable single crystals were obtained by recrystallization from toluene (3), pentane (4), or from hexane (6), at -30 °C and were mounted on glass fibers.

Diffraction measurements of **3** and **4** were made on a Rigaku AFC-7R automated four-circle diffractometer with graphite-monochromated Mo K α radiation ($\lambda = 0.71069$ Å). The data collections were carried out at 23 ± 2 °C using the ω -2 θ scan technique. Cell constants and an orientation matrix for data collection were determined from 25 reflections with 2 θ angles in the range 29.77–29.98° for **3** and 29.67–29.98° for **4**, respectively. In the reduction of data, Lorentz and polariza-

tion corrections and an empirical absorption correction (Ψ scan) were made.

A diffraction measurement of **6** was made on an Enraf-Nonius CAD4 diffractometer by using graphitemonochromated Mo K α radiation ($\lambda = 0.71069$ Å). The data collections were carried out at 23 ± 1 °C using the ω -2 θ scan technique. Cell constants and an orientation matrix for data collection were determined from 25 reflections with 2 θ angles in the range 20.84–36.06°. In the reduction of data, Lorentz and polarization corrections and an empirical absorption correction (Ψ scan) were made.

Crystallographic data and the results of measurements are summarized in Table 1. The structures were solved by heavy-atom Patterson methods (DIRDIF94 PATTY) [8] for 3 or by direct methods (SIR 92) [9] for 4 and 6, and expanded using Fourier techniques [10]. Least-squares refinements were carried out using SHELXL-97 [11] linked to TEXSAN [12]. All of the nonhydrogen atoms were refined anisotropically. All hydrogen atoms were introduced at the ideal positions with the C-H bond distance of 0.96 Å. The methyl hydrogen atoms were refined by using riding models and the rest of hydrogen atoms were fixed at the calculated positions.

3. Results and discussion

3.1. Reaction of $[Mo_2(\mu - OAc)_4](1)$ with Li(amidinato) (2). Formation of mixed-ligand lantern-type complexes

In order to systematically investigate on the reaction of dimolybdenum complex 1 with Li(amidinato), we selected three amidinato ligands containing a series of substituents on the central carbon, $\text{Li}[({}^{i}\text{PrN})_{2}\text{CR}]$ (R = ${}^{t}\text{Bu}$; 2a, Me; 2b, Ph; 2c), which are easily prepared by the reaction of 1,3-diisopropylcarbodiimide with the corresponding RLi (Chart 2).

Firstly, the reaction of dimolybdenum complex 1 with Li(amidinato) **2a** in THF was examined (Scheme 1). The reaction mixture was changed from a yellow solution to a homogeneous red solution from which a dark-red solid was obtained, which was, however, too unstable to be characterized. Cotton has reported that the fully chelated red crystalline dimolybdenum complex, $[Mo_2(\eta-o-Me_2NCH_2C_6H_4)_4]$, is very air-sensitive [13]. Taking into account that most of lantern-type complexes, most of which are yellow, are relatively stable toward air and moisture, it is feasible to consider that instability of the present product might come from the formation of non-lantern-type complex.

In the reaction of 1 with acetamidinato 2b, tris(amidinato)acetato complex 3 was obtained as a greenish yellow crystal in good yield (Scheme 2). X-ray diffraction study on the product revealed that the complex 3 in a

Table 1
Summary of crystal data for 3, 4, and 6

	3	4	6
Empirical formula	$C_{26}H_{54}Mo_2N_6O_2$	C ₃₀ H ₄₄ Mo ₂ N ₄ O ₄	C ₃₀ H ₄₄ Mo ₂ N ₄ O ₇
Formula weight	674.63	716.58	764.58
Crystal color, habit	yellow, plate	yellow, prismatic	red, plate
Crystal size (mm)	$0.25 \times 0.18 \times 0.08$	$0.25 \times 0.15 \times 0.15$	$0.45 \times 0.38 \times 0.15$
Crystal system	triclinic	monoclinic	triclinic
Space group	$P\overline{1}(\#2)$	$P2_1/c$ (#14)	$P\bar{1}(#2)$
Lattice parameters			
a (Å)	8.860(3)	9.735(2)	12.774(1)
b (Å)	10.396(2)	9.876(1)	13.743(2)
c (Å)	18.121(3)	17.741(1)	10.8262(9)
α (°)	89.99(1)	90	95.405(9)
β (°)	80.64(2)	91.13(1)	107.914(8)
γ (°)	74.57(2)	90	96.15(1)
$V(Å^3)$	1586.0(7)	1705.4(4)	1781.7(4)
Ζ	2	2	2
$D_{\rm c} ({\rm g}{\rm cm}^{-3})$	1.413	1.395	1.425
F(000)	704.00	736.00	784.00
μ (Mo K α) (cm ⁻¹)	8.20	7.70	7.48
$2\theta_{\rm max}$ (°)	60.0	60.0	54.9
Reflections measured	9818	5511	8529
Independent reflections (R_{int})	9265 (0.026)	4969 (0.022)	8162 (0.013)
Number of observed $(I > 2.0\sigma(I))$	6558	3151	6630
Number of variables	341	186	398
Residuals: R^{a} ; R_{w}^{b}	$0.030; 0.090^{\rm d}$	0.033; 0.101 ^e	$0.025; 0.070^{\rm f}$
GOF °	1.03 ^d	1.02 ^e	1.05 ^f
$\delta \rho_{\max,\min} (e \text{ Å}^{-3})$	0.47, -0.65	0.34, -0.35	0.29, -0.40

^a $R = \Sigma ||F_0| - |F_c|| \Sigma |F_0|$ for observed data. ^b $R_w = [\Sigma w (F_o^2 - F_c^2)^2 / \Sigma w (F_o^2)^2]^{1/2}$ for all data.

^c GOF = $[\Sigma w(|F_o| - |F_c|)^2 / (N_o - N_v)]^{1/2}$.

 $\begin{array}{l} & \text{d} \quad w = [\sigma^2(F_o^2) + (0.0404P^2 + 0.0560P]^{-1}, \text{ where } P = (F_o^2 + 2F_c^2)/3. \\ & \text{e} \quad w = [\sigma^2(F_o^2) + (0.0421P)^2 + 0.3913P]^{-1}, \text{ where } P = (F_o^2 + 2F_c^2)/3. \\ & \text{f} \quad w = [\sigma^2(F_o^2) + (0.0328P)^2 + 0.5551P]^{-1}, \text{ where } P = (F_o^2 + 2F_c^2)/3. \end{array}$



Chart 2. Entry of amidinato ligands employed in this research.



solid state possesses a lantern-type skeleton bearing three amidinato ligands and one acetato ligand. One of the three amidinato ligands is located in the coplanar with the acetato ligand and the rest two amidinato ligands are located in mutually trans positions (vide infra). This structure was found to be maintained in the solution state, too. In the ¹H NMR spectrum, three sets



of doublets with the same integration (12 protons each), assignable to ⁱPr-methyl groups on the amidinato ligands, were observed. Methine protons on the amidinato ligands displayed two sets of septets and the integration ratio was 4H/2H. The pathway for the formation of non-lantern-type complex in this reaction is not clear at the present stage.

Treatment of 1 with two equivalents of 2c in THF under refluxing conditions vielded a homogeneous vellow solution from which yellow crystals were obtained in 93% yield. Elemental analysis, ¹H and ¹³C NMR spectra, and X-ray structure analysis confirmed the formation of the symmetrical lantern-type complex bearing two amidinato and two acetato ligands (4) (Scheme 3).



Scheme 3.

In ¹H NMR spectrum, isopropyl protons on the amidinato ligands were seen as a doublet at 0.92 ppm and as a septet at 4.02 ppm with a coupling constant of 6.6 Hz. Methyl protons on the acetato ligands were observed at 2.59 ppm as a singlet.

The ORTEP drawings of 3 and 4 are displayed in Figs. 1 and 2, respectively. The crystal data and selected bond distances and angles are listed in Tables 1-3, respectively. The molecular structure of 3 is almost identical to those of $[Mo_2(\mu-OAc){\mu-(NPh)_2CMe}_3]$ [14]. The Mo-Mo distance, 2.0702(3) Å, is consistent with a Mo-Mo quadruple bond. The Mo-N bond distances that are *trans* to the acetato oxygen are 2.125(2) Å for Mo(1)-N(3) and 2.134(2) Å for Mo(2)-N(4). These distances are slightly shorter than the remaining Mo-N bond distances (2.153(2)–2.158(2) Å). These structural features are also similar to those in $[Mo_2(\mu-OAc)]$ $(NPh)_2CMe_{3}$ [14]. The structure of complex 4 is almost similar to those of $[Mo(\mu-OAc)_2{\mu-(NSiMe_3)_2CPh}_2]$ and $[Mo(\mu-OAc)_2{\mu-(N,N'-di(2-methoxyphe-$ [15] nyl)formamidinato)₂}] [16]. The quadruply bonded Mo–Mo distance in 4 is 2.0677(4) Å.



Fig. 1. ORTEP drawing of complex **3** with thermal ellipsoid drawn at the 30% probability level. All hydrogen atoms are omitted for clarity.



Fig. 2. ORTEP drawing of complex **4** with thermal ellipsoid drawn at the 30% probability level. All hydrogen atoms are omitted for clarity.

3.2. Reinvestigation on the reaction of 1 with 2c. Formation of a non-lantern-type dinuclear complex, $[Mo_2(\mu-OAc)_2\{\eta-(N^iPr)_2CPh\}_2]$ (5)

The reaction of 1 with 2c in THF was investigated in detail by ¹H NMR (Scheme 4). The reaction mixture of 1 with 2c showed a homogeneous red solution at the

Table 2 Selected bond distances (Å) and angles (°) for complex 3

	0 ()	
Mo(1)–Mo(2)		2.0702(3
Mo(1)-O(1)		2.175(2)
Mo(1)–N(1)		2.158(2)
Mo(1)-N(3)		2.125(2)
Mo(1)-N(5)		2.156(2)
Mo(2)–O(2)		2.174(2)
Mo(2)–N(2)		2.153(2)
Mo(2)–N(4)		2.134(2)
Mo(2)-N(6)		2.156(2)
O(1)-Mo(1)-N(3)		173.94(7)
N(1)-Mo(1)-N(5)		171.73(7)
O(1)-Mo(1)-N(1)		88.23(8)
O(1)-Mo(1)-N(5)		85.56(7)
N(1)-Mo(1)-N(3)		94.83(8)
N(3)-Mo(1)-N(5)		90.87(8)
O(2)-Mo(2)-N(4)		174.83(7)
N(2)-Mo(2)-N(6)		171.24(9)
O(2)-Mo(2)-N(2)		88.21(8)
O(2)-Mo(2)-N(6)		85.47(8)
N(2)-Mo(2)-N(4)		94.05(8)
N(4)-Mo(2)-N(6)		91.78(8)

Table 3 Selected bond distances (Å) and angles (°) for complex **4**

Mo(1)–Mo(1*)	2.0677(4)
Mo(1)–O(1)	2.123(2)
Mo(1)-O(2*)	2.122(2)
Mo(1)–N(1)	2.135(2)
Mo(1)–N(2*)	2.132(3)
O(1)-Mo(1)-O(2*)	175.52(8)
N(1)-Mo(1)-N(2*)	174.02(9)
O(1)-Mo(1)-N(1)	89.16(9)
O(1)-Mo(1)-N(2*)	90.26(9)
O(2*)-Mo(1)-N(1)	90.59(9)
O(2*)-Mo(1)-N(2*)	89.53(9)
N(1)-Mo(1)-N(2*)	174.02(9)



initial stage. After treating 1 with 2c in THF at -78 °C, the reaction mixture was gradually allowed to be warmed to room temperature. After removing the volatiles, the obtained red solid was subjected to ¹H NMR measurement. The ¹H NMR spectrum showed that the formation of 4 was accompanied with another complex (5). The latter complex showed the two doublets ($\delta = 0.97$ and 1.57) and one septet ($\delta = 3.75$) assignable to ^{*i*}Pr-methyl and -methine protons, respectively, with a coupling constant of 6.3 Hz. Acetato methyl protons were observed at 2.63 ppm as a singlet signal. Although we tried to isolate this complex (5), a solid isolated from the solution was consisted of only 4. On monitoring the time-course of the mixture of complexes 4 and 5 by 1 H NMR, the intensity of the signals due to complex 5 was found to be reduced gradually and the signals for complex 4 were observed finally. From this observation and the results of thermal synthetic conditions mentioned above, it is plausible to consider that the complex 5 is a stereoisomer of 4 and that the complex 5 is a kinetic product and **4** is a thermodynamic one.

On the basis of spectral evidence, we proposed three plausible structures for **5** as depicted in Chart 3. The structure **A** has a lantern-type skeleton and two acetate



Chart 3. Plausible structures for complex 5.

and two amidinato ligands are located in mutually *cis* position, respectively. Structures **B** and **C** exhibit nonlantern-type skeleton. In the case of **B**, two amidinato ligands act as a bridging ligand and each acetato ligand coordinates to the molybdenum center in a chelating fashion. The structure **C** is a reverse to the structure **B**. Recently, Zou and Ren [15] have reported that dinuclear complex [Mo₂(OAc)₂{(NSiMe₃)₂CPh}₂] possesses a set of stereoisomers; one is a lantern-type complex which is an isostructure to **4** and the other is a non-lantern-type complex corresponding to the structure **C** in Chart 3. The tentative assignment of complex **5** to the structure **C** was further supported by its reaction with O₂ (vide infra).

3.3. Reaction of $[Mo_2(\mu - OAc)_2 \{\eta - (N^i Pr)_2 CPh\}_2]$ (5) with O_2

We are interested in the reactivity of the dinuclear complex 5 with various molecules, because it has the structure of "open" quadruply bonded Mo_2 framework allowing the direct reaction toward the Mo–Mo quadruple bond. To examine the reactivity of 5, we used the mixture of complexes 5 and 4 because the former was not able to be isolated as single product as mentioned above. The reactions of 5 with some unsaturated molecules such as olefin and acetylene resulted in isomerization to 4.

On treatment of the mixture of 4 and 5 with dry O_2 (1 atm) in THF at -78 °C, oxo complex of dimolybdenum was obtained as a red crystal (Scheme 5). In this reaction, complex 4 remained almost intact. X-ray diffraction study revealed that the product has two terminal oxo ligands attached to each molybdenum center and one bridging oxo ligand between Mo₂ cores and that two amidinato and two acetato ligands act as chelating and bridging modes, respectively, as shown by the OR-TEP drawing in Fig. 3. Each molybdenum center shows the pseudo-pentagonal bipyramidal geometry positioning terminal oxo and acetato oxygen in axial sites. From the skeleton of complex 6, it may be plausible to assign the structure C depicted in Chart 1 as a possible geometry for complex 5.

The crystal data and selected bond distances and angles are listed in Tables 1 and 4, respectively. The Mo-Mo distance in 6, 2.8088(3) Å, is somewhat longer than the range of the single bond distances in Mo(V)-Mo(V)



Scheme 5



Fig. 3. ORTEP drawing of complex 6 with thermal ellipsoid drawn at the 30% probability level. All hydrogen atoms are omitted for clarity.

Table 4 Selected bond distances (Å) and angles (°) for complex $\bf 6$

Mo(1)–Mo(2)	2.8088(3)
Mo(1)–O(1)	2.210(2)
Mo(1)–O(3)	2.127(2)
Mo(1)–O(5)	1.671(2)
Mo(1)–O(7)	1.921(1)
Mo(1)–N(1)	2.105(2)
Mo(1)–N(2)	2.135(2)
Mo(2)–O(2)	2.253(2)
Mo(2)–O(4)	2.098(1)
Mo(2)–O(6)	1.669(2)
Mo(2)–O(7)	1.914(2)
Mo(2)–N(3)	2.116(2)
Mo(2)–N(4)	2.142(2)
O(1)-Mo(1)-O(5)	168.71(8)
N(1)-Mo(1)-N(2)	61.91(7)
O(2)-Mo(2)-O(6)	171.05(7)
N(3)-Mo(2)-N(4)	61.36(7)
Mo(1)–O(7)–Mo(2)	94.15(6)

(2.73–2.80 Å) [17]. Complex **6** showed the diamagnetic nature [17a] indicated by NMR spectroscopy (see Section 2). Therefore, the Mo–Mo bond in complex **6** is considered to be a single bond. The terminal oxo–Mo bond distances are 1.671(2) and 1.669(2) Å, distances of which are consistent with the reported Mo(V) = O distances [18]. The bridging oxo–Mo bond distances (1.921(1) and 1.914(2) Å) are longer than terminal oxo–Mo distances.

Recently, Cotton et al. [4] reported $[Mo_2(\eta-OAc)_2{\mu-(NXyl)_2CH}_2(\mu-oxo)_2]$ complex, which has bridging amidinato and chelating acetato ligands. This complex has a coordination mode reverse to **6**. It is interesting to note that the Cotton's complex was obtained by the reaction of the lantern-type complex formulated as $[Mo_2(\mu-OAc)_2{\mu-(NXyl)_2CH}_2]$ with O₂ and that it has the formal oxidation state of Mo(IV). Although the reaction of the lantern-type complex **4** with O₂ did not take place, complex **6** was formed by the reaction of **5** with O₂ in our case.

For the purpose of transforming the complex 6 into dimolybdenum (IV) complex similar to that reported by Cotton, we examined the reduction of 6 with triphenylphosphine as a reducing agent. In this reaction, the formation of O = PPh₃ was observed by ³¹P NMR spectroscopy (δ = 27.9). The ¹H NMR spectrum showed the consumption of complex **6**, whereas the product formed was not able to be identified because of the complexity of the products.

4. Concluding remarks

We investigated the systematic reaction of dimolybdenum complex 1 with Li(amidinato) in order to produce non-lantern-type complexes by introduction of sterically hindered amidinato ligands onto Mo₂ core. These investigations resulted in the formation and isolation of lantern-type mixed-ligand dimolybdenum complexes (3 and 4). Although non-lantern-type complex was not isolated, the evidence for the formation of such complex (5) was obtained. Complex 5 showed high reactivity toward O_2 to give dinuclear oxo complex (6). High potential reactivity seems to be accumulated on the quadruple bond in Mo₂ core and thus it is hoped that utilization of this potential for the activation of various substrates will contribute to the development of the novel catalytic processes. Further investigations on the syntheses and reactions of non-lantern-type complexes of Mo₂ are now in progress.

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Appendix A. Supplementary data

ORTEP drawings of complexes 3, 4, and 6 with the atom-numbering scheme have been deposited at the editorial office. Atomic coordinates, thermal parameters, and bond lengths and distances in CIF format have been deposited at the Cambridge Crystallographic Data Center, 12 Union Road, Cambridge CB2 1EZ, UK and

copies can be obtained on request, free of charge, by quoting the publication citation and the deposition numbers 260458–260460. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.ica.2005.01.002.

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