

Synthesis of Novel Amidinato(amidine) Complexes of Molybdenum via Bis(amidine) Complexes

Yoshitaka Yamaguchi,* Kenichi Ogata, Kimiko Kobayashi,¹ and Takashi Ito*

Department of Materials Chemistry, Graduate School of Engineering, Yokohama National University, 79-5, Tokiwadai, Hodogaya-ku, Yokohama 240-8501

¹The Institute of Physical and Chemical Research (RIKEN), 2-1 Hirosawa, Wako 351-0198

Received July 25, 2003; E-mail: t-ito@ynu.ac.jp

The molybdenum complex $[\text{Mo}(\eta^3\text{-allyl})\text{Cl}(\text{CO})_2(\text{NCMe})_2]$ (**1**) reacted with two equivalents of amidines, $\text{ArN}=\text{C}(\text{R})\text{NHA}r$ ($\text{R} = \text{H}, \text{CH}_3$; $\text{Ar} = \text{C}_6\text{H}_5, p\text{-CH}_3\text{-C}_6\text{H}_4$) (**2**), to give corresponding bis(amidine) complexes, $[\text{Mo}(\eta^3\text{-allyl})\text{Cl}(\text{CO})_2(\text{amidine})_2]$ (**3**). Upon a treatment of bis(amidine)molybdenum complexes (**3**) with a base, such as *n*-butyllithium, complexes (**4**) bearing both amidinato and amidine ligands were formed and isolated as a yellow solid. The amidine ligand in complexes **4** was easily substituted by PEt_3 to give amidinato(phosphine) complexes of molybdenum (**5**) as a red solid. These complexes were characterized spectroscopically as well as by X-ray analyses.

The amidinato ligand is known to play an important role as an ancillary ligand to stabilize complexes of transition metals, main-group elements, or rare earth metals because of its ability to act as both a chelating and bridging ligand toward metals.^{1,2} In respect concerning amidinato complexes of molybdenum, much effort has been made for their syntheses and reactivities. In particular, an excellent study was developed by Cotton and co-workers concerning quadruply bonded dinuclear molybdenum complexes utilizing a bridging amidinato ligand,³ and numerous investigations have been undertaken by Vrieze,⁴ Kilner,⁵ and Brunner,⁶ independently, relating to mononuclear molybdenum complexes bearing a chelating amidinato ligand, $[\text{Mo}(\eta^5\text{-C}_5\text{H}_5)(\text{amidinato})(\text{CO})_2]$. Although miscellaneous types of complexes of this kind have also been studied,^{1,2} typical amidinato complexes of molybdenum are limited in number, as mentioned above. In order to prepare the new type of amidinato complex of Mo, our effort focused on the combination of the $\text{Mo}(\text{allyl})(\text{CO})_2$ fragment with an amidinato ligand.

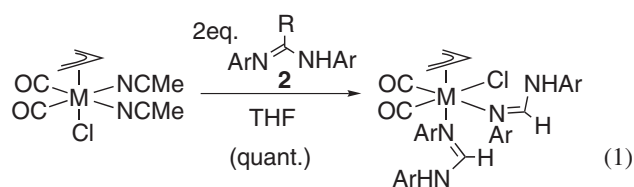
$[\text{Mo}(\text{allyl})\text{Cl}(\text{CO})_2(\text{NCMe})_2]$, which has two labile acetonitrile ligands and one chloride ligand, is a most useful starting material for the synthesis of a series of allyl complexes of molybdenum,⁷ and is known to be a key compound for a Mo-catalyzed allylic alkylation reaction.⁸ Although a series of allyl complexes of molybdenum have been studied using 4-electron donating neutral nitrogen⁹ or phosphorus-containing ligands¹⁰ as well as anionic oxygen¹¹ or sulfur containing ligands,¹² to our best knowledge there has been no investigation concerning the amidinato ligand. In this paper, we report on the syntheses and crystal structures of novel amidinato(amidine) complexes of molybdenum possessing the $\text{Mo}(\eta^3\text{-allyl})(\text{CO})_2$ fragment.

Results and Discussion

Preparation of Bis(amidine) Complexes, $[\text{Mo}(\eta^3\text{-allyl})\text{Cl}(\text{CO})_2(\text{amidine})_2]$. One of the most convenient synthetic procedures for amidinato complexes is a reaction of the metal halide precursor with the lithiated amidinate compound, which

is easily prepared by the treatment of 1,3-disubstituted carbo-diimido with appropriate alkylolithium.¹ In order to prepare an unprecedented type of amidinato complex of molybdenum, we first chose $[\text{Mo}(\eta^3\text{-allyl})\text{Cl}(\text{CO})_2(\text{NCMe})_2]$ (**1-Mo**) as the starting material, and examined its reaction with $\text{Li}(\text{amidinate})$. However, the reaction resulted in the formation of complicated products, and the desired complex was not obtained. We next examined the reaction of **1-Mo** and its tungsten analogue (**1-W**) with amidines, since amidine, which is a precursor of amidinate, has been reportedly known to coordinate to a transition metal by its imine nitrogen.¹³

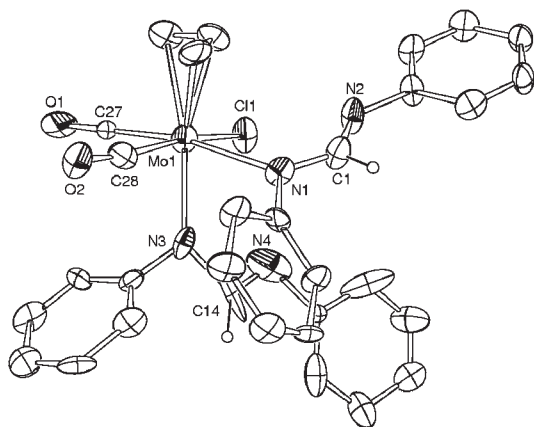
Upon a treatment of the yellow complex of **1-Mo** with two equivalents of *N,N'*-diphenylformamidine **2a** in THF at room temperature, a clean substitution reaction took place, and after a work-up, a two-amidines coordinated molybdenum complex, **3a-Mo**, was isolated as a yellow powder in quantitative yield (Eq. 1). In a similar fashion, complexes **3b-Mo**, **3c-Mo**, **3d-Mo**, and **3a-W** were successfully prepared and isolated in quantitative yield (Eq. 1).



	R	Ar
a	H	Ph
b	H	<i>p</i> -tolyl
c	Me	Ph
d	Me	<i>p</i> -tolyl

Table 1. IR Spectral Data for Starting Materials and Bis(amidine) Complexes **3**

	1-Mo	3a-Mo	3b-Mo	3c-Mo	3d-Mo	1-W	3a-W
ν_{CO} /cm ⁻¹	1942 1849	1937 1844	1931 1836	1932 1832	1932 1822	1933 1836	1914 1810
ν_{CN} /cm ⁻¹		2317 2285				2317 2286	

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

In the IR spectra, the starting complex, **1-Mo**, showed two stretching bands (2317, 2285 cm⁻¹) due to CH₃CN and two stretching bands (1942, 1849 cm⁻¹) due to CO ligands. In the complex **3a-Mo**, the former bands fully disappeared and the latter bands were shifted slightly to lower frequencies (1937, 1844 cm⁻¹) than those for complex **1-Mo**. A similar tendency was observed for the rest of complexes **3b-Mo**, **3c-Mo**, **3d-Mo**, and **3a-W**. The IR spectral data for starting compounds **1** and amidine complexes **3** are summarized in Table 1. In the ¹H NMR spectra, the bis(formamidine) complex **3a-Mo** showed broadened signals in the temperature range from -80 °C to 70 °C. In other bis(amidine) complexes **3**, similar broadened signals were observed at room temperature. These features might have come from the low isomerization energy barrier for the trigonal twist mechanism of these complexes.^{14,15} Although we could not confirm the structure of complex **3** in solution to be bis(amidine) complexes, [Mo(η³-allyl)Cl(CO)₂·{N(C₆H₅)=C(H)N(H)C₆H₅}₂]·1/2toluene (**3a-Mo**·1/2toluene) was characterized by a single-crystal X-ray diffraction study. An ORTEP drawing of **3a-Mo**·1/2toluene is shown in Fig. 1. The crystal data and the selected bond distances and an-

Table 2. Summary of Crystal Data for **3a-Mo**, **4a-Mo**, and **5a-Mo**

	3a-Mo ·1/2toluene	4a-Mo	5a-Mo
Empirical formula	C _{34.50} H ₃₃ ClMoN ₄ O ₂	C ₃₁ H ₂₈ MoN ₄ O ₂	C ₂₄ H ₃₁ MoN ₂ O ₂ P
Formula weight	667.06	584.53	506.43
Crystal color, Habit	yellow, plate	yellow, prismatic	dark-orange, prismatic
Crystal size/mm	0.30 × 0.10 × 0.05	0.20 × 0.08 × 0.08	0.50 × 0.23 × 0.13
Crystal system	monoclinic	orthorhombic	monoclinic
Space group	P2 ₁ /n (#14)	P2 ₁ 2 ₁ 2 ₁ (#19)	P2 ₁ /n (#14)
Lattice parameters			
<i>a</i> /Å	18.39(1)	13.532(9)	12.255(2)
<i>b</i> /Å	22.64(1)	17.00(1)	14.787(2)
<i>c</i> /Å	7.545(3)	11.967(6)	13.670(1)
β/deg	97.87(5)	90	100.501(9)
<i>V</i> /Å ³	3112(3)	2753(3)	2435.6(4)
<i>Z</i> value	4	4	4
<i>D</i> _{calc} /g cm ⁻³	1.423	1.410	1.381
<i>F</i> ₀₀₀	1372.00	1200.00	1048.00
μ(Mo-Kα)/cm ⁻¹	5.44	5.10	6.25
Reflections measured	7043	2771	7676
Independent reflections	1342 (<i>R</i> _{int} = 0.160)	2747 (<i>R</i> _{int} = 0.679)	7106 (<i>R</i> _{int} = 0.016)
No. Variables	368	344	316
Reflection/parameter ratio	8.41	7.99	22.56
Residuals: <i>R</i> ; <i>R</i> _w	0.226; 0.287	0.155; 0.166	0.053; 0.110
Residuals: <i>R</i> 1	0.138	0.077	0.033
No. of reflections to calc <i>R</i> 1	2411 (<i>I</i> > 2.0σ(<i>I</i>))	1375 (<i>I</i> > 2.0σ(<i>I</i>))	5258 (<i>I</i> > 2.0σ(<i>I</i>))
Goodness of Fit Indicator	2.80	1.14	1.26
Maximum peak in Final Diff. Map/e Å ⁻³	1.53	1.17	0.53
Minimum peak in Final Diff. Map/e Å ⁻³	-2.39	-0.83	-0.36

Table 3. Selected Bond Distances (Å) for **3a-Mo**, **4a-Mo**, and **5a-Mo**

	3a-Mo		4a-Mo		5a-Mo	
Allyl	Mo(1)–C(29)	2.34(2)	Mo(1)–C(29)	2.29(2)	Mo(1)–C(22)	2.339(3)
	Mo(1)–C(30)	2.22(2)	Mo(1)–C(30)	2.21(2)	Mo(1)–C(23)	2.224(3)
	Mo(1)–C(31)	2.36(2)	Mo(1)–C(31)	2.25(2)	Mo(1)–C(24)	2.327(3)
CO	Mo(1)–C(27)	1.92(2)	Mo(1)–C(14)	1.94(2)	Mo(1)–C(14)	1.953(3)
	Mo(1)–C(28)	1.91(2)	Mo(1)–C(15)	1.94(2)	Mo(1)–C(15)	1.959(3)
	O(1)–C(27)	1.18(2)	O(1)–C(14)	1.18(2)	O(1)–C(14)	1.155(3)
	O(2)–C(28)	1.21(2)	O(2)–C(15)	1.17(2)	O(2)–C(15)	1.148(3)
	Mo(1)–N(1)	2.36(2)	Mo(1)–N(1)	2.21(1)	Mo(1)–N(1)	2.237(2)
Amidinato or Amidine	Mo(1)–N(3)	2.24(1)	Mo(1)–N(2)	2.27(1)	Mo(1)–N(2)	2.243(2)
	N(1)–C(1)	1.29(2)	Mo(1)–N(3)	2.25(2)	N(1)–C(1)	1.317(3)
	N(2)–C(1)	1.37(2)	N(1)–C(1)	1.31(2)	N(2)–C(1)	1.320(3)
	N(3)–C(14)	1.58(4)	N(2)–C(1)	1.37(2)		
	N(4)–C(14)	1.09(3)	N(3)–C(16)	1.32(2)		
			N(4)–C(16)	1.29(2)		
Others	Mo(1)–Cl(1)	2.608(6)			Mo(1)–P(1)	2.5621(6)

Table 4. Selected Bond Angles (deg) for **3a-Mo**, **4a-Mo**, and **5a-Mo**

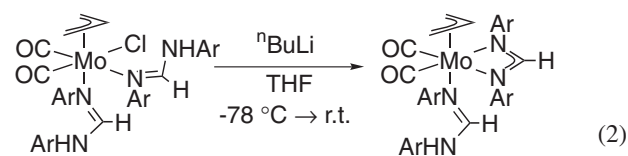
	3a-Mo		4a-Mo		5a-Mo	
CO	Mo(1)–C(27)–O(1)	177(2)	Mo(1)–C(14)–O(1)	172(2)	Mo(1)–C(14)–O(1)	179.1(3)
	Mo(1)–C(28)–O(2)	173(2)	Mo(1)–C(15)–O(2)	176(1)	Mo(1)–C(15)–O(2)	179.5(3)
Amidinato or Amidine	Mo(1)–N(1)–C(1)	130(1)	N(1)–Mo(1)–N(2)	59.3(5)	N(1)–Mo(1)–N(2)	58.76(6)
	Mo(1)–N(1)–C(2)	119(1)	Mo(1)–N(1)–C(1)	96(1)	Mo(1)–N(1)–C(1)	94.3(1)
	N(1)–C(1)–N(2)	124(2)	Mo(1)–N(1)–C(2)	144(1)	Mo(1)–N(1)–C(2)	140.7(1)
	C(1)–N(1)–C(2)	111(2)	C(1)–N(1)–C(2)	119(1)	C(1)–N(1)–C(2)	124.9(2)
	C(1)–N(2)–C(8)	127(2)	Mo(1)–N(2)–C(1)	92(1)	Mo(1)–N(2)–C(1)	94.0(1)
	Mo(1)–N(3)–C(14)	137(1)	Mo(1)–N(2)–C(8)	145(1)	Mo(1)–N(2)–C(8)	141.1(1)
	Mo(1)–N(3)–C(15)	120(1)	C(1)–N(2)–C(8)	122(2)	C(1)–N(2)–C(8)	124.8(2)
	C(14)–N(3)–C(15)	102(1)	Mo(1)–N(3)–C(16)	121(2)	N(1)–C(1)–N(2)	112.9(2)
	N(3)–C(14)–N(4)	103(4)	Mo(1)–N(3)–C(17)	121(1)	N(1)–C(1)–H(1)	120(1)
	C(14)–N(4)–C(21)	104(4)	C(16)–N(3)–C(17)	117(2)	N(2)–C(1)–H(1)	126(1)
			C(16)–N(4)–C(23)	121(2)		
			N(1)–Mo(1)–N(3)	83.7(5)	P(1)–Mo(1)–N(1)	80.68(5)
Mo	Cl(1)–Mo(1)–N(1)	88.8(4)	N(1)–Mo(1)–C(14)	168.0(7)	P(1)–Mo(1)–N(2)	84.53(5)
	Cl(1)–Mo(1)–N(3)	84.1(4)	N(1)–Mo(1)–C(15)	106.5(6)	P(1)–Mo(1)–C(14)	89.29(9)
	Cl(1)–Mo(1)–C(27)	93.5(5)	N(2)–Mo(1)–N(3)	79.0(5)	P(1)–Mo(1)–C(15)	86.42(9)
	Cl(1)–Mo(1)–C(28)	166.8(5)	N(2)–Mo(1)–C(14)	113.2(7)	N(1)–Mo(1)–C(14)	165.0(1)
	N(1)–Mo(1)–N(3)	78.8(5)	N(2)–Mo(1)–C(15)	164.2(7)	N(1)–Mo(1)–C(15)	109.4(1)
	N(1)–Mo(1)–C(27)	169.2(7)	N(3)–Mo(1)–C(14)	85.6(7)	N(2)–Mo(1)–C(14)	109.38(9)
	N(1)–Mo(1)–C(28)	98.4(7)	N(3)–Mo(1)–C(15)	93.2(6)	N(2)–Mo(1)–C(15)	166.2(1)
	N(3)–Mo(1)–C(27)	91.0(7)	C(14)–Mo(1)–C(15)	79.4(8)	C(14)–Mo(1)–C(15)	80.9(1)
	N(3)–Mo(1)–C(28)	86.6(7)				

gles for **3a-Mo**·1/2toluene are listed in Tables 2–4, respectively. An X-ray study revealed that complex **3a-Mo** has two amidine ligands; one is located in trans position to the π -allyl ligand and the other to the CO ligand.¹⁶ An elemental analysis supported the formation of complex **3a-Mo** containing 0.5 molecule of toluene.

Conversion of Bis(amidine) Complexes 3 into Amidinato-(amidine) Complexes 4. It is reported that the amidine complex of iron, having a halogen ligand, was successfully converted into the amidinato complex by alkyllithium.^{13b} We therefore examined the reaction of bis(amidine) complexes **3** with a base, such as ⁿBuLi, to prepare the amidinato complex.

After bis(formamidine) complex **3a-Mo** was treated with one equivalent of ⁿBuLi in THF at –78 °C, the reaction mixture

was allowed to warm to room temperature. After a work-up, amidinato(amidine) complex **4a-Mo** was isolated as a yellow solid in 64% yield. A similar reaction of complex **3b-Mo** with ⁿBuLi yielded complex **4b-Mo** as a yellow solid (79%) (Eq. 2).



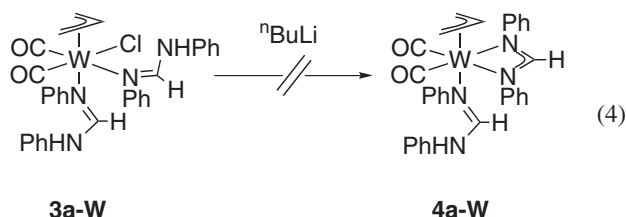
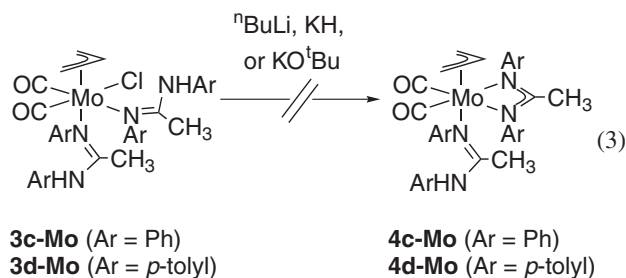
3a-Mo (Ar = Ph)
3b-Mo (Ar = *p*-tolyl)

4a-Mo (Ar = Ph)
4b-Mo (Ar = *p*-tolyl)

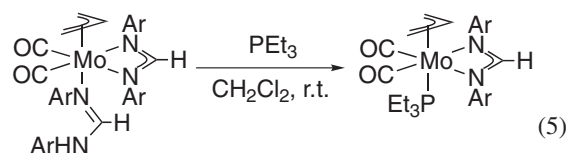
(2)

In IR spectra, complexes **4a-Mo** and **4b-Mo** showed two CO stretching bands (1927, 1826 cm^{-1} for **4a-Mo** and 1926, 1832 cm^{-1} for **4b-Mo**, respectively), which are lower frequency than those for the starting complexes **3a-Mo** (1937, 1844 cm^{-1}) and **3b-Mo** (1931, 1836 cm^{-1}). In ^1H NMR spectra, both complexes showed complicated signals, possibly due to the fluxional geometrical rearrangement of the molecule in solution.^{14,17} Complex **4a-Mo** was characterized by a single-crystal X-ray diffraction study (vide infra).

Next, we examined the reaction of complexes **3c-Mo** and **3d-Mo**, having acetamidine ligands, with $^n\text{BuLi}$ (Eq. 3). In these reactions, the desired reaction did not occur and unidentified products were formed. The employment of another base, such as KH or KO^tBu , in the place of $^n\text{BuLi}$ also resulted in the formation of uncharacterized products. These complicated results might have come from abstraction of the hydrogen atom of the methyl group on the acetamidine ligand, though there is no compelling evidence to support it. In the case of a tungsten complex, the desired product (**4a-W**) was also not obtained by the reaction of **3a-W** with an equimolar amount of $^n\text{BuLi}$ (Eq. 4). A further investigation of the preparation of these compounds is now in progress.



Reaction of Amidinato(amidine) Complexes of Molybdenum with Triethylphosphine. We next examined the reaction of amidinato(amidine) complexes of molybdenum (**4a-Mo**, **4b-Mo**) with triethylphosphine (PEt_3), hoping that the substitution reaction of the amidine with PEt_3 might proceed. In a treatment of complex **4a-Mo** with one equimolar amount of PEt_3 in CH_2Cl_2 at ambient temperature, an initial yellow solution changed to a homogenous red solution. The product was isolated by column chromatography as a red solid (70%). Elemental analysis as well as IR and ^1H , ^{13}C , and ^{31}P NMR spectra established the formation of an amidinato complex of molybdenum bearing PEt_3 (**5a-Mo**). In a similar procedure, complex **5b-Mo** was isolated as a red solid in 61% yield, whose complex was also characterized spectroscopically as well as by elemental analysis (Eq. 5). Complex **5a-Mo** was determined by a single-crystal X-ray diffraction study (vide infra).



4a-Mo (Ar = Ph)
4b-Mo (Ar = *p*-tolyl)

5a-Mo (Ar = Ph)
5b-Mo (Ar = *p*-tolyl)

The IR spectrum of **5a-Mo** showed two CO stretching bands at 1921 and 1836 cm^{-1} . In ^{31}P NMR, a singlet signal was observed at 13.7 ppm, which suggests that PEt_3 binds to the molybdenum center. In the ^1H NMR spectrum, methyl and methylene groups in PEt_3 were observed at 1.04 ppm as a double triplet and at 1.75 ppm as quintet, respectively. The ^1H NMR spectrum also showed a doublet at 8.79 ppm ($J = 4.0$ Hz) due to a formamidinato CH proton. This pattern resulted from coupling with coordinated PEt_3 . The ^{13}C NMR spectrum showed a doublet signal at 227.4 ppm with $^2J_{\text{PC}} = 14.7$ Hz due to the carbonyl carbons. Two signals being assignable to the allyl ligand were observed at 60.5 ppm as a singlet and at 86.2 ppm as a doublet, and four sets of singlets due to phenyl carbons were observed. These results suggest that the phosphine is located in the cis position to two CO ligands and in the trans position to the allyl ligand in solution. Similar spectra were obtained for complex **5b-Mo**.

Crystal Structures of Molybdenum Complexes 4a-Mo and 5a-Mo. X-ray structure analyses of complexes **4a-Mo** and **5a-Mo** were undertaken. ORTEP drawings of **4a-Mo** and **5a-Mo** are displayed in Figs. 2 and 3, respectively. The crystal data and the selected bond distances and angles for **4a-Mo** and **5a-Mo** are listed in Tables 2–4, respectively.

Both complexes have a pseudo octahedral geometry around the Mo atom, and the amidinato ligand is located on a coplanar with two CO ligands. The amidine ligand in **4a-Mo**, which is coordinated to molybdenum through an imine nitrogen, is positioned trans to the η^3 -allyl ligand. In **5a-Mo**, the PEt_3 ligand is also positioned trans to the η^3 -allyl ligand, whose geometrical structure coincide with that suggested by NMR spectroscopy (vide supra).

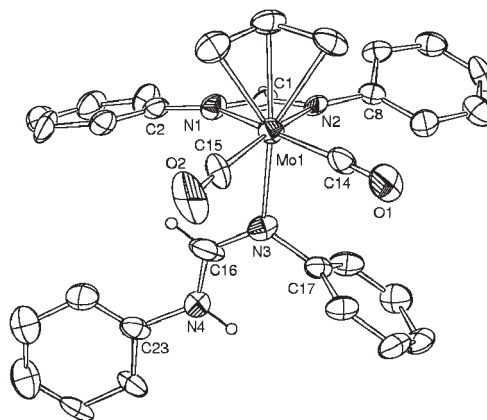


Fig. 2. ORTEP drawing of **4a-Mo** with thermal ellipsoids drawn at the 30% probability level. Some hydrogen atoms are omitted for clarity.

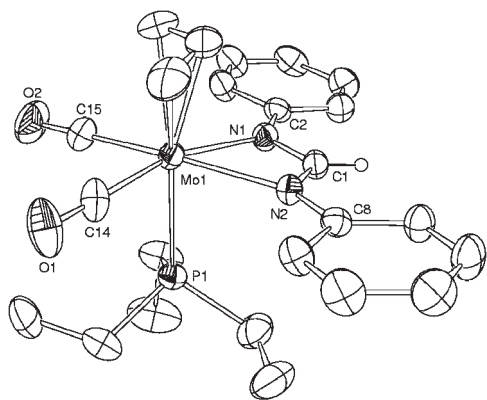


Fig. 3. ORTEP drawing of **5a-Mo** with thermal ellipsoids drawn at the 30% probability level. Some hydrogen atoms are omitted for clarity.

In complex **4a-Mo**, the Mo(1)–N(3) (amidine nitrogen) bond distance is 2.25(2) Å, which is similar to that found for Mo–amidinato N bond distances (Mo(1)–N(1); 2.21(1) Å and Mo(1)–N(2); 2.27(1) Å). The amidinato N–C bond distances are 1.34(2) Å for N(1)–C(1) and 1.31(2) Å for N(2)–C(1). This result indicates that the amidinato N–C–N bond electrons are delocalized. Furthermore, the nitrogen atoms in the amidinato ligand have a trigonal-planar structure; the sum of the angles is 359.0° for N(1) and 358.0° for N(2), respectively. The N–C bond distances in the amidine ligand are 1.32(2) Å for N(3)–C(16) and 1.29(2) Å for N(4)–C(16) and are in good agreement with the mean value of the N–C double bond (1.24 Å) and the N–C single bond (1.48 Å).¹ These observations stand for the delocalized nature of the two N–C bonds in amidine ligand. Similar results were reported for a tantalum complex bearing both amidine and amidinato ligands.^{13c}

The Mo(1)–P(1) distance (2.5621(6) Å) of **5a-Mo** is in good agreement with the reported value for the normal Mo–P dative bond distances falling in the range of 2.40–2.57 Å.¹⁸ Other bond distances and angles concerning the molybdenum fragment, Mo(η^3 -allyl)(amidinato)(CO)₂, in complex **5a-Mo** bore a close parallel to those of the parent complex, **4a-Mo**.

Conclusion

In an examination of the preparative method of a new type of amidinato complexes possessing the Mo(η^3 -allyl)(CO)₂ fragment, we found an effective method utilizing the bis(amidine) complex as a starting material. Conversion of the bis(amidine) complex of molybdenum to the amidinato(amidine) complex was successfully achieved by abstraction of HCl with a base, such as ⁿBuLi. However, in cases of acetamidine complexes of molybdenum (**3c-Mo**, **3d-Mo**), or a tungsten analogue (**3a-W**), the desired products were not obtained. The observed facile displacement of the amidinato ligand in amidinato(amidine) complexes (**4**) by tertiary phosphine allows us to expect novel reactions involving these complexes. A further investigation along this line is under progress in our laboratory.

Experimental

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. Mo(CO)₆ and W(CO)₆ were purchased from Kanto Chemical Co., Inc., and used as received. ⁿBuLi in a hexane solution was purchased from Kanto Chemical Co., Inc. and titrated prior to use. Other reagents employed in this research were used without further purification. [Mo(η^3 -allyl)Cl(CO)₂(NCMe)₂] (**1-Mo**),⁷ [W(η^3 -allyl)Cl(CO)₂(NCMe)₂] (**1-W**),⁷ *N,N'*-disubstituted formamidines,¹⁹ N(C₆H₅)=C(H)N(H)C₆H₅ (**2a**) and N(C₆H₄-*p*-CH₃)=C(H)N(H)C₆H₄-*p*-CH₃ (**2b**), and *N,N'*-disubstituted acetamidines,¹⁹ N(C₆H₅)=C(CH₃)N(H)C₆H₅ (**2c**) and N(C₆H₄-*p*-CH₃)=C(CH₃)N(H)C₆H₄-*p*-CH₃ (**2d**), were prepared according to the literature methods.

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 H₃PO₄. All coupling constants were recorded in Hz. The splitting patterns are indicated as s, singlet; d, doublet; t, triplet; quint, quintet. IR spectra were recorded on a Perkin-Elmer 1600 FT-IR spectrometer. Melting points were measured using a YAZAWA Micro Melting Point BY-2 apparatus. Column chromatography was performed under air.

Preparation of [Mo(η^3 -allyl)Cl(CO)₂{N(C₆H₅)=C(H)N(H)-C₆H₅}₂] (3a-Mo**).** [Mo(η^3 -allyl)Cl(CO)₂(NCMe)₂] (**1-Mo**) (130 mg, 0.42 mmol) and formamidine, N(C₆H₅)=C(H)N(H)C₆H₅ (**2a**), (170 mg, 0.87 mmol) were put into a Schlenk tube and then THF (10 mL) was added via a syringe. The mixture was stirred over-night at ambient temperature. After removing the volatiles under reduced pressure, a residual yellow powder was washed with hexane several times and dried in vacuo to give spectroscopically pure **3a-Mo** as a yellow powder (250 mg, 0.40 mmol, yield 95%). For the purpose of elemental analysis, the product was further purified recrystallization from toluene to give yellow crystals of **3a-Mo**·0.5toluene. Found: C, 62.38; H, 5.04; N, 8.41%. Calcd for C₃₁H₂₉ClMoN₄O₂·0.5C₇H₈: C, 62.12; H, 4.99; N, 8.40%. Mp 105.0–107.0 °C.

Preparation of [Mo(η^3 -allyl)Cl(CO)₂{N(*p*-CH₃C₆H₄)=C(H)NH(*p*-CH₃C₆H₄)₂] (3b-Mo**).** Complex **3b-Mo** was prepared from **1-Mo** (125 mg, 0.40 mmol) and formamidine, N(C₆H₄-*p*-CH₃)=C(H)N(H)C₆H₄-*p*-CH₃ (**2b**), (215 mg, 0.96 mmol) in the same manner as that for **3a-Mo**. **3b-Mo** was isolated as a yellow powder (270 mg, 0.40 mmol, yield quant.). Analytically pure sample was obtained by recrystallization from toluene. Found: C, 61.66; H, 5.70; N, 7.99%. Calcd for C₃₅H₃₇ClMoN₄O₂: C, 62.09; H, 5.51; N, 8.27%. Mp 106.0–107.0 °C.

Preparation of [Mo(η^3 -allyl)Cl(CO)₂{N(C₆H₅)=C(CH₃)-N(H)(C₆H₅)₂] (3c-Mo**).** Complex **3c-Mo** was prepared from **1-Mo** (200 mg, 0.64 mmol) and acetamidine, N(C₆H₅)=C(CH₃)-N(H)C₆H₅ (**2c**), (275 mg, 1.31 mmol) in the same manner as that for **3a-Mo**. **3c-Mo** was isolated as a yellow powder (400 mg, 0.62 mmol, yield 97%). Correct elemental analysis data could not be obtained.

Preparation of [Mo(η^3 -allyl)Cl(CO)₂{N(C₆H₄-*p*-CH₃)=C(CH₃)N(H)C₆H₄-*p*-CH₃}₂] (3d-Mo**).** Complex **3d-Mo** was prepared from **1-Mo** (80 mg, 0.26 mmol) and acetamidine, N(C₆H₄-*p*-CH₃)=C(CH₃)N(H)C₆H₄-*p*-CH₃ (**2d**), (155 mg, 0.65 mmol) in the same manner as that for **3a-Mo**. **3d-Mo** was isolated as a yellow powder (180 mg, 0.26 mmol, yield quant.). Correct elemental analysis data could not be obtained.

Preparation of [W(η^3 -allyl)Cl(CO)₂{N(C₆H₅)=C(H)N(H)-

C₆H₅]₂) (3a-W). Complex **3a-W** was prepared from [W(η^3 -allyl)Cl(CO)₂(NCMe)₂] (**1-W**) (75 mg, 0.19 mmol) and formamidine, N(C₆H₅)=C(H)N(H)C₆H₅ (**2a**), (75 mg, 0.38 mmol) in the same manner as that for **3a-Mo**. **3a-W** was isolated as a yellow powder (130 mg, 0.18 mmol, yield 95%). Analytically pure sample was obtained by recrystallization from toluene. Found: C, 54.40; H, 4.68; N, 7.26%. Calcd for C₃₁H₂₉ClN₄O₂W·0.5C₇H₈: C, 54.89; H, 4.41; N, 7.42%. Mp 114.0–115.0 °C.

Preparation of [Mo(η^3 -allyl){(NC₆H₅)₂CH}(CO)₂-N(C₆H₅)=C(H)N(H)C₆H₅}] (4a-Mo). A solution of complex **3a-Mo** (430 mg, 0.69 mmol) in THF (20 mL) was cooled to –78 °C, and then a hexane solution of ⁿBuLi (1.50 mol dm^{–3}, 0.46 mL, 0.69 mmol) was added. The mixture was stirred at –78 °C for 2 h and then allowed to warm to room temperature. After several hours, the volatiles were removed under reduced pressure. The residual solid was extracted with toluene. The filtrate was evaporated off under high vacuum. The residue was washed with hexane several times, and dried in vacuo to give **4a-Mo** as a yellow powder (260 mg, 0.44 mmol, yield 64%). Found: C, 63.20; H, 4.49; N, 9.37%. Calcd for C₃₁H₂₈MoN₄O₂: C, 63.70; H, 4.83; N, 9.59%. Mp 116.0–117.0 °C. IR (ν_{CO} , KBr) 1927, 1826 cm^{–1}.

Preparation of [Mo(η^3 -allyl){(NC₆H₄-*p*-CH₃)₂CH}(CO)₂-N(*p*-CH₃C₆H₄)=C(H)NH(*p*-CH₃C₆H₄)] (4b-Mo). Complex **4b-Mo** was prepared from complex **3b-Mo** (550 mg, 0.81 mmol) and a hexane solution of ⁿBuLi (1.50 mol dm^{–3}, 0.55 mL, 0.83 mmol) in the same manner as that for **4a-Mo**. **4b-Mo** was isolated as a yellow powder (410 mg, 0.64 mmol, yield 79%). Found: C, 66.18; H, 5.88; N, 8.27%. Calcd for C₃₅H₃₆MoN₄O₂: C, 65.62; H, 5.66; N, 8.75%. Mp 86.0–87.0 °C. IR (ν_{CO} , KBr) 1926, 1832 cm^{–1}.

Preparation of [Mo(η^3 -allyl){(NC₆H₅)₂CH}(CO)₂PtEt₃] (5a-Mo). To a solution of complex **4a-Mo** (103 mg, 0.18 mmol) in CH₂Cl₂ (10 mL) was added PtEt₃ (28 μ L, 0.19 mmol) at room temperature. After being stirred for 1.5 h, the volatiles were removed under reduced pressure. The residual material was loaded on an alumina column (ϕ 14 mm $\times$ 40 mm) and eluted with CH₂Cl₂/hexane (1/1 v/v %). The eluted red band was collected and solvent was removed in vacuo to give a red powder of **5a-Mo** (63 mg, 0.12 mmol, yield 67%). Found: C, 56.77; H, 6.03; N, 5.46%. Calcd for C₂₄H₃₁MoN₂O₂P: C, 56.92; H, 6.17; N, 5.53%. Mp 108.0–109.0 °C. IR (ν_{CO} , KBr) 1921, 1836 cm^{–1}. ¹H NMR (δ , in CDCl₃) 1.04 (dt, *J* = 14.2, 7.6 Hz, 9H, CH₃), 1.70 (d, *J* = 9.9 Hz, 2H, allyl-CH₂), 1.75 (quint, *J* = 7.6 Hz, PCH₂), 3.77 (m, 1H, allyl-CH), 3.84 (dd, *J* = 7.3, 1.7 Hz, 2H, allyl-CH₂), 6.93 (d, *J* = 7.3 Hz, 4H, Ph), 7.23 (m, 6H, Ph), 8.79 (d, *J* = 4.0 Hz, 1H, amidinato-CH). ¹³C{¹H} NMR (δ , in CDCl₃) 7.6 (d, *J* = 2.5 Hz, CH₃), 15.5 (d, *J* = 19.5 Hz, PCH₂), 60.5 (s, allyl-CH₂), 86.2 (d, *J* = 4.9 Hz, allyl-CH), 117.7, 121.6, 129.2, 146.0 (s, Ph), 151.5 (d, *J* = 6.1 Hz, amidinato-CH), 227.4 (d, *J* = 14.7 Hz, CO). ³¹P{¹H} NMR (δ , in CH₂Cl₂) 13.7 (s).

Preparation of [Mo(η^3 -allyl){(NC₆H₄-*p*-CH₃)₂CH}(CO)₂-PEt₃] (5b-Mo). Complex **5b-Mo** was prepared from complex **4b-Mo** (115 mg, 0.18 mmol) and PEt₃ (28 μ L, 0.19 mmol) in the same manner as that for **5a-Mo**. **5b-Mo** was isolated as a red powder (58 mg, 0.11 mmol, yield 61%). Found: C, 58.00; H, 6.24; N, 5.31%. Calcd for C₂₆H₃₅MoN₂O₂P: C, 58.43; H, 6.60; N, 5.24%. Mp 125.0–126.0 °C. IR (ν_{CO} , KBr) 1921, 1837 cm^{–1}. ¹H NMR (δ , in CDCl₃) 1.04 (dt, *J* = 14.8, 7.6 Hz, 9H, CH₃), 1.67 (d, *J* = 9.9 Hz, 2H, allyl-CH₂), 1.74 (quint, *J* = 7.6 Hz, 6H, PCH₂), 2.28 (s, 6H, PhCH₃) 3.74 (m, 1H, allyl-CH), 3.84 (d, *J* = 6.9 Hz, 2H, allyl-CH₂), 6.82 (d, *J* = 8.3 Hz, 4H, Ph), 7.03 (d, *J* = 8.3 Hz, 4H, Ph), 8.73 (d, *J* = 3.6 Hz, 1H, amidinato-

CH). ¹³C{¹H} NMR (δ , in CDCl₃) 7.7 (d, *J* = 2.4 Hz, PCH₂CH₃), 15.6 (d, *J* = 19.5 Hz, PCH₂), 20.7 (s, C₆H₄CH₃), 60.5 (s, allyl-CH₂), 86.2 (d, *J* = 6.1 Hz, allyl-CH), 117.4, 129.7, 130.9, 143.7 (s, Ph), 151.2 (d, *J* = 4.9 Hz, amidinato-CH), 227.5 (d, *J* = 14.6 Hz, CO). ³¹P{¹H} NMR (δ , in CH₂Cl₂) 13.7 (s).

Experimental Procedure for X-ray Crystallography. Suitable single crystals were obtained by recrystallization from toluene (**3a-Mo**), toluene/hexane (**4a-Mo**), or from hexane (**5a-Mo**), and were mounted on glass fibers.

A diffraction measurement of **3a-Mo** was made on a Rigaku RAXIS IV imaging plate area detector with Mo K α radiation (λ = 0.71069 Å). Indexing was performed from four oscillation images, which were exposed for 22 min. The crystal-to-detector distance was 100 mm. The data were collected at a temperature of –50 °C to a maximum 2 θ value of 60°. A total of 28 5.00° oscillation images were collected, each being exposed for 22 min. Readout was performed in the 0.100 mm pixel mode. The data processing was performed on an SGI Indy computer.

Diffraction measurements of **4a-Mo** and **5a-Mo** were made on a Rigaku AFC-7R automated four-circle diffractometer by using graphite-monochromated Mo K α radiation (λ = 0.71069 Å). The data collections were carried out at 23 °C using the ω –2 θ scan technique to a maximum 2 θ value of 50.0° for **4a-Mo**, and 60.0° for **5a-Mo**, respectively. Cell constants and an orientation matrix for data collection were determined from 11 reflections with 2 θ angles in the range 22.40–24.21° for **4a-Mo** and from 25 reflections with 2 θ angles in the range 29.73–29.99° for **5a-Mo**. Three standard reflections were monitored at every 150 measurements. The data processing (data collection) was performed on a personal computer. 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 2. The structures were solved by heavy-atom Patterson methods (PATTY)²⁰ for **3a-Mo** or by direct methods (SIR 92)²¹ for **4a-Mo** and **5a-Mo**, and expanded using Fourier techniques.²² All of the non-hydrogen atoms, except for the toluene solvates in **3a-Mo**·1/2toluene, were refined anisotropically. Except for complex **5a-Mo**, all hydrogen atoms were located at the calculated positions (C–H 0.95 Å) and not refined. In complex **5a-Mo**, the hydrogen atoms were located from difference Fourier maps and refined isotropically, except for the ethyl hydrogen atoms, which were located calculated positions (C–H 0.95 Å). All calculations were performed on an SGI Indy computer using the teXsan crystallographic software package of Molecular Structure Corporation.²³ Crystallographic data have been deposited at the CCDC, 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 219635–219637.

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- 15 In order to confirm whether the mechanism of this site-exchange process is dissociative or associative, we monitored the reaction of **3a-Mo** with 5 equivalents of amidine **2a** by ¹HNMR spectrum, and found that the broad signals due to **3a-Mo** remained intact throughout the reaction. Thus, the mechanism associated with the dissociation of the amidine ligand from **3a-Mo** could not be ruled out completely at the present stage.
- 16 The yellow crystals of complex **3a-Mo**·1/2toluene were so low crystallinity due to containing solvated toluene molecules that high quality intensity data were not obtained. Therefore, we could not discuss the bond distances and angles for **3a-Mo**·1/2toluene. However, the geometrical structure of the molecule can be discussed unequivocally.
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