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Dimolybdenum complexes with mixed formamidinate ligands

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Abstract

A series of dimolybdenum complexes containing mixed formamidinate ligand are discussed. The reactions of *trans*-$Mo_2(O_2CCH_3)_2$(*o*-DMophF)$_2$ [*o*-HDMophF = *N*,*N*′-di(2-methoxyphenyl)formamidine] with *N*,*N*′-di(2-pyridyl)formamidine (HD pyF), *N*,*N*′-di(2-pyrimidyl)formamidine (HDpmF) and *N*,*N*′-di(6-methyl-2-pyridyl)formamidine (HDMepyF), in refluxing CH_2Cl_2 afforded the complexes, *trans*-$Mo_2(O_2CCH_3)$(DpyF)(*o*-DMophF)$_2$ (**1**), *trans*-$Mo_2(O_2CCH_3)$(DpmF)(*o*-DMophF)$_2$ (**2**), and *trans*-$Mo_2(O_2CCH_3)$(DMepyF)(*o*-DMophF)$_2$ (**3**), respectively. The *o*-DMophF$^-$ and DMepyF$^-$ ligands in these complexes adopt the *s-cis, s-trans* conformation, resulting in Mo–O short distances [2.889 (3) and 2.861(2) Å for **1**; 2.880(3) and 3.024(4) Å for **2**], while the DpyF$^-$ ligand adopts the *s-cis, s-trans* conformation, resulting in a Mo–N [3.208(4) Å] and a Mo–H [2.90 (3) Å] short distances. The reactions of *trans*-$Mo_2(O_2CCH_3)_2$(*o*-DMophF)$_2$ with HDMepyF in CH_3CN gave complexes **3**, *trans*-$Mo_2(O_2CCH_3)$(DMepyF)$_2$(*o*-DMophF) (**4**), and *trans*-Mo_2(DMepyF)$_2$(*o*-DMophF)$_2$ (**5**). The *o*-DMophF$^-$ ligands in **4** and **5** adopt the *s-cis, s-cis* conformation while DMepyF$^-$ assumes an *s-cis, s-trans* conformation. Complexes **1**–**5** are the first dimolybdenum complexes containing mixed formamidinate ligands.

Keywords: Dimolybdenum complex; Formamidinate ligand; Conformation; *o*-HDMophF

1. Introduction

The coordination chemistry of formamidinate compounds has been investigated extensively during recent years [1–5]. Many efforts have been concentrated in their ability to form bridges between metal atoms. Preparations, structures and spectroscopic properties of tetrakis(μ-diarylformamidinato)dimolybdenum complexes of the type Mo_2(form)$_4$, where form is the generic formamidine, were the subjects of several studies [6]. Crystalline Mo_2(form)$_4$ can be prepared by stoichiometric ligand metathesis between the dimolybdenum tetraacetate $Mo_2(O_2CR)_4$ and the lithiated formamidine. This type of reaction was used to prepare the first Mo_2(form)$_4$ compound, Mo_2(DTolF)$_4$ (DTolF$^-$ = [(*p*-tol)NCHN(*p*-tol)]$^-$) [7]. Recently, dimolybdenum complexes containing mixed acetate–formamidinate ligands of the types $Mo_2(O_2CCH_3)_3$(*o*-DMophF), *trans*-$Mo_2(O_2CR)_2$(*o*-DMophF)$_2$ (R = CH_3, CF_3 and Pr^n) and $Mo_2(O_2CCH_3)$(*o*-DMophF)$Cl_2(PMe_3)_2$, which contain three, two or one bridging acetate ligands and anions of *N*,*N*′-di(2-methoxyphenyl)formamidine (*o*-HDMophF) have been reported [8]. These complexes can be envisaged as the intermediates of the stepwise decarboxylation of $Mo_2(O_2CR)_4$ to form Mo_2(form)$_4$.

To our knowledge, no dimolybdenum species containing two types of formamidinate ligands has been reported. The only dinuclear complexes with mixed formamidinate ligands are the two unexpected products *trans*-$Ru_2(O_2CCH_3)_2$(μ-*N*,*N*′-η^2-N-O-*o*-MeOForm)(μ-*N*,*N*′-η^2-N-O-*o*-MeOForm′) and $Ru_2(O_2CCH_3)$(μ-*N*,*N*′-*o*-MeOForm)(μ-*N*,*N*′-η^2-N-O-*o*-MeOForm)(μ-*N*,*N*′-η^2-N-O-*o*-MeOForm′), where *o*-MeOForm is di(o-methoxyphenyl)formamidinate, and *o*-MeOForm′ is the *O*-demethylation derivative of *o*-MeOForm, (*o*-methoxyphenyl)(*o*-oxyphenyl)formamidinate [9]. Introducing two different types of formamidinate ligands to the dimolybdenum units may drastically changes the

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conformations of the formamidinate ligands. As a continuous study on the dimolybdenum complexes supported by formamidinate ligands and to study the influence of weak interactions on the conformation of the formamidinate ligand, we have synthesized five dimolybdenum complexes containing two different formamidinate ligands. Hereby, the syntheses, structures and characterization of these complexes are reported.

2. Experimental

2.1. General procedures

All manipulations were carried out under dry, oxygen-free nitrogen by using Schlenk techniques, unless otherwise noted. Solvents were dried and deoxygenated by refluxing over the appropriate reagents before use. Hexanes and ether were purified by distillation from sodium/benzophenone, acetonitrile from CaH_2 and dichloromethane from P_2O_5. The Visible absorption spectra were recorded on a Hitachi U-2000 spectrophotometer. NMR spectra were measured on a Bruker Avance 300 MHz spectrometer. IR spectra were obtained from a Jasco FT/IR-460 plus spectrometer. Elemental analyses were obtained from a PE 2400 series II CHNS/O analyzer.

2.2. Materials

The compounds *trans*-$Mo_2(O_2CCH_3)_2$(*o*-DMophF)$_2$ [8], *N*,*N*′-di(2-pyridyl)formamidine (HDpyF) [10], *N*,*N*′-di(2-pyrimidyl)-formamidine (HDpmF) [11], and *N*,*N*′-di(6-methyl-2-pyridyl)formamidine (HDMepyF) [12] were prepared according to previously reported procedures.

2.3. Preparation of trans-$Mo_2(O_2CCH_3)$(DpyF)(*o*-DMophF)$_2$ (**1**)

Trans-$Mo_2(O_2CCH_3)_2$(*o*-DMophF)$_2$ (0.50 g, 0.61 mmol) and HDpyF (0.12 g, 0.61 mmol) was placed in a flask containing 10 mL CH_2Cl_2. The mixture was then refluxed for 2 days to yield an orange–yellow solution. The solvent was removed under vacuum to leave an orange–yellow solid which was dissolved in 30 mL ether to give an orange–yellow solution. The solvent was then removed, followed by addition of 2 mL ether and 30 mL hexanes. The solid was filtered and dried under vacuum to give a yellow product. Yield: 0.26 g (44.5%). UV–Vis: 462 nm (CH_2Cl_2, $\varepsilon = 2247$ M^{-1} cm^{-1}). ^{1}H NMR ($CDCl_3$, ppm): 9.73 (s, 1H, C*H*), 8.78 (s, 2H, C*H*), 7.60 (d, 2H, H^{meta}), 7.14 (d, 4H, H^{ortho}), 6.89 (t, 2H, H^{meta}), 6.81 (t, 4H, H^{para}), 6.79 (t, 4H, H^{meta}), 6.52 (d, 4H, H^{meta}), 6.44 (t, 2H, H^{para}), 5.62 (d, 2H, H^{ortho}), 3.15 (s, 12H, OCH_3), 2.69 (s, 3H, CH_3). ^{13}C{^{1}H} NMR ($CDCl_3$, ppm): 179.14 (C), 160.82 (C), 158.53 (CH), 154.57 (CH), 151.40 (C), 147.35 (CH), 139.92 (C), 136.29 (CH), 123.34 (CH), 122.44 (CH), 120.57 (CH), 117.15 (CH), 113.70 (CH), 111.26 (CH), 55.71 (CH_3), 24.21 (CH_3). *Anal.* Calc. for $C_{43}H_{42}Mo_2N_8O_6$ (Mw = 958.73): C, 53.87; H, 4.42; N, 11.69. Found: C, 53.66; H, 4.53; N, 11.74%. IR (KBr disk): 2934(w), 2832(w), 1594(m), 1540(s), 1494(s), 1461(s), 1426(s), 1311(s), 1247(s), 1208(m), 1175(w), 1148(w), 1115(m), 1049(m), 1022(m), 935 (w), 858(w), 782(m), 744(s), 674(m), 447(w).

2.4. Preparation of trans-$Mo_2(O_2CCH_3)$(DpmF)(*o*-DMophF)$_2$ (**2**)

Trans-$Mo_2(O_2CCH_3)_2$(*o*-DMophF)$_2$ (1.00 g, 1.22 mmol) and HDpmF (0.49 g, 2.45 mmol) were placed in a flask containing 10 mL CH_2Cl_2. The mixture was then refluxed for 5 h to yield a red solution. The solvent was removed under vacuum to leave a red solid which was dissolved in 80 mL ether to give a red solution. The solvent was removed and the solid was filtered, washed by 30 mL hexanes and dried under vacuum to give the red product. Yield: 0.73 g (62.5 %). UV–Vis: 491 nm (CH_2Cl_2, $\varepsilon = 1701$ M^{-1} cm^{-1}). ^{1}H NMR ($CDCl_3$, ppm): 10.39 (s, 1H, C*H*), 8.78 (s, 2H, C*H*), 7.66 (d, 4H, H^{meta}), 7.11 (d, 4H, H^{ortho}), 6.76 (t, 4H, H^{para}), 6.66 (t, 4H, H^{meta}), 6.47 (d, 4H, H^{meta}), 6.31 (t, 2H, H^{para}), 3.14 (s, 12H, OCH_3), 2.77 (s, 3H, CH_3). ^{13}C{^{1}H}NMR ($CDCl_3$, ppm): 179.39 (C), 165.09 (C), 158.58 (CH), 157.61 (CH), 156.67 (CH), 151.88 (C), 140.18 (C), 123.09 (CH), 122.51 (CH), 120.07 (CH), 114.27 (CH), 110.55 (CH), 54.88 (CH_3), 24.41 (CH_3). *Anal.* Calc. for $C_{41}H_{40}Mo_2N_{10}O_6$ (Mw = 960.71): C, 51.26; H, 4.20; N, 14.58. Found: C, 51.29; H, 4.27; N, 14.45% IR (KBr disk): 2952(w), 2830(w), 1577(m), 1541(s), 1493(s), 1456(m), 1431(w), 1384(s), 1308(s), 1248(s), 1205(m), 1176(m), 1115(m), 1051(w), 1026(m), 986(w), 933(w), 876(w), 809(m), 745(m), 675(w), 642(w), 447(w).

2.5. Preparation of trans-$Mo_2(O_2CCH_3)_2$(DMepyF)(*o*-DMophF)$_2$ (**3**)

Trans-$Mo_2(O_2CCH_3)_2$(*o*-DMophF)$_2$ (0.30 g, 0.37 mmol) and HDMepyF (0.08 g, 0.37 mmol) were placed in a flask containing 10 mL CH_2Cl_2. The mixture was then refluxed for 2 days to yield a brown solution. The solvent was removed, followed by addition 30 mL ether to give a yellow solution. The solvent was then removed and the solid washed by hexanes and then dried under vacuum to give a yellow product. Yield: 0.08 g (22.2 %). UV–Vis: 462 nm (CH_2Cl_2, $\varepsilon = 3193$ M^{-1} cm^{-1}). ^{1}H NMR ($CDCl_3$, ppm): 9.72 (s, 1H, C*H*, 8.70 (s, 2H, C*H*), 7.13 (d, 4H, H^{ortho}), 6.83 (t, 2H, H^{meta}), 6.79 (t, 4H, H^{para}), 6.69 (t, 4H, H^{meta}), 6.54 (d, 4H, H^{meta}), 6.27 (d, 2H, H^{para}), 5.62 (d, 2H, H^{ortho}), 3.27 (s, 12H, OCH_3),

2.71 (s, 3H, CH_3), 1.76 (s, 6H, CH_3). $^{13}C\{^1H\}$ NMR ($CDCl_3$, ppm): 178.84 (C), 160.32 (C), 158.99 (CH), 156.44 (C), 153.29 (CH), 151.60 (C), 140.26 (C), 136.53 (CH), 123.22 (CH), 123.08 (CH), 120.65 (CH), 116.23 (CH), 111.83 (CH), 109.59 (CH), 55.46 (CH_3), 24.18 (CH_3), 23.41 (CH_3). *Anal.* Calc. for $C_{45}H_{46}Mo_2N_8O_6$ (Mw = 986.79): C, 57.77; H, 4.70; N, 11.36. Found: C, 57.46; H, 4.49; N, 11.70%. IR (KBr disk): 2930(w), 2832(w), 1583(m), 1544(s), 1494(s), 1442(s), 1315(m), 1282(m), 1244(s), 1178(w), 1158(w), 1114(m), 1024(m), 932(w), 783(w), 743(m), 676(w), 532(w), 449(w).

2.6. Preparations of trans-$Mo_2(O_2CCH_3)(DMepyF)_2$(o-DMophF), 4 and trans-$Mo_2(DMepyF)_2$(o-DMophF)$_2$ (5)

Trans-$Mo_2(O_2CCH_3)_2$(*o*-DMophF)$_2$ (0.50 g, 0.61 mmol) and HDMepyF (0.41 g, 1.82 mmol) were placed in a flask containing 10 mL CH_3CN. The mixture was then refluxed for 2 days to yield a brown solution and an orange solid. The solvent was removed under vacuum to leave a yellow solid. The ^1H NMR spectrum of the yellow solid showed that there were three complexes in a ratio of 1:10:20. The spectrum of the complex with the least amount is the same as that of complex **3**, which was not obtained after the purification process. 30 mL ether was then added to a flask containing the yellow solid to give a yellow solution and an orange solid. The solvent of the yellow solution was removed and the solid washed by 2 mL ether and 30 mL hexanes and then dried under vacuum to give complex **4**. The orange solid was washed by 20 mL ether and then dried under vacuum to give complex **5**. Yield for **4**: 0.07 g (12.0%). UV–Vis: 471 nm (CH_2Cl_2, $\varepsilon = 5617\ M^{-1}\ cm^{-1}$). ^1H NMR ($CDCl_3$, ppm): 10.22 (s, 2H, C*H*), 8.09 (s, 1H, C*H*), 7.16 (t, 4H, H^{meta}), 6.73 (t, 2H, H^{para}), 6.50 (d, 4H, H^{para}), 6.46 (d, 2H, H^{ortho}), 6.37 (d, 2H, H^{meta}), 6.30 (t, 2H, H^{meta}), 6.02 (d, 4H, H^{ortho}), 3.12 (s, 6H, OCH_3), 2.51 (s, 3H, CH_3), 1.95 (s, 12H, CH_3). $^{13}C\{^1H\}$ NMR ($CDCl_3$, ppm): 179.90 (C), 161.36 (CH), 160.23 (C), 157.03 (C), 153.41 (C), 152.84 (CH), 139.76 (C), 137.48 (CH), 127.45 (CH), 124.37 (CH), 119.16 (CH), 116.71 (CH), 110.16 (CH), 109.86 (CH), 54.74 (CH_3), 25.58 (CH_3), 23.60 (CH_3). *Anal.* Calc. for $C_{43}H_{44}Mo_2N_{10}O_4$ (Mw = 956.76): C, 53.98; H, 4.64; N, 14.64. Found: C, 53.39; H, 4.87; N, 14.39%. IR (KBr disk): 2962(w), 2837(w), 1685(m), 1591(m), 1545(s), 1494(m), 1447(s), 1384 (w), 1292(s), 1249(m), 1214(m), 1180(w), 1158(w), 1111(w), 1046(w), 1025(m), 988(w), 782(w), 745(m), 672(w), 558(w), 450(w). Yield for **5**: 0.18 g (25.6%). UV–Vis: 473 nm (CH_2Cl_2, $\varepsilon = 3319\ M^{-1}\ cm^{-1}$). ^1H NMR ($CDCl_3$, ppm): 10.32 (s, 2H, C*H*), 8.40 (s, 2H, C*H*), 6.94 (t, 4H, H^{meta}), 6.78 (t, 4H, H^{para}), 6.44 (d, 4H, H^{para}), 6.41 (d, 4H, H^{ortho}), 6.36 (d, 4H, H^{meta}), 6.23 (t, 4H, H^{meta}), 5.65 (d, 4H, H^{ortho}), 3.17 (s, 12H, OCH_3), 1.63 (s, 12H, CH_3). *Anal.* Calc. for $C_{56}H_{56}Mo_2N_{12}O_4$ (Mw = 1153.01): C, 58.34; H, 4.90; N, 14.58, Found: C, 58.54; H, 4.76; N, 14.38%. IR (KBr disk): 2960(w), 2827(w), 1637(m), 1586(m), 1540(s), 1515(s), 1495(m), 1445 (s), 1383(w), 1289(s), 1242(m), 1215(m), 1157(w), 1115(w), 1048(w), 1030(w), 939(w), 791(m), 744(m), 733(m), 671(w), 565(w), 455(w).

3. X-ray crystallography

The diffraction data of **1**, **2**, **4** and **5** were collected on a Bruker Smart 1000 or a Bruker AXS diffractometer, which was equipped with a graphite-monochromated Mo-Kα ($\lambda_\alpha = 0.71073$ Å) radiation. Data reduction was carried by standard methods with use of well-established computational procedures [13]. The structure factors were obtained after Lorentz and polarization corrections. The positions of some of the heavier atoms including the molybdenum atoms were located by the direct method. The remaining atoms were found in a series of alternating difference Fourier maps and least-square refinements. The final residuals of the refinement were $R_1 = 0.0359$ and $wR_2 = 0.0494$. The X-ray crystallographic procedures for other complexes were similar to those for **1**. Basic information pertaining to crystal parameters and structure refinement is summarized in Table 1.

4. Results and discussions

4.1. Synthesis

The starting complex *trans*-$Mo_2(O_2CCH_3)_2$(*o*-DMophF)$_2$ was prepared by a reaction of $Mo_2(O_2CCH_3)_4$ with Li(*o*-DMophF). Reactions of *trans*-$Mo_2(O_2CCH_3)_2$(*o*-DMophF)$_2$ with *N*,*N*′-di(2-pyridyl)formamidine (HDpyF), *N*,*N*′-di(2-pyrimidyl)formamidine (HDpmF) and *N*,*N*′-di(6-methyl-2-pyridyl) ormamidine (HDMepyF) in refluxing CH_2Cl_2 afforded the complexes, *trans*-$Mo_2(O_2CCH_3)$(DpyF)(*o*-DMop F)$_2$ (**1**), *trans*-$Mo_2(O_2CCH_3)$(DpmF)(*o*-DMo phF)$_2$ (**2**), and *trans*-$Mo_2(O_2CCH_3)$(DMepyF)(*o*-DMophF)$_2$ (**3**), respectively. Reactions of *trans*-$Mo_2(O_2CCH_3)_2$(*o*-DMo phF)$_2$ with HDMepyF in CH_3CN gave the complexes **3**, *trans*-$Mo_2(O_2CCH_3)$(DMepyF)$_2$(*o*-DMophF) (**4**), and *trans*-Mo_2(DMepyF)$_2$(*o*-DMophF)$_2$ (**5**) in a 1:10:20 ratio as measured by ^1H NMR spectrum. The structures of complexes **1**, **2**, **4** and **5** were characterized by X-ray crystallography while that of **3** was characterized by elemental analysis and spectroscopic studies. Fig. 1 show the ^1H–^{13}C COSY NMR spectrum for **3**. The ^1H NMR spectrum shows three singlets centered at 3.27 (12H), 2.71 (3H) and 1.76 (6H) ppm, which can be assigned to the methyl hydrogen atoms of the *o*-DMophF$^-$, $CH_3CO_2^-$ and DMepyF$^-$ ligands, respectively. The observations of only one singlet for the methyl hydrogen

Table 1
Crystal data for **1**, **2**, **4** and **5**·CH_2Cl_2

Compound	**1**	**2**·CH_2Cl_2	**4**	**5**
Formula	$C_{43}H_{42}Mo_2N_8O_6$	$C_{42}H_{42}Cl_2Mo_2N_{10}O_6$	$C_{43}H_{44}Mo_2N_{10}O_4$	$C_{56}H_{56}Mo_2N_{12}O_4$
Fw	958.73	1045.64	956.76	1153.01
Crystal system	monoclinic	monoclinic	monoclinic	monoclinic
Space group	$P2_1/c$	$P2_1/c$	$C2/c$	$C2/c$
a (Å)	19.569(1)	18.191(3)	26.100(4)	25.617(2)
b (Å)	15.102(1)	16.682(3)	10.804(1)	13.672(2)
c (Å)	15.036(1)	15.356(2)	15.084(1)	15.463(1)
β (°)	106.193(1)	106.59(2)	95.38(1)	96.946(5)
V (Å^3)	4267.4(5)	4466.1(12)	4234.8(8)	5375.9(9)
Z	4	4	4	4
d_{calc} (g/cm^3)	1.492	1.555	1.501	1.425
$F(000)$	1952	2120	1952	2368
Crystal size (mm)	$0.05 \times 0.6 \times 0.6$	$0.6 \times 0.8 \times 0.8$	$0.3 \times 0.3 \times 0.5$	$0.15 \times 0.3 \times 0.5$
μ(Mo-Kα) (mm^{-1})	0.644	0.739	0.647	0.524
Data collection instruments	Bruker Smart 1000	Bruker AXS P4	Bruker AXS P4	Bruker AXS P4
Radiation monochromated in incident beam (λ(Mo-Kα) (Å))	0.71073	0.71073	0.71073	0.71073
Orientation reflections number; range(2θ) (°)		42; $11.29 \leqslant 2\theta \leqslant 25.09$	57; $11.69 \leqslant 2\theta \leqslant 24.93$	40; $9.26 \leqslant 2\theta \leqslant 24.88$
Range(2θ) for data collection (°)	$3.90 \leqslant 2\theta \leqslant 55.02$	$3.70 \leqslant 2\theta \leqslant 50.00$	$4.08 \leqslant 2\theta \leqslant 50.00$	$4.18 \leqslant 2\theta \leqslant 50.00$
Temperature (°C)	25	25	25	25
Limiting indices	$-25 \leqslant h \leqslant 22$, $-19 \leqslant k \leqslant 19$, $-19 \leqslant l \leqslant 18$	$-21 \leqslant h \leqslant 21$, $-19 \leqslant k \leqslant 1$, $-1 \leqslant l \leqslant 18$	$-1 \leqslant h \leqslant 30$, $-1 \leqslant k \leqslant 12$, $-17 \leqslant l \leqslant 17$	$-1 \leqslant h \leqslant 30$, $-1 \leqslant k \leqslant 16$, $-18 \leqslant l \leqslant 18$
Reflections collected	26,474	9340	4423	5464
Independent reflections	9758 [$R_{int} = 0.0685$]	7786 [$R_{int} = 0.0416$]	3705 [$R_{int} = 0.0257$]	4671 [$R_{int} = 0.0324$]
Refinement method	full-matrix least-squares on F^2	full-matrix least-squares on F^2	full-matrix least-squares on F^2	full-matrix least-squares on F^2
Data/restraints/parameters	9785/0/670	7786/0/647	3705/0/359	4671/0/342
Quality-of-fit indicator[c]	0.759	1.015	1.091	1.029
Final R indices [$I > 2\sigma(I)$][a,b]	$R_1 = 0.0359$, $wR_2 = 0.0494$	$R_1 = 0.0480$, $wR_2 = 0.1256$	$R_1 = 0.0328$, $wR_2 = 0.0774$	$R_1 = 0.0538$, $wR_2 = 0.1255$
R indices (all data)	$R_1 = 0.1146$, $wR_2 = 0.0563$	$R_1 = 0.0682$, $wR_2 = 0.1386$	$R_1 = 0.0459$, $wR_2 = 0.0832$	$R_1 = 0.0938$, $wR_2 = 0.1445$
Largest differences peak and hole (e/Å^3)	0.525 and −0.587	0.552 and −0.757	0.341 and −0.351	0.764 and −0.412

[a] $R_1 = \sum \| F_o | - | F_c \| / \sum | F_o |$.

[b] $wR_2 = \left[\sum w(F_o^2 - F_c^2)^2 \Big/ \sum w(F_o^2)^2 \right]^{1/2}$. $w = 1/[\sigma^2(F_o^2) + (ap)^2 + (bp)]$, $p = [\max(F_o^2 \text{ or } 0) + 2(F_c^2)]/3$. $a = 0$, $b = 0$, **1**; $a = 0.0766$, $b = 4.3750$, **2**·CH_2Cl_2. $a = 0.0310$, $b = 7.5459$, **4**; $a = 0.0626$, $b = 17.6367$, **5**.

[c] Quality-of-fit $= \left[\sum w(|F_o^2| - |F_c^2|)^2 / N_{observed} - N_{parameters} \right]^{1/2}$.

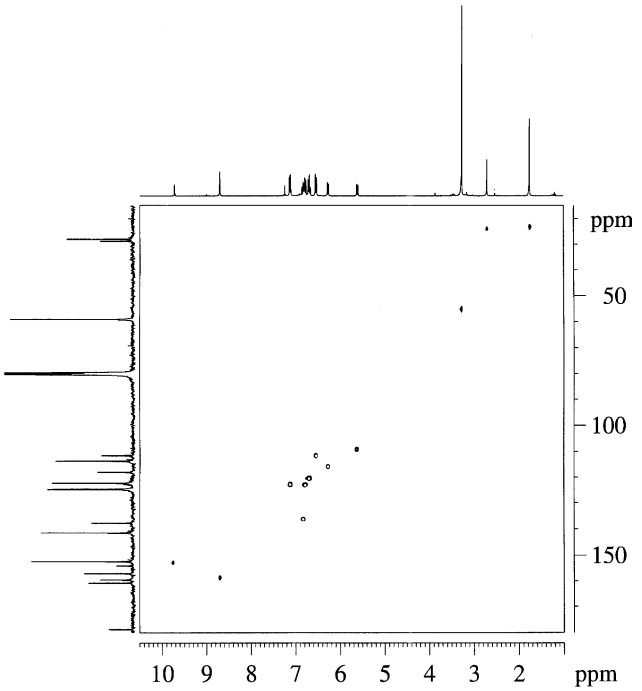


Fig. 1. ^{1}H–^{13}C COSY NMR spectrum for complex **3**.

atoms of the *o*-DMophF^{-} ligands and an integration of twelve hydrogen atoms indicate that complex **3** is coordinated by two *o*-DMophF^{-} ligands which are *trans* to each other. Complexes **1** and **2** show similar spectra to that of **3**.

4.2. Structures

Orange crystals of **1** and **2** conform to the space group $P2_1/c$ with four molecules in a unit cell. Figs. 1–3 shows the ORTEP diagram for complexes **1** and **2**, respectively, and selected bond distances and angles are

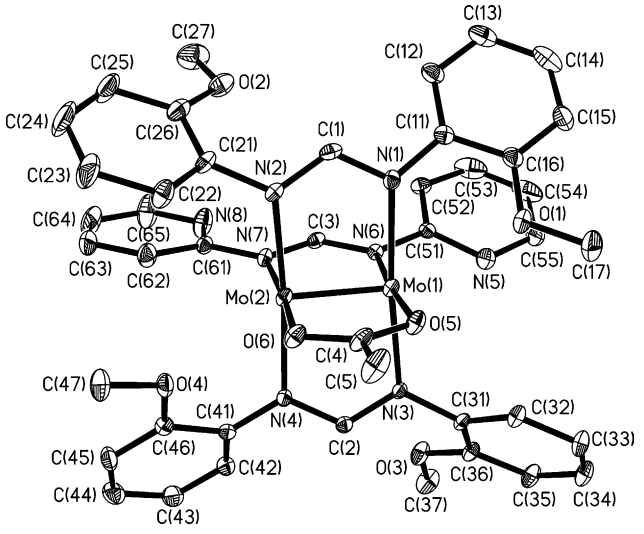


Fig. 2. ORTEP drawing of *trans*-$Mo_2(O_2CCH_3)$(DpyF)(*o*-DMophF)$_2$ (**1**).

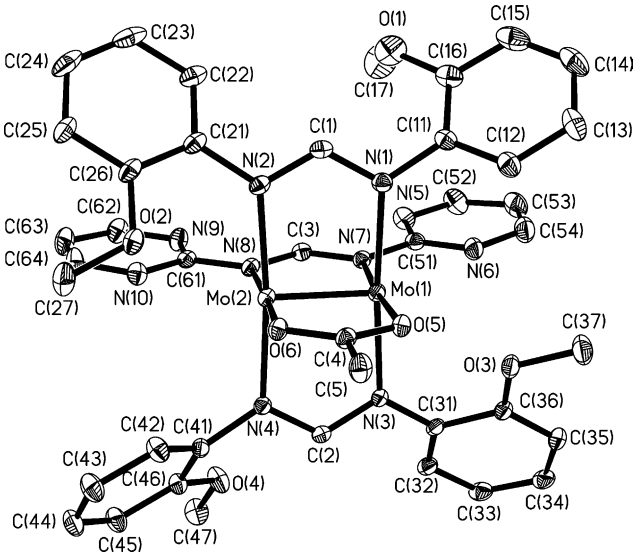


Fig. 3. ORTEP drawing of *trans*-$Mo_2(O_2CCH_3)$(DpmF)(*o*-DMophF)$_2$ (**2**).

listed in Tables 2 and 3, respectively. The molecular structure of **1** consists of two molybdenum atoms [Mo–Mo = 2.0961 (5) Å], which are spanned by one bridging acetate, two *o*-DMophF^{-} and one DpyF^{-} ligands, while the two molybdenum atoms [Mo–Mo = 2.1057(6) Å] of **2** are spanned by one bridging acetate, two *o*-DMophF^{-} and one DpmF^{-} ligands. The two *trans o*-DMophF^{-} ligands in complexes **1** and **2** coordinate to the molybdenum centers through the two central nitrogen atoms and adopt the *s-cis, s-trans* conformation [14], resulting in a Mo–O short distance [2.889 (3) and 2.861 (2) Å for **1** and 2.880 (3) and 3.024 (4) Å for **2**, respectively] for each *o*-DMophF^{-} ligand. The DpyF^{-} ligand in **1** also adopts an *s-cis, s-trans* conformation, resulting in a Mo–N [3.208(4) Å] and a Mo–H [2.90 (3) Å, to pyridyl hydrogen atom attached to C(62)] short distances. Although single crystal X-ray structure was not obtained for **3**, on the basis of spectroscopic studies and elemental analysis, its structure is proposed to be similar to those for **1** and **2**.

Yellow crystals of **4** and orange crystals of **5** both conform to the space group $C2/c$ with four molecules in each unit cell. Figs. 4(a) and 5(a) show the ORTEP diagram for complexes **4** and **5**, respectively. Selected bond distances and angles for **4** and **5** are listed in Tables 4 and 5, respectively. The molecular structures of **4** consists of two molybdenum atoms [Mo–Mo = 2.1021(6) Å] which are spanned by one acetate, two *trans* DMepyF^{-} and one *o*-DMophF^{-} ligands while the two molybdenum atoms [Mo–Mo = 2.1071(9) Å] in **5** are spanned by two trans DMepyF^{-} ligands and two *trans o*-DMophF^{-} ligands. All the *o*-DMophF^{-} ligands in complexes **4** and **5** adopt the *s-cis, s-cis* conformation and the oxygen atoms of the methoxy groups are positioned away from the

Table 2
Selected bond distances (Å) and angles (°) for **1**

Bond distances			
Mo(1)–Mo(2)	2.0961(5)	Mo(1)–N(6)	2.130(3)
Mo(1)–N(1)	2.139(3)	Mo(1)–O(5)	2.146(2)
Mo(1)–N(3)	2.148(3)	Mo(2)–N(2)	2.129(3)
Mo(2)–O(6)	2.138(2)	Mo(2)–N(4)	2.142(3)
Mo(2)–N(7)	2.144(3)	Mo(2)–O(4)	2.861(2)
Mo(1)–O(1)	2.889(3)		
Bond angles			
Mo(2)–Mo(1)–N(6)	91.57(8)	Mo(2)–Mo(1)–N(1)	92.71(8)
N(6)–Mo(1)–N(1)	85.00(10)	Mo(2)–Mo(1)–O(5)	91.96(7)
N(6)–Mo(1)–O(5)	175.57(10)	N(1)–Mo(1)–O(5)	92.17(10)
Mo(2)–Mo(1)–N(3)	92.65(8)	N(6)–Mo(1)–N(3)	92.87(10)
N(1)–Mo(1)–N(3)	174.29(12)	O(5)–Mo(1)–N(3)	89.62(9)
Mo(1)–Mo(2)–N(2)	92.46(9)	Mo(1)–Mo(2)–O(6)	91.46(7)
N(2)–Mo(2)–O(6)	88.86(10)	Mo(1)–Mo(2)–N(4)	92.41(8)
N(2)–Mo(2)–N(4)	174.94(12)	O(6)–Mo(2)–N(4)	92.41(10)
O(6)–Mo(2)–N(7)	174.20(10)	N(2)–Mo(2)–N(7)	87.87(10)
N(4)–Mo(2)–N(7)	90.44(10)		

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

Bond distances			
Mo(1)–Mo(2)	2.1057(6)	Mo(1)–O(5)	2.148(3)
Mo(1)–N(3)	2.148(4)	Mo(1)–N(1)	2.149(4)
Mo(1)–N(7)	2.154(4)	Mo(2)–N(4)	2.138(4)
Mo(2)–O(6)	2.147(3)	Mo(2)–N(8)	2.155(4)
Mo(2)–N(2)	2.157(4)	Mo(2)–O(2)	3.024(4)
Mo(1)–O(3)	2.880(3)		
Bond angles			
Mo(2)–Mo(1)–O(5)	91.3(1)	Mo(2)–Mo(1)–N(3)	92.8(1)
O(5)–Mo(1)–N(3)	91.5(1)	Mo(2)–Mo(1)–N(1)	92.1(1)
O(5)–Mo(1)–N(1)	88.8(2)	N(3)–Mo(1)–N(1)	175.7(2)
Mo(2)–Mo(1)–N(7)	92.5(1)	O(5)–Mo(1)–N(7)	175.8(1)
N(3)–Mo(1)–N(7)	90.0(1)	N(1)–Mo(1)–N(7)	89.4(2)
N(4)–Mo(2)–O(6)	89.1(1)	Mo(1)–Mo(2)–N(8)	91.5(1)
N(4)–Mo(2)–N(8)	91.8(1)	O(6)–Mo(2)–N(8)	176.7(1)
O(6)–Mo(2)–N(2)	90.7(1)	N(4)–Mo(2)–N(2)	174.5(2)
N(8)–Mo(2)–N(2)	88.2(1)		

molybdenum metal centers. Noticeably, although all the *o*-DMophF$^-$ ligands in complexes **4** and **5** adopt the *s-cis, s-cis* conformation, the orientations of the methoxy groups in each *o*-DMophF$^-$ ligand are different. Figs. 4(b) and 5(b) show the ORTEP diagrams looking down the Mo–Mo axes for complexes **4** and **5**, respectively. It is seen that while the two methoxy groups in **4** are positioned opposite to each other, those in **5** are on the same side. It is also noted that all the DMepyF$^-$ ligands in complexes **4** and **5** adopt the *s-cis, s-trans* conformation, resulting in the formation of Mo–N and Mo–H short distances for both complexes. The distances are Mo–N = 2.882 (**3**) and Mo–H = 2.79 (**4**) Å for **4** and Mo–N = 2.863 (**5**) and Mo–H = 2.98 Å for **5**, respectively. It seems that formation of both Mo–N and Mo–H short distances are more favorable than Mo–O short distance.

Complexes **1**–**5** are of significance because they are the first dimolybdenum complexes containing two different types of formamidinate ligands.

4.3. Structural comparisons

A comparison of distances and conformations, as well as ^{1}H- and ^{13}C NMR chemical shifts, observed for dimolybdenum complexes containing anion of *N*, *N*′-di(2-methoxyphenyl)formamidine (*o*-DMophF$^-$) is listed in Table 6. Two short Mo–O distances for each *o*-DMophF$^-$ ligand are observed in the complex $Mo_2(O_2CCH_3)_3$(*o*-DMophF), in which the *o*-DMophF$^-$ ligand adopts the *s-trans, s-trans* conformation [8]. In complexes *trans*-$Mo_2(O_2CR)_2$(*o*-DMophF)$_2$ (R = CH_3, CF_3 and Pr^n), **1** and **2**, the *o*-DMophF$^-$ ligands adopt the *s-cis, s-trans* conformation, resulting in one Mo–O

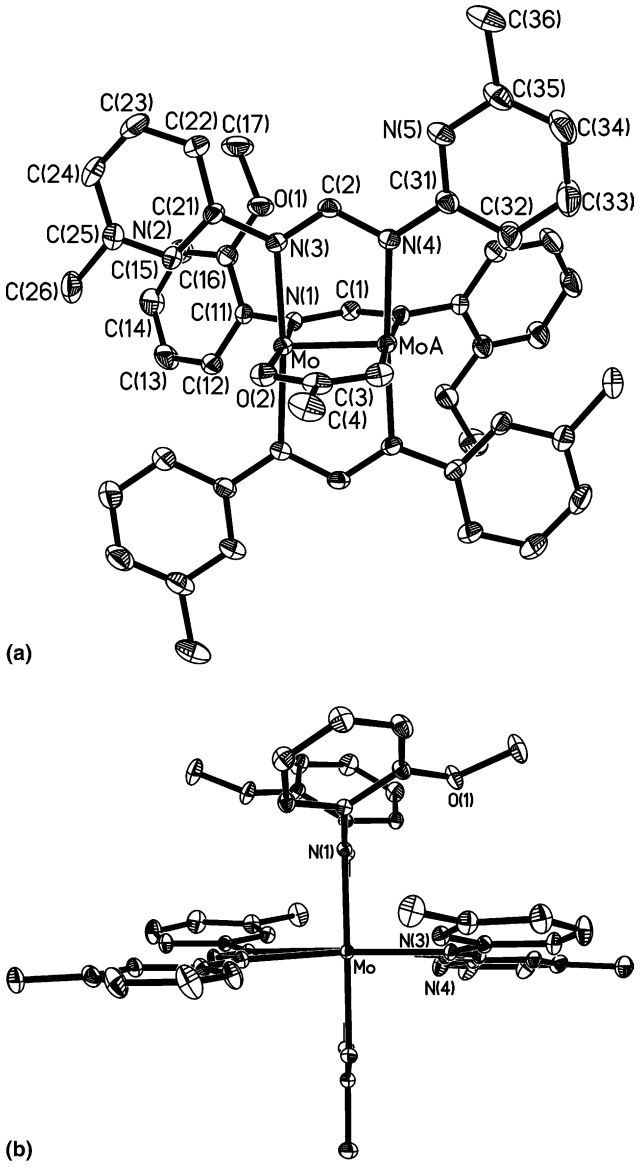


Fig. 4. ORTEP drawing of *trans*-$Mo_2(O_2CCH_3)(DMepyF)_2$(*o*-DMophF) (**4**).

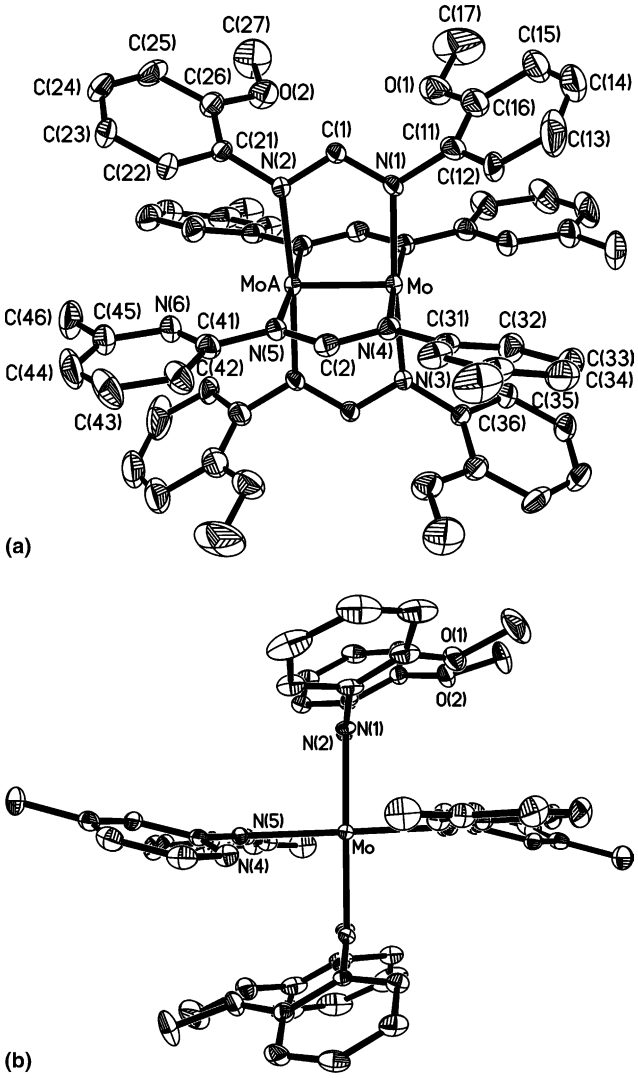


Fig. 5. ORTEP drawing of *trans*-$(DMepyF)_2$(*o*-$DMophF)_2$ (**5**).

short distance for each *o*-$DMophF^-$ ligand. These complexes are in marked to the *s-cis, s-cis* conformation in complexes **4** and **5**, where no Mo–O interaction is observed. It is noted that for all the complexes with *s-cis, s-trans* conformation, the two complexes with two different formamidinate ligands, i.e., complexes **1** and **2**, have the longer Mo–O distances, presumably do to the steric effect imposed by the other formamidinate ligands.

The variable-temperature ^1H NMR spectra of all the complexes in Table 6, except $Mo_2(O_2CCH_3)$(*o*-DMophF)$Cl_2(PMe_3)_2$ [8], show only a sharp singlet for the protons of OCH_3 groups, indicating that the solid state *s-cis, s-trans* conformation of the *o*-HDMophF ligands in these complexes are not retained in solution. Since all the complexes show similar ^1H and ^{13}C NMR chemical shifts for the methoxy hydrogen and carbon atoms, respectively, the *s-trans, s-trans* and *s-cis, s-cis* conformations are most probably not retained in solution either. Similar situations were seen in the complexes Cr_2(*o*-$DMophF)_4$ [15] and $Cr_2(O_2CCH_3)_2$(*o*-$DMophF)_2$ [16]. Due to the asymmetry of the molecules, two singlets for the two methoxy hydrogen atoms were observed for the complex $Mo_2(O_2CCH_3)$(*o*-DMophF)$Cl_2(PMe_3)_2$ [8].

4.4. Formation scheme for complexes 3–5

The formation of **4** from the starting complex *trans*-$Mo_2(O_2CCH_3)_2$(*o*-$DMophF)_2$ is worthy of discussion. In the complexes *trans*-$Mo_2(O_2CCH_3)_2$(*o*-$DMophF)_2$ and **3**, the two *o*-$DMophF^-$ ligands which are positioned *trans* to each other are *cis* to the acetate ligands, while in complex **4** the *o*-$DMophF^-$ ligand is positioned *trans* to the acetate ligand. Scheme 1 shows the proposed formation mechanism for complexes **3**–**5**, where the

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

Bond distances			
Mo–Mo(A)	2.1021(6)	Mo–N(1)	2.115(3)
Mo–N(3)	2.141(3)	Mo–O(2)	2.146(3)
Mo–N(4A)	2.181(3)		
Bond angles			
Mo(A)–MoN(1)	92.48(7)	Mo(A)–Mo–N(3)	89.95(8)
N(1)–Mo–N(3)	91.59(10)	Mo(A)–Mo–O(2)	91.68(7)
N(1)–Mo–O(2)	175.82(10)	N(3)–Mo–O(2)	88.86(10)
Mo(A)–Mo–N(4A)	94.42(8)	N(1)–Mo–N(4A)	92.46(10)
N(3)–Mo–N(4A)	173.91(11)	O(2)–Mo–N(4A)	86.77(10)

Table 5
Selected bond distances (Å) and angles (°) for **5**

Bond distances			
Mo–Mo(A)	2.1071(9)	Mo–N(1)	2.144(4)
Mo–N(2A)	2.146(4)	Mo–N(5A)	2.146(5)
Mo–N(4)	2.184(5)		
Bond angles			
Mo(A)–MoN(1)	92.5(1)	Mo(A)–Mo–N(2A)	92.4(1)
N(1)–Mo–N(2A)	175.1(2)	Mo(A)–Mo–N(5A)	90.2(1)
N(1)–Mo–N(5A)	87.2(2)	N(2A)–Mo–N(5A)	92.3(2)
Mo(A)–Mo–N(4)	93.5(1)	N(1)–Mo–N(4)	92.0(2)
N(2A)–Mo–N(4)	88.2(2)	N(5A)–Mo–N(4)	176.2(2)

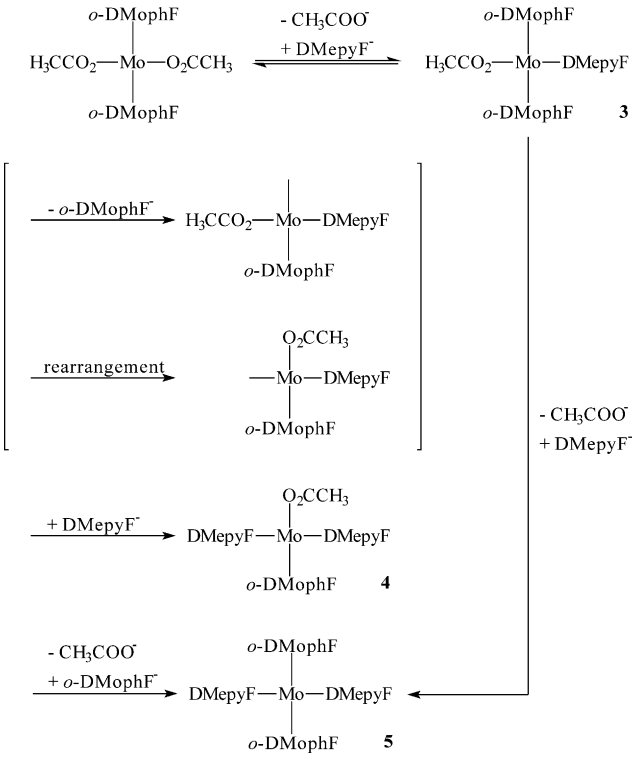
Table 6
Some important parameters for dimolybdenum complexes containing anion of *N*, *N*′-di(2-methoxyphenyl)formamidine (*o*-DMophF$^-$)

Compound	Mo–Mo (Å)	Mo–O (Å)	Conformation of *o*-DMophF$^-$	δ ^{1}H(^{13}C) for the methoxy groups of *o*-DMophF$^-$
$Mo_2(O_2CCH_3)_3$ (*o*-DMophF)	2.0933(3)	2.681(2) 2.667(2)	*s-trans, s-trans*	3.26(55.05)
trans-$Mo_2(O_2CCH_3)_2$ (*o*-DMophF)$_2$	2.108(1)	2.600(7) 2.615(6)	*s-cis, s-trans*	3.15(55.71)
trans-$Mo_2(O_2CCF_3)_2$ (*o*-DMophF)$_2$	2.133(2)	2.576(5) 2.576(5)	*s-cis, s-trans*	3.09(55.38)
trans-$Mo_2(O_2CCPr^n)_2$ (*o*-DMophF)$_2$	2.1088(6)	2.602(2) 2.602(2)	*s-cis, s-trans*	3.16(55.78)
$Mo_2(O_2CCH_3)$(*o*-DMophF)$Cl_2(PMe_3)_2$	2.1239(6)	2.562(4)	*s-cis, s-trans*	3.23(55.88) 3.40(54.15)
1	2.0961(5)	2.889(3) 2.861(2)	*s-cis, s-trans*	3.15(55.71)
2	2.1057(6)	3.024(4) 2.880(3)	*s-cis, s-trans*	3.14(54.88)
3				3.27(55.46)
4	2.1021(6)		*s-cis, s-cis*	3.12(54.74)
5	2.1071(9)		*s-cis, s-cis*	3.17

complexes are represented by the side views looking down the Mo–Mo bonds, showing the relative positions of the ligands. The first step is that one of the acetate ligands was replaced by the DMepyF$^-$ ligand to give complex **3**. Upon addition of another DMepyF$^-$ ligand, one of the *o*-DMophF$^-$ ligands departs from the metal centers and the intermediate rearrange to position the acetate and *o*-DMophF$^-$ ligands *trans* to each other. The DMepyF$^-$ ligand then coordinates to the dimolybdenum unit to form complex **4**. As shown in Scheme 1, two possible pathways can be undertaken to form complex **5**.

5. Concluding remarks

Five complexes, which are the first dimolybdenum complexes containing mixed formamidinate ligands, have been structurally characterized. The *o*-DMophF$^-$ ligands in complexes **1**–**3** adopt the *s-cis, s-trans* conformation, resulting in a Mo–O short distance for each *o*-DMophF$^-$ ligand, while those in complexes **4** and **5** adopt the *s-cis, s-cis* conformation, where no Mo–O interaction is observed. Noticeably, although the *o*-DMophF$^-$ ligands in complexes **4** and **5** adopt the same conformation, the orientations of the two methoxy



Scheme 1. Formation scheme for complexes **3**, **4** and **5**.

groups are different. A mechanism involving *cis–trans* isomerization process has been proposed for the formation of complex **4**. On the basis of the conformations adopted by *o*-DMophF$^-$and DMepyF$^-$ ligands, it seems that formation of both Mo–N and Mo–H short distances are more favorable than Mo–O short distance, although the subtle difference in the structures of the two ligands can be influential.

6. Supplementary material

Crystallographic data (excluding structure factors) for the structures in this paper has been deposited with the Cambridge Crystallographic Data Centre as supplementary publication numbers CCDC 208105–208108. Copies of the data can be obtained, free of charge, on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [fax: +44(0)-1223-336033 or e-mail: deposit@ccdc.cam.ac.uk].

Acknowledgements

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