

Systematic Preparation of  $\text{Mo}_2^{4+}$  Building Blocks for Supramolecular Assemblies

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The preparation of additional and useful building blocks for the construction of supramolecular entities with quadruply bonded  $\text{Mo}_2^{4+}$  units has been explored, and five new mixed-ligand complexes with three types of ligands and various basicities are reported. The ligands used were the DAniF (*N,N'*-di-*p*-anisylformamidinate) anion, the acetate anion, and neutral acetonitrile molecules. The formamidinate ligands are the least labile, and the acetonitrile molecules are the most labile. This difference as well as a relatively strong *trans* directing influence by the formamidinate anions in ligand substitution reactions allows designed synthesis of various mixed-ligand building blocks, including rare pairs of *cis* and *trans* isomers. The new compounds are *cis*- $\text{Mo}_2(\text{DAniF})_2(\text{O}_2\text{CCH}_3)_2$  (**1**), *trans*- $\text{Mo}_2(\text{DAniF})_2(\text{O}_2\text{CCH}_3)_2$  (**2**), *trans*- $[\text{Mo}_2(\text{DAniF})_2(\text{O}_2\text{CCH}_3)(\text{CH}_3\text{CN}_{eq})_2]\text{BF}_4$  (**3**), *trans*- $[\text{Mo}_2(\text{DAniF})_2(\text{CH}_3\text{CN}_{eq})_4](\text{BF}_4)_2$  (**4**), and  $[\text{Mo}_2(\text{O}_2\text{CH}_3)(\text{CH}_3\text{CN}_{eq})_6(\text{CH}_3\text{CN}_{ax})](\text{BF}_4)_3$  (**5**), where *eq* and *ax* designate equatorial and axial ligands, respectively. A comparison with some previously synthesized complexes is given along with a discussion of the overall reactivity of all compounds.

## Introduction

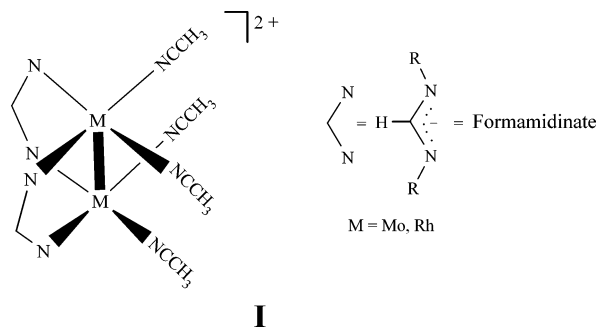
In the past few years there has been great interest in supramolecular entities,<sup>1</sup> in particular those that contain building blocks with metal species joined by appropriate polydentate linkers.<sup>2</sup> The development of designed, convergent strategies for their synthesis has a high priority. Depending on the substituents, the coordination number, and the geometry of such metal containing species, it is possible to produce corner pieces that will favor triangular, square, or other polygonal arrangements.<sup>3</sup> Much work to date has been done using  $\text{M}(\text{diamine})^{2+}$  or  $\text{M}(\text{diphosphine})^{2+}$ ,  $\text{M} = \text{Pd}$  and  $\text{Pt}$ , corner pieces and neutral bidentate linkers which form supramolecular ions with high positive charges. A

significant number of papers have appeared in which  $\text{Zn}^{2+}$  and other ions have been employed too.<sup>2b</sup>

In our laboratory, we have introduced and developed the idea of combining metal–metal bonded species containing two nonlabile bridging formamidinate ligands with polycarboxylate linkers. This has resulted in a variety of  $\text{M}_2$ -containing architectures, including loops, squares, triangles, complex polygons, and extended three-dimensional materials for systems where  $\text{M} = \text{Mo},^4 \text{Rh},^4$  and  $\text{Ru}.^5$  Most of the work has been done with *cis*- $\text{M}_2(\text{formamidinate})_2^{2+}$  corner piece precursors such as **I** which favor square and sometimes triangular assemblies. Previous efforts to produce the iso-

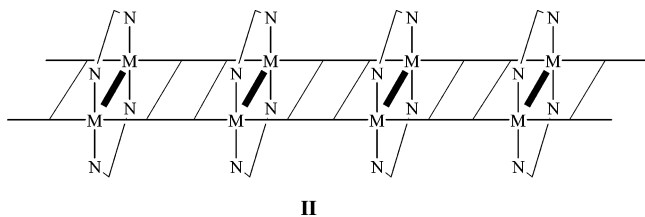
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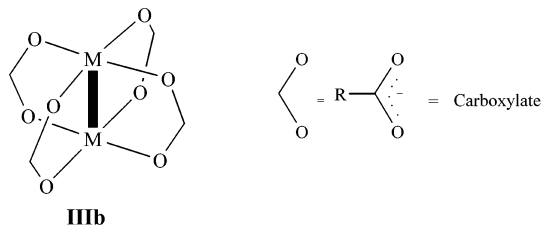
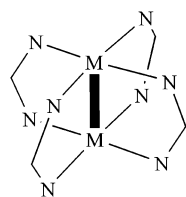
meric *trans*- $\text{M}_2(\text{formamidinate})_2^{2+}$  species, which might be used to assemble other geometrical entities such as ladders

of the type **II**, have also been successful, but so far only



with methyl groups present in the 2 and 6 positions of the aryl groups of the formamidinate anions, as in *trans*-Cr<sub>2</sub>(DXylF)<sub>2</sub>(O<sub>2</sub>CCH<sub>3</sub>)<sub>2</sub>(THF)<sub>2</sub>, DXylF = *N,N'*-dixyllylformamidinate.<sup>6</sup> Other isolated examples of dimolybdenum compounds having mixed amidinate and carboxylate ligands, some with trans arrangements, have also been prepared.<sup>7</sup>

The first systematic approach to the production of various M<sub>2</sub> building blocks was done using dimolybdenum species with a mixture of formamidinate and acetonitrile ligands.<sup>8</sup> These generally have from four to zero *N,N'*-diarylformamidinate groups (DArF) occupying the equatorial positions (*eq*) of the paddlewheel Mo<sub>2</sub><sup>4+</sup> species, with the rest of the equatorial positions occupied by acetonitrile molecules. Axial (*ax*) acetonitrile molecules might also be present. These compounds, of general formula Mo<sub>2</sub>(DArF)<sub>4-n</sub>(CH<sub>3</sub>CN<sub>eq</sub>)<sub>2n-</sub>(CH<sub>3</sub>CN<sub>ax</sub>)<sub>m</sub>, *m* = 0–2, are useful in substitution reactions because the formamidinate ligands are not displaced in reactions with dicarboxylate linkers while the acetonitrile molecules are. These useful starting materials are made by reacting quadruply bonded Mo<sub>2</sub>(DArF)<sub>4</sub>, **IIIa**, where Ar is often Ani = anisyl, in acetonitrile as solvent with the necessary quantities of acids such as OEt<sub>3</sub>BF<sub>4</sub> or HBF<sub>4</sub> to give species such as Mo<sub>2</sub>(DArF)<sub>3</sub>(CH<sub>3</sub>CN<sub>eq</sub>)<sub>2</sub><sup>+</sup>, *cis*-Mo<sub>2</sub>(DArF)<sub>2</sub>(CH<sub>3</sub>CN<sub>eq</sub>)<sub>2</sub><sup>2+</sup>, and Mo<sub>2</sub>(DArF)(CH<sub>3</sub>CN<sub>eq</sub>)<sub>6</sub><sup>3+</sup>.<sup>8</sup> The fully

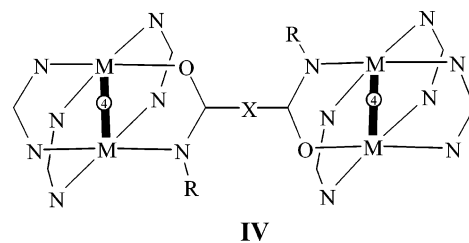


solvated species, Mo<sub>2</sub>(CH<sub>3</sub>CN<sub>eq</sub>)<sub>8</sub><sup>4+</sup>, is obtained similarly from Mo<sub>2</sub>(O<sub>2</sub>CCH<sub>3</sub>)<sub>4</sub>, **IIIb**.<sup>9</sup> These mixed formamidinate–acetonitrile species can be successfully used in the construction of supramolecular entities by reacting them with

tetraalkylammonium salts of dicarboxylic acids.<sup>4</sup> The use of carboxylate analogues, e.g., *cis*-Mo<sub>2</sub>(O<sub>2</sub>CBu<sup>t</sup>)<sub>3</sub>(CH<sub>3</sub>CN<sub>eq</sub>)<sub>2</sub><sup>+</sup>, as building blocks has turned out to be problematical.<sup>10,11</sup> The isolation of products in crystalline form has proven very difficult because of the higher lability of the carboxylate anions, compared to that of the formamidinate ligands, during substitution reactions with dicarboxylate linkers.

The strategy for success in consistent, designed, convergent synthesis of specific structures as compounds that can be isolated as pure, well-formed crystals is to employ starting materials with a hierarchy of ligand labilities. The series, in order of increasing lability, that has served our purposes well is DAniF<sup>-</sup> < RCO<sub>2</sub><sup>-</sup> < CH<sub>3</sub>CN.

Recently, we expanded our efforts in the construction of molecules with pairs of Mo<sub>2</sub> units, **IV**, by using the more basic diamidate linkers which enable better electronic communication between Mo<sub>2</sub> units.<sup>12</sup> However, in early synthetic



efforts reactions of Mo<sub>2</sub>(DArF)<sub>4-n</sub>(CH<sub>3</sub>CN<sub>eq</sub>)<sub>2n</sub><sup>n+</sup> species with diamidate anions did not provide the target molecules because acetonitrile molecules are very reactive toward the more basic ligands. Nucleophilic attacks by bases upon coordinated acetonitrile are known, for example in reactions producing acetamidate groups, and such reactions are catalyzed by transition metal ions.<sup>13</sup> To obviate this problem we employed Mo<sub>2</sub>(formamidinate)<sub>3</sub>(acetate) as a useful and reactive starting material from which the labile acetate groups are preferentially replaced by the diamidate linkers.<sup>14</sup> The acetate displacement approach has also been used successfully for the synthesis of Ru<sub>2</sub><sup>5+</sup> compounds.<sup>15</sup>

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In the present work we examine in more detail the preparation of mixed-ligand complexes having an Mo<sub>2</sub><sup>4+</sup> nucleus where the ligands are formamidinates, acetate, and acetonitrile, and report five new compounds. These are *cis*-Mo<sub>2</sub>(DAniF)<sub>2</sub>(O<sub>2</sub>CCH<sub>3</sub>)<sub>2</sub> (**1**), *trans*-Mo<sub>2</sub>(DAniF)<sub>2</sub>(O<sub>2</sub>CCH<sub>3</sub>)<sub>2</sub> (**2**), *trans*-[Mo<sub>2</sub>(DAniF)<sub>2</sub>(O<sub>2</sub>CCH<sub>3</sub>)(CH<sub>3</sub>CN<sub>eq</sub>)<sub>2</sub>](BF<sub>4</sub>) (**3**), *trans*-[Mo<sub>2</sub>(DAniF)<sub>2</sub>(CH<sub>3</sub>CN<sub>eq</sub>)<sub>4</sub>](BF<sub>4</sub>)<sub>2</sub> (**4**), and [Mo<sub>2</sub>(O<sub>2</sub>CCH<sub>3</sub>)(CH<sub>3</sub>CN<sub>eq</sub>)<sub>6</sub>(CH<sub>3</sub>CN<sub>ax</sub>)](BF<sub>4</sub>)<sub>3</sub> (**5**). Compounds **1** and **2**, and also **4** and the previously reported *cis*-[Mo<sub>2</sub>(DAniF)<sub>2</sub>(CH<sub>3</sub>CN<sub>eq</sub>)<sub>4</sub>](BF<sub>4</sub>)<sub>2</sub>,<sup>8</sup> are both pairs of *cis* and *trans* stereoisomers, which have so far been uncommon in dimetal chemistry.<sup>16</sup> Each of the isomers has been synthesized selectively, and by a different synthetic route. This provides a unique opportunity to study the factors that influence ligand substitution and reactivity of dimolybdenum compounds. A general discussion of the syntheses of mixed-ligand compounds is provided.

## Experimental Section

**Materials and Methods.** Solvents used were freshly distilled under N<sub>2</sub> by employing standard procedures or dried and degassed using a Glass Contour solvent purification system. All synthetic operations were conducted under N<sub>2</sub> using Schlenk line techniques. The materials used for the study, Mo<sub>2</sub>(O<sub>2</sub>CCH<sub>3</sub>)<sub>4</sub>,<sup>17</sup> **IIIb** or **B**, Mo<sub>2</sub>(DAniF)<sub>4</sub>,<sup>18</sup> **IIIa** or **D**, *cis*-Mo<sub>2</sub>(O<sub>2</sub>CCH<sub>3</sub>)<sub>2</sub>(CH<sub>3</sub>CN<sub>eq</sub>)<sub>4</sub>](BF<sub>4</sub>)<sub>2</sub>,<sup>19</sup> **A**, *cis*-[Mo<sub>2</sub>(DAniF)<sub>2</sub>(CH<sub>3</sub>CN<sub>eq</sub>)<sub>4</sub>](BF<sub>4</sub>)<sub>2</sub>, **E**, (DAniF = *N,N'*-di-*p*-anisylformamidinate), [Mo<sub>2</sub>(DAniF)(CH<sub>3</sub>CN<sub>eq</sub>)<sub>6</sub>](BF<sub>4</sub>)<sub>3</sub>, **C**,<sup>8</sup> were prepared by following a literature procedure. Other commercially available chemicals were used as received.

**Physical Measurements.** Elemental analyses were performed by Canadian Microanalytical Service, Delta, British Columbia, Canada. <sup>1</sup>H NMR spectra were recorded on a Mercury-300 NMR spectrometer with chemical shifts (δ ppm) referenced to CDCl<sub>3</sub> for **1** and **2**, CD<sub>3</sub>CN for **3** and **4**, and DMSO-*d*<sub>6</sub> for **5**.

**Preparation of *cis*-Mo<sub>2</sub>(DAniF)<sub>2</sub>(O<sub>2</sub>CCH<sub>3</sub>)<sub>2</sub>, **1**.** To *cis*-[Mo<sub>2</sub>(DAniF)<sub>2</sub>(CH<sub>3</sub>CN<sub>eq</sub>)<sub>4</sub>](BF<sub>4</sub>)<sub>2</sub> (1.04 g, 1.00 mmol) was added an excess amount of anhydrous NaO<sub>2</sub>CCH<sub>3</sub> (0.25 g, 3.05 mmol) in 20 mL of acetonitrile. A yellow precipitate formed in ca. 10 min. The mixture was stirred at room temperature for 2 h. After filtration, the solid was extracted with ca. 15 mL of dichloromethane; addition of 40 mL of hexanes gave a light yellow precipitate, which was collected by filtration and dried under vacuum. Yield: 0.680 g (83%). <sup>1</sup>H NMR (δ, ppm in CDCl<sub>3</sub>): 8.41 (s, 2H, -NCHN-), 6.61 (d, 8H, aromatic C-H), 6.55 (d, 8H, aromatic C-H), 3.71 (s, 12H, -OCH<sub>3</sub>), 2.65 (s, 6H, -CH<sub>3</sub>). Anal. Calcd for C<sub>34</sub>H<sub>36</sub>Mo<sub>2</sub>N<sub>4</sub>O<sub>8</sub>: C, 49.56; H, 4.40; N, 6.80. Found: C, 49.50; H, 4.34; N, 6.79.

**Preparation of *trans*-Mo<sub>2</sub>(DAniF)<sub>2</sub>(O<sub>2</sub>CCH<sub>3</sub>)<sub>2</sub>, **2**.** To a suspension of Mo<sub>2</sub>(OCCH<sub>3</sub>)<sub>4</sub> (2.14 g, 5.00 mmol) and *N,N'*-di-*p*-anisyl-

formamidine (2.56 g, 10.0 mmol) in 100 mL of THF was added slowly, and with stirring, 20 mL of a 0.5 M solution of NaOCH<sub>3</sub> in methanol. The color turned red, then brown. The reaction mixture was stirred for 5 h at room temperature, after which some colorless sodium acetate was visible. Then the solvent was removed under reduced pressure, and dichloromethane (ca. 40 mL) was added to the residue; then the mixture was filtered. The volume of the filtrate was then reduced to about 15 mL under vacuum. While the mixture was stirred vigorously, ethanol (ca. 40 mL) was added, producing a light yellow solid and a dark brown solution. The solid was separated and then washed with ethanol (2 × 20 mL), followed by 20 mL of hexanes, and dried under vacuum. Yield: 3.50 g (86%). <sup>1</sup>H NMR (δ, ppm in CDCl<sub>3</sub>): 8.45 (s, 2H, -NCHN-), 6.72 (d, 8H, aromatic C-H), 6.71 (d, 8H, aromatic C-H), 3.72 (s, 12H, -OCH<sub>3</sub>), 2.61 (s, 6H, -CH<sub>3</sub>). Anal. Calcd for C<sub>34</sub>H<sub>36</sub>Mo<sub>2</sub>N<sub>4</sub>O<sub>8</sub>: C, 49.56; H, 4.40; N, 6.80. Found: C, 49.69; H, 4.33; N, 6.69.

**Preparation of *trans*-[Mo<sub>2</sub>(DAniF)<sub>2</sub>(O<sub>2</sub>CCH<sub>3</sub>)(CH<sub>3</sub>CN<sub>eq</sub>)<sub>2</sub>](BF<sub>4</sub>)<sub>3</sub>, **3**.** *trans*-Mo<sub>2</sub>(DAniF)<sub>2</sub>(O<sub>2</sub>CCH<sub>3</sub>)<sub>2</sub> (0.410 g, 0.500 mmol) was dissolved in a mixture of 15 mL of dichloromethane and 5 mL of acetonitrile. To the yellow solution was added 1.00 mL of triethyloxonium tetrafluoroborate dropwise, with stirring. The mixture was stirred for 30 min, generating a golden yellow solution. The volume was reduced to ca. 10 mL; then, with vigorous stirring, 30 mL of ether was added, precipitating a sticky brown solid. After the solvent was decanted, the residue was dissolved in 5 mL of acetonitrile, and ether (20 mL) was added with stirring. This produced a golden yellow solid, which was washed with an additional 10 mL of ether after filtration. The product was dried under vacuum. Yield: 0.258 g (55%). A golden yellow crystalline product was obtained by diffusion of ether into a dichloromethane-acetonitrile solution (5:5 mL) of the product. <sup>1</sup>H NMR (δ, ppm in CD<sub>3</sub>CN): 8.92 (s, 2H, -NCHN-), 6.912 (d, 8H, aromatic C-H), 6.88 (d, 8H, aromatic C-H), 3.78 (s, 12H, -OCH<sub>3</sub>), 2.61 (s, 3H, -CH<sub>3</sub> from acetate), 2.02 (s, 6H, -CH<sub>3</sub> from acetonitrile). Anal. Calcd for C<sub>36</sub>H<sub>40</sub>BF<sub>4</sub>Mo<sub>2</sub>N<sub>6</sub>O<sub>7</sub> (3·H<sub>2</sub>O): C, 45.42; H, 4.23; N, 8.83. Found: C, 45.06; H, 4.17; N, 8.47.

**Preparation of *trans*-[Mo<sub>2</sub>(DAniF)<sub>2</sub>(CH<sub>3</sub>CN<sub>eq</sub>)<sub>4</sub>](BF<sub>4</sub>)<sub>2</sub>, **4**.** A purple solution containing [Mo<sub>2</sub>(DAniF)(CH<sub>3</sub>CN)<sub>6</sub>](BF<sub>4</sub>)<sub>3</sub> (0.479 g, 0.500 mmol) in 10 mL of acetonitrile was mixed with a solution of HDAniF (0.128 g, 0.500 mmol) in 10 mL of acetonitrile. With stirring, the color of the mixture turned to orange red. After 1 h, 40 mL of ether was added to produce an orange solid, which was washed first with ether (2 × 20 mL) and then with dichloromethane (2 × 10 mL). The solid was then collected by filtration and dried under vacuum. Yield: 0.330 g (64%). Single crystals for X-ray analysis were obtained by diffusion of ether into an acetonitrile solution. <sup>1</sup>H NMR (δ, ppm in CD<sub>3</sub>CN): 9.18 (s, 2H, -NCHN-), 7.04 (d, 8H, aromatic C-H), 6.89 (d, 8H, aromatic C-H), 3.77 (s, 12H, -OCH<sub>3</sub>), 1.99 (s, 12H, -CH<sub>3</sub>). Anal. Calcd for C<sub>38</sub>H<sub>42</sub>B<sub>2</sub>F<sub>8</sub>Mo<sub>2</sub>N<sub>8</sub>O<sub>4</sub>: C, 43.72; H, 4.06; N, 10.73. Found: C, 43.58; H, 3.90; N, 10.38.

**Preparation of [Mo<sub>2</sub>(O<sub>2</sub>CCH<sub>3</sub>)(CH<sub>3</sub>CN)<sub>6</sub>(CH<sub>3</sub>CN<sub>ax</sub>)](BF<sub>4</sub>)<sub>3</sub>, **5**.** To a suspension of Mo<sub>2</sub>(O<sub>2</sub>CCH<sub>3</sub>)<sub>4</sub> (0.535 g, 1.25 mmol) in 20 mL of acetonitrile was added slowly 8 mL of triethyloxonium tetrafluoroborate (1.0 M in CH<sub>2</sub>Cl<sub>2</sub>), with stirring. A red solution which formed immediately was stirred for 1 h while the color turned magenta. Solvent removal under reduced pressure left a magenta solid, which was washed thoroughly with diethyl ether and dried under vacuum. Yield: 0.660 g (70%). The crystalline product was obtained by layering an acetonitrile solution (15 mL) with hexanes (0.5 mL) followed by diethyl ether (40 mL). <sup>1</sup>H NMR (δ, ppm in DMSO-*d*<sub>6</sub>): 2.82 (s, 3H, -CH<sub>3</sub> from acetate), 2.05 (s, 18H, -CH<sub>3</sub>

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 (16) There is a pair of isomers which have the composition Mo<sub>2</sub>(*μ*-acetate)<sub>2</sub>(*N,N'*-bis(trimethylsilyl)benzamidinate)<sub>2</sub> which were isolated from the same reaction mixture. Only one of them has a paddlewheel structure with two *trans* acetate and two bridging benzamidinate groups, while the other has two cisoid acetate bridges but each of the benzamidinate groups is chelated to one Mo atom. See ref 7c.  
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**Table 1.** X-ray Crystallographic Data for **1–5**

	<b>1</b>	<b>2</b>	<b>3</b> ·1.5C <sub>4</sub> H <sub>10</sub> O	<b>4</b>	<b>5</b> ·0.5CH <sub>3</sub> CN
empirical formula	C <sub>34</sub> H <sub>36</sub> Mo <sub>2</sub> N <sub>4</sub> O <sub>8</sub>	C <sub>34</sub> H <sub>36</sub> Mo <sub>2</sub> N <sub>4</sub> O <sub>8</sub>	C <sub>42</sub> H <sub>54</sub> BF <sub>4</sub> Mo <sub>2</sub> N <sub>6</sub> O <sub>7.5</sub>	C <sub>38</sub> H <sub>42</sub> B <sub>2</sub> F <sub>8</sub> Mo <sub>2</sub> N <sub>8</sub> O <sub>4</sub>	C <sub>17</sub> H <sub>15.5</sub> B <sub>3</sub> F <sub>12</sub> Mo <sub>2</sub> N <sub>7.5</sub> O <sub>2</sub>
fw	820.55	820.55	1041.60	1040.3	819.26
space group	<i>P</i> 2 <sub>1</sub> (No. 4)	<i>P</i> 2 <sub>1</sub> 2 <sub>1</sub> 2 <sub>1</sub> (No. 19)	<i>P</i> 2 <sub>1</sub> / <i>c</i> (No. 14)	<i>P</i> 2 <sub>1</sub> / <i>n</i> (No. 14)	<i>P</i> 1̄ (No. 2)
<i>a</i> , Å	8.087(2)	10.7893(5)	17.860(1)	12.9175(5)	11.1461(7)
<i>b</i> , Å	22.374(4)	17.5542(9)	21.679(1)	9.6959(5)	16.220(1)
<i>c</i> , Å	19.358(4)	18.2354(9)	12.3258(8)	18.294(1)	19.106(1)
α, deg	90	90	90	90	101.377(1)
β, deg	101.747(4)	90	94.761(1)	104.471(1)	95.957(1)
γ, deg	90	90	90	90	106.340(1)
<i>V</i> , Å <sup>3</sup>	3461.0(1)	3453.7(3)	4755.7(5)	2218.5(2)	3202.5(4)
<i>Z</i>	4	4	4	2	4
<i>T</i> , K	213	213	213	213	213
λ, Å	0.71073	0.71073	0.71073	0.71073	0.71073
<i>d</i> <sub>calcd</sub> , g/cm <sup>3</sup>	1.575	1.578	1.455	1.557	1.699
μ, mm <sup>-1</sup>	0.780	0.782	0.596	0.647	0.882
<i>R</i> 1 <sup>a</sup> ( <i>wR</i> 2 <sup>b</sup> )	0.078(0.164)	0.024(0.059)	0.048(0.106)	0.031(0.073)	0.066(0.128)

$$^a R1 = \sum ||F_o| - |F_c|| / \sum |F_o|. \quad ^b wR2 = [\sum [w(F_o^2 - F_c^2)^2] / \sum [w(F_o^2)^2]]^{1/2}.$$

**Table 2.** Selected Bond Lengths (Å) for **1–5**

	<b>1</b> <sup>a</sup>	<b>2</b>	<b>3</b> ·1.5C <sub>4</sub> H <sub>10</sub> O	<b>4</b>	<b>5</b> ·0.5CH <sub>3</sub> CN <sup>a</sup>
Mo(1)–Mo(2)	2.092(2)	2.0831(3)	2.114(1)		2.1558(5)
Mo(1)–Mo(1A)				2.1056(4)	
Mo(1)–N(1)	2.155(12)	2.140(2)	2.152(5)	2.137(2)	2.154(4)
Mo(1)–N(3)	2.121(14)	2.136(2)	2.142(5)	2.114(2)	2.126(4)
Mo(1)–N(5)			2.149(4)		2.136(4)
Mo(2)–N(2)	2.162(14)	2.152(2)	2.170(8)	2.146(2)	2.153(4)
Mo(2)–N(4)	2.121(14)	2.132(2)	2.126(5)	2.123(2)	2.140(4)
Mo(2)–N(6)			2.121(4)		2.127(4)
Mo(1)–O(1)	2.129(10)	2.125(2)	2.170(4)		2.089(3)
Mo(1)–O(3)	2.156(11)	2.122(2)			
Mo(2)–O(2)	2.125(11)	2.113(2)	2.071(5)		2.066(3)
Mo(2)–O(4)	2.150(11)	2.118(2)			

<sup>a</sup> Data for one of the two crystallographically independent but chemically similar molecules in **1** and **5**.

from acetonitrile). Anal. Calcd for C<sub>14</sub>H<sub>21</sub>B<sub>3</sub>F<sub>12</sub>Mo<sub>2</sub>N<sub>6</sub>O<sub>2</sub>: C, 22.07; H, 2.78; N, 11.03. Found: C, 22.30; H, 3.95; N 10.80.

**X-ray Structure Determinations.** Each of the single crystals for **1–5** was mounted on the tip of a quartz fiber attached to a goniometer head. Data were collected on a Bruker SMART 1000 CCD area detector system. The structures were solved by direct methods using the SHELXS-97 program<sup>20</sup> and refined using the SHELXL-97 program.<sup>21</sup> Crystals of **1** were racemic twins, and the structure was refined to a BASF coefficient of 0.64. Non-hydrogen atoms were refined with anisotropic displacement parameters. Hydrogen atoms were added in calculated positions. Crystallographic data for **1**, **2**, **3**·1.5(C<sub>2</sub>H<sub>5</sub>)<sub>2</sub>O, **4**, and **5**·0.5CH<sub>3</sub>CN are in Table 1, and selected bond distances in Table 2.

## Results and Discussion

**Synthetic Overview.** Reactions pertinent to the syntheses of all five new compounds are summarized in Scheme 1, where compounds **1–5** are in red boxes. Other species with an Mo<sub>2</sub><sup>4+</sup> unit that play a role in this study are labeled **A–E**, and are in blue boxes. All reactions are coded by arrows with lower case italic letters (*a–o*). Solid arrows indicate reactions that lead exclusively to the species to which the arrows are pointing, while an X over the arrow indicates an attempted reaction that did not lead to the target product.

(20) Sheldrick, G. M. SHELXS-97. Program for crystal structure solution. *Acta Crystallogr.* **1990**, *A46*, 467.

(21) Sheldrick, G. M. SHELXL-97. Program for Crystal Structure Analysis; University of Göttingen: Göttingen, Germany, 1997.

Double arrows with an X signify an interconversion of *cis/trans* isomer pairs that was not observed. Letters O and N represent oxygen atoms of acetate groups or nitrogen atoms of formamidinate groups, respectively, and L represents an equatorial CH<sub>3</sub>CN molecule. The identity of each previously known compound was confirmed by comparing the <sup>1</sup>H NMR spectrum of the prepared sample with that of an authentic sample made as described in the literature, and/or by comparing values of the crystal unit cell dimensions. The absence of an arrow indicates that the reaction was not studied. Reaction conditions for each process are described briefly in the scheme footnote. In all cases, crystallographic characterization and <sup>1</sup>H NMR spectra are available (*vide infra*). It should be noted that Scheme 1 shows 10 species of a total of 21 possible combinations for the three ligands (formamidinate, acetate, and acetonitrile) under study. Of those not shown, three have been studied before and are described elsewhere, namely, Mo<sub>2</sub>(CH<sub>3</sub>CN<sub>eq</sub>)<sub>8</sub><sup>4+</sup>,<sup>9</sup> Mo<sub>2</sub>(DAniF)<sub>3</sub>-(O<sub>2</sub>CCH<sub>3</sub>),<sup>12</sup> and Mo<sub>2</sub>(DAniF)<sub>3</sub>(CH<sub>3</sub>CN<sub>eq</sub>)<sub>2</sub><sup>+</sup>.<sup>22</sup> Others which remain unreported, e.g., *trans*-Mo<sub>2</sub>(O<sub>2</sub>CCH<sub>3</sub>)<sub>2</sub>(CH<sub>3</sub>CN<sub>eq</sub>)<sub>4</sub><sup>2+</sup>, were not studied because we did not deem them likely to be useful synthetic building blocks, nor did we see them as essential for understanding the patterns of chemical reactivity.

The scheme permits several useful generalizations and a few specific observations:

(1) Replacement of formamidinate groups by acetonitrile molecules requires the strongest conditions, such as the use of Et<sub>3</sub>OBf<sub>4</sub> with a trace amount of H<sub>2</sub>O or even HBF<sub>4</sub>.

(2) Acetate ligands are replaced also by acetonitrile in the presence of CF<sub>3</sub>SO<sub>3</sub>H, Et<sub>3</sub>OBf<sub>4</sub>, or HBF<sub>4</sub>·Et<sub>2</sub>O, or other acids with weakly coordinating anions.

(3) Acetonitrile molecules can be readily substituted by carboxylate and formamidinate anions.

(4) Carboxylates can be replaced by formamidinates, but the opposite is not possible under any of the conditions studied. Thus, ligand lability decreases from acetonitrile to acetate to formamidinate ligands.

(5) Whenever *cis* and *trans* isomers exist, each can be made in pure form, but it is necessary to use different

(22) (a) Cotton, F. A.; Donahue, J. P.; Lin, C.; Murillo, C. A. *Inorg. Chem.* **2001**, *40*, 1234. (b) Cotton, F. A.; Donahue, J. P.; Murillo, C. A. *J. Am. Chem. Soc.* **2003**, *125*, 5436.



the *trans* isomer **4**. It should be noted that a random substitution would be expected to yield a mixture of *cis* to *trans* products in a 2:1 ratio but only **4** is observed. In this reaction, strong base or deprotonated DAniF anion should be avoided to prevent possible nucleophilic attack upon the coordinated acetonitrile molecules.<sup>23</sup> The addition of diethyl ether, a Lewis base, shifts the equilibrium toward the products by removing the acid that is produced as HBF<sub>4</sub>·(OEt<sub>2</sub>).

(6) In some reactions such as that of **E** to give **1**, the stereochemistry is retained and both reactants and product have a *cis* conformation. However, in process *l* (reaction of **2** to produce **E**) the *trans* disposition of the formamidinate anions changes and a *cis* species is formed. Likewise, *cis* **A** gives only *trans* **2** but no *cis* **1**.

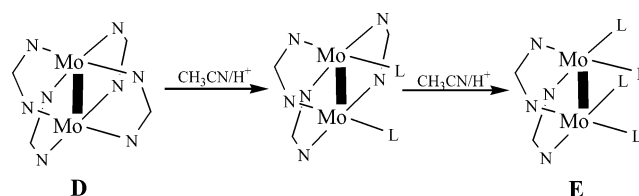
**General Stability of Isomers 1 and 2, and 4 and E.** Once isolated, the four compounds are indefinitely stable in the solid state under an inert atmosphere. They are also stable in solution at room temperature. For each pair of *cis* and *trans* isomers the <sup>1</sup>H NMR spectra show small but distinct differences that allow unambiguous identification of each compound. To evaluate the possible interconversion of isomers, yellow solutions of **1** and **2** were taken independently to reflux in toluene for 2 h (reaction *h*). Under these conditions, no isomer interconversion was observed.<sup>24</sup>

Similarly, orange-red solutions of **4** and **E**, prepared in CD<sub>3</sub>CN in an NMR tube, were heated slowly under nitrogen from 50 to 85 °C over a period of 1.5 h and then refluxed gently at this temperature for an additional 0.5 h (reaction *i*). The <sup>1</sup>H NMR spectra did not change. Thus, heating under these conditions does not cause interchange between the two isomers.

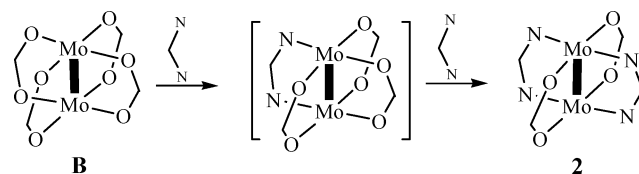
**Reactivity and Evidence of a *Trans* Effect.** The isolation and lack of interconversion of *cis* and *trans* isomers of these mixed-ligand species indicate that their formation is not thermodynamically regulated but kinetically controlled in much the same way as kinetic control determines the substitution reactions in the common textbook example of formation of the square planar complexes *cis*-Pt(NH<sub>3</sub>)<sub>2</sub>Cl<sub>2</sub> and *trans*-Pt(NH<sub>3</sub>)<sub>2</sub>Cl<sub>2</sub>. Indeed the similarities go beyond the selective formation of isomers. The basicity of the three ligands studied here decreases in the order DAniF<sup>-</sup> > O<sub>2</sub>CCH<sub>3</sub><sup>-</sup> > CH<sub>3</sub>CN. Accordingly the observed lability is the opposite, with formamidinates being more difficult to displace while the acetonitrile molecules are the most easily displaced. Furthermore, it appears that each of these ligands exerts a *trans* effect that is proportional to its basicity. This *trans* effect seems to be the major factor influencing the geometry of the product in any given substitution reaction, and it is also manifested in the bond distances (*vide infra*).

Earlier work supports the idea that, in substitution reactions of quadruply bonded dimolybdenum compounds, bond formation and breaking takes place via an associative (A)

Scheme 2



Scheme 3



or intermediate associative mechanism (Ia).<sup>25</sup> For such mechanisms, the axial sites are the most likely pathway for ligands to enter or leave the M<sub>2</sub> unit.

Let us first consider the replacement of formamidinate groups in Mo<sub>2</sub>(DAniF)<sub>4</sub>, **D**, by CH<sub>3</sub>CN molecules in the presence of acid (reaction *o*). Presumably, substitution reactions occur in a stepwise manner; protonation forms an intermediate with one monodentate, neutral HDAniF group, and the open coordination site is occupied by an acetonitrile molecule. Then the neutral formamidinate is displaced by another acetonitrile molecule to give a species that has been reported earlier (but made by a different synthetic route), namely, the [Mo<sub>2</sub>(DAniF)<sub>3</sub>(CH<sub>3</sub>CN)<sub>2</sub>]<sup>2+</sup> cation.<sup>22</sup> This process is shown in Scheme 2. Because of the stronger *trans* directing influence of the bridging formamidinate group relative to that of that of the monodentate acetonitrile ligands, replacement of a second bridging group is expected to occur giving a *cis* geometry, as confirmed by the transformation of **D** into **E**. Similarly **B** yields **A** in the acetate analogues, although no intermediate Mo<sub>2</sub>(O<sub>2</sub>CCH<sub>3</sub>)<sub>3</sub>(CH<sub>3</sub>CN)<sub>2</sub><sup>+</sup> has been observed.

For the replacement of acetate groups in Mo<sub>2</sub>(O<sub>2</sub>CCH<sub>3</sub>)<sub>4</sub>, **B**, by formamidinate ligands, the substitution leading to the *trans* **2** is also easily understood in terms of a stepwise, *trans* directing effect as shown in Scheme 3.<sup>26</sup> In the intermediate compound Mo<sub>2</sub>(DAniF)(O<sub>2</sub>CCH<sub>3</sub>)<sub>3</sub> (which has not been observed), the strong *trans* directing DAniF makes replacement of the acetate *trans* to the DAniF ligand, resulting in formation of the *trans* isomer, the preferred choice.

The methodology to synthesize *trans*-[Mo<sub>2</sub>(DAniF)<sub>2</sub>(CH<sub>3</sub>CN<sub>eq</sub>)<sub>4</sub>](BF<sub>4</sub>)<sub>2</sub>, **4**, was explicitly designed with the concept of a *trans* effect in mind. This compound is potentially useful for the development of ladder-type molecular chains, **II**, but this building block precursor has not been accessible by direct synthesis.<sup>8</sup> This preparation also provided an opportunity to test the proposed stepwise mechanism and the *trans*-directing influence. Indeed, addition of 1 equiv of DAniF (as HDAniF) to [Mo<sub>2</sub>(DAniF)(CH<sub>3</sub>CN<sub>eq</sub>)<sub>6</sub>]<sup>3+</sup>, **C**,

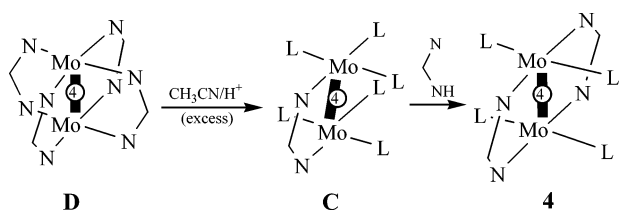
(23) Cotton, F. A.; Daniels, L. M.; Donahue, J. P.; Liu, C. Y.; Murillo, C. A. *Inorg. Chem.* **2002**, *41*, 1354.

(24) The only changes observed in the <sup>1</sup>H NMR spectra were due a small amount of disproportionation with apparent formation of Mo<sub>2</sub>(DAniF)<sub>3</sub>(O<sub>2</sub>CCH<sub>3</sub>).

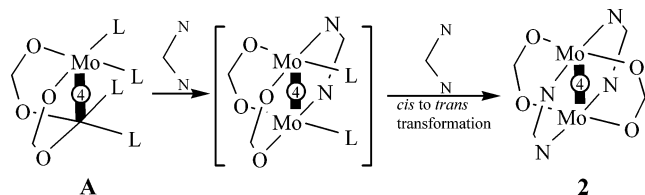
(25) Casas, J. M.; Cayton, R. H.; Chisholm, M. H. *Inorg. Chem.* **1991**, *30*, 360.

(26) Here and in all other schemes, the species in brackets have not been isolated; furthermore, the charges on all ions have been removed for simplicity.

Scheme 4



Scheme 5



displaces two CH<sub>3</sub>CN molecules, and gives *trans* **4** as the only product. Scheme 4 shows a cartoon of the reaction.

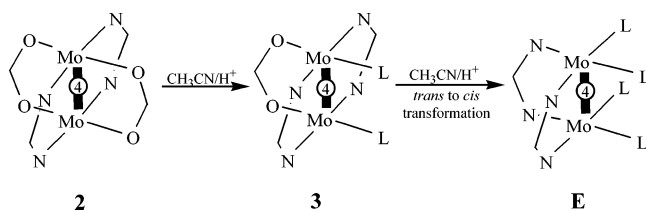
However, an attempt to prepare *trans*-[Mo<sub>2</sub>(O<sub>2</sub>CCH<sub>3</sub>)<sub>2</sub>(CH<sub>3</sub>CN<sub>eq</sub>)<sub>4</sub>]<sup>2+</sup> using a similar approach, viz., by reaction of [Mo<sub>2</sub>(O<sub>2</sub>CCH<sub>3</sub>)(CH<sub>3</sub>CN<sub>eq</sub>)<sub>6</sub>]<sup>3+</sup>, **5**, with 1 equiv of NaO<sub>2</sub>CCH<sub>3</sub>, led exclusively to *cis*-[Mo<sub>2</sub>(O<sub>2</sub>CCH<sub>3</sub>)<sub>2</sub>(CH<sub>3</sub>CN<sub>eq</sub>)<sub>4</sub>]<sup>2+</sup>, **A**. This indicates that the fairly labile and less basic acetate groups are not capable inducing the *trans* substitution. Thus, it is likely that in this case the kinetic factors do not offset the higher thermodynamic stability of the *cis* isomer.

The reaction of *cis*-[Mo<sub>2</sub>(DAniF)<sub>2</sub>(CH<sub>3</sub>CN<sub>eq</sub>)<sub>4</sub>](BF<sub>4</sub>)<sub>2</sub>, **E**, with NaO<sub>2</sub>CCH<sub>3</sub> leading to *cis*-Mo<sub>2</sub>(DAniF)<sub>2</sub>(O<sub>2</sub>CMe)<sub>2</sub>, **1**, is also understandable in terms of the proposed kinetic considerations. In the cation *cis*-[Mo<sub>2</sub>(DAniF)<sub>2</sub>(CH<sub>3</sub>CN<sub>eq</sub>)<sub>4</sub>]<sup>2+</sup>, the labile CH<sub>3</sub>CN molecules are *trans* to the DAniF ligands. The addition of one acetate group produces *cis*-[Mo<sub>2</sub>(DAniF)<sub>2</sub>(O<sub>2</sub>CCH<sub>3</sub>)(CH<sub>3</sub>CN<sub>eq</sub>)<sub>2</sub>]<sup>+</sup> as the intermediate product. Because of the strong *trans* directing influence of the formamidinate ligands, the second incoming acetate ligand displaces the remaining acetonitrile molecules, which are also *trans* to a DAniF ligand, maintaining the *cis* geometry of the precursor.

**Cis/Trans Geometry Transformations.** The initial *cis* or *trans* configuration of a given reactant does not guarantee that the geometry will be retained in the product. An example is provided by reaction *e*, in which **A** yields **2**. Here a rearrangement of ligands and conversion of geometry from *cis* to *trans* is involved, as shown in Scheme 5. In the intermediate cation [Mo<sub>2</sub>(DAniF)(O<sub>2</sub>CCH<sub>3</sub>)<sub>2</sub>(CH<sub>3</sub>CN)<sub>2</sub>]<sup>+</sup>, which has not been observed but appears to be the logical intermediate in the stepwise addition of a formamidinate ligand to **A**, the labile acetonitrile molecules are expected to be the leaving ligands. If a second step were to proceed similarly, this would give **1**, which cannot be formed in this manner, as shown in reaction *f*. It should be noted that, in the intermediate monocation, the species that is opposite to the *trans* directing DAniF group is an acetate anion while the very labile acetonitrile molecules are *cis* to the DAniF ligands.

Another example of change in geometry is observed in the reaction of **2** to **E**, which is expected to proceed via **3** (Scheme 6). Here, strict control of the acidity is necessary and only 2 equiv of triethyloxonium tetrafluoroborate is used

Scheme 6



for the substitution of each acetate group. In the first step, replacement of a labile acetate anion by two acetonitrile molecules does not change the geometry. Therefore, a geometry conversion must take place during the replacement of the second acetate group by two additional acetonitrile molecules. However, direct replacement of the second labile acetate group would produce a *trans*, and not the observed *cis* species. Because interconversion of the isomers **E** and **4** does not occur, the geometry change must take place during the second substitution process and it is probably effected by the presence of a trace of water in the OEt<sub>3</sub><sup>+</sup> precursor which can react with the formamidinate groups.

These two geometry transformation reactions are not straightforward and show that other factors can be important too. It appears that the geometry of the final product is determined by the basicity of the ligands and the geometric arrangement of the ligands in the precursor at the last step. Contrary to those reactions in Schemes 2–4, where the intermediates have the most labile ligands opposite to the *trans* directing ligands, those in Schemes 5 and 6 have intermediates with the most labile ligands in positions other than *trans* to the formamidinate groups. Therefore in the latter, the lability of the ligands and the *trans* directing effect do not work synergistically. It is only under these circumstances that a change of geometry has been observed. Although it is not immediately obvious how the change takes place, it is reasonable to suppose that some degree of axial coordination is involved in the transition states. For example, in Scheme 5, the acetate group *trans* to the formamidinate ligand could be activated with concomitant dissociation of one of the oxygen atoms.<sup>27</sup> With support from the associative mechanism mentioned earlier,<sup>25</sup> a possible sequence for the substitution of DAniF for acetonitrile can be described in this way: the acetate group is displaced from the *trans* position by the incoming DAniF, and then, through axial coordination, this acetate anion displaces the labile CH<sub>3</sub>CN molecules, completing the substitution and geometry conversion. Because these effects are not expected to be exclusive to those reactions in Schemes 5 and 6, they must be slower than those in which there is a *trans* inducing effect.

It should also be noted that a geometric conversion from *cis* to *trans* occurs when *cis*-[Mo<sub>2</sub>(DPhF)<sub>2</sub>(CH<sub>3</sub>CN)<sub>4</sub>]<sup>2+</sup> reacts with pyridine, DPhF = *N,N'*-diphenylformamidinate, giving *trans*-[Mo<sub>2</sub>(DPhF)<sub>2</sub>(py)<sub>4</sub>]<sup>2+</sup>.<sup>8</sup> In the former, weaker ligands (CH<sub>3</sub>CN) displace a stronger acetate ligand, but in the latter, stronger (more basic) pyridine ligands substitute the weaker

(27) A related pathway has been invoked for dirhodium complexes. See for example: Crawford, C. A.; Matonic, J.; Streib, W. E.; Huffman, J. C.; Dunbar, K. R.; Christou, G. *Inorg. Chem.* **1993**, *32*, 3125.

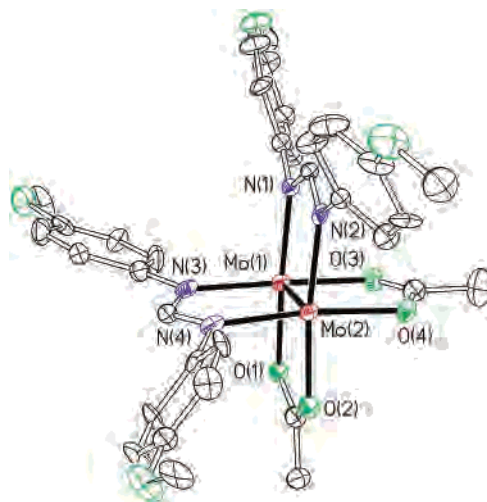
CH<sub>3</sub>CN ligands. In this case, the bulky pyridine molecules adopt a transoid configuration.

**Other Observations.** Compound **E** is the most extensively used building block precursor in the construction of supramolecular species with dicarboxylate anions. It is made by reaction of **D** with trialkyloxonium tetrafluoroborate as a source of acid. However, **E** is not suitable for making an assembly with more basic ligands, such as diamidates.<sup>23</sup> Because **1** has the same geometry setting as **E**, we believe that it will be useful for the synthesis of square or triangular supramolecular entities with strongly basic ligands.<sup>28</sup> Similarly, **3** and **4** should provide the basis for the construction of ladder type arrangements, **II**.

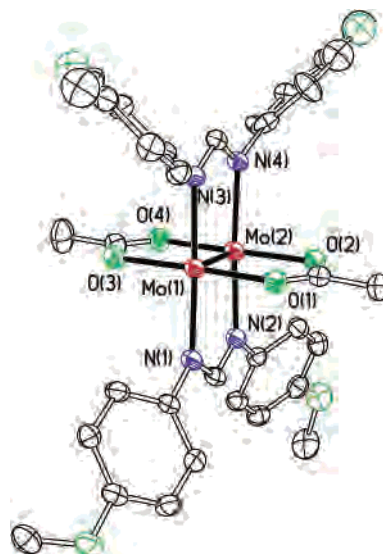
Because of the variety of ligands in **3**, this compound offers some interesting possibilities that will be explored in due course. The compound can be prepared using a method similar to the procedures for other dimetal acetonitrile derivatives using triethyloxonium tetrafluoroborate in the presence of a trace of water.<sup>8</sup> However, the reaction must be handled very carefully. To remove one of the acetate ligands from **2**, *trans*-Mo<sub>2</sub>(DAniF)<sub>2</sub>(O<sub>2</sub>CMe)<sub>2</sub>, 2 equiv of the acidic reagent is required and the stoichiometry must be strictly controlled because of the lability of the acetate ligand; a mixture of dichloromethane and acetonitrile is used to create a homogeneous reaction system. It is also important to wash the crude product thoroughly.

**Colors of the Compounds.** It is well-known that the electronic spectra of compounds of the type Mo<sub>2</sub>(carboxylate)<sub>4</sub> and Mo<sub>2</sub>(formamidinate)<sub>4</sub> is dominated by the  $\delta \rightarrow \delta^*$  transition which gives them a yellow color.<sup>29</sup> Replacement of some of these groups by acetonitrile molecules causes a significant change in color from yellow to blue as the number of CH<sub>3</sub>CN groups increases. Thus, Mo<sub>2</sub>(CH<sub>3</sub>CN<sub>eq</sub>)<sub>3</sub>-(CH<sub>3</sub>CN<sub>ax</sub>)<sub>2</sub><sup>4+</sup> is blue-purple,<sup>9</sup> while **5** is pink<sup>30</sup> and **C** is purple.<sup>8</sup> Compounds **E** and **4** are orange-red, and **A** is red. All others shown in Scheme 1 are yellow.

**Structures.** As shown in Figures 1 and 2, compounds **1** and **2** are stereoisomers having a paddlewheel structure in which the four paddles are two formamidinate and two acetate groups. In the former the formamidinate ligands are cisoid to each other but transoid in the latter. The isomer *cis*-Mo<sub>2</sub>(DAniF)<sub>2</sub>(O<sub>2</sub>CCH<sub>3</sub>)<sub>2</sub> crystallizes in the monoclinic space group *P*2<sub>1</sub> while the corresponding *trans* complex is found in the orthorhombic space group *P*2<sub>1</sub>2<sub>1</sub>2<sub>1</sub>. The Mo–Mo bond distances for **1**, 2.089(2) and 2.092(2) Å for the two crystallographically independent molecules in the unit cell, are essentially the same as 2.0831(3) Å for **2**, which is consistent with the presence of quadruple bonds in the Mo<sub>2</sub><sup>4+</sup> units.<sup>18,31</sup> However, there are some notable differences in Mo–N and Mo–O bond distances as seen in Tables 2



**Figure 1.** Molecular structure of **1** showing the paddlewheel structure with cisoid formamidinate and acetate groups. Displacement ellipsoids have been drawn at the 40% probability level, and hydrogen atoms have been omitted for clarity.



**Figure 2.** A drawing of the molecular structure of **2** with 40% probability ellipsoids showing the transoid configuration of the acetate and formamidinate groups. All hydrogen atoms have been omitted for clarity.

**Table 3.** Cisoid and Transoid Mo–Ligand Distances (Å) Relative to a Formamidinate<sup>a</sup> Group

		<b>1</b> and <b>2</b>	<b>E</b> and <b>4</b>	<b>5</b>	<b>C</b>
Mo–N <sub>DAniF</sub>	<i>trans</i>	2.140[3] ( <b>2</b> )			
	<i>cis</i>	2.13[1] ( <b>1</b> )			
Mo–O <sub>Acetate</sub>	<i>trans</i>	2.14[1] ( <b>1</b> )			
	<i>cis</i>	2.120[2] ( <b>2</b> )			
Mo–N <sub>acetonitrile</sub>	<i>trans</i>		2.181[4] ( <b>E</b> )	2.152[2]	2.16[1]
	<i>cis</i>		2.141[2] ( <b>4</b> )	2.132[5]	2.14[2]

<sup>a</sup> Acetate in **5**.

and **3**. The Mo–N bond lengths in **1**, with an average of 2.13[1] Å, are slightly shorter than those in **2** (average of 2.140[3] Å), but the Mo–O bond distances in **1** are longer than those in **2** (averages of 2.14[1] Å vs 2.120[2] Å, respectively). Thus, all bonds *trans* to formamidinate nitrogen atoms are slightly elongated. These data are collected in Table 3 to facilitate the comparison between Mo-to-ligand distances in these *cis/trans* isomers and other similar species.

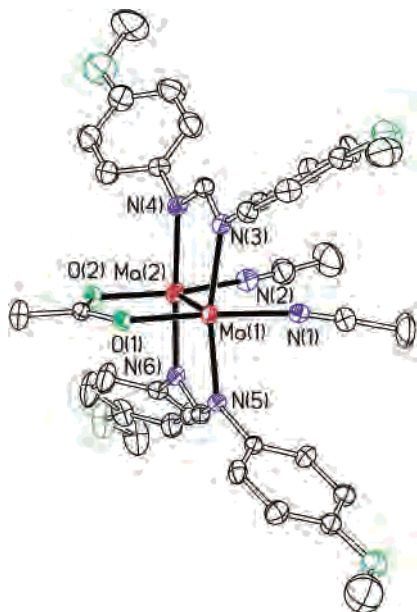
(28) Indeed, we have isolated a molecular triangle from a reaction with *N,N'*-diphenyltetraphthaloyldiamidate: Cotton, F. A.; Liu, C. Y.; Murillo, C. A. Unpublished results.

(29) Cotton, F. A.; Nocera, D. G. *Acc. Chem. Res.* **2000**, *33*, 483.

(30) A pink compound that has not been structurally characterized but reported to be [Mo<sub>2</sub>(O<sub>2</sub>CCH<sub>3</sub>)<sub>2</sub>(CH<sub>3</sub>CN)<sub>5</sub>](BF<sub>3</sub>OH)<sub>2</sub> is likely to be analogous to **5**, because of the color. See: Telser, J.; Drago, R. L. *Inorg. Chem.* **1984**, *23*, 1798.

(31) Cotton, F. A.; Mester, Z. C.; Webb, T. R. *Acta Crystallogr.* **1974**, *B30*, 2768.



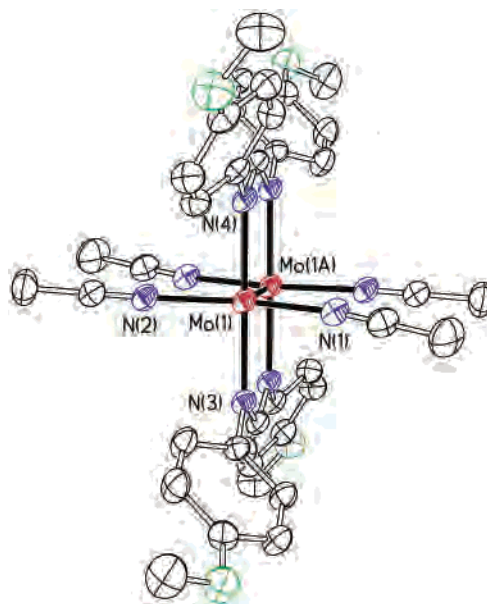


**Figure 3.** A view of the cation in **3**·1.5Et<sub>2</sub>O showing the three different types of ligands and the transoid configuration of the formamidinate groups. Displacement ellipsoids have been drawn at the 40% probability level, and all hydrogen atoms have been omitted for clarity.

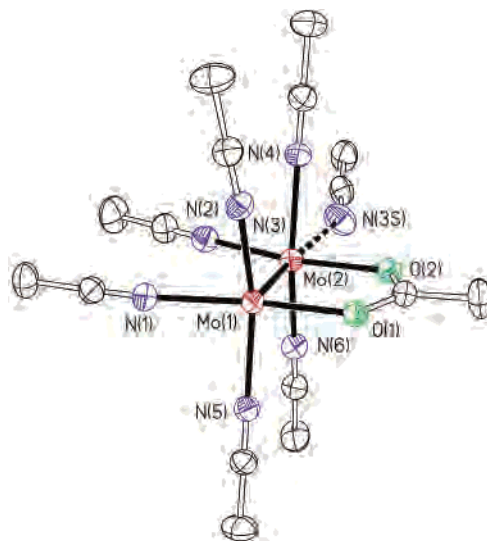
This lengthening of bond distances of the groups that are *trans* to the formamidinate ligands is consistent with the kinetic *trans* influence of the formamidinate groups relative to those of the acetate groups.<sup>32</sup>

The cation in **3**·1.5(C<sub>2</sub>H<sub>5</sub>)<sub>2</sub>O, shown in Figure 3, resides on a general position in the monoclinic space group *P*<sub>2</sub><sub>1</sub>/*c* and has three different types of ligands: two transoid, bridging formamidinates, one bridging acetate, and two acetonitrile molecules that occupy equatorial positions. The interstitial molecules of diethyl ether are far from the Mo<sub>2</sub><sup>4+</sup> unit and do not interact with it. The Mo–Mo bond distance of 2.114(1) Å is longer than those in the paddlewheel compounds **1** and **2**, which is in accord with the presence of only three bridging groups. All the Mo–ligand distances, 2.135[5] Å for Mo–N<sub>DAniF</sub>, 2.161[6] Å for Mo–N<sub>acetonitrile</sub>, and 2.121[5] Å for Mo–O, are in the expected range.<sup>8</sup>

Compound **4** crystallizes in a monoclinic space group *P*<sub>2</sub><sub>1</sub>/*n*, with the midpoint of each Mo–Mo bond on an inversion center. Figure 4 shows the *trans* geometry of the dication which is accompanied by two BF<sub>4</sub><sup>−</sup> counteranions. In contrast to the *cis* analogue and *cis*-[Mo<sub>2</sub>(O<sub>2</sub>CCH<sub>3</sub>)<sub>2</sub>(CH<sub>3</sub>CN<sub>eq</sub>)<sub>4</sub>(CH<sub>3</sub>CN<sub>ax</sub>)<sub>2</sub>](BF<sub>4</sub>)<sub>2</sub>, in which there are two axial CH<sub>3</sub>CN molecules,<sup>8,19,33</sup> the axial sites in **4** are empty. Also, there are no interstitial solvent molecules in the unit cell. The Mo–Mo bond distance of 2.1056(4) Å is noticeably shorter than that of 2.1439(6) Å in the *cis* isomer **E** and that of 2.134(2) Å for the *cis* acetate compound, **A**. This may be due, at least in part, to the lack of axial ligation which generally shortens the metal–metal bond lengths.<sup>34</sup> An interesting issue is why there are no CH<sub>3</sub>CN molecules in the axial positions in the



**Figure 4.** A view of the cation in **4** drawn with 40% probability ellipsoids. All hydrogen atoms have been omitted for clarity.



**Figure 5.** A view of one of the two crystallographically independent cations in **5**·0.5CH<sub>3</sub>CN showing the weak interaction with an axial acetonitrile molecule. Displacement ellipsoids are drawn at the 40% probability level. Hydrogen atoms have been omitted for clarity.

*trans* compound **4**, despite the fact that it is a cation. It is known that electronic, structural, or crystallographic factors may affect the axial interactions on dimetal units. Thus, the structural parameters might render some hints. The average Mo–N<sub>DAniF</sub> bond distance of 2.119[2] Å is slightly longer than that of the *cis* analogue, 2.101[3] Å; but, as shown in Table 3, the average Mo–N<sub>acetonitrile</sub> bond distance of 2.141[2] Å is significantly shorter than that of 2.181[4] Å in the *cis* isomer.<sup>8</sup> Here, again, we see the impact of the nature of the coordination of ligands that elongate the bonds that are *trans* to the nonlabile DAniF group. For this reason, the equatorial coordination of the CH<sub>3</sub>CN molecules to the Mo<sub>2</sub><sup>4+</sup> unit is stronger in the *trans* isomer than in the *cis* isomer. In

(32) Similar elongations, which have been attributed to a *trans* influence, have been observed recently in singly bonded dirhodium compounds. See for example: Chifotides, H. T.; Catalan, K. V.; Dunbar, K. R. *Inorg. Chem.* **2003**, *42*, 8739–8747.

(33) Pimblett, G.; Garner, C. D. *J. Chem. Soc., Dalton Trans.* **1986**, 1257.

(34) Cotton, F. A.; Hillard, E. A.; Murillo, C. A.; Zhou, H.-C. *J. Am. Chem. Soc.* **2000**, *122*, 416.

other words, the electron density in the  $\text{Mo}_2^{4+}$  unit is larger in the *trans* isomer than in the *cis* one, which reduces the attraction of molybdenum atoms for the axial ligands in **4**.

Complex **5** crystallizes in space group  $P\bar{1}$ , with  $Z = 4$ . There are two crystallographically independent, but similar cations (one is shown in Figure 5) which reside on general positions. Each has only one bridging acetate group. The remaining equatorial positions are occupied by acetonitrile molecules. Furthermore, one of the axial sites is occupied by a loosely bound acetonitrile molecule with an Mo–N distance of 2.605 or 2.716 Å; the other axial position is empty. The Mo–Mo bond distances of 2.1558(5) and 2.1539(5) Å are very similar to that of 2.152(1) Å found in the formamidinate analogue, **C**. For **5** and **C**, the  $\text{CH}_3\text{CN}$  molecules *trans* to the acetate or DAniF ligands, respectively, have Mo–N<sub>acetonitrile</sub> distances longer than those corresponding to the *cis* Mo–N<sub>acetonitrile</sub> groups (see Table 3).

**Concluding Remarks.** The systematic preparation of various building block precursors usable for the construction of supramolecular species has been accomplished using

formamidinate, acetate, and acetonitrile ligands, all of which show different substitution rates, which permits the selective replacement of ligands. Furthermore, a significant *trans* effect of the formamidinate ligands permits significant control in the syntheses of *cis* and *trans* species. This is somewhat similar to that found in square platinum(II) compounds. The possibility that this methodology can be extended to other  $\text{M}_2$  species will be investigated soon.

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**Supporting Information Available:** X-ray crystallographic data in CIF format for **1**, **2**, **3**·1.5(C<sub>2</sub>H<sub>5</sub>)<sub>2</sub>O, **4**, and **5**·0.5CH<sub>3</sub>CN. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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