Inorganic Chemistry
Communication

Inorg. Chem. **2009**, *48*, 9069–9071 **9069**
DOI: 10.1021/ic901360c

Synthesis and Characterization of a Benzene−Dimolybdenum Complex with a New Bridging Mode

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Received July 13, 2009

A novel dimolybdenum complex, $[Mo_2(^{iPr}L')_2(C_6H_6)]$ ($\mathbf{1}^{C_6H_6}$), has been synthesized and characterized as a benzene-ring-bridged dimolybdenum complex with a *cis*-μ-$\eta^2(1,2)$:$\eta^2(4,5)$ binding mode. Complex $\mathbf{1}^{C_6H_6}$ reacts with MeMgBr to form **2**, where μ-benzene is methylated to form μ-xylene.

The unusual binding modes of transition metals to organic π-system molecules have historically played a very important role in the development of the field of organometallic chemistry.[1] Arene molecules represent one of the most important classes of π ligands and have the potential to provide up to six electrons for coordination. Numerous donor−acceptor complexes with various hapticities (η^1−η^6) between the arene ligands and metal centers are known. Most of these complexes have been identified as crucial intermediates in homogeneous metal complex catalysis for various aromatic reactions.[2] However, the chemical features of multinuclear π-arene complexes have not yet been clarified because they are quite rare relative to mononuclear π-arene complexes.[3]

Multinuclear metal−arene complexes may exhibit useful and intriguing chemical properties because of unusual chemical structures and/or reactivities as a result of the cooperative effect between metal ions. A diimine ligand can be bridged between two metal ions to induce the formation of a metal−metal bond and to produce interesting structures with very short metal−metal bonds.[4]

Herein, we report on the synthesis and structural characterization of the first benzene-ring-bridged dimolybdenum complex $\mathbf{1}^{C_6H_6}$ and its reactivity with methylmagnesium bromide (MeMgBr).

Compound $\mathbf{1}^{C_6H_6}$ is synthesized by the reaction of ^{iPr}L with $MoCl_4(THF)_2$[5] in the presence of excess magnesium powder in benzene under argon (Scheme 1).

Compound $\mathbf{1}^{C_6H_6}$ is stable in a nonpolar solvent such as *n*-hexane, benzene, and diethyl ether and decomposes in H_2O and CH_2Cl_2. The electrospray ionization/time-of-flight (ESI/TOF) mass spectrum of $\mathbf{1}^{C_6H_6}$ indicates the isotopic features of $[M]^+$ ($M = \mathbf{1}^{C_6H_6}$) at m/z = 1023.1. Compound $\mathbf{1}^{C_6H_6}$ is recrystallized from a MeOH/benzene solution. X-ray structural analysis of $\mathbf{1}^{C_6H_6}$ (Figure 1) reveals that the complex includes two Mo atoms bridged by two ^{iPr}L ligands and a benzene. The complex does not include any counteranions or cations. The coordination mode of the μ-benzene is *cis*-μ-$\eta^2(1,2)$:$\eta^2(4,5)$, which represents a unique molybdenum complex. Similar binding modes have been observed in complexes with different metal centers.[6] The C−N bond

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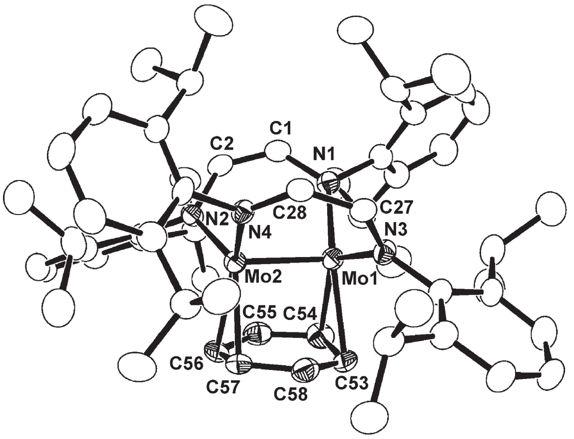
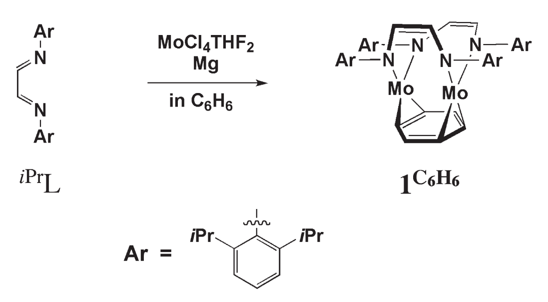


Figure 1. X-ray structure of $1^{C_6H_6}$ with the atom numbering scheme (50% probability thermal ellipsoids). Selected bond lengths (Å) for $1^{C_6H_6}$: Mo1−Mo2 2.1968(4), Mo1−N1 2.018(3), Mo1−N3 2.052(3), Mo1−C53 2.261(3), Mo1−C54 2.194(3), Mo2−N2 2.061(3), Mo2−N4 2.010(3), Mo2−C56 2.253(3), Mo2−C57 2.189(3), C1−C2 1.349(5), C1−N1 1.398(4), C2−N2 1.389(5), C27−C28 1.347(5), C27−N3 1.405(4), C28−N4 1.396(5), C53−C54 1.456(5), C54−C55 1.442(5), C55−C56 1.365(5), C56−C57 1.463(5), C57−C58 1.433(5), C58−C53 1.384(5).

Scheme 1



lengths of ^{iPr}L are as follows: 1.398(4) Å for C1−N1, 1.389(5) Å for C2−N2, 1.405(4) Å for C27−N3, and 1.396(5) Å for C28−N4. The C1−C2 and C27−C28 bond lengths are 1.349(5) and 1.347(5) Å, respectively. These bond lengths are very close to those of previously reported bis(diamido) complexes with Zr^{IV}, Na, Mg, or Zn.[7] It therefore appears that the ^{iPr}L ligands have been reduced by magnesium to form diamido ligands ^{iPr}L′. This result is in accordance with the observed disappearance of the ν(CH=N) stretching vibration in the IR measurement of $1^{C_6H_6}$ [ν(CH=N) of ^{iPr}L: 1626 cm^{-1}]. The two Mo atoms are reduced to Mo^{2+} by excess magnesium. The Mo−N bond lengths for **1** are 2.018(3) Å for Mo1−N1, 2.052(3) Å for Mo1−N3, 2.061(3) Å for Mo2−N2, and 2.010(3) Å for Mo2−N4. These Mo−N bond lengths are shorter than those in Mo^0 complexes with imine ligands (2.2−2.3 Å)[8] and close to those in Mo^{II} complexes with diamido ligands (2.06−2.07 Å).[9] The Mo−C distances are 2.261(3) Å for Mo1−C53, 2.194(3) Å for Mo1−C54, 2.253(3) Å for Mo2−C56, and 2.189(3) Å for Mo2−C57. Small differences are seen in the lengths of the Mo−C bonds. The distance between the two Mo atoms is 2.1968(4) Å. This value is close to a quadruple bond order (2.0−2.2 Å) rather than a triple bond order (2.5−2.6 Å).[10] The coordinated benzene is distorted, as evidenced by two highly extended bonds [1.456(5) and 1.463(5) Å], two slightly extended bonds [1.433(5) and 1.442(5) Å], and two normal bonds with comparisons made with respect to a free benzene molecule contained in the unit cell [from 1.335(8) to 1.388(9) Å; Figure S2 in the Supporting Information). The average of these C−C bonds (1.424 Å) is longer than those of previously reported μ-$\eta^2(1,2)$:$\eta^2(4,5)$-benzene complexes.[6e,j] On the basis of the C−C bond order of benzene reported by Pauling,[2a,11] the bond orders of these six C−C bonds are estimated to be 1.1−1.2 for C53−C54, 1.2 for C54−C55, 1.7−1.8 for C55−C56, 1.1 for C56−C57, 1.2−1.3 for C57−C58, and 1.6 for C58−C53. The two C−C bonds involved in π bonding with molybdenum are both close to the average length of a C−C single bond.[2a]

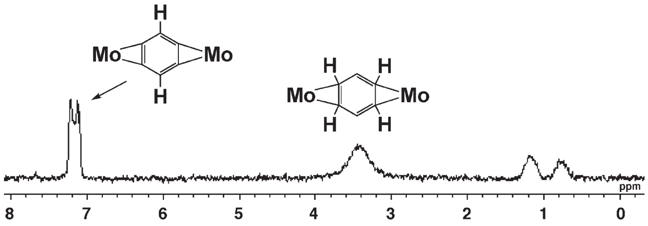


Figure 2. ^{2}H NMR spectrum of $1^{C_6D_6}$ in *n*-hexane at 20 °C (δ/ppm vs TMS).

The ^{1}H NMR spectrum of $1^{C_6H_6}$ in *n*-hexane-d_{14} indicates the presence of six aromatic H atoms, two ethylene H atoms, four methine H atoms, and eight methyl H atoms originating from the ligated ^{iPr}L′ (Figure S3 in the Supporting Information). The ^{13}C NMR spectrum has 12 aromatic C atoms, 2 ethylene C atoms, 4 methane C atoms, and 8 methyl C atoms (Figure S4 in the Supporting Information). These features indicate that, in solution, $1^{C_6H_6}$ has C_2 symmetry. The ^{1}H NMR peaks are assigned from the ^{2}H NMR spectrum of $1^{C_6D_6}$ prepared using benzene-d_6 because the broad peaks could not be assigned from the ^{1}H NMR spectrum in *n*-hexane-d_{14}. The ^{2}H NMR spectrum at 20 °C showed two sharp peaks at 7.23 and 7.17 ppm and a broad peak at 4.0−3.0 ppm (vs TMS in *n*-hexane; Figure 2). The peaks at 7.17 and 4.0−3.0 ppm are assigned as originating from μ-benzene. The broad peak contains signals from the four protons that are located on the C atoms bound to the Mo atoms. These signals have a large shift to the high-field region relative to the analogous signals of free benzene at 7.23 ppm. The two peaks of μ-benzene were broadened with a

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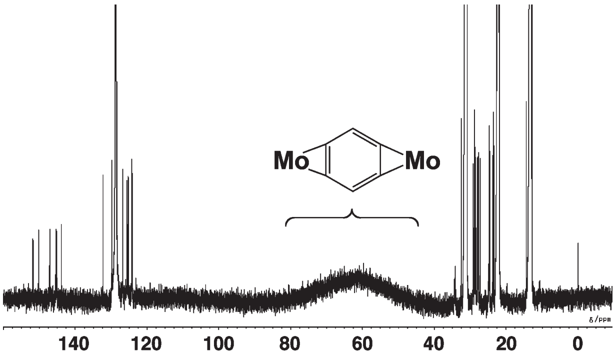

Figure 3. ^{13}C NMR spectrum of $\mathbf{1}^{^{13}\mathrm{C_6H_6}}$ in *n*-hexane-d_{14} at 20 °C (δ/ppm vs TMS).

decrease in the temperature from +20 to −80 °C (Figure S5 in the Supporting Information). In the ^{13}C NMR experiment at 20 °C, μ-benzene has a very broad peak detected by using $\mathbf{1}^{^{13}\mathrm{C_6H_6}}$, which is synthesized by the same method as that used for the synthesis of $\mathbf{1}^{\mathrm{C_6H_6}}$ using $^{13}C_6H_6$ in place of $^{12}C_6H_6$ (Figure 3). Carbon peaks of the μ-benzene moiety are not detected for $\mathbf{1}^{\mathrm{C_6H_6}}$. The broad peak in the ^{13}C NMR spectrum is centered at 61.2 ppm and spread out in the range of 40−80 ppm. Such a large shift was previously observed in the coordinated μ-η^2:η^2-benzene ligands.[3h,i,6c−6g,6i] In a variable-temperature ^{13}C NMR experiment, the broad peak of μ-benzene was split into three sharp peaks at 123.6, 71.3, and 50.8 ppm with a decrease in the temperature from +20 to −70 °C. The peaks at 71.3 and 50.8 ppm are assigned as the C atoms that are linked with long and short bonds to the Mo atoms, respectively. These indicate that μ-benzene is rotating in a binuclear unit, and the rotation rate slows with a decrease in the temperature (Figure S6 in the Supporting Information). These observations provide clear experimental evidence that the μ-benzene moiety provides a bridge between the two Mo atoms in solution. Additionally, we preliminarily confirmed using NMR and ESI mass spectrometry experiments that μ-benzene cannot be replaced with C_6D_6, toluene, xylene, or anisole.

Aromatic C−H bond activation reactions of arene ligands have been reported for an η^2 complex.[2c,d,12,13] It was recognized that the bridging benzene moiety of $\mathbf{1}^{\mathrm{C_6H_6}}$ may react in a similar manner, and thus we examined the reaction of the μ-benzene of $\mathbf{1}^{\mathrm{C_6H_6}}$ with excess MeMgBr in *n*-hexane at room temperature. The formation of a dimethylated $\mathbf{1}^{\mathrm{C_6H_6}}$ (**2**) is confirmed by a ESI-MS spectrum (Figure 4), although monomethylated $\mathbf{1}^{\mathrm{C_6H_6}}$ was not detected. Although the yields were low, the ratio of $\mathbf{1}^{\mathrm{C_6H_6}}$/**2** was estimated to be about 5/1 by comparing MS peak intensities. Although **2** could not be isolated, we expect that **2** is a dimethylated μ-benzene complex and not a dimethylated diimine complex. The production of xylene can be explained by the ESI-MS experiment of the reaction products of $\mathbf{1}^{\mathrm{C_6D_6}}$ with MeMgBr. Compound $\mathbf{1}^{\mathrm{C_6D_6}}$ also reacts with MeMgBr to give **2**-*d*. The ESI-MS spectrum has an isotope feature of **2**-*d* at m/z = 1055.5, which is shifted by m/z = 4 from that of **2** (Figure 4). Thus, μ-benzene reacts with MeMgBr to form μ-xylene. Gas chromatography (GC) analysis of the decomposed products of **2** (Figure S7 in the Supporting Information) demonstrates the generation of *o*-/*m*-/*p*-xylenes in a ratio of 33/18/49, indicating that two C atoms at ortho and para positions of the μ-benzene are particularly activated by the dimolybdenum center. This is a particularly interesting reaction because benzene itself cannot be directly dialkylated. Although monoalkylation and monohalogenation reactions of aromatic rings coordinated to metal ions have been reported,[2a,d,12,13] to the best of our knowledge, this work represents the first report of dialkylation of an aromatic ring coordinated to a dinuclear metal center.

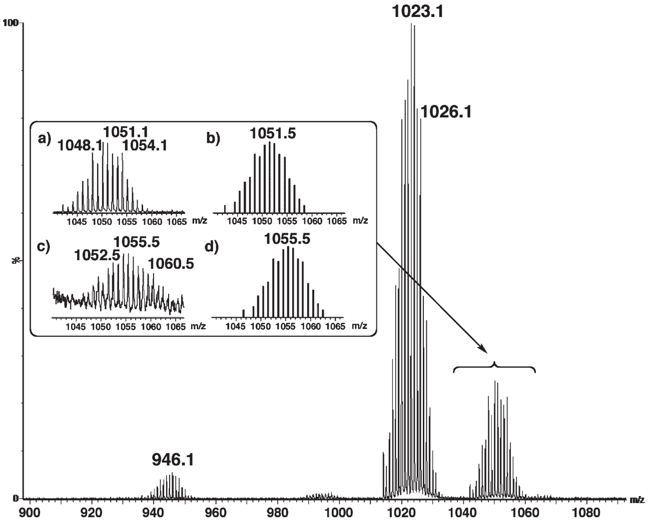

Figure 4. ESI-MS spectrum of the reaction products of $\mathbf{1}^{\mathrm{C_6H_6}}$ with MeMgBr. Inset: Expanded views of the range of m/z = 1040−1065 for **2**-*d* (a), for the simulation of **2**-*d* (b), **2** (c), and for the simulation of **2** (d).

In summary, a novel dimolybdenum complex with a cis-μ-η^2(1,2):η^2(4,5)-benzene moiety, $\mathbf{1}^{\mathrm{C_6H_6}}$, has been synthesized and characterized by X-ray and NMR analyses. We also demonstrated the reactivity of complex $\mathbf{1}^{\mathrm{C_6H_6}}$ with MeMgBr as a preliminary result toward a useful reaction of this π-arene complex.

Acknowledgment. We gratefully acknowledge the support of this work from a Grant-in-Aid for Scientific Research from the Ministry of Education, Science, Sports and Culture.

Supporting Information Available: Experimental procedures, detailed characterization data, and X-ray crystallographic data files in CIF format for $\mathbf{1}^{\mathrm{C_6H_6}}$: crystallographic experimental details, final atomic coordinates, thermal parameters, and full bond lengths and angles for $\mathbf{1}^{\mathrm{C_6H_6}}$ (Tables S1−S8), ORTEP views of independent molecules and local structures around μ-benzene for $\mathbf{1}^{\mathrm{C_6H_6}}$ crystal (Figures S1 and S2), ^{1}H and ^{13}C NMR spectra (Figures S3 and S4), variable-temperature ^{2}H and ^{13}C NMR spectra (Figures S5 and S6), and GC chromatogram for products obtained from the reaction of $\mathbf{1}^{\mathrm{C_6H_6}}$ with MeMgBr (Figure S7). This material is available free of charge via the Internet at http://pubs.acs.org.

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