Synthesis and Reactions of Bis(arylimino)isoindoline Complexes of Dimolybdenum

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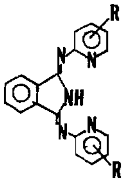
Abstract

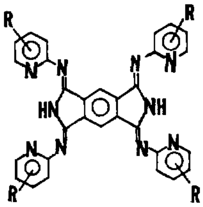
Several dimolybdenum complexes have been synthesized which contain the planar tridentate ligand bis(arylimino)isoindoline, BAII. The BAII derivatives which have been successfully coordinated to the dimolybdenum unit include those in which the aryl group is pyridine, 4-methylpyridine, and 4-ethylpyridine. It was found that only one BAII ligand would attach to the dimolybdenum unit and that complexes with the formula $Mo_2(OAc)_3$-(BAII) resulted. These complexes have one molybdenum coordinated to the BAII and one monodentate acetate while the other molybdenum is coordinated to two bidentate acetates. This structural assignment is supported by NMR, infrared and electronic absorption data. This is the first dimolybdenum complex which contains non-bridging acetates as well as being the first dimolybdenum complex with a planar tridentate ligand. Reaction of the complexes with excess acetic acid regenerates molybdenum acetate thus showing that the quadruple bond is intact in the BAII complexes.

Introduction

There have been a large number of dimolybdenum complexes reported over the past twenty years or so [1, 2]. The bis(porphyrin) complex reported by Collman [3] is the only one report of a dimolybdenum complex of a planar tri- or tetradentate ligand system. This is rather surprising since these ligand types represent some of the most heavily studied and most interesting complexes for other metal systems [4]. With the recent interest in the electronic properties of planar complexes [5] it seems natural that compounds in which two planar ligands such as tetraphenylporphyrin or phthalocyanine are held close together by a strong metal–metal bond would be important as candidates for synthesis and study. Our approach has been to first focus on the planar tridentate ligand bis(arylimino)isoindoline, BAII represented below.



We chose this sytem for two reasons. The solubility of many porphyrin and phthalocyanine complexes is unfavorable, whereas it is reasonably simple to increase the solubility of BAII ligands by changing the identity of the R-group [6]. In addition, it is fairly simple to synthesize a binucleating analog of BAII [7], shown below, which is not available for the previously mentioned ligands.



We wondered if two BAII molecules could get close enough so that each molybdenum in the dimolybdenum unit could be coordinated to one BAII? In the event that only one BAII could be coordinated we wondered if the reactivity of the remaining acetates would be altered by the presence of a tridentate ligand. It was assumed that the BAII could not bridge the two metal atoms.

The successful synthesis of some dimolybdenum complexes containing the planar delocalized BAII groups are reported herein along with the structural assignment of the compounds. In addition, the details of their reactions with carboxylic acids are discussed along with the potential implications these reactions have on possible oxidative–addition reactions to bridged quadruple molybdenum–molybdenum bonds.

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Experimental

Materials

Molybdenum acetate was prepared by the method of Wilkinson [8]. All reactions were performed under an Ar atmosphere using standard Schlenk techniques. Methanol was freshly distilled from calcium sulfate where it had been stored. The BAII ligands were prepared by the method of Siegl using the template reaction with $CaCl_2$ as the catalyst [9].

Spectroscopic Measurements and Methods

Electronic absorption spectra were recorded on a Perkin-Elmer 552 spectrophotometer in methylene chloride solutions. Infrared spectra were obtained as KBr pellets on a Perkin-Elmer 1306 spectrophotometer as KBr pellets which were prepared under inert conditions. NMR spectra were collected using a Varian EM-360A spectrometer using d^2-methylene chloride, which was purchased in sealed ampules, as the solvent. Elemental analyses were performed by Atlantic Microlabs, Atlanta, Ga.

Reactions

Synthesis of $Mo_2(OAc)_3(BAII)$

Typically 1 g of $Mo_2(OAc)_4$ was reacted with 1 equivalent of the appropriate BAII ligand in 50 ml of dry, degassed methanol under an argon atmosphere. The solution immediately turned an emerald green color. Unreacted, undissolved molybdenum acetate was visible in the mixture for about 2 h. Upon stirring overnight a large amount of the dark green complex precipitated. The crude product was purified by dissolution in about 25 ml of dry degassed methylene chloride followed by addition of an equal volume of dry degassed hexane. Large green needles of the complex were deposited from this solution over a 24 to 48 hour period. *Anal.* for $Mo_2(OAc)_3(BAII)$ (R = Me). Calc. for $C_{26}H_{27}N_5O_6Mo_2$: C, 44.91; H, 3.62; N, 10.06. Found: C, 42.79; H, 3.93; N, 9.66%.

Reaction of $Mo_2(OAc)_3(BAII)$ with acetic acid

The acetic acid was prepared by refluxing 15 ml of glacial acetic acid with 2 ml of acetic anhydride for 1 h. The solution was cooled and argon gas was bubbled through it for 1 h. The $Mo_2(OAc)_3(BAII)$ was then added and the bright green solution was stirred overnight. During this period small yellow crystals precipitated. The crystals were determined to be $Mo_2(OAc)_4$ since the infrared spectrum of the compound was identical to that of authentic $Mo_2(OAc)_4$ prepared as mentioned above.

Results

Synthesis of the Complexes

Original reactions were run with a ligand-to-dimolybdenum ratio of 2-to-1, and later, ratios of greater than 2-to-1 were used. In each case an emerald green solution resulted. After stirring the solution overnight a green precipitate formed but, unfortunately, it was mixed with unreacted molybdenum acetate. These two were difficult to separate due to the extreme air-sensitivity of the green $Mo_2(OAc)_3$-(BAII). When separation was accomplished elemental analyses always indicated that only one BAII had been incorporated into the dimolybdenum complex. As a result later reactions were run with a BAII to molybdenum acetate ratio of 1-to-1. In these cases only $Mo_2(OAc)_3(BAII)$ was isolated. BAII complexes have also been reported to result from the template reaction of *o*-dicyanobenzene and the appropriately substituted 2-aminopyridine in the presence of a transition metal acetate [6]. Attempts to prepare the dimolybdenum–BAII complexes in this manner resulted in complex mixtures which were not green and as a result this method of synthesis was abandoned.

Spectroscopic Studies

The NMR spectra were taken in d^2-methylene chloride at 30 °C. The important NMR features of all of the complexes were similar except for the resonances due to the R-group so only the R = Me spectrum will be discussed in detail.

The spectrum of the $Mo_2(OAc)_3(BAII)$ complex with R = methyl displays three singlet resonances at 2.35, 2.70 and 2.83 ppm. These three bands occur in a ratio of 6:6:3 and correspond to the methyl protons of the BAII and the bidentate and monodentate acetates from the complex respectively. Much more interesting is the aromatic region between 6.5 and 8.5 ppm. In the spectrum of the ligand alone five bands appear in this region with a ratio of 2:2:2:2:2. These bands correspond to the five differient types of aromatic protons on the BAII molecule and can be assigned to H-5, H-3, H_α, H_β and H-6 respectively, see Fig. 1.

In the complex spectrum, on the other hand, six resonances occur in this region with a ratio of 1:1:4:

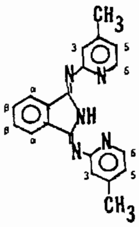

Fig. 1. Proton assignments for NMR spectra at BAII and BAII complexes.

2:1:1; This is apparently due to the inequivalence of the 5- and 6-protons of the two different pyridine rings of the BAII ligand. The assignment of the bands can be made based on a comparison of the spectrum of the free ligand with the dimolybdenum complex. The H-6 resonance in the spectrum of the ligand occurs at 8.45 ppm as a doublet while the H-6 and H-6′ resonances in the complex spectrum are near 8.45 ppm occurring at 8.37 and 7.83 ppm. Likewise the H-5 proton resonance in the ligand spectrum occurs at 6.91 ppm while the H-5 and H-5′ resonances in the complex spectrum appear at 6.82 ppm and 6.49 ppm. The benzo-proton resonances have overlapped somewhat to form a broad multiplet which integrates as 4 protons and the H-3 resonance in the ligand spectrum occurs at 7.28 ppm while in the complex spectrum it occurs at 7.12 ppm.

The spectra of the R = ethyl ligand and the dimolybdenum complex of this ligand compare in the same way and therefore the structure of the ethyl derivative is not significantly different from the structure of the complex of the methyl derivative. The R = H derivative is not soluble enough for NMR spectra to be obtained.

The infrared spectra of the complexes were informative as to the structures of the BAII complexes. The spectra of all of the complexes showed a strong absorbance between 1600 and 1650 cm^{-1}. This was assigned to the C=O stretch of the monodentate acetate ligand [10]. This band did not occur in the spectrum of either the ligand or the molybdenum acetate. There have been reports that complexes which contain non-deprotonated BAII show a strong band at 1600 cm^{-1} [11]. We do not believe that this is the case for Mo$_2$(OAc)$_3$(BAII) since the complex does not appear to be ionic in nature and it would be ionic if in fact the BAII ligands were not deprotonated.

The electronic absorption spectra of the complexes showed the bands typical of the BAIIs in the ultraviolet region. The pure ligand has no visible bands in its spectrum. The spectra of the complexes each exhibited a band very near to 690 nm. We assign this band to the $\delta \rightarrow \delta^*$ transition. While this is a rather low energy band for the $\delta \rightarrow \delta^*$ transition it appears to be a correct assignment since the energy of the band is independent of the R = group attached to the pyridine ring of the BAII ligand, see Table I. There is not a great amount of difference in the inductive effect of the ethyl and methyl groups [12], however, the fact that there no change at all on going from H– to Et– to Me– tends to support the assignment as the $\delta \rightarrow \delta^*$ band, which is a metal centered transition, as opposed to at metal-to-ligand charge transfer band. Other compounds have appeared in the literature with the $\delta \rightarrow \delta^*$ band near 670 nm and at even higher wavelengths [13, 14]. The compounds Mo$_2$I$_2$(PP)$_2$, where PP is a bidentate phosphine ligand, exhibit the $\delta \rightarrow \delta^*$ band between 690 and 920 nm depending on the δ-overlap which is a function of the twist of the molybdenum–molybdenum bond.

TABLE I. $\delta \rightarrow \delta^*$ Transition for Mo$_2$(OAc)$_3$BAII

R	λ (nm)
H	675
Me	685
Et	685

Discussion

The NMR and electronic absorption data support the assignment of a structure in which one of the molybdenums of the dimolybdenum unit is coordinated by the three nitrogens of the BAII ligand. From the NMR data there must be three acetates, two of one kind and one of another kind. The only way to satisfy the above conditions is for one monodentate acetate to be bonded to the molybdenum coordinated to the BAII ligand while the other molybdenum is coordinated by two bidentate acetate ligands as shown in Fig. 2. This is the first example of a dimolybdenum complex which contains non-bridging acetates.

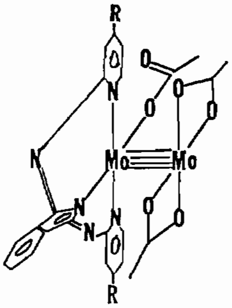

Fig. 2. Proposed structure of Mo$_2$(OAc)$_3$BAII.

It is interesting in light of the synthesis of Mo$_2$-(porphyrin)$_2$ that only one BAII ligand can be added to the dimolybdenum unit. The method of synthesis used by Collman involved initial formation of mononuclear porphyrin precursors which were then coupled in a thermal reaction to form the dimolybdenum complex [3a]. In addition, the same bis(porphyrin) complex has been formed from reaction of MoCl$_2$(CO)$_4$ with H$_2$OEP in refluxing toluene [3b]. Our method involved much milder conditions. Whether the second BAII addition is hindered by steric or electronic factors has not been determined. However, electronic spectra suggest that the metal–metal bond may be twisted away from the usual eclipsed configuration, *vide infra*. This twist may result from some steric interaction of the BAII on one molybdenum with the acetates on the other molybdenum. If this is the case then approach of a second BAII would most likely be blocked sterically.

The structure is supported by the NMR spectra particularly in the aromatic region between 6.5 and 8.5 ppm. Five proton resonances appear in this area for the pure ligand spectra whereas six resonances appear in the same area in the complex spectra. This fact can be explained based on the proposed structure. One of the pyridine rings of the BAII ligand is across the quadruple metal–metal bond from one of the bidentate acetates while the other pyridine ring is across the quadruple bond from the space in between the bidentate acetates. This difference is apparently enough to cause the H-5 and H-6 protons on the two pyridine rings to be inequivalent.

The low energy of the $\delta \rightarrow \delta^*$ transition in the electronic spectra of the complexes suggests weak δ-bonding in the complex and therefore a smaller overlap of the two d_{xy} orbitals on the two molybdenum atoms. If the δ-bonding is weak then the δ and δ^* molecular orbitals would be closer together in energy than if the bonding were stronger. As a result the highest occupied molecular orbital, the δ-orbital, will be raised in energy. This suggests that $Mo_2(OAc)_3(BAII)$ may readily be oxidized. The low energy of the band in the title compounds also suggests that the two ends of the metal–metal bond may be twisted relative to one another. In a totally eclipsed configuration the twist angle would be zero and the δ-overlap would be maximized while if the twist of one end of the metal–metal bond relative to the other end is 45° the δ-overlap should theoretically be zero. This has been demonstrated by Cotton and co-workers for a series of compounds with the formula $Mo_2X_2(PP)_2$ in which the $\delta \rightarrow \delta^*$ band shifts to lower energy as the metal–metal bond becomes increasingly twisted [13, 14].

Once the structure was shown to have only one BAII per dimolybdenum unit it became of interest to investigate the reactions of the complex to see if the BAII ligand affected the acetates still bonded to the metals. In particular we wanted to find out if the acetate on the molybdenum chelated by the BAII had a significantly different reactivity than the acetates on the non-chelated molybdenum. Toward this end $Mo_2(OAc)_3(BAII)$ was reacted with isobutyric acid. It was felt that either the acetates would all be replaced or only the monodentate acetate or bidentate acetates would be replaced. Upon reaction of $Mo_2(OAc)_3(BAII)$ with isobutyric acid a yellow microcrystalline material is produced. It is difficult to say if there are any acetates left bonded to the dimolybdenum since NMR spectra could not be obtained but the infrared spectrum of the complex clearly showed that the BAII had been removed and that there were carboxylates bonded to the metals. This led us to react $Mo_2(OAc)_3(BAII)$ with acetic acid and the resulting product was shown to be $Mo_2(OAc)_4$. The NMR and infrared spectra of the yellow compound obtained in this reaction are identical to those of $Mo_2(OAc)_4$ which had been prepared by the method of Wilkinson. This result suggests that, in fact, the quadruple bond is still intact in $Mo_2(OAc)_3(BAII)$. In addition, this reaction demonstrates the flexibility of the acetates in changing binding modes. This suggests that the acetates, or other bridging ligands, could get out of the way for the quadruple bond to react. For example, there has been much interest in the possibility of oxidative–addition reactions to metal–metal multiple bonds [15]. The present study suggests that bridging ligands, and particularly acetates, may not hinder such reactions.

Acknowledgement

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