DOI: 10.1002/ejic.200801103

Adduct Formation of Dichloridodioxidomolybdenum(VI) and Methyltrioxidorhenium(VII) with a Series of Bidentate Nitrogen Donor Ligands

Ahmad M. Al-Ajlouni,[a,b] Alev Günyar,[a] Ming-Dong Zhou,[a] Paul N. W. Baxter,[c] and Fritz E. Kühn*[a]

Keywords: Molybdenum / Rhenium / N ligands / Oxido ligands / Stability constants

The stability of a variety of bidentate N-base adducts of MoO_2Cl_2 and $(CH_3)ReO_3$ (MTO) was investigated in thf and CH_2Cl_2 as solvents. The formation constants were determined from the spectrophotometric data based on 1:1 adduct formation. The adduct formation constants for $[MoO_2Cl_2L_2]$ (L_2 = bidentate nitrogen ligand) are 10^4–10^6 times higher than those for $[(CH_3)ReO_3L_2]$ with the same ligands under the same conditions. The adduct stability of both systems is very sensitive to the electronic nature of the ligands and increases with their donor ability. Hammett correlations of the formation constants against σ give relatively large negative values for the reaction constants ($\rho_{Re} = -5.9$, $\rho_{Mo} = -6.6$). The stability is also governed by steric and strain factors. Thus, sterically hindered 6,6′-disubstituted-2,2′-bipyridines do not form adducts with MTO, and only 6,6′-dimethyl- and 6,6′-diphenyl-2,2′-bipyridines form adducts with MoO_2Cl_2. However, these adducts are much less stable than other methyl derivatives of 2,2′-bipridine adducts. The steric strain between the two methyl groups in 3,3-dimethyl-2,2′-bipyridine influences the bipyridine planarity upon complexation and reduces the adduct stability. The thermodynamic parameters (enthalpy and entropy) were determined from temperature-dependence studies. The adduct stability is mainly due to the strongly exothermic binding of the nitrogen-bidentate ligand. The entropy change is small and has little effect on adduct stability.

Introduction

High-valent d^0 early transition metal oxides are well known for their catalytic oxidation activities in the presence of peroxides.[1] Among these, methyltrioxidorhenium(VII) (MTO) and dichloridodioxidomolybdenum(VI) complexes have been most widely utilized as catalysts or catalyst precursors for oxygen-atom transfer reactions to a plethora of substrates.[2] MTO is very stable and has been used in aqueous, semi-aqueous, and organic solutions under homogeneous and heterogeneous conditions,[3] whereas dioxidomolybdenum(VI) complexes, such as MoO_2X_2 (X = Cl, Br, or methyl), are coordinatively unsaturated (or coordinated to labile solvent molecules) and highly sensitive to moisture. The MoO_2X_2 moiety can be stabilized by adduct formation with relatively strong basic donor ligands, such as 2,2′-bipyridine and derivatives. Many papers have been published on the effect of nitrogen donor ligands on the stability and activity of MTO and, to a lesser extent, MoO_2X_2 complexes.[4] Adducts of the composition $[MoO_2X_2L_2]$ are formed with Lewis bases such as pyridine and 2,2′-bipyridine.[5,6] The first X-ray crystal structure of an $[MoO_2X_2L_2]$-type complex was reported in 1966.[7] $[MoO_2X_2L_2]$ complexes are monomeric and display a distorted octahedral geometry, with the oxido ligands *cis* to each other in order to maximize donation into the empty t_{2g} set orbitals.[8] Such Mo^{VI}-oxido complexes have been used as active catalysts for olefin epoxidation by organic peroxides, particularly homogeneous phase systems.[9,10] A series of papers has been published in recent years showing that complexes of the type $[MoO_2X_2L_2]$ are excellent catalyst precursors for olefin epoxidation in the presence of *tert*-butylhydroperoxide (TBHP).[11] As regards the reaction mechanism, it has been generally agreed that formation of a Mo^{VI} alkyl peroxide occurs followed by transfer of the distal oxygen atom of the alkyl peroxide rather than an oxido ligand.[12] The activity of d^0 M-oxido catalysts in olefin epoxidation depends on the Lewis bases, the redox stability of the ligands, and particularly on the stability of the ad-

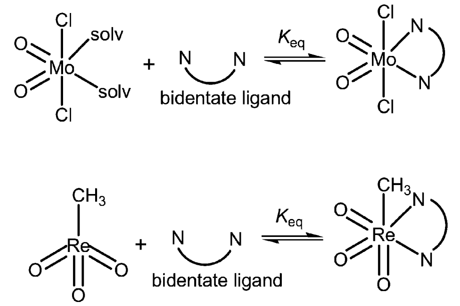
---

[a] Molecular Catalysis, Catalysis Research Center, Technische Universität München,
Lichtenbergstrasse 4, 85747 Garching bei München, Germany
E-mail: fritz.kuehn@ch.tum.de
[b] Department of Applied Chemical Sciences, Jordan University of Science and Technology,
Irbid 22110, Jordan
E-mail: aajlouni@just.edu.jo
[c] Institut Charles Sadron, Université Louis Pasteur,
23 rue du Loess BP 20, 67083 Strassbourg, France
E-mail: baxter@ics.u-strasbg.fr

Supporting information for this article is available on the WWW under http://www.eurjic.org or from the author.

duct complexes.[13,14] The activity was also found to be influenced by both the electronic and steric nature of the ligands.[15] In addition, substituted bipyridines can enhance the catalyst solubility in organic solvents.[16] Adduct stability and loss of the bipyridine ligand in solution (especially in donor solvents such as thf or CH_3CN) is a major concern when using these catalysts under homogeneous conditions. The release of the Lewis base ligand affects the activity of the catalyst (due to polymerization and precipitation of MoO_2X_2) and leads to the oxidation of the free bipyridine ligand.[13] Accordingly, the whole catalytic system is destroyed.

In this work, we set out to investigate the complexation of a new series of bidentate (mainly 2,2′-bipyridines) ligands with MTO and MoO_2X_2 in two organic solvents (thf as a coordinating solvent and CH_2Cl_2 as a non-coordinating solvent). The formation constants were determined to provide direct information about the adduct stability and the results correlated with the electron-donating and -withdrawing abilities of the bidentate ligands to reconcile their electronic effect on the adducts' stabilities. Additionally, both steric and strain factors were investigated. A comparison between MoO_2Cl_2 and MTO adducts is further presented. To the best of our knowledge, this is the first study that presents experimental details on the formation constants and relative stability of bidentate nitrogen adducts of MoO_2X_2.



N N = 2,2'-bipyridine (**1**)
3,3'-dimethyl-2,2'-bipyridine (**2**)
4,4'-dimethyl-2,2'-bipyridine (**3**)
5,5'-dimethyl-2,2'-bipyridine (**4**)
6,6'-dimethyl-2,2'-bipyridine (**5**)
4,4'-dibromo-2,2'-bipyridine (**6**)
5,5'-dibromo-2,2'-bipyridine (**7**)
5,5'-dinitro-2,2'-bipyridine (**8**)
5,5'-diamino-2,2'-bipyridine (**9**)
5,5'-dicarboxyethyl-2,2'-bipyridine (**10**)
6-phenyl-2,2'-bipyridine (**11**)
6,6'-diphenyl-2,2'bipyridine (**12**)
4,5-diazofluoren-9-one (**13**)
1,10-phenanthroline-5,6-dione (**14**)
2,2':6',2''-terpyridine (**15**)
2,2'-biquinoline-4,4-dicarboxylic acid, diethyl ester (**16**)
6,6'-dimethoxy-3,3' bipyridazine (**17**)
3,6'-bis(2-pyridyl)pyridazine (**18**)

Scheme 1. Adduct formation of MoO_2Cl_2 and MTO with bidentate nitrogen ligands in solution.

Results and Discussion

Methyltrioxidorhenium (MTO) and dioxidomolybdenum(VI) compounds are Lewis acidic and electrophilic catalysts. In organic solution, good Lewis bases (or nucleophiles) replace the solvent molecules and form stable adducts. Depending on the nature of the ligand and the solvent, the adduct exists in equilibrium with the M-solvent complex and the free ligand. Adducts of dioxidomolybdenum(VI) with the formula $[MoO_2X_2L_2]$ (X = halogen or alkyl; L_2 = mono- or bidentate nitrogen ligands) have been used in catalytic reactions, such as oxidations with organoperoxides, but their adduct-formation constants have never been determined. In this work, the formation constants of various bidentate nitrogen adducts of MoO_2Cl_2 and MTO are examined in CH_2Cl_2 and thf. MoO_2Cl_2 is very labile in solution and reacts rapidly with bidentate Lewis bases to form a 1:1 adduct (Scheme 1). The bidentate nitrogen ligands enhance the complex stability and lead to electronic and steric saturation of the Mo center. In addition, the ligands significantly affect the catalytic activity of the resulting compounds.[13] Adduct formation between mono- and bidentate nitrogen Lewis bases and MTO has been investigated in various organic solvents.[17] Some 2,2′-bipyridine- and other bidentate nitrogen adducts of MTO have been prepared before and their stabilities in solution have been investigated.[4,17] They also form 1:1 adducts as shown in Scheme 1.

Determination of Formation Constants

The formation constants were determined from the absorbance changes as the equilibrium depicted in Scheme 1 is established. A new absorption band in the range 300–450 nm (Figure 1) is usually observed upon formation of the $[MoO_2Cl_2L_2]$ adduct with any of the bidentate ligands above. The absorbance of $[MoO_2Cl_2(solv)_2]$ above 315 nm is negligible and can be ignored (see Figure 1). The free ligand has a tiny absorption in this region but cannot be ignored because it exists in large excess. The reaction leads to a 1:1 adduct, $[MoO_2Cl_2(bipy)]$, which exists in equilibrium with the original $[MoO_2Cl_2(solv)_2]$ and the free nitrogen ligand (Scheme 1).

The changes in absorbance (*Abs*) above 315 nm due to the formation of $[MoO_2Cl_2(bipy)]$ can be expressed by Equation (1) (assuming a 1.0-cm path-length), where ε_L and ε_{ML} are the molar absorptivities for the free bipy ligand (L) and the $[MoO_2Cl_2(bipy)]$ adduct (ML), respectively.

$$Abs = \varepsilon_L[L] + \varepsilon_{ML}[ML] \quad (1)$$

Substituting the formation constant (*K*) for the formation of the $[MoO_2Cl_2(bipy)]$ adduct into Equation 1, and using the molar balance $[M]_T = [MoO_2Cl_2] + [MoO_2Cl_2(bipy)]$, gives Equation (2). Complete derivation of Equation (2) is shown in Appendix I (Supporting Information).

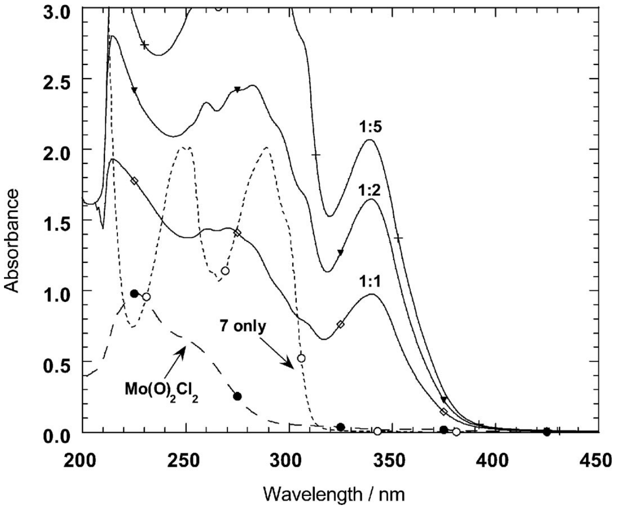


Figure 1. UV/Vis spectra of MoO_2Cl_2 before and after the addition of 5,5′-dibromo-2,2′-bipyridine (**7**) in thf at 25 °C. The solid line spectra are for mixtures of $Mo(O)_2Cl_2$ and **7** in 1:1 (○), 1:2 (▼), and 1:5 (+) ratios, respectively.

$$Abs = \varepsilon_L[L] + \frac{\varepsilon_{ML}\cdot[M]_T\cdot K_{eq}[L]}{1 + K_{eq}[L]} \tag{2}$$

The molar absorptivity of the bipy ligand (ε_L) was determined in the absence of the metal complex and used in Equation (2). If the absorbance of the free ligand at the chosen wavelength is negligible and can be ignored (i.e. $\varepsilon_L \approx 0$), then Equation (3) can be used to determine the formation constant.

$$Abs = \frac{\varepsilon_{ML}\cdot[M]_T\cdot K_{eq}[L]}{1 + K_{eq}[L]} \tag{3}$$

The absorbance vs. concentration diagram of solutions of the $[MoO_2Cl_2(bipy)]$ complex with [bipy] is not like a titration curve (see Figure 2). Instead, as more bipy is added, it increases monotonically until finally a plateau is reached. Fitting of the experimental absorbance data (at equilibrium) as a function of [L] to Equations (2) or (3) allows values for the equilibrium constants to be calculated (Table 1).

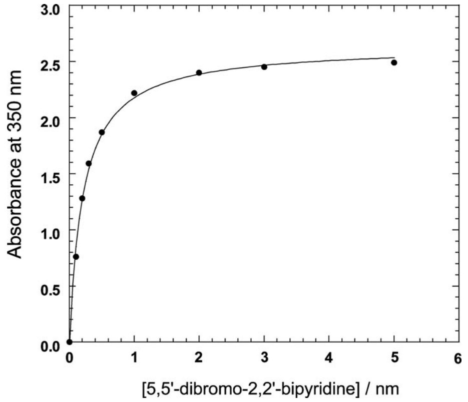


Figure 2. Plot of the absorbance change at 350 nm versus the concentration of 5,5′-dibromo-2,2′-bipyridine (**7**) in thf at 25 °C. The solid line is the calculated data based on Equation (3) with $K_{eq} = (4.7 \pm 0.2) \times 10^3$ and $\varepsilon_{ML} = 2.6 \times 10^4\ \mathrm{M^{-1}\,cm^{-1}}$.

This fitting can only be used for adducts with relatively low formation constants ($K < 10^3$) where the equilibrium concentrations of the bipy ligand are known and the assumption that $[L]_T \approx [L]_{eq} > [M]_T$ is valid. When K is large ($K > 10^3$) the saturation is reached with relatively low $[L]_T$, therefore $[L]_T$ must not be very much greater than $[M]_T$ (i.e. $[L]_T \neq [L]_{eq}$). In these cases, the program PSEQUAD was used to determine the equilibrium constants.[18] This method has been used for the determination of relatively large formation constants based upon spectrophotometric

Table 1. Formation constants and UV/Vis spectroscopic data for MoO_2Cl_2 adducts with different N-bidentate ligands in thf and CH_2Cl_2 at 25 °C.

Ligand	K_{eq} in thf	K_{eq} in CH_2Cl_2	$\lambda^{[a]}$ $(\varepsilon_\lambda)^{[b]}$ in thf	$\lambda^{[a]}$ $(\varepsilon_\lambda)^{[b]}$ in CH_2Cl_2
1	$(9.2 \pm 1.2) \times 10^5$	–	317 (1.4×10^4)	–
2	$(1.6 \pm 0.2) \times 10^4$	–	330 (1×10^4)	–
3	$(9 \pm 3) \times 10^6$	–	320 (1×10^4)	–
4	$(2.4 \pm 0.5) \times 10^6$	–	318 (1.5×10^4)	–
5	$(6.9 \pm 0.7) \times 10^3$	$(2.2 \pm 0.3) \times 10^6$	330 (4.9×10^3)	330 (5×10^3)
6	$(5.7 \pm 0.6) \times 10^4$	–	325 (1.4×10^4)	–
7	$(4.7 \pm 0.2) \times 10^3$	–	350 (2.6×10^4)	–
8	15 ± 5	$(9.6 \pm 0.2) \times 10^2$	360 (2.1×10^4)	360 (2.3×10^4)
9	$(3.8 \pm 0.9) \times 10^6$	–	450 (3.0×10^3)	–
10	$(3.7 \pm 0.36) \times 10^4$	–	340 (5.6×10^3)	–
11	$(2.4 \pm 0.2) \times 10^3$	$(1.4 \pm 0.2) \times 10^6$	350 (2.9×10^3)	350 (3.5×10^3)
12	$(1.2 \pm 0.4) \times 10^3$	$(7 \pm 3) \times 10^5$	330 (2.0×10^4)	355 (9.2×10^3)
13	$(3.9 \pm 0.4) \times 10^3$	–	340 (4.8×10^3)	340 (5×10^3)
14	$(1.0 \pm 0.2) \times 10^4$	–	350 (5.2×10^3)	–
15	$(1.9 \pm 0.1) \times 10^3$	–	330 (8.6×10^3)	–
16	$(1.9 \pm 0.2) \times 10^3$	$(1.1 \pm 0.2) \times 10^6$	360 (2.8×10^4)	385 (1.7×10^4)
17	$(2.7 \pm 0.4) \times 10^3$	$(1.5 \pm 0.2) \times 10^6$	350 (1.7×10^3)	360 (1.5×10^3)
18	$(1.5 \pm 0.4) \times 10^4$	–	350 (5.3×10^3)	–

[a] nm. [b] $\mathrm{M^{-1}\,cm^{-1}}$.

data.[17,19] The PSEQUAD program is designed to calculate the best values for the formation constants of the proposed equilibrium model by employing a nonlinear least-squares approach. The data for 5,5′-dibromo-2,2′-bipyridine (**7**) were checked by both methods, and the agreement in the values of K was found to be within the experimental errors of 4.2×10^3 and 4.5×10^3 for the nonlinear least-squares and PSEQUAD approaches, respectively. Another method (*competition method*, see Exp. Sect.) was used to determine formation constants with large values. The UV/Vis absorbance data used to obtain information about the equilibrium concentrations were collected in the presence of two competing bidentate ligands, both of which are in equilibrium with the complex. If both ligands are present in large enough amounts, which means that the free complex does not exist, the following equilibrium [Equation (4)] is considered.

$$\mathrm{ML'} + \mathrm{L''} \rightleftharpoons \mathrm{ML''} + \mathrm{L'} \quad r = K''/K' \tag{4}$$

To ensure that the complex exists only in the adduct forms, this method is used in the presence of an excess of L′ and L″ with respect to the Mo complex, in other words L′ and L″ > $[\mathrm{M}]_\mathrm{T}$ (at least 10 times larger). The changes in absorbance were measured at a wavelength at which neither L′ nor L″ absorb significantly. Under these conditions, the changes in absorbance due to the formation of ML″ from ML′ can be expressed by Equation (5) (in a 1.0-cm path length).

$$Abs = \varepsilon_{\mathrm{ML'}}[\mathrm{ML'}] + \varepsilon_{\mathrm{ML''}}[\mathrm{ML''}] \tag{5}$$

where $\varepsilon_{\mathrm{ML'}}$ and $\varepsilon_{\mathrm{ML''}}$ are the molar absorptivities for the adducts (ML′) and (ML″), respectively. Substituting the formation constants, or their ratio ($r = K''/K'$), into Equation (5), and using the molar balance $[\mathrm{M}]_\mathrm{T} = [\mathrm{ML'}] + [\mathrm{ML''}]$, gives Equation (6). Complete derivation of Equation (6) is given in Appendix II (Supporting Information).

$$Abs = \{\varepsilon_{\mathrm{ML'}} + \frac{(\varepsilon_{\mathrm{ML''}} - \varepsilon_{\mathrm{ML'}})\cdot r\cdot[\mathrm{L''}]}{[\mathrm{L'}] + r\cdot[\mathrm{L''}]}\}[\mathrm{M}]_\mathrm{T} \tag{6}$$

The spectrophotometric data obtained at fixed $[\mathrm{M}]_\mathrm{T}$ and [L′] and by varying [L″] can be fitted to Equation (6) to determine the unknown formation constant (K'') of an adduct from the known value (K') of another one. As shown in Equation (6), if ML′ has a higher molar absorptivity than ML″ at the measuring wavelength (i.e. $\varepsilon_{\mathrm{ML'}} > \varepsilon_{\mathrm{ML''}}$), the absorbance will decrease upon the addition of L″ to a solution of ML′. In the opposite case, the absorbance will increase when L″ is added. Equation (6) can therefore always be used under the condition that $\varepsilon_{\mathrm{ML'}} \neq \varepsilon_{\mathrm{ML''}}$. Under our experimental conditions ($[\mathrm{M}]_\mathrm{T} \approx 0.1$ mM), accurate absorbance measurements were obtained with $\varepsilon_{\mathrm{ML'}}/\varepsilon_{\mathrm{ML}} \geq 100$. Each value of the formation constant was evaluated by at least one method and the results are summarized in Table 1.

Similar methods and treatments were used to calculate the adduct-formation constants of MTO with several bidentate ligands in thf and CH_2Cl_2. The results of these are summarized in Table 2.

The Solvent Effect

Adduct stability in solution is greatly influenced by the nature of the solvent. Thf, for example, is a far stronger coordinating solvent than CH_2Cl_2, therefore the adduct-formation constants in CH_2Cl_2 are much larger. The linear correlation of the formation constants obtained for CH_2Cl_2 [K_eq(DCM)] with those obtained for thf [K_eq(THF)] for the Mo adducts is shown in Figure 3. The slope of the line represents the relative stability of $[MoO_2Cl_2(thf)]$ as compared to $[MoO_2Cl_2(CH_2Cl_2)]$. The results show that the parent complex, MoO_2Cl_2, is about 500 times more stable in thf than in CH_2Cl_2. Similar results were found for the MTO system.

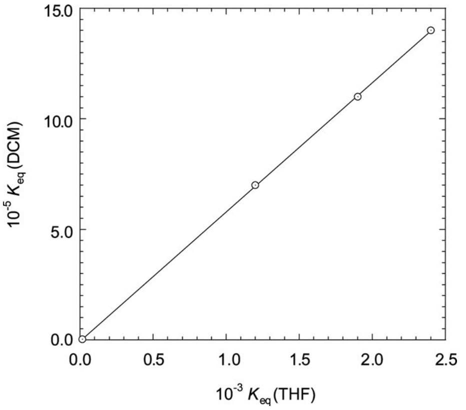


Figure 3. Correlation of the adduct-formation constants in CH_2Cl_2 (DCM) and thf. Data are from Table 1 at 25 °C, and the solid line is a linear fit.

Table 2. Formation constants and UV/Vis spectroscopic data for MTO adducts with 2,2′-bipyridine ligands in thf and CH_2Cl_2 at 25 °C.

Ligand	K_eq in thf	K_eq in CH_2Cl_2	$\lambda^{[a]}$ $(\varepsilon_\lambda)^{[b]}$ in thf	$\lambda^{[a]}$ $(\varepsilon_\lambda)^{[b]}$ in CH_2Cl_2
1	–	$(3.9 \pm 0.2) \times 10^2$	–	360 (8.2×10^2)
2	–	2.9 ± 0.5	–	370 (2.9×10^3)
3	21 ± 2	$(3.9 \pm 0.2) \times 10^3$	360 (9.7×10^2)	360 (1.0×10^3)
4	9.1 ± 1.6	$(1.3 \pm 0.1) \times 10^3$	370 (2.0×10^3)	360 1.0×10^3
5	–	1.2 ± 0.3	–	360 (1.7×10^3)
6	–	12 ± 2	–	350 (3.2×10^3)
9	$(4.1 \pm 0.2) \times 10^3$	$(6 \pm 2) \times 10^5$	376 (1.8×10^4)	370 (3.1×10^4)

[a] nm. [b] $\mathrm{M}^{-1}\,\mathrm{cm}^{-1}$.

The formation constants of MTO-bipy adducts in CH_2Cl_2 are also larger than those in thf. However, the solvent effect is less than that observed for MoO_2Cl_2-bipy adducts. The smaller effect of the solvent on MTO-bipy adduct-formation constants can be attributed to the fact that MTO is highly stable and its coordination to a solvent does not greatly affect its stability.

The Electronic Effect

We have investigated the stability of adducts of MoO_2Cl_2 and MTO with a broad variety of bidentate nitrogen ligands with different groups bound at different positions. Upon coordination, the ligand affects both the electronic and the steric environment of the complex, therefore the presence of electron-donating or electron-withdrawing group(s) on the bidentate ligands influences the stability of the adduct.[17]

The values of the formation constants (shown in Tables 1 and 2) obtained for both Mo and Re systems are highly sensitive to the electronic nature of the ligand, with bidentate ligands bearing more strongly donating groups forming more stable adducts in solution. For example, the presence of CH_3 groups at the 5,5′ positions of 2,2′-bipyridine enhances the stability by a factor of 500 with respect to Br groups. The steric difference between CH_3 and Br groups at these positions can be ignored. The adduct stability of MTO and MoO_2Cl_2 with different 2,2′-bipyridines follows the order 4,4′-dimethyl- > 5,5′-dimethyl- > H > 4,4′-dibromo- > 5,5′-dibromo- >> 5,5′-dinitro-2,2′-bipyridine.

The electronic effect was examined more closely using the Hammett correlation for 4,4′- (*para*) and 5,5′-disubstituted 2,2′-bipyridine (*meta*), as shown in Figure 4. The linear correlation between $\log(K_X/K_H)$ and σ shows that the adduct-formation constant increases with the donating ability of the bidentate ligand.

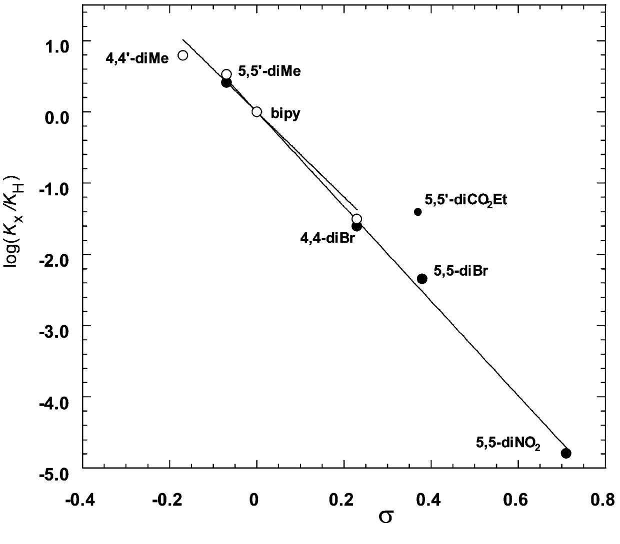


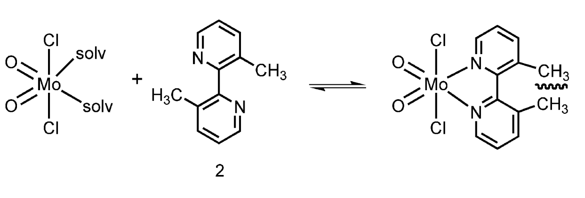
Figure 4. Hammett correlations of the adduct-formation constant for MTO (○) and MoO_2Cl_2 (●) with 2,2′-bipyridine ligands against σ. The reaction constants are $\rho_{Re} = -5.9 \pm 0.6$ and $\rho_{Mo} = -6.6 \pm 0.3$.

Linear correlations, with negative values for the reaction constants ($\rho_{Re} = -5.9$, $\rho_{Mo} = -6.6$), were obtained from the above plots using the Hammett equation [$\log(K_X/K_H) = \rho\sigma$]. This indicates that the metal centers are highly electrophilic and that adduct stability increases with the donating ability of the ligand. The reaction constants have relatively large negative values ($\rho = -2.5$ for MTO-py adducts), which confirms the strong dependence of the adduct stability on the electronic nature of the bidentate ligand, as shown in Tables 1 and 2. This stability trend is also related to the ligand basicity.[17]

The Steric Effect

The coordinating affinity of the bidentate ligands to the Mo^{VI} and Re^{VII} compounds is influenced by both the electronic nature of the ligand and its steric effect, with the formation constants of 6,6′-disubstituted-2,2′-bipyridine adducts with MoO_2Cl_2 being much smaller than other disubstituted 2,2′-bipyridines containing the same groups. For example, the formation constants for 4,4′- and 5,5′-dimethyl-2,2′-bipyridine adducts are three to four orders of magnitude larger than that for sterically hindered 6,6′-dimethyl-2,2′-bipyridine adducts. Only 6,6′-disubstituted 2,2′-bipyridines with electron donating groups, such as methyl, are able to form adducts with MoO_2Cl_2. However, 2,2′-bipyridines with chloro or bromo (electron-withdrawing) groups at the 6,6′-positions do not form adducts with MoO_2Cl_2 in either thf or CH_2Cl_2. In the case of MTO, none of the 6,6′-disubstituted-2,2′-bipyridines are able to form an adduct in both solvents, even at low temperature (0 °C). These results show that MTO is more sensitive to the steric bulk of the bidentate ligands, whereas both MTO and MoO_2Cl_2 adducts show similar sensitivity to electronic factors, as reflected by the Hammett correlation, the values of which (ρ_{Re} and ρ_{Mo}) are very similar.

The results obtained for the adducts with ligands **2**, **13**, and **14** indicate a rigidity (strain) factor. If one considers the electronic factor only, 3,3′-dimethyl-2,2′-bipyridine (**2**) should be similar to 5,5′-dimethyl-2,2′-bipyridine (**4**) as they both have methyl groups at the positions *meta* to the pyridine nitrogens. However, the formation constants of their adducts with MoO_2Cl_2 and MTO show a large difference. Ligand **4** forms adducts with MoO_2Cl_2 and MTO that are 10^2–10^3 times more stable than the adducts formed with ligand **2**. As shown in Scheme 2, 3,3′-dimethyl-2,2′-bipyridine (**2**) is planar (aromatic) with the pyridine nitrogens *trans* to each other to minimize the repulsion between the two methyl groups. Coordination to the metal places the



Scheme 2.

two nitrogens on the same side, which causes a steric strain between the methyl groups and leads to a less stable adduct.

Enthalpy and Entropy of Ligand Formation

The thermodynamic stability of adducts is controlled by both enthalpy and entropy parameters. Negative values of both the enthalpy and entropy have been reported previously for the formation of bipyridine adducts with MTO.[17] The adduct formation constants of MoO_2Cl_2 with 6,6-dimethyl-2,2-bipyridine (**5**) were investigated in CH_2Cl_2 over the temperature interval 5–35 °C. The values of the enthalpy change (ΔH^o = –42.1 ± 0.4 kJ mol^{-1}) and the entropy change (ΔS^o = –18.5 ± 11.6 J K^{-1} mol^{-1}) for the adduct-formation reactions were determined from the temperature dependence of the formation constant by making use of Equation (7) (see Figure 5).

$$\ln(K_{eq}) = \Delta S^o/R - \Delta H^o/R(1/T) \qquad (7)$$

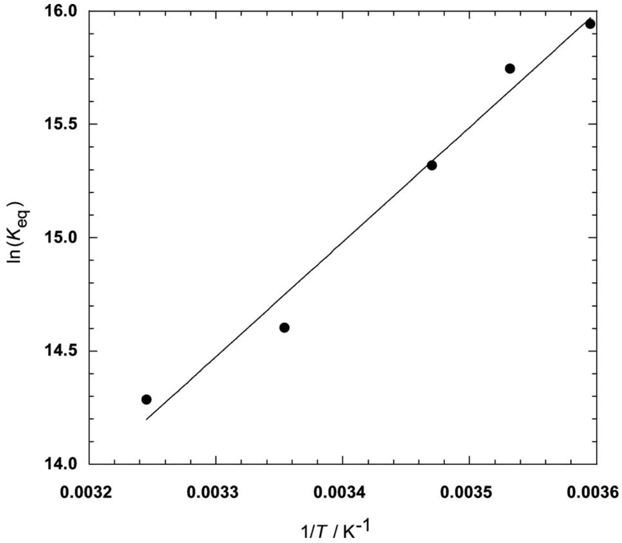


Figure 5. A plot of $\ln(K_{eq})$ vs. $1/T$ for adduct formation between MoO_2Cl_2 and 6,6′-dimethyl-2,2′-bipyridine (**5**) in CH_2Cl_2.

A negative enthalpy is expected[17] due to the replacement of relatively weak ligands (i.e. solvent) with strong ones (i.e. bipyridine). The value obtained for the MoO_2Cl_2/**5** adduct (ΔH^o = –42.1 kJ mol^{-1}) is within the range of enthalpy values for 2,2′-bipyridine adducts of d^0-metal complexes.

The entropy changes are due to the changes in the entropies of the solvent and the bipyridine ligand (i.e $\Delta S^o = \Delta S^s + \Delta S^l$).[20] Two solvent molecules are released during adduct formation, therefore ΔS^s must be positive. Similarly, the change in ligand entropy (ΔS^l) upon complexation is responsible for the negative reaction entropy and must also be negative. The small negative entropy change indicates that the stability is mainly governed by enthalpic rather than entropic considerations. In conclusion, the reaction thermodynamic parameters are mostly dependent on the nature of the ligand – it is the binding strength of the bipyridine ligand and the associated entropy change that make the most important contribution to the values of ΔH^o and ΔS^o, respectively. However, the value of ΔS^o is small and has little effect on the adduct stability. The donor ability of the ligand, which is clearly demonstrated by the Hammett correlation above, must therefore play a major role in adduct formation and stability.

MTO vs. MoO_2Cl_2 Adducts

In the absence of strongly coordinating ligands, such as pyridines and bipyridines, MTO is much more stable than MoO_2Cl_2 in solution. MTO is known for its high stability in most organic solvents and aqueous solutions, whereas MoO_2Cl_2 is only stable in strong (and dry) coordinating organic solvents, such as thf and DMSO. Mono- and bidentate nitrogen ligands greatly enhance the stability of MoO_2Cl_2 by forming 1:1 or 1:2 (M:L) adducts. The results of this study clearly show that MTO-bipy adducts are less stable in solution (relative to the solvent adduct depicted in Scheme 1) than the MoO_2Cl_2-bipy adducts. MTO adducts with Lewis base ligands are usually prepared in weakly coordinating solvents, such as $CHCl_3$ or diethyl ether, and are not stable in strongly coordinating solvents such as thf. The formation constants of MTO-L adducts in thf are, relatively speaking, very small. In fact, most pyridine and bipyridine ligands (especially those with electron-withdrawing groups) do not form adducts with MTO in thf solution. This agrees with our previous observation of ligand exchange results on both systems[4e,11b] – the exchange is rapid and complete when a better donor ligand is added to a solution of MTO adduct. In the case of MoO_2Cl_2 adducts, the exchange is not prominent and the adducts are of comparatively high stability even in strongly coordinating solvents such as thf. As repeatedly stated above, MoO_2Cl_2 is not stable (solvent dependent) and its applications in catalytic oxidation are therefore limited due to decomposition. Bidentate nitrogen ligands are therefore of significant importance for the catalytic application of the MoO_2Cl_2 system, especially in epoxidation reactions at elevated temperatures.

Conclusions

Bidentate nitrogen ligands form highly stable adducts with MoO_2Cl_2 and relatively less stable adducts with MTO in organic solvents. The formation constant (adduct stability) is governed by both electronic and steric effects. Thus, whereas 6,6-disubstituted 2,2-bipyridine ligands do not form adducts with MTO, they form (less stable) adducts with MoO_2Cl_2. It seems that bidentate ligands fit well with systems of the form MoO_2X_2 (X = halo or alkyl) whereas monodentate ligands are more suitable for the MTO system. The MTO adducts are not stable in solution, except when the ligand contains good donor groups such as methyl or amino, and a large excess of ligand is needed to force complexation. This would lead to a basic solution (Brønsted basicity) and enhance the decomposition of

MTO, especially under catalytic oxidation conditions with H_2O_2.[21] The $[MoO_2Cl_2L_2]$ (L_2 is a bidentate N-ligand) adducts with strong donor ligands are almost completely formed when the metal and the ligand are present in a 1:1 ratio. The adduct formation is crucial for Mo catalytic applications. With this large variety of ligands, one can choose a suitable adduct for a certain reaction based on stability, solubility, activity, and other reaction conditions.

Experimental Section

Material and Methods: All experimental work and manipulations were carried out using standard Schlenk techniques under argon. Solvents were dried by standard procedures (thf, hexane, and diethyl ether over Na/benzophenone ketyl; CH_2Cl_2 and CH_3CN over CaH_2), distilled, and kept under argon over molecular sieves. Solution NMR spectra were measured with Bruker CXP 300 (^1H: 300 MHz), Bruker Avance DPX-400 (^1H: 400 MHz; ^{13}C: 100.28 MHz; ^{95}Mo: 26.07 MHz), and JEOL NMR GX-400 (^{13}C: 100.28 MHz; ^{17}O: 54.14 MHz) spectrometers. The UV spectra were measured with a JASCO UV/Vis V-550 spectrophotometer connected to a water-circulating temperature control unit.

MoO_2Cl_2 was purchased from Aldrich and used as received. The starting complex $[MoO_2Cl_2(thf)_2]$ was prepared by treating MoO_2Cl_2 with thf according to published procedures.[5] The bipy ligands 2,2′-bipyridine, 4,4′-dimethyl-2,2′-bipyridine, and 3,6′-bis(2-pyridyl)pyridazine, were obtained from Aldrich and used without further purification. The remaining nitrogen ligands[22] and MTO[3a,23] were prepared according to known literature procedures.

Formation Constant Measurements: The formation constants of MTO and MoO_2Cl_2 adducts with a series of bidentate nitrogen ligands were determined from spectrophotometric data obtained from homogeneous solutions at equilibrium containing the metal complex, the bidentate ligand(s), and the adduct, using the following methods:

I. Direct Method: A UV/Vis spectrophotometric method was used to determine the formation constants of the bidentate ligand adducts with MoO_2Cl_2 and MTO (Scheme 1). In a typical experiment, a 0.1–0.2 mM solution of $[MoO_2Cl_2(thf)_2]$ (or MTO) in thf or CH_2Cl_2 in a quartz cuvette with a 1-cm path length (total volume: 3.0 mL) was treated with successive aliquots of a solution of the ligand, of known concentration, in the same solvent. The UV/Vis spectra were recorded in the range 200–500 nm for the solution before and after each addition of the ligand aliquot. The values of the formation constants and extinction coefficients of each adduct at a certain wavelength were determined by fitting the equilibrium absorbance to Equation (2) or (3) by the nonlinear least-squares method or using the PSEQUAD computer program.[18]

II. Competition Method: This method is based on the replacement of a weaker bidentate ligand (L', for which K' is known) with a stronger one (L'', for which K'' is unknown) and was used for the MoO_2Cl_2 adducts which had relatively high formation constants ($K \geq 10^4$). First, the formation of the weaker adduct $[MoO_2Cl_2L_2']$ (0.1–0.2 mM), with known formation constant (K'), was established in the presence of at least a 10-fold excess of L' with respect to Mo in thf or CH_2Cl_2 solution in a quartz cuvette (1-cm path length, total volume = 3.0 mL). Then, successive aliquots of a solution of L'', of known concentration and in the same solvent, were added. After equilibrium was reached in the solution (waiting period 10–30 min), UV/Vis spectra were recorded in the range 200–500 nm for the solution before and after each addition of L''. The ratio ($r = K''/K'$) was determined by fitting the equilibrium absorbance to Equation (6) using the nonlinear least-squares method with the Kaleidagraph program.

Supporting Information (see also the footnote on the first page of this article): Full derivations of Equations (2) and (6).

Acknowledgments

A. M. A. thanks the Alexander von Humboldt Foundation for a Georg Forster Fellowship. A. G. acknowledges the Bavarian elite network NanoCat for a Ph. D. grant and for financial support of the project. M.-D. Z. thanks the International Graduate School of Science and Engineering for a Ph.D. grant. Dr. Hugh Chaffey-Millar and Ms. Sci. Kavita R. Jain are acknowledged for proofreading the manuscript.

[1] a) F. E. Kühn, A. M. Santos, M. Abrantes, *Chem. Rev.* **2006**, *106*, 2455; b) J.-M. Bregeault, *Dalton Trans.* **2003**, 3289; c) K. A. Jørgensen, *Chem. Rev.* **1989**, *89*, 431.

[2] a) F. E. Kühn, J. Zhao, W. A. Herrmann, *Tetrahedron: Asymmetry* **2005**, *16*, 3469; b) S. B. Kumar, M. Chaudhury, *J. Chem. Soc., Dalton Trans.* **1991**, 2169; c) P. Palanca, T. Picher, V. Sanz, P. Gomez-Romero, E. Llopis, A. Domenech, A. Cervilla, *J. Chem. Soc., Chem. Commun.* **1990**, 531; d) J. P. Wilshire, L. Leon, P. Bosserman, D. T. Sawyer, *J. Am. Chem. Soc.* **1979**, *101*, 3379; e) J. M. Berg, R. H. Holm, *J. Am. Chem. Soc.* **1985**, *107*, 925; f) J. P. Caradonna, E. W. Harlan, R. H. Holm, *J. Am. Chem. Soc.* **1986**, *108*, 7856; g) F. J. Feher, K. Rahimian, T. A. Budzichowski, J. W. Ziller, *Organometallics* **1995**, *14*, 3920; h) R. Clarke, M. Gahagan, R. K. Mackie, D. F. Foster, D. J. Cole-Hamilton, M. Nicol, A. W. Montford, *J. Chem. Soc., Dalton Trans.* **1995**, 1221; i) J. R. Backhouse, H. M. Lowe, E. Sinn, S. Suzuki, S. Woodward, *J. Chem. Soc., Dalton Trans.* **1995**, 1489; j) U. Piarulli, D. N. Williams, C. Floriani, G. Gervasio, D. Viterbo, *J. Chem. Soc., Dalton Trans.* **1995**, 3329.

[3] a) E. Tosh, J. K. M. Mitterpleininger, A. M. J. Rost, D. Veljanovski, W. A. Herrmann, F. E. Kühn, *Green Chem.* **2007**, *9*, 1296; b) W. Wang, Y. Jiang, M. Hunger, *Catal. Today* **2006**, *113*, 102; c) J. Q. Chen, A. Bozzano, B. Glover, T. Fuglerud, S. Kvisle, *Catal. Today* **2005**, *106*, 103; d) F. E. Kühn, M. Groarke in *Applied Homogeneous Catalysis with Organometallic Compounds*, vol. 3 (Eds.: B. Cornils, W. A. Herrmann), Wiley-VCH, Weinheim, New York, **2002**; e) A. M. Al-Ajlouni, J. H. Espenson, *J. Org. Chem.* **1996**, *61*, 3969; f) A. M. Al-Ajlouni, J. H. Espenson, *J. Am. Chem. Soc.* **1995**, *117*, 9243.

[4] a) C. Freund, W. Herrmann, F. E. Kühn, *Topics in Organometallic Chemistry*, vol. 22, Springer, Berlin, Heidelberg, **2007**, p. 39; b) F. E. Kühn, *Multiphase Homogeneous Catalysis*, vol. 1, Wiley-VCH, Weinheim, **2005**, p. 210; c) F. E. Kühn, A. M. Santos, W. A. Herrmann, *Dalton Trans.* **2005**, *15*, 2483; d) F. E. Kühn, R. W. Fischer, W. A. Herrmann, *Transition Metals for Organic Synthesis*, vol. 2, 2nd ed., Wiley-VCH, Weinheim, **2004**, p. 357; e) P. Ferreira, W. M. Xue, E. Bencze, E. Herdtweck, F. E. Kühn, *Inorg. Chem.* **2001**, *40*, 5834.

[5] H. L. Krauss, W. Huber, *Chem. Ber.* **1961**, *94*, 183.

[6] R. H. Fenn, *J. Chem. Soc. A* **1969**, 1764.

[7] C. G. Hull, M. B. H. Stiddart, *J. Chem. Soc. A* **1966**, 1633.

[8] G. Barea, A. Lledos, F. Maseras, Y. Jean, *Inorg. Chem.* **1998**, *37*, 3321.

[9] M. N. Sheng, G. J. Zajaczek, ARCO, GB 1,136,923, **1968**.

[10] J. Kollar, Halcon, US 3,350,422 and US 3,351,635, **1967**.

[11] a) F. E. Kühn, E. Herdtweck, J. J. Haider, W. A. Herrmann, I. S. Goncalves, A. D. Lopes, C. C. Romao, *J. Organomet. Chem.* **1999**, *583*, 3; b) F. E. Kühn, A. D. Lopes, A. M. Santos, E. Herdtweck, J. J. Haider, C. C. Romao, A. G. Santos, *J. Mol.*

Catal. A **2000**, *151*, 147; c) F. E. Kühn, A. M. Santos, A. D. Lopes, I. S. Goncalves, E. Herdtweck, C. C. Romao, *J. Mol. Catal. A* **2000**, *164*, 25; d) F. E. Kühn, A. M. Santos, A. D. Lopes, I. S. Goncalves, J. E. RodrIguez-Borges, M. Pillinger, C. C. Romao, *J. Organomet. Chem.* **2001**, *621*, 207; e) A. M. Santos, F. E. Kühn, K. Bruus-Jensen, I. Lucas, C. C. Romao, E. Herdtweck, *J. Chem. Soc., Dalton Trans.* **2001**, 1332; f) I. S. Goncalves, C. C. Romao, A. M. Santos, A. D. Lopes, J. E. Rodrigues-Borges, M. Pillinger, P. Ferreira, F. E. Kühn, J. Rocha, *J. Organomet. Chem.* **2001**, *626*, 1.

[12] J. M. Mitchell, N. S. Finney, *J. Am. Chem. Soc.* **2001**, *123*, 862.

[13] F. E. Kühn, A. M. Santos, I. S. Goncalves, C. C. Romao, A. D. Lopes, *Appl. Organomet. Chem.* **2001**, *15*, 43.

[14] a) F. E. Kühn, A. M. Santos, P. W. Roesky, E. Herdtweck, W. Scherer, P. Gisdakis, I. V. Yudanov, C. D. Valentin, N. Rösch, *Chem. Eur. J.* **1999**, *5*, 5603; b) W. R. Thiel, J. Eppinger, *Chem. Eur. J.* **1997**, *3*, 696.

[15] A. M. Al-Ajlouni, A. A. Valente, C. D. Nunes, M. Pillinger, A. M. Santos, J. Zhao, C. C. Romao, I. S. Goncalves, F. E. Kühn, *Eur. J. Inorg. Chem.* **2005**, 1716.

[16] a) A. Togni, L. M. Venanzi, *Angew. Chem.* **1994**, *106*, 517; *Angew. Chem. Int. Ed. Engl.* **1994**, *33*, 497; b) F. Fache, E. Schulz, M. L. Tommasino, M. Lemaire, *Chem. Rev.* **2000**, *100*, 2159; c) F. Fache, B. Dunjic, P. Gamez, M. Lemaire, *Top. Catal.* **1997**, *4*, 201; d) A. K. Ghosh, P. Mathivanan, J. Cappiello, *Tetrahedron: Asymmetry* **1998**, *9*, 1.

[17] a) S. M. Nabavizadeh, *Inorg. Chem.* **2003**, *42*, 4204; b) S. M. Nabavizadeh, *Dalton Trans.* **2005**, 1644; c) S. M. Nabavizadeh, A. Akbari, M. Rashidi, *Eur. J. Inorg. Chem.* **2005**, 2368.

[18] a) L. Zekan, I. Nagypal, in *Computational methods for the determination of formation constants* (Ed.: D. Leggett), Plenum Press, New York, **1985**; b) L. Zekan, I. Nagypal, *PSEQUAD: A comprehensive program for the evaluation of potentiometric or spectrophotometric equilibrium data using analytical derivatives*, in *Computational methods for the determination of formation constants* (Ed.: D. Leggett), Plenum Press: New York, USA, **1991**.

[19] a) . M. Asadi, E. Safaei, B. Ranjbar, L. Hasani, *New J. Chem.* **2004**, *28*, 1227; b) A. K. Bordbar, M. Keshavarz, H. Aghaei, K. Zare, *Phys. Chem. Liq.* **2006**, *44*, 457.

[20] a) S. Gronert, *Acc. Chem. Res.* **2003**, *36*, 848; b) H. C. Bajaj, P. A. Tregloan, R. van Eldik, *Inorg. Chem.* **2004**, *43*, 1429.

[21] C. Zhang, I. A. Guzei, J. H. Espenson, *Organometallics* **2000**, *19*, 5257.

[22] a) C. P. Whittle, *J. Heterocycl. Chem.* **1977**, *14*, 191; b) G. Maerker, F. H. Case, *J. Am. Chem. Soc.* **1958**, *80*, 2745; c) C. Hiort, P. Lincoln, B. Nordén, *J. Am. Chem. Soc.* **1993**, *115*, 3448.

[23] W. A. Herrmann, A. M. J. Rost, J. K. M. Mitterpleininger, N. Szesni, W. Sturm, R. W. Fischer, F. E. Kühn, *Angew. Chem. Int. Ed.* **2007**, *46*, 7901.

Received: November 12, 2008