Adduct Formation and Stability of Methyltrioxorhenium(VII) with a Series of Aliphatic and Aromatic Nitrogen–Donor Ligands

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Abstract

The stability of a variety of aromatic and aliphatic N-donor ligands adducts of methyltrioxorhenium(VII) (CH_3ReO_3, MTO) was investigated using acetonitrile (CH_3CN) as a solvent. The formation constants were determined by utilization of the obtained spectrophotometric data based on a 1:1 adduct formations. The adduct formation constants (K_f) for MTO**:**L (L = nitrogen donor ligand) are very sensitive to the electronic nature of the ligand and increases with the ligand donating ability. Adducts of aliphatic N-donor ligands are less stable towards decomposition by basic solutions and produce polymeric rhenium material, methane and perrhenate. The kinetics of the adduct decomposition were investigated in solution at room temperature under pseudo-first-order conditions. Linear correlations between the adduct decomposition rate constants (k_d) and (K_a) values of the N-donor ligand have shown that the decomposition rate constants increasing with the N-donor ligand basicity. A comparative study between the values of K_f and k_d revealed that imidazole forms the most stable adduct with MTO among the N-donor ligands investigated in this study.

Keywords: Methyltrioxorhenium; Nitrogen ligands; Adduct formation; Adduct stability; Formation constants.

Introduction

In the presence of peroxides, high-valent d^0 early transition metal oxides are well known for their catalytic oxidative activities.[1] Among these, methyltrioxorhenium(VII), (CH_3ReO_3, MTO), has been most widely utilized as a catalyst or catalyst precursor for the oxidation of different substrates such as olefins, sulfides, amines, halides, and cyclic ketones with hydrogen peroxide.[2] MTO activates H_2O_2 through the formation of two active species (monoperoxide, **A**, and diperoxide, **B**) which exist in equilibrium with MTO and H_2O_2 in solution (Scheme 1). Both species are active oxidants, and they are 10^4-10^5 more reactive than H_2O_2 itself. [3]

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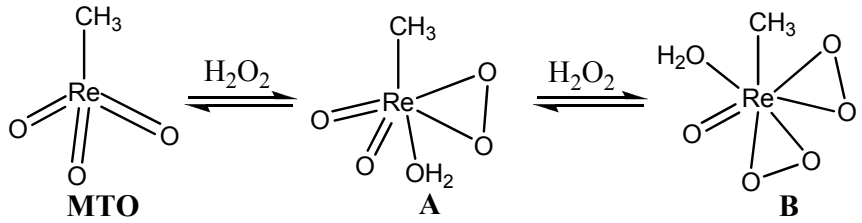


Scheme 1

MTO has been used in aqueous, semi-aqueous, and organic solutions under homogeneous and heterogeneous conditions. [2, 3] It is stable in the solid state as well as in neutral or acidic aqueous and organic solutions. A glance at the literature shows that many articles have been published regarding the effect of aromatic N-donor ligands on the stability and activity of MTO and, to a lesser extent, on MTO adducts with aliphatic N- donor ligands.[4] With mono- and bidentate ligands, such as pyridine and 2,2'-bipyridine, 1:1 adducts of the composition [CH_3ReO_3:L] are formed.[5,6] The activity of d^0 M-oxo catalysts in olefin epoxidation depends on the Lewis base, the redox stability of the ligands, and particularly on the stability of the adduct complexes.[7,8] It was also found that the catalyst activity is affected by the electronic nature of the ligands.[9] As a matter of fact, nitrogen ligands are of great importance in homogeneous catalysis, and can enhance the catalyst solubility in organic solvents.[10] When applying these adducts as catalysts under homogeneous conditions, adduct stability and loss of the N-donor ligand in solution (especially in donor solvents, such as THF or CH_3CN) are of major concern. Even the adduct formation can enhance the activity of MTO and its utilization under different homogeneous and heterogeneous conditions, the ligand Bronsted basicity may lead to MTO decomposition.[11] Therefore, a search for suitable N-donor ligands that form stable adducts with MTO is still going on.

In this work, we investigate the complexation of a series of aliphatic and aromatic N- donor ligands with MTO in CH_3CN. The formation constants were determined to provide direct information about the adduct stability. In addition, the decomposition of MTO due to the basic nature of the N-donor ligand was studied. The electronic and steric effects of the ligands on adduct and MTO stabilities and comparisons between aliphatic and aromatic N- donor ligands are also investigated.

Experimental

Materials and methods:

Acetonitrile was dried over CaH_2, distilled and kept under nitrogen over molecular sieves. Solution NMR spectra were measured on a Bruker CXP 300 (^1H, 300 MHz), Bruker Avance DPX-400 (^1H: 400 MHz; ^{13}C: 100.28 MHz). The UV-vis spectra were carried out on a Shimadzu UV-2401-PC Spectrophotometer connected with a water-circulating temperature control unit. Nitrogen ligands were purchased

from Aldrich and used as received. MTO was prepared according to a literature known procedure.[12]

Formation Constant Measurements:

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

I. *Direct method*: The formation constants of the MTO:L adducts (L = N-donor ligand, see Table 1) were determined using UV-vis absorption data. In a typical experiment, a 0.2-0.5 mM solution of MTO in CH_3CN 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, in the range 200-500 nm, were recorded for the solutions before and after each addition of the ligand aliquots. The values of formation constants of each adduct at a certain wavelength were determined by fitting the equilibrium absorbance using the nonlinear least-squares method shown in the results and discussion section.

II. *Competition method*: This method is based on a replacement of a weaker ligand (L', for which K' is known) with a stronger one (L", for which K" is unknown) and was used for the MTO:L adducts that have relatively high formation constants ($K \geq 10^3$). First, the formation of the weaker adduct MTO:L' (0.2-0.5 mM), with known formation constant (K'), is established in the presence of at least 10 fold excess of L' over MTO in CH_3CN solution in a quartz cuvette. Then, successive aliquots of a solution of L" ligand, of known concentration and in the same solvent, were added. After the equilibrium is established in the solution (waiting period 10-30 min.), the UV-vis spectra in the range 200-500 nm were recorded for the solution before and after each addition of L" aliquot. The ratio (r = K"/K') was determined by fitting the equilibrium absorbance to the method of nonlinear least-squares, as shown in the results and discussion section, using the KaleidaGraph program, version 3.09.

Kinetic studies

All decomposition reactions were carried out in CH_3CN at 25.0 ± 0.5 °C (controlled by water-circulating cooling/heating system). Kinetic data were collected by following the absorbance changes due to the decomposition of the MTO:L adduct in the region 300-400 nm. All UV-vis experiments were done in the presence of 10 fold excess [ligand] over the [MTO]. The MTO concentrations were varied (0.05-1.0 mM). The change in the absorbance followed first-order kinetics. The observed-first-order rate constants were evaluated by nonlinear least-square fitting of the absorbance-time curves to a single exponential equation (Eq. 1), where Abs_t, Abs_o and Abs_∞

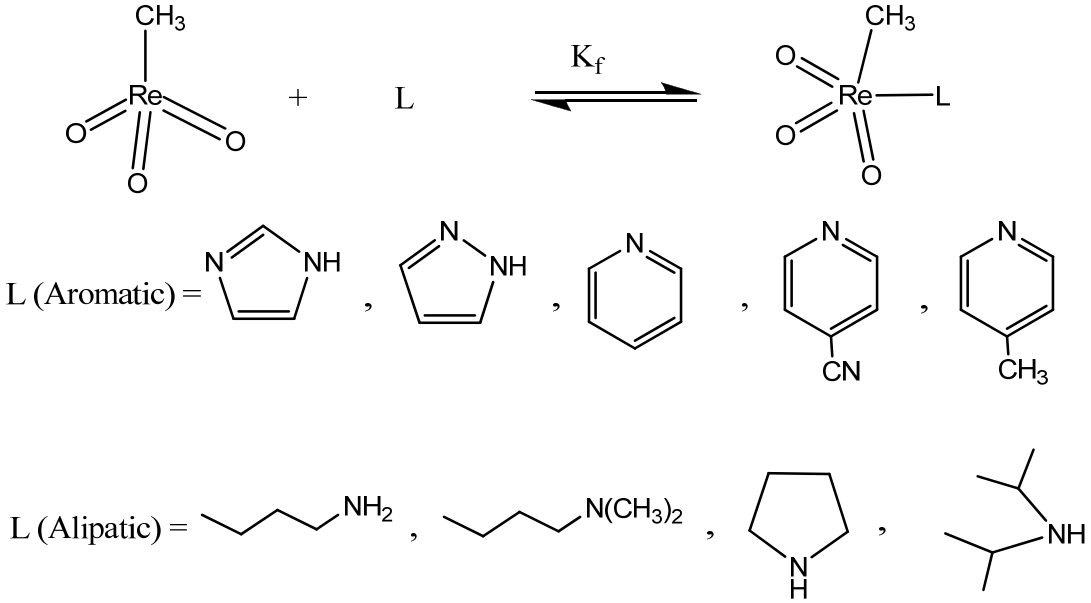
$$\mathbf{Abs_t = Abs_\infty + (Abs_o - Abs_\infty)exp(-k_d t)} \qquad \mathbf{(1)}$$

are the absorbance at anytime, initial and final, respectively; and k_d is the observed-first-order rate constant. The data were also analyzed by the KaleidaGraph program.

Results and discussion

Methyltrioxorhenium (MTO) is a Lewis acid and an electrophilic catalyst.[13,14] In organic solution, good Lewis bases (or nucleophiles) replace the solvent molecules and form stable adducts. Depending on the nature of the ligand and solvent, the formed adduct exists in equilibrium with the Re-solvent complex and free ligand. It is worth mentioning that adducts of many aromatic N-donor ligands, such as pyridine and bipyridine, with MTO have been used in catalysis. Their adduct formation constants have also been determined.[13,15] In this work, the formation constants of the MTO adducts with various aliphatic and aromatic nitrogen containing bases (shown in Scheme 2) were examined in CH_3CN. Recently, adduct formations of mono- and bi-dentate aromatic nitrogen Lewis bases with MTO have been investigated in various organic solvents. Their stabilities in solution were also investigated.[7,14]

As shown in Scheme 2, a 1:1 adduct is formed between MTO and the N-ligand. The Lewis acid-base adduct formation should lead to electronic and steric saturation of the Re center. In addition, the ligand significantly affects the catalytic activity of the resulting compounds.[7]



Scheme 2

Formation Constants Determination

The formation constants have been determined from the absorbance changes as the equilibrium depicted in Scheme 2 is established. A new absorption band in the range 250 – 400 nm (Figure 1) is usually observed upon formation of the MTO:L adduct with any of the ligands above. The absorbance of the N-donor ligand above

300 nm is negligible and can be ignored (see figure 1). The reaction leads to a 1:1 adduct, existing in equilibrium with the original solvent complex, MTO.solv, and the free nitrogen ligand (Scheme 2). The changes in absorbance due to the formation of MTO:L can be expressed by Eq. 2, where ε_{MTO} and

$$\mathbf{Abs = \varepsilon_{MTO}[MTO] + \varepsilon_{MTO:L}[MTO:L]} \qquad \mathbf{(2)}$$

$\varepsilon_{MTO:L}$ are the molar absorptivities for the free complex and the MTO:L adduct, respectively. Substituting the formation constant (K) for the formation of the MTO:L adduct into Eq. 2, and using the molar balance $[M]_T = [MTO] + [MTO:L]$ we obtain Eq. 3. Complete derivation of Eq 3 is shown in Appendix I (supplementary material).

$$\mathbf{Abs. = \varepsilon_{MTO}[MTO] + \frac{\varepsilon_{MTO.L}.[M]_T.\, K_{eq}\,[L]}{1 + K_{eq}\,[L]}} \qquad \mathbf{(3)}$$

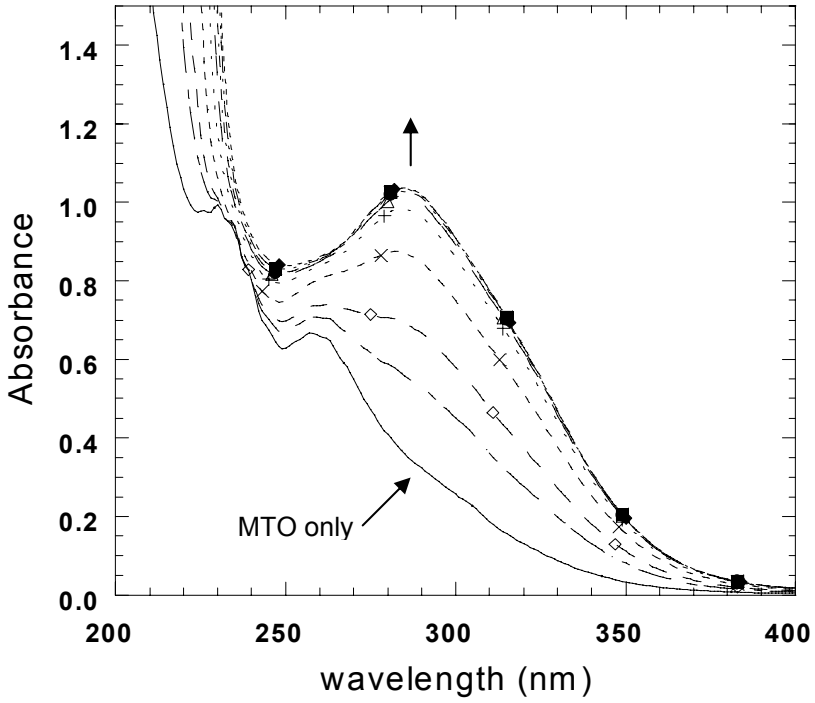


Figure 1: UV-visible spectra of MTO (0.5 mM) before (solid line) and after the addition of imidazole (0.5 (dashed), 1.0 (◊), 2.0 (x), 5.0 (+), 10 (■), 15 (♦)) in CH_3CN at 25 ^oC.

The molar absorptivity of MTO (ε_{MTO}) was determined in the absence of the N-donor ligand and used in Eq. 3. The absorbance versus concentration diagram of solutions of the MTO:L complex with [L] is not like a titration curve (see figure 2). Instead, as more L 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 Eq. 3 allows values for the equilibrium constants to be calculated (Table 1).

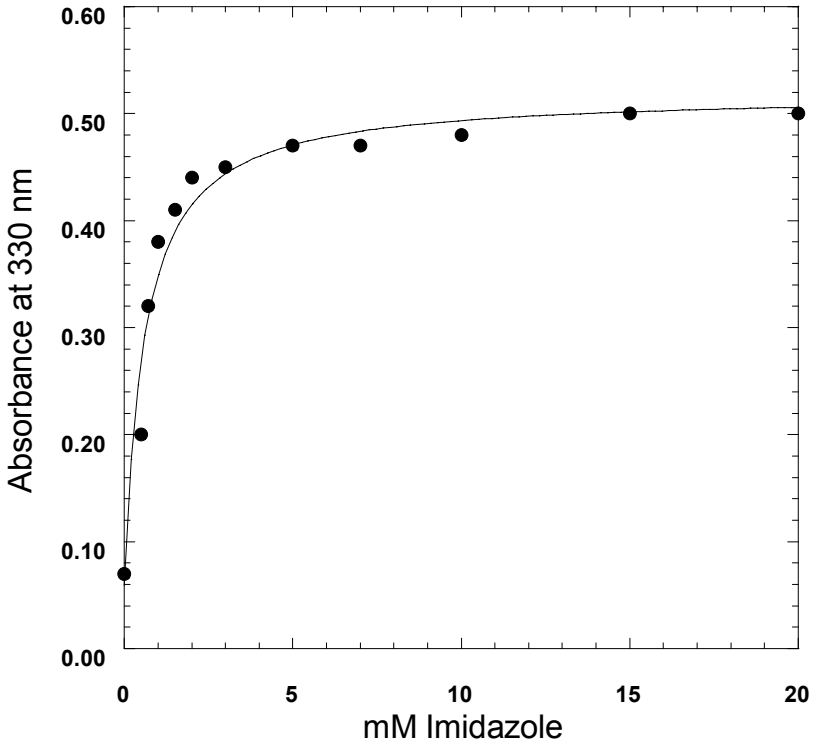


Figure 2: The absorbance change at 330 nm against the concentration of imidazole in CH_3CN at 25 ^oC. The solid line is the calculated data based on Eq. 2 with K_{eq} = (1.7 ± 0.34) x10^3 and $\varepsilon_{MTO.L}$ = 2.6 x 10^4 $M^{-1}cm^{-1}$.

Another method (*competition method*, see experimental section) was used to determine the formation constants with large values. The UV-vis absorbance data, which have been used to obtain information about the equilibrium concentrations, are collected in the presence of two competing ligands, both of which are in equilibrium with the complex. If both ligands are present in large amounts, meaning that the free complex does not exist, the following equilibrium (Eq. 4) is considered. This method is applied in the presence of an excess L'

Table 1: Formation constants and the decomposition rate constants of MTO adducts with aromatic and aliphatic N-donor ligands in CH_3CN at 25 °C.

Ligand	K_a	K_f	k_d/ $10^3 s^{-1}$	10^{-3} K_f/k_d
imidazole	6.99	(1.7 ± 0.34) x 10^3	0.050	34
pyrazole	2.49	36 ± 6	0.025	1.4
pyridine	5.23	(2.0 ± 0.2) x 10^2	0.035	5.7
3-cyanopyridine	1.78	7.5 ± 1.5	0.023	0.33
4-methylpyridine	5.95	(7.4 ± 0.5) x 10^2	0.040	18.5
n-butyl amine	10.59	(5.5 ± 0.8) x 10^2	1.1	0.50
pyrrolidine	11.3	(1.5 ± 0.3) x 10^3	3.0	0.50
N,N-diisopropyl amine	11.05	(8.3 ± 2.2) x 10^2	1.7	0.49
N-butyl-N,N-dimethyl amine	9.99	(2.0 ± 0.4) x 10^2	0.41	0.50

$$ML' + L'' \rightleftharpoons ML'' + L' \qquad r = K''/K' \qquad (4)$$

and L" with respect to the MTO complex, i.e. L' and L" > $[M]_T$.[15] The changes in absorbance are measured at a wavelength for 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 Eq. 5, where $\varepsilon_{ML'}$ and $\varepsilon_{ML''}$ are the molar absorptivities for the adducts (ML') and (ML"), respectively. Substituting the formation constants or their ratio (r = K"/K') into Eq. 5, and

$$\mathbf{Abs = \varepsilon_{ML'}[ML'] + \varepsilon_{ML''}[ML'']} \qquad (5)$$

using the molar balance $[M]_T$ = [ML'] + [ML"], we obtain Eq. 6. Complete derivation of Eq 6 is shown in Appendix II (supplementary material).

$$\mathbf{Abs.} = \left\{ \varepsilon_{ML'} + \frac{(\varepsilon_{ML''} - \varepsilon_{ML'}).r.[L'']}{[L'] + r.[L'']} \right\} [M]_T \qquad (6)$$

Eq. 6 is always applied under the condition that $\varepsilon_{ML'} \neq \varepsilon_{ML''}$. The absorbance change with [L"] obtained at fixed $[M]_T$ and [L'], can be fitted to Eq. 6 to determine the unknown formation constant (K") of an adduct from the known value (K') of another one. Therefore, each value of the formation constant was evaluated by at least one method and the results are summarized in table 1.

The Electronic Effect

In this study, we investigated the adduct formation of MTO with a broad variety of nitrogen-donor ligands. Upon coordination, the ligand affects both the electronic and the steric environment of the complex. The values of the formation constants (shown in table 1) are highly sensitive to the electronic nature of the ligand. Ligands bearing more strongly donating groups form more stable adducts in solution. For example, the presence of CH_3 groups in pyridine increases the formation constant (K_f) by a factor of 3-4 times. On the other hand, the presence of a cyano group decreases K_f by a factor of almost 2 orders of magnitude (~100 times). The electronic effect was also examined by correlating K_f values with the ligand basicity (pK_a). As shown in Figure 3, linear correlations between log(K_f) and pKa for aliphatic and aromatic N-donor ligands clearly indicate that the adduct formation constant is highly sensitive to the ligand basicity confirming that the adduct formation constant increases with the donating ability of the ligand.

The Steric Effect

The coordinating affinity of the N-ligands to MTO is not only influenced by the electronic nature of the ligand but also by its steric effects. The formation constant of MTO:pyrrolidine is ~20 times higher than that of MTO-(N,N-diisopropylamine). Both ligands are secondary amines, and the difference in their K_f values is attributed to the

large steric factor exerted by the latter ligand. For the same reason, the formation constant of the 3°-amine adduct, MTO-(N-butyl-N,N-dimethylamine), is the smallest.

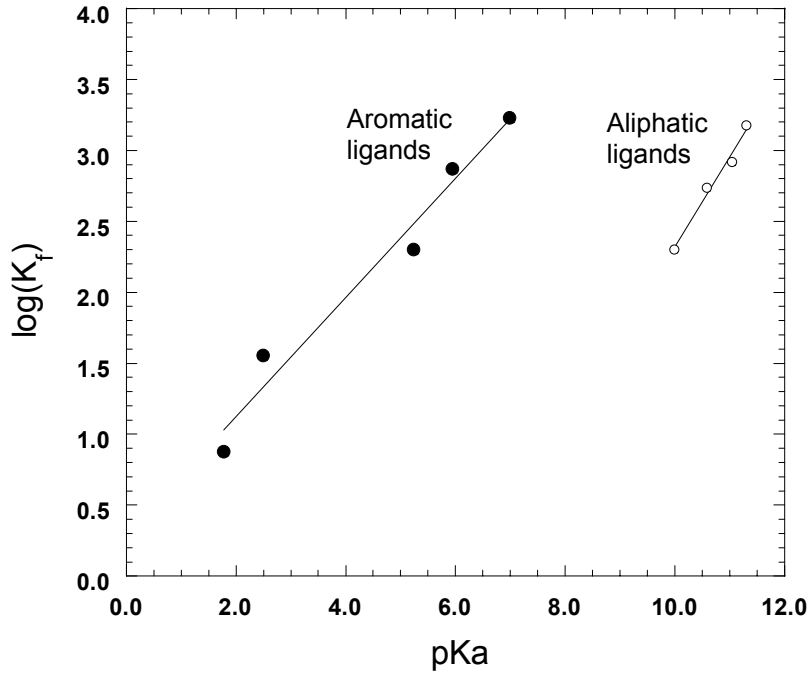


Figure 3: Correlation of the logarithm of the adduct formation constants ($\log K_f$) with pKa of the N-donor ligand. Data are from Table 1 at 25 °C, and the solid lines are linear fit.

The complex stability and decomposition

After formation of the adduct (and equilibrium between the adduct and free MTO and the N-ligand is established), a slow decomposition of MTO:L adduct in CH_3CN is observed. The decomposition rate depends on the electronic and steric nature of the N-ligand. The decomposition rate constants for some of these adducts were determined in the presence of at least 10 fold excess ligand. The decomposition is first order with respect to the adduct, and produces the free ligand, perrhenate and methane.[11] In the presence of H_2O_2, methanol and the N-ligand oxide, in addition to the free ligand and perrhenate, are formed (Scheme 3).

As shown in table 1, the decomposition rate constant, k_d, increases with the ligand basicity. The adducts of aromatic N-ligands are significantly more stable than those of the aliphatic ones. This is probably attributed to the fact that aromatic N-ligands are relatively "soft" bases (due to the presence of the π-system electrons) and form more stable complexes with transition metal ions. The decomposition rate is also correlated with pK_a of the N-ligand and the linear correlation (presented in figure 4) shows the direct effect of the ligand basicity on the complex stability.

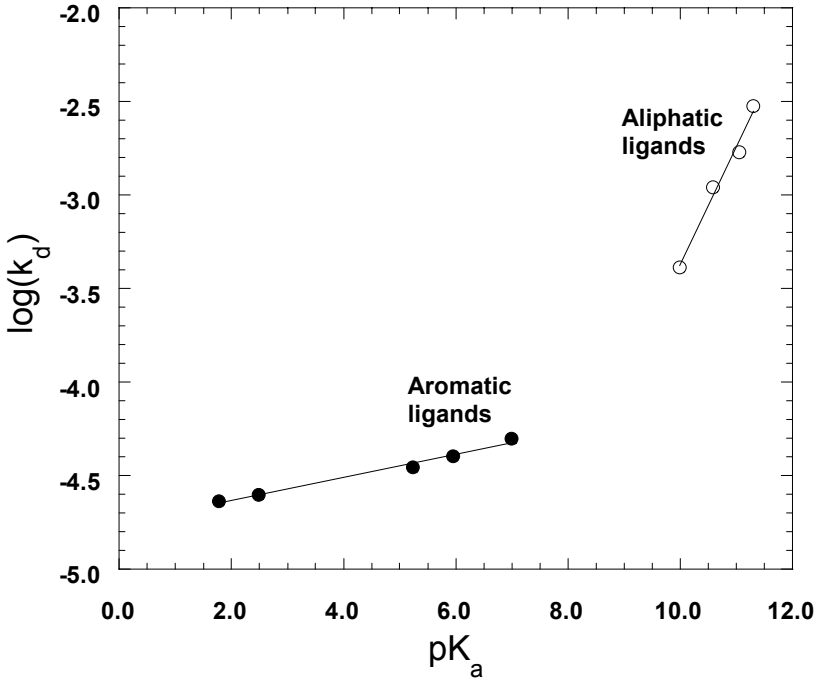
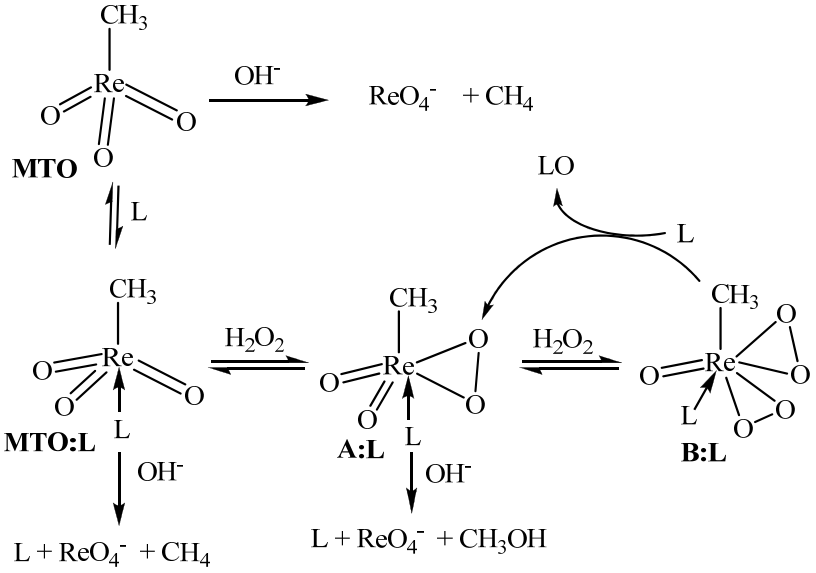


Figure 4: Correlation of the logarithm of the decomposition rate constants of the adduct ($logk_d$) with pKa of the N-donor ligands. Data are from Table 1 at 25 °C, and the solid lines are linear fit.

Furthermore, the results in Table 1 show that k_d for pyrrolidine (2°) is more than k_d for N,N-diisopropylamine (2°), indicating that the steric factor of the N-ligand does not significantly influence the decomposition rate of the adduct. Confirming the finding that the adduct decomposition is directly related to the basic strength of the N-ligand. In a previous study it has shown that MTO decomposes in basic media, Scheme 3,[16] and the solution Bronsted basicity is responsible for the decomposition of the MTO and/or MTO:L adduct.



Scheme 3

Conclusion

The adduct stability of aromatic heterocyclic N-donor ligands with MTO is significantly higher than that of aliphatic ones. In both cases, however, the adduct formation constant values of MTO:L are highly sensitive to the basic strength of the ligand. On the other hand, the adduct decomposition in solution is sensitive to the aromatic/aliphatic nature of the ligand and to the ligand Bronsted basicity. Steric hindrance does not significantly influence the adduct decomposition rate. This is in agreement with the previous proposed mechanism for the decomposition of MTO in basic solutions. In fact, a basic solution enhances the formation of a carbene intermediate that leads to MTO decomposition rather than coordination of the base to MTO in a Lewis base/Lewis acid fashion.[16] Harder bases prefer to attack the methyl (or H) group and softer bases prefer to bind to the metal center. Compared to the aliphatic N-donor ligands, aromatic heterocyclic N-donor ligands have proven to form more stable adducts in solutions toward ligand binding to the Re center and decomposition of MTO to perrhenate. In a closer look to the values of K_f and k_d, imidazole has the highest K_f/k_d ratio (Table 1) which reflects the MTO-ligand binding strength relative to the decomposition rate. Naturally, imidazole (as part of the amino acid histidine) binds to many metal centers in enzymes and other biological molecules, such as hemes, peroxidase and catalase enzymes.

Acknowledgements

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References

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

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

[3] a) Tosh, E.; Mitterpleininger, J. K.; Rost, A. M.; Veljanovski, D.; Herrmann, W. A.; Kühn, F. E., *Green Chem.,* 2007, *9*(12), 1296. b) Wang, W.; Jiang, Y.; Hunger, M., *Cat. Today,* 2006, *113*(1-2), 102. c) Al-Ajlouni, A. M.; Espenson, J. H., *J. Org. Chem.,* 1996, *61*, 3969. d) Al-Ajlouni, A. M.; Espenson, J. H., *J. Am. Chem. Soc.,* 1995, *117*, 9243.

[4] a) Freund, C. ; Herrmann, W. ; Kühn, F. E., *Top. Organomet. Chem*., 2007, *22*, 39. b) Kühn, F. E., *Multiphase Homogeneous Catalysis,* 2005, *1*, 210. c) Kühn, F. E. ; Santos, A. M. ; Herrmann, W. A., *J. Chem. Soc. Dalton Trans*., 2005, *15*, 2483. d) Kühn, F. E. ; Fischer, R. W. ; Herrmann, W. A., ''Transition Metals for Organic Synthesis'', Beller , M.; Bolm, C.; Eds.; 2nd Edn. ; Wilrey: New York, 2004, Vol. 2, 357. e) Ferreira, P. ; Xue, W. M. ; Bencze, E. ; Herdtweck, E.; Kühn, F. E., *Inorg. Chem*., 2001, *40*, 5834.

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

[6] Fenn, R. H., *J. Chem. Soc. A,* 1969, 1764.
[7] Kühn, F. E.; Santos, A. M.; GonAalves, I. S.; Romao, C. C.; Lopes, A. D., *Appl. Organomet. Chem*., 2001, *15*, 43.
[8] a) Kühn, F. E.; Santos, A. M.; Roesky, P. W.; Herdtweck, E.; Scherer, W. ; Gisdakis, P.; Yudanov, I. V.; Valentin, C. D.; Rösch, N., *Chem. Eur. J*., 1999, *5*(12), 5603. b) Thiel, W. R.; Eppinger, J., *Chem. Eur. J*., 1997, *3*(5), 696.
[9] Al-Ajlouni, A. M.; Valente, A. A.; Nunes, C. D. ; Pillinger, M.; Santos, A. M.; Zhao, J.; Romão, C. C. ; Gonçalves,I. S.; Kühn, F. E., *Eur. J. Inorg. Chem*., 2005, 1716.
[10] a) Togni, A.; Venanzi, L. M., *Angew. Chem., Int. Ed. Engl.,* 1994, *33*, 497-526; *Angew. Chem.,* 1994, *106*, 517. b) Fache, F.; Schulz, E.; Tommasino, M. L.; Lemaire, M., *Chem. Rev.,* 2000, *100*, 2159. c) Fache, F.; Dunjic, B.; Gamez, P.; Lemaire, M., *Top. Catal.,* 1997, *4*, 201. d) Ghosh, A. K.; Mathivanan, P.; Cappiello, J., *Tetrahedron Asymm.,* 1998, *9*, 1.
[11] Kuhn , F. E.; Scherbaum, A.; Herrmann, W. A., J. Organomet. Chem., 2004, 689, 4149.
[12] a) Herrmann, W. A.; Rost, A. M.; Mitterpleininger, J. K.; Szesni, N.; Sturm, W.; Fischer, R. W.; Kühn, F. E., *Angew. Chem. Int. Ed.,* 2007, *46*, 7901. b) Tosh, E.; Mitterpleininger, H. K.; Rost, A. M.; Veljanovski, D.; Herrmann, W. A.; Kühn, F. E., *Green Chem.,* 2007, *12*, 1296.
[13] a) Nabavizadeh, S. M., *Inorganic Chemistry*, 2003, *42* (13), 4204. b) Nabavizadeh, S. M., *J. Chem. Soc. Dalton Trans.,* 2005, 1644. c) Nabavizadeh, S. M.; Akbari, A.; Rashidi, M., *Eur. J. Inorg. Chem.,* 2005, 2368.
[14] Nabavizadeh, S. M.; Rashidi, M.*, J. Am. Chem. Soc.,* 2006, *128*, 351.
[15] Al-Ajlouni, A. M.; Günyar, A.; Zhou, M-D.; Baxter, P. N.; Kühn, F. E., *Eur. J. Inorg. Chem.,* 2009, 1019.
[16] a) Wang, W-D.; Espenson, J. H., *J. Am. Chem. Soc*., 1998, 120, 11335 b) Zhang, C.; Guzei, I. A.; Espenson, J. H., *Organometallics*, 2000, *19*, 5257-525.

Appendix I: *Derivation of Eq. 3*

According to the adduct formation equilibrium (Scheme 2 text), the absorbance at λ can be expressed as follow:

$$Abs = Abs_M + Abs_{ML} = [M].\varepsilon_M + [ML].\varepsilon_{ML} \quad (1)$$

where Abs_M and Abs_a are the absorbance of the free metal (M) and the adduct (ML), and ε_M and ε_{ML} are their extinction coefficients, respectively.

Using the equilibrium expression:

$$K_{eq} = [ML]/[M][L] \quad (2)$$

With the total mass balance expression, $[M]_T = [M] + [ML]$, Eq. 2 can be written as follow:

$$[ML] = K_{eq}[M]_T[L]/(1 + K_{eq}[L]) \quad (3)$$

Replacing [ML] in Eq. 1 by using Eq. 3 gives:

$$Abs = [M].\varepsilon_M + \varepsilon_{ML}.K_{eq}[M]_T[L]/(1+K_{eq}[L]) \quad (4)$$

Appendix II: *Derivation of Eq. 6*

The absorption data were collected at wavelength (λ) where both adducts (Eq. 5 text) absorb light. Therefore, the absorbance at λ can be expressed as follow:

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

where $\varepsilon_{ML'}$ and $\varepsilon_{ML''}$ are the extinction coefficients of ML' and ML", respectively.

With the total mass balance expression, $[M]_T = [ML'] + [ML'']$, Eq. 1 can be written as follow:

$$Abs = \varepsilon_{ML'}[M]_T + (\varepsilon_{ML''} - \varepsilon_{ML'})\,[ML''] \quad (2)$$

Using the equilibrium expression, $r = K''/K' = [ML''][L']/[ML'][L'']$ and the total mass balance expression, $[M]_T = [ML'] + [ML'']$, the concentration of [ML"] at equilibrium is:

$$[ML''] = r.[M]_T[L'']/([L'] + r.[L'']) \quad (3)$$

Replacing [ML"] in Eq. 2 by using Eq. 3 gives:

$$Abs = [M]_T.\varepsilon_{ML'} + (\varepsilon_{ML''} - \varepsilon_{ML'}).r.[M]_T[L'']/([L']+ r.[L'']) \quad (4)$$