Double deprotonation of coordinated ethylimide to CH_3CN: molecular mechanism and relevance to the chemistry of Mo and W organoimides

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Received 10th February 2006, Accepted 31st March 2006
First published as an Advance Article on the web 21st April 2006
DOI: 10.1039/b602038k

Reaction of $[MCl(NEt)(dppe)_2]Cl$ (M = Mo, W) with *n*-BuLi in *tert*-butyl methyl ether under an N_2 atmosphere yields the M(0) bis(dinitrogen) complexes $[M(N_2)_2(dppe)_2]$ and acetonitrile. A mechanism is proposed for this reaction which involves an anionic chloro–acetonitrile intermediate. The implications of these findings to the chemistry of Mo and W organoimides are discussed.

Introduction

The derivatization of N-containing ligands in order to introduce nitrogen into organic molecules is an issue of continuing interest.[1] Nitrido complexes of the type $[MX(N)(diphos)_2]$ (M = Mo, W; diphos = dppe, depe) are well suited for this purpose as their preparation is relatively straightforward and the nitrido group is nucleophilic.[2] These systems in particular react with alkyl halides to give the corresponding alkyl imido complexes.[3] The ligand-centered chemistry of the latter compounds has been intensively investigated, and reactivity patterns have emerged.[1,4] Release of the final N-functionalized products (*i.e.*, substituted amines) can be effected electrochemically, as demonstrated for the synthesis of amino acids.[5] Pickett and coworkers have identified the intermediates occuring in these transformations.[6] Specifically, they found that two-electron reduction of alkylimides $[MoX(NR)(dppe)_2]^+$ (X = halide, R = alkyl) leads to the five-coordinate Mo(II) complexes $[Mo(NR)(dppe)_2]$. In the course of attempts to generate such species by chemical reduction we detected that treatment of $[MCl(NEt)(dppe)_2]^+$ (M = Mo, W) with *n*-BuLi leads to the Mo/W dinitrogen complexes and acetonitrile, which must involve a double deprotonation of the ethylimido ligand.

Experimental

All syntheses were carried out in atmospheres of dinitrogen or argon using standard Schlenk techniques. All solvents were dried over appropriate drying agents under inert gas atmospheres. $[M(N_2)(CH_3CN)(dppe)_2]$ (M = Mo, W) was synthesized using literature procedures.[4,7]

Reaction of $[M(N_2)(CH_3CN)(dppe)_2]$ with HCl

Hydrochloric acid was condensed onto a frozen solution of $[Mo(N_2)(CH_3CN)(dppe)_2]$ (0.24 g, 0.22 mmol) in benzene (25 ml), and the reaction mixture was stirred at room temperature for 2 h and filtered through a sintered-glass frit. The filtrate was concentrated and upon addition of diethyl ether an orange yellow solid precipitated. The solid was separated by filtration and washed with diethyl ether to give analytically pure $[MoCl(NEt)(dppe)_2]Cl$.[4] The corresponding tungsten system was prepared analogously.

Reaction of $[MoCl(NEt)(dppe)_2]Cl$ with *n*-BuLi

n-Butyllithium (1.6 M hexane solution) was added to a suspension of $[MoCl(NEt)(dppe)_2]Cl$ in *tert*-butyl methyl ether and stirred for 0.5 h to give an orange–yellow solution. The solution was concentrated and *n*-hexane was added; upon cooling to −25 °C a bright orange solid precipitated. The solid was filtered off and washed with *n*-hexane to give analytically pure $[Mo(N_2)_2(dppe)_2]$ (69% yield). The same reaction was performed with $[WCl(NEt)(dppe)_2]Cl$ giving $[W(N_2)_2(dppe)_2]$ in 67% yield. The products were characterized by comparison of their spectroscopic properties with the literature.[8]

Results and discussion

The starting compounds $[MCl(NEt)(dppe)_2]Cl$ (**1**; M = Mo/W) were prepared by reaction of the mixed acetonitrile–N_2 complexes $[M(N_2)(CH_3CN)(dppe)_2]$ (M = Mo, W) with HCl in benzene (Scheme 1).[7] Under these conditions, the acetonitrile ligands are protonated to yield the corresponding M(IV) ethylimido complexes.[7,9] Recently we investigated this reaction in more detail and found that in complexes of the type $[M(N_2)(CH_3CN)(diphos)_2]$ (M = Mo, W; diphos = dppe, depe) the nitrile ligand is activated towards protonation at the sp carbon center after exchange of dinitrogen by a Lewis base X, in general the conjugated base of the acid HX employed for protonation.[10] In the context of the present study, X = Cl and diphos = dppe (Scheme 1). The corresponding anionic species $[MCl(CH_3CN)(dppe)_2]^-$ (M = Mo, W; **3**) promote electron transfer to the nitrile ligand, making it susceptible to protic attack at C_β. Under the described reaction conditions (*vide supra*) the subsequent protonation steps leading to **2** and **1** are *irreversible.* This ensures that the whole reaction proceeds unidirectionally although the reactive, anionic intermediates **3** may only be present in small concentrations.

Addition of an excess of *n*-BuLi (hexane solution) to suspensions of $[MCl(NEt)(dppe)_2]Cl$ (M = Mo, W; **1**) in *tert*-butyl methyl ether afforded the dinitrogen complexes $[M(N_2)_2(dppe)_2]$ (**5**) in about 70% yield (Scheme 2). Acetonitrile formed in this reaction was detected by gas chromatography. Importantly, the

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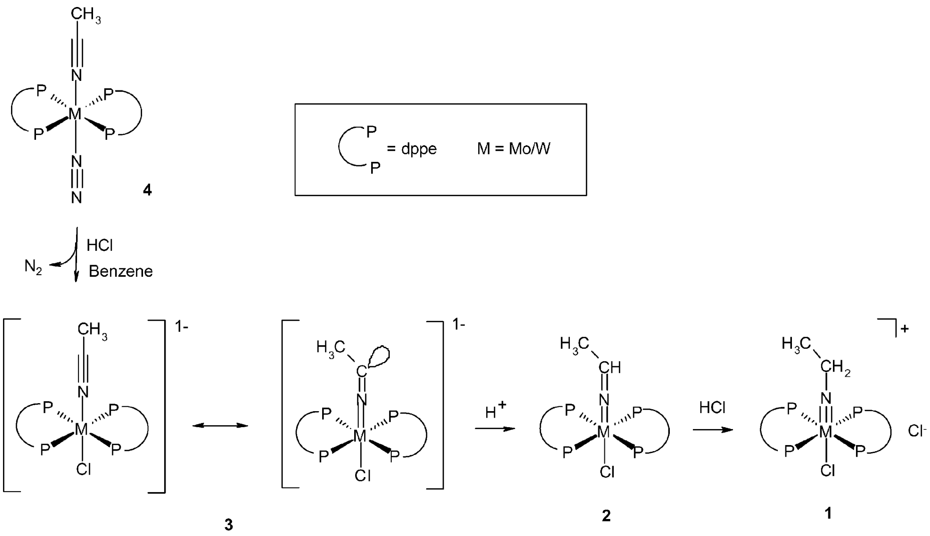
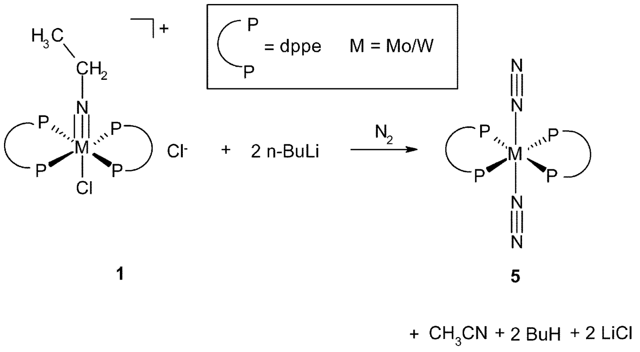


Scheme 1

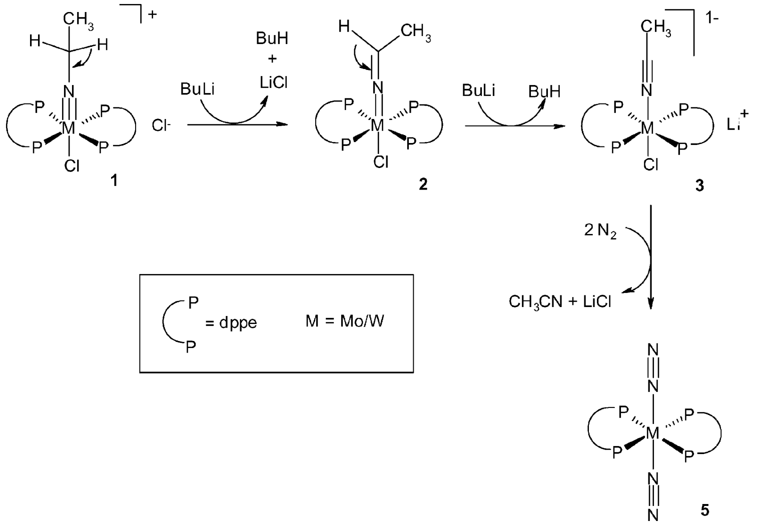


Scheme 2

deprotonation of coordinated ethylimide corresponds to a reversal of the protonation described in Scheme 1. Based on a comparison with the latter reaction, we propose the following mechanism for the deprotonation: initial reaction of *n*-BuLi with the chloro–ethylimido complex **1** leads to a chloro–azavinylidene intermediate **2** which in a second reaction with *n*-BuLi generates the anionic M(0) chloro–acetonitrile species **3**. Subsequent ligand exchange reactions of acetonitrile and chloride for N_2 generate the final products; *i.e.*, the M(0) bis(dinitrogen) complexes **5** (Scheme 3).

On the basis of Schemes 1 and 3 both the protonation of coordinated acetonitrile and the deprotonation of coordinated ethylimide thus would involve the anionic intermediates $[MCl(CH_3CN)(dppe)_2]^-$ (**3**; M = Mo, W). Mechanistic evidence for the existence of such species has been presented in our previous study,[10] where we showed that acetonitrile is only activated towards protonation if it is coordinated to a zerovalent metal center in the presence of an additional Lewis-basic ligand (*vide supra*).

Double deprotonation of coordinated methylene imide groups has not been known so far, except for Mo complexes with imide esters; *i.e.*, $[MoCl(NCH_2COOR)(dppe)_2]^+$.[4,11] These compounds have been deprotonated with strong bases such as methoxide or K[OBu^t], leading in the presence of N_2 or CO to the free



Scheme 3

cyanoformic acid esters NCCOOR and [Mo(N_2)$_2$(dppe)$_2$] or [Mo(CO)$_2$(dppe)$_2$]. A mechanism has been suggested which is analogous to Scheme 3 and, in particular, also involves anionic chlorocyanoformic acid ester intermediates.[4] In these reactions, however, the acidity of the methylene protons is increased due to the vicinity of an electron-withdrawing ester group whereas in our case such additional activation of C–H bonds is absent.[12]

Single deprotonation reactions of the active methylene group of ethylimido complexes have been known as well. Thus, 10% formation of the azavinylidene complex **2** has been observed during the electrochemical reduction of **1**.[6] Moreover, electrochemistry has been employed to show that **1** reacts quantitatively with K[OBu^t] in thf to give **2**.[4] The latter species has further been trapped by addition of MeI, leading to the isopropylimide cation [MoCl(NCHMe$_2$)(dppe)$_2$]$^+$, which again could be deprotonated to give the corresponding azavinylidene complex.[4] Deprotonation of a d^4 chloro–azavinylidene to a d^6 chloro–nitrilo complex has also been observed before. Thus, Re(I) chloro–arylnitrile complexes could be prepared by treatment of the corresponding Re(III) chloro arylazavinylidene complexes with [NBu$_4$]OH.[13] The corresponding M(0) chloro–nitrile complexes **3** (M = Mo, W), in contrast, cannot be isolated and in the presence of N_2 are converted the bis(dinitrogen) complexes **5**.

Conclusion

We have shown that treatment of the M(IV) ethylimido complexes **1** with *n*-BuLi causes a double deprotonation of the ligand to generate acetonitrile and the M(0) bis(dinitrogen) complexes **5** (M = Mo, W), which constitutes the counterpart to the well-known transition-metal mediated diprotonation of acetonitrile to ethylimide. Whereas double deprotonation reactions on *activated* and single deprotonation reactions on *non-activated* methylene imide ligands as well as on coordinated azavinylidene groups have been known, it herewith has been demonstrated that two sequential deprotonations on *non*-activated methylene imide groups can be achieved by employing *n*-BuLi as a base in these reactions.

Acknowledgements

Funding of this research by DFG Tu58-12 and FCI is gratefully acknowledged.

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