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Mass Spectrometric Studies of Reductive Elimination from Pd(IV) Complexes

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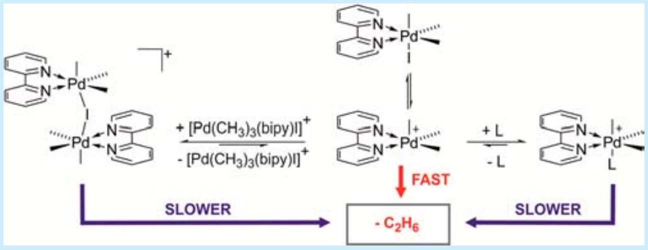
Ⓢ *Supporting Information*

ABSTRACT: Reductive elimination of ethane from the palladium(IV) complex [$PdMe_3(bpy)I$] (bpy = 2,2′-bipyridine) is studied by electrospray ionization mass spectrometry. Palladium(IV) complexes can be detected as binuclear clusters [$Pd_2Me_6I(bpy)_2$]$^+$ or as complexes [$PdMe_3(bpy)(L)$]$^+$ stabilized by an electron-donating ligand L. Fragmentation of all palladium(IV) complexes is dominated by elimination of ethane which corresponds to the reductive elimination coupling of the methyl groups. The associated energy demands for different complexes reveal that the mononuclear complexes with poorly electron-donating ligands provide the fastest reaction.

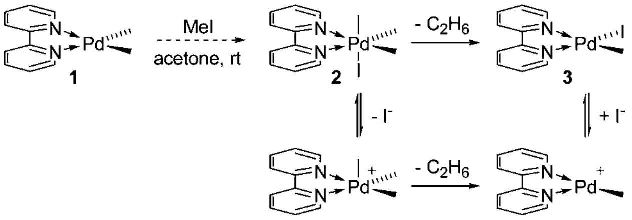


Palladium-catalyzed reactions are well established in modern organic chemistry, and their importance is highlighted by an enormous list of effective and useful transformations in synthetic chemistry.[1] Reactions involving Pd^0/Pd^{II} intermediates in a catalytic cycle are probably the most explored area in transition-metal-catalyzed chemistry.[2]

The scope of palladium chemistry was extended by transformations operating with higher oxidation states of palladium in recent years.[3] Contrary to the well-explored Pd^0/Pd^{II} reactions, the reaction mechanisms in Pd^{II}/Pd^{IV} catalysis were not clear for a long period of time due to the absence of direct evidence for a Pd^{IV} reaction intermediate.[4] The main obstacle in the research of reactions involving Pd^{IV} species is their instability in comparison to Pd^{II} compounds. The first reaction with a proven Pd^{IV} intermediate was introduced by Allan J. Canty in 1986. In this report, a hydrocarbyl Pd^{IV} complex was isolated and fully characterized.[5] Subsequent work revealed the reaction mechanism of reductive elimination from the Pd^{IV} complex **2** (Scheme 1).[6]

The most recent milestone in high-oxidation-state palladium chemistry was the isolation of a binuclear $Pd^{III}-Pd^{III}$ intermediate in the acetoxylation of 2-phenylpyridine.[7a] It was demonstrated in several examples that the $Pd^{II}-Pd^{II}/Pd^{III}-Pd^{III}$ catalytic cycle is more general and operates in some transformations which were previously considered to work on the $Pd^{II/IV}$ platform.[7]

Scheme 1. Suggested Reaction Mechanism for the Reductive Elimination of Ethane from [$PdMe_3(bpy)I$][6]



The low stability of high-oxidation-state palladium complexes represents a great challenge for chemists. It is necessary to design a model compound which would lead in the course of the reaction to the potential high-oxidation-state palladium intermediates such that they would be stable enough to be detected and characterized.[8] An alternative solution could be electrospray ionization mass spectrometry (ESI-MS) which has been successfully utilized in the elucidation of other mechanisms of palladium-catalyzed reactions.[9] The great advantage of this approach is the ability to identify possible intermediates which are in very low concentrations and hence below the detection limits of other methods that work with the whole reaction mixture.[10] When intermediates are successfully transferred to the gas phase, their lifetime can be much longer because they do not interact with other possible reactants. As a result, their structure and reactivity can be further studied.[11]

Here, we report an ESI-MS study of high-oxidation-state palladium complexes.[12,13] We have directly addressed reactions proceeding in the [$PdMe_3(bpy)I$] (**2**, bpy = 2,2′-bipyridine) model system. Reductive elimination reactions from various suggested intermediates are studied by means of collision-induced dissociation (CID) experiments.

As the starting point, a solution of *in situ* prepared [$PdMe_3(bpy)I$] (**2**) in acetone was investigated via ESI-MS in the positive ion mode (Figure 1; we note in passing that no

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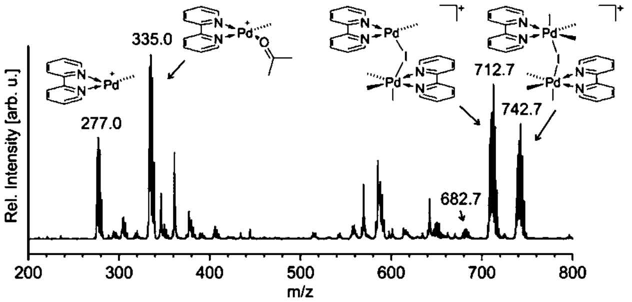

Figure 1. ESI-MS spectrum of $[PdMe_3(bpy)I]$ (**2**) in acetone under soft ionization conditions.

signals of ions containing palladium were detected in the negative mode). The spectrum shows two dominant groups of peaks for mono- and dipalladium complexes. The peaks corresponding to the complexes with one palladium atom can be assigned to $[PdMe(bpy)]^+$ (m/z 277) and $[PdMe(bpy)(Me_2CO)]^+$ (m/z 335).[14] Hence, both complexes represent products of reductive elimination. We have detected neither the mononuclear Pd^{IV} species suggested originally by Canty (i.e., $[PdMe_3(bpy)]^+$) nor their suggested adducts with solvent molecules (e.g., $[PdMe_3(bpy)(Me_2CO)]^+$) (Scheme 1).[6] The absence of the cationic mononuclear Pd^{IV} complexes could be a sign that their high reactivity prevents their detection.

The most abundant ions among the binuclear complexes correspond to $[Pd_2IMe_4(bpy)_2]^+$ (m/z 713) and $[Pd_2IMe_6(bpy)_2]^+$ (m/z 743). Both complexes have a high valence number in that the first complex contains either Pd^{II}/Pd^{IV} centers or two Pd^{III} centers and the second complex contains two Pd^{IV} centers. The fact that binuclear Pd^{IV} clusters form one of the most abundant groups of ions suggests that the binding of a counterion (here I^-) increases the stability of Pd^{IV} complexes. We have therefore tested this hypothesis with a charge-tagged counterion[15] and also with neutral ligands with higher electron donor ability than acetone.

A simple charge-tagged counterion is derived from glycine by transforming the amino group to the permanently charged trimethylammonium group ($Me_3N^+CH_2COO^-$ = betaine). Coordination of betaine to the palladium center thus creates a neutral environment at palladium while maintaining a positive charge in the ligand sphere. The dominant signal in the ESI-MS spectrum obtained for the solution of $[PdIMe_3(bpy)]$ and betaine (1 equiv) corresponds to $[PdMe_3(bpy)(Me_3N^+CH_2COO^-)]^+$ (m/z 424) (Figure S1 in the Supporting Information (SI)). Similarly, experiments with the addition of electron-donating ligands L led to the generation of the corresponding Pd^{IV} complexes $[PdMe_3(bpy)(L)]^+$. The ligands were triphenylphosphine (PPh_3), triethylphosphite ($P(OEt)_3$), imidazole (Imi), 4-(*N*,*N*-dimethylamino)pyridine (DMAP), pyridine (Py), cyclohexylamine ($CyNH_2$), and 1,4-diazabicyclo[2.2.2]octane (DABCO).

In the next step, we have investigated the reductive elimination of ethane from the Pd^{IV} complexes using collision-induced dissociation (CID) experiments. The aim was to examine the energy demands for ethane elimination in relation to the structure of the complex. The common fragmentation motif is elimination of ethane followed by or associated with loss of the ligand. The energy demands can be compared with energy-resolved CID experiments. It has been shown that for LCQ ion trap instruments the collision energy scale can be calibrated[16] and thus the determined appearance energies are reasonable estimates for the corresponding bond-dissociation energies.[17] Hence, we have evaluated the appearance energies for our system (see the SI and Table 1).

The appearance energies for the elimination of ethane from $[PdMe_3(bpy)(L)]^+$ are clearly dependent on the ligand L (Table 1). The largest appearance energy (155 kJ mol^{-1}) was found for the complex with betaine (Figure 2). It can be explained by the largest charge compensation on palladium from all investigated complexes. For the complexes with neutral donor ligands, the appearance energies associated with reductive elimination gradually decrease along with ligand donor ability down to the value of 101 kJ mol^{-1}. In these cases, reductive elimination is followed by or associated with the elimination of the respective ligand. For L = DMAP, imidazole, triethylphosphite, or triphenylphosphine, the product formed after reductive elimination ($[PdMe(bpy)(L)]^+$) can be trapped, whereas for L = pyridine, cyclohexylamine, or DABCO, only the products of simultaneous elimination of ethane and the ligand are detected. We note in passing that the activation barriers for reductive elimination of ethane from $[PdMe_3(bpy)I]$ in acetone and methanol were determined as 65 and 30 kJ mol^{-1}, respectively.[6]

Table 1. Experimental and Theoretical[a] Energy Demands for the Eliminations of Ethane and Ligands from Various Pd Complexes

parent ion	*AE*(loss of C_2H_6) (kJ mol^{-1})	*AE*(loss of L + C_2H_6) (kJ mol^{-1})	$BDE_{theor}(C_2H_6)^a$	$BDE_{theor}(L)^a$ in the Pd^{IV} complex	$BDE_{theor}(L)^a$ in the Pd^{II} complex
$[PdMe_3(bpy)(betaine)]^+$	155 ± 2	–	−146		
$[PdMe_3(bpy)(DMAP)]^+$	151 ± 1	147 ± 3	−162	116	215
$[PdMe_3(bpy)(Imi)]^+$	135 ± 2	129 ± 1	−157	106	200
$[PdMe_3(bpy)((EtO)_3P)]^+$	128 ± 1	133 ± 4			
$[PdMe_3(bpy)(Ph_3P)]+$	126 ± 2	133 ± 1			
$[PdMe_3(bpy)(Py)]^+$		111 ± 1	−157	88	182
$[PdMe_3(bpy)(CyNH_2)]^+$		108 ± 1			
$[PdMe_3(bpy)(DABCO)]^+$		101 ± 1	−137	69	143
$[PdMe_3(bpy)]^+$			−63		
$[Pd_2IMe_6(bpy)_2]^+$	1. 122 ± 5	130 ± 2			
	2. 129 ± 1				
$[Pd_2IMe_4(bpy)_2]^+$	119 ± 3				

[a] The results are obtained for the structures optimized at the mPW1PW91/cc-pVDZ:LanL2DZ(Pd) level of theory. The energies include zero-point vibrational energy and refer thus to 0 K.

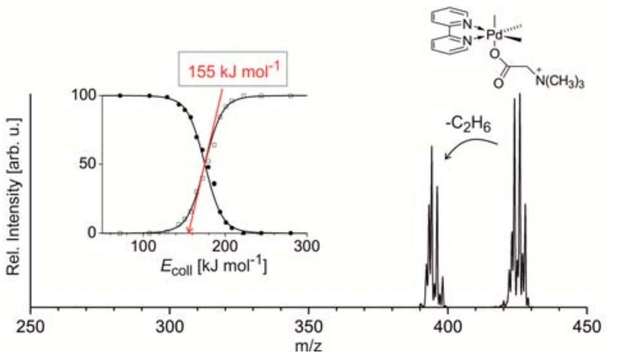

Figure 2. CID spectrum of [PdMe$_3$(bpy)(Me$_3$N$^+$CH$_2$COO$^-$)]$^+$ (m/z 424, mass selection: $\Delta m/z = 15$) leading exclusively to [PdMe(bpy)(Me$_3$N$^+$CH$_2$COO$^-$)]$^+$ (m/z 394). The insert shows the dependence of the fragmentation on the collision energy and the extrapolation to determine the appearance energy (the points correspond to the integral of all isotopic peaks of the parent ions (●) and the daughter ions (□)).

The fragmentation behavior is clearly related both to the binding energy of the ligand to the product ion [PdMe(bpy)]$^+$ and to the exothermicity of ethane elimination from [PdMe$_3$(bpy)(L)]$^+$. We have performed exploratory density functional calculations to qualitatively evaluate the observed results for L = DMAP, imidazole, pyridine, and DABCO.

The exothermicities of the reductive eliminations are rather similar (162, 157, 157, and 137 kJ mol^{-1}, respectively). A difference can be observed in the binding energies of the ligands to the Pd(IV) complexes and to the product Pd(II) complexes (Table 1). If we concentrate on Pd(II), then the binding energies drop in the order DMAP > imidazole > pyridine > DABCO (215, 200, 182, and 143 kJ mol^{-1}, respectively). Hence, the lower binding energies of pyridine and DABCO could explain why the product ions [PdMe(bpy)(L)]$^+$ were not observed. At the same time, the determined appearance energies for the reductive elimination are lower for pyridine and DABCO compared to DMAP and imidazole, which could be related to the smaller binding energies of the former ligands to the Pd(IV) complex. Hence, the more the palladium(IV) complex is stabilized by a strongly bound ligand, the more activation energy is necessary to promote the reductive elimination. This *inter alia* implies that the smallest activation energy should be expected for the bare cation [PdMe$_3$(bpy)]$^+$, and the reductive elimination from this ion should thus proceed most rapidly. This view is consistent with the fact that the activation barriers determined in acetone and methanol[6] are lower than those determined here for the ligated cations here.

With respect to the possible involvement of palladium clusters, we have evaluated appearance energies for the reductive elimination from [Pd$_2$IMe$_6$(bpy)$_2$]$^+$ (m/z 743) and [Pd$_2$IMe$_4$(bpy)$_2$]$^+$ (m/z 713). As mentioned above, the first complex involves two Pd^{IV} centers, whereas the second one is composed from either Pd^{II}/Pd^{IV} centers or two Pd^{III} centers. The [Pd$_2$IMe$_6$(bpy)$_2$]$^+$ complex can undergo 2-fold reductive elimination. The determined appearance energies are rather similar and amount to 122 and 129 kJ mol^{-1}, respectively. The complex [Pd$_2$IMe$_4$(bpy)$_2$]$^+$ can eliminate just one molecule of ethane, and the corresponding appearance energy is 119 kJ mol^{-1}. Hence, there is no significant difference between the appearance energies for the elimination of ethane from [Pd$_2$IMe$_6$(bpy)$_2$]$^+$ and [Pd$_2$IMe$_4$(bpy)$_2$]$^+$, which suggests that both processes are similar and thus probably proceed at the Pd^{IV} center. There is no reason to assume that the reductive elimination from the complex [Pd$_2$IMe$_4$(bpy)$_2$]$^+$ involves cooperation between two Pd^{III} centers. If so, then this variant does not induce any significant energetical advantage.

The second important finding follows from the comparison of the energy demands for the reductive eliminations from the mononuclear and binuclear complexes. The appearance energies for ethane elimination from the binuclear palladium complexes are slightly larger than those from the mononuclear complexes with weakly bound ligands. This means that reductive elimination most probably occurs from mononuclear palladium complexes.

In conclusion, we have shown that palladium(IV) complexes can be detected and studied by ESI-MS. The reductive elimination of ethane from [PdMe$_3$(bpy)I] can proceed either in mononuclear cationic complexes [PdMe$_3$(bpy)(L)]$^+$ (where L is a ligand) or in binuclear complexes [Pd$_2$Me$_6$I(bpy)$_2$]$^+$. In the series of mononuclear complexes [PdMe$_3$(bpy)(L)]$^+$, the energy demands for reductive eliminations decrease with decreasing binding energies of L to the palladium atom, and thus the fastest reaction is expected for the bare [PdMe$_3$(bpy)]$^+$ cation. The energy demands for the reductive eliminations from the binuclear clusters are on the order of or larger than those for the mononuclear ligated complexes, and therefore their involvement in the reactivity is not expected to be significant.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Experimental and computational details, MS and MS/MS spectra, and energy-resolved collision induced dissociation experiments with evaluation of the appearance energies. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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