

Table 1. Comparison of data derived from determinations of the ionic conductivity, rotational (Grotthuss Mechanism) and translational (Vehicle Mechanism) modes for two proton conductors.

Compound	Process	Activation Enthalpy [eV]	Jump Frequency at Room Temperature [s <sup>-1</sup> ]	Measurement
H <sub>2</sub> UO <sub>2</sub> AsO <sub>4</sub> ·4H <sub>2</sub> O	conductivity	0.64 ± 0.03	10 <sup>9</sup>	complex impedance
	H <sub>2</sub> O rotation	0.27 ± 0.02	10 <sup>6</sup>	<sup>1</sup> H-NMR [a]
	H <sub>2</sub> O translation	0.8 ± 0.2	3 × 10 <sup>9</sup>	<sup>18</sup> O self-diffusion, H <sub>2</sub> O desorption
LiN <sub>2</sub> H <sub>3</sub> SO <sub>4</sub>	conductivity	0.75 ± 0.07	—	complex impedance [4]
	—NH <sub>3</sub> <sup>+</sup> rotation	0.19 ± 0.01	—	<sup>1</sup> H-NMR [5]
	N <sub>2</sub> H <sub>3</sub> <sup>+</sup> translation	0.7 ± 0.04	—	<sup>1</sup> H-NMR [5]

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conductors are good ion-exchangers, in which oxonium ions are always exchanged, but individual protons never, *e. g.*,



Using the Vehicle Mechanism as a working principle a series of new proton conductors have been found<sup>[3a]</sup>. In particular proton conduction in zeolites has been optimized. Since the Vehicle Mechanism no longer requires an infinite hydrogen bond network, much stronger basic species, *e. g.* NH<sub>3</sub>, which have a high self-diffusion coefficient, can be used. In the case of zeolites this is particularly important, since NH<sub>3</sub>, in contrast to H<sub>2</sub>O, is capable of binding a proton from the amphoteric host lattice with formation of NH<sub>4</sub><sup>+</sup>.

The concept of the Vehicle Mechanism leads to new applications of solid proton conductors in electrochemical cells<sup>[3b]</sup>. Whereas the previously discussed mechanisms are based on pure proton transport between electrodes of different H-activity—as, *e. g.*, mixed conducting hydrides—electrodes of different oxygen activity can now also be taken into consideration. The transport of protons and water molecules in opposite direction give together an overall transport of O<sup>2-</sup>. For example, proton conductors have already been used as electrolytes in metal-air and metal/metal oxide cells (Table 2).

Table 2. Properties of some galvanic elements with hydrated NH<sub>4</sub>-zeolite A as separator material.

Anode	Cathode	Observed Open Cell Potential [V]	Observed Short Circuit Current Density [ $\mu\text{A cm}^{-2}$ ]
Fe	MnO <sub>2</sub>	0.7—1.2	120
Sn	MnO <sub>2</sub>	0.85	80
Zn	MnO <sub>2</sub>	1.3	800
Zn	PbO <sub>2</sub>	1.7	5000

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[2] Groups such as OH<sup>+</sup> or even NH<sub>3</sub><sup>+</sup> have been detected IR spectroscopically in solid proton conductors.

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## Photochemical Oxidative Addition of Chlorine from Chloroform to 2,2'-Bipyridylchloroplatinum(II)\*\*

By Arnd Vogler\* and Horst Kunkely

The mechanism of light-induced multielectron transfer has been little studied. Increasing interest is being shown in reactions of this type in relation to photosynthesis, or to the photochemical splitting of water. Particularly important two-electron redox reactions of complexes are reductive elimination and oxidative addition. Some light-induced reductive eliminations have been studied in depth<sup>[1a]</sup>. In addition, a series of photolytic oxidative additions is known<sup>[1b]</sup>. However, in all cases the primary photochemical step consists of the release of a ligand. Consequently, oxidative addition is not strictly a photochemical reaction, but occurs more frequently as a thermal reaction at coordinatively unsaturated, reactive metal complexes. We report the first oxidative addition as the primary step in a photochemical reaction.

Irradiation of [Pt<sup>II</sup>(bpy)Cl<sub>2</sub>]<sup>[2]</sup> in acetonitrile led, in the absence of side-reactions, to substitution of chloride with formation of [Pt(bpy)(CH<sub>3</sub>CN)Cl]<sup>+</sup>; irradiation at the long wavelength band of the complex ( $\lambda \geq 320$  nm) was sufficient. The reaction did not proceed in CHCl<sub>3</sub> solutions. In contrast [Pt<sup>II</sup>(bpy)Cl<sub>2</sub>] is smoothly oxidized to

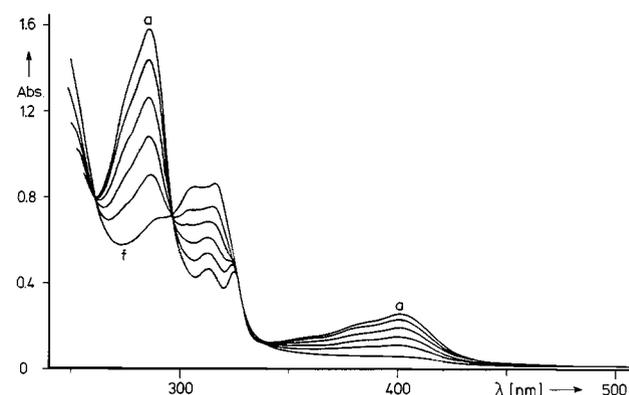


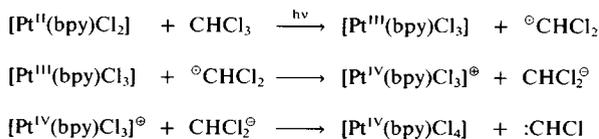
Fig. 1. Changes in the absorption spectrum during photolysis of [Pt(bpy)Cl<sub>2</sub>] ( $8.78 \times 10^{-5}$  mol/L) in CHCl<sub>3</sub> in a 1 cm cuvette, excitation light:  $\lambda > 280$  nm, irradiation time: a = 0, f = 10 min.

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[Pt<sup>IV</sup>(bpy)Cl<sub>4</sub>]<sup>[2]</sup> when shorter wavelength light (280 < λ < 300 nm) is used for the irradiation. The spectral changes during photolysis (Fig. 1) can be simulated by oxidation of [Pt(bpy)Cl<sub>2</sub>] with Cl<sub>2</sub>, or by reduction of [Pt(bpy)Cl<sub>4</sub>] with NaBH<sub>4</sub>. The quantum yield of the photooxidation was φ = 0.06 for irradiation with λ = 280 nm.

From these results it is improbable that a coordinatively unsaturated complex is formed in the primary photochemical step by release of a ligand. Summarizing, the following mechanism is proposed:



Two-electron reductions are well known for geminal dichlorides CR<sub>2</sub>Cl<sub>2</sub><sup>[3]</sup>. In the initial step an electron is taken up *via* formation of <sup>⊖</sup>CR<sub>2</sub>Cl and Cl<sup>⊖</sup>. The radicals <sup>⊖</sup>CR<sub>2</sub>Cl are powerful oxidizing agents, which are able to rapidly add a further electron to form the CR<sub>2</sub>Cl<sup>⊖</sup> anion. This reaction mechanism is thus to be expected in all cases involving the reaction of geminal dichlorides with a two-electron reducing agent such as Pt<sup>II</sup>. Presumably the intermediate products [Pt<sup>III</sup>(bpy)Cl<sub>3</sub>] and <sup>⊖</sup>CHCl<sub>2</sub> have a very short lifetime and rapidly exchange a further electron to form Pt<sup>IV</sup>. In accord with this assumption radicals could not be detected during the photolysis. ESR signals could neither be registered during low temperature photolysis at 77 K nor by irradiation at room temperature in the presence of *N*-benzylidene-*tert*-butylamine *N*-oxide (*N*-*tert*-butylphenylnitron) as spin trap.

In the last step of the oxidative addition, the anion CHCl<sub>2</sub><sup>⊖</sup> could add directly as a sixth ligand to the coordinatively unsaturated complex [Pt<sup>IV</sup>(bpy)Cl<sub>3</sub>]<sup>⊖</sup> to form [Pt<sup>IV</sup>(bpy)Cl<sub>3</sub>(CHCl<sub>2</sub>)]. This type of oxidative addition of chlorinated alkanes such as dichloromethane to Pt<sup>II</sup> complexes is a well known thermal reaction<sup>[4]</sup>. In our example, however, the complex removes a chloride ion from the anion CHCl<sub>2</sub><sup>⊖</sup>. Thereby [Pt<sup>IV</sup>(bpy)Cl<sub>4</sub>] is formed as a stable end product together with monochlorocarbene. Apparently, this carbene reacts with a further chloroform molecule by insertion into its C—Cl bond resulting in formation of 1,1,2,2-tetrachloroethane, which was detected by gas chromatography. This insertion reaction is a well known reaction type of carbenes<sup>[5]</sup>. Attempts to trap the monochlorocarbene with 2,3-dimethyl-2-butene did not lead to unambiguous results. At low concentrations of olefin (*ca.* 10<sup>-3</sup> mol/L) the carbene reacts preferentially with solvent. With markedly higher concentrations of olefin the solubility of the complex is too low. In addition, complications from substitution reactions arise.

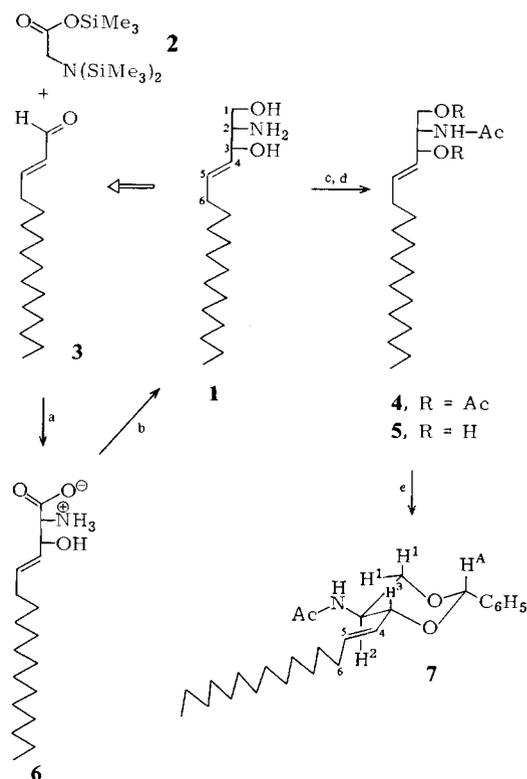
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## Diastereoselective Synthesis of D,L-Sphingosine\*\*

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Sphingosine **1**, an important membrane component, was previously accessible from achiral educts only *via* several steps involving formation of *threo*- and *erythro*-products<sup>[1,2]</sup>. The natural product could be prepared—albeit in low yields—in more than ten steps from D-glucose<sup>[3]</sup>. According to the progress made in the diastereoselective synthesis of acyclic systems<sup>[4]</sup> it should be possible to prepare *erythro*-configured D,L-sphingosine.



Scheme 1. a: LDA in THF, -80°C, 1.5 h; yield 59–75% **6**, m.p. = 192–193°C (dec.) from DMF. —b: 7 equiv. LiAlH<sub>4</sub> in THF, reflux, 36 h; yield 90% **1**; R<sub>1</sub> = 0.2 (DC, silica gel, CHCl<sub>3</sub>:methanol = 1:1). —c: pyridine/Ac<sub>2</sub>O, RT, 15 h; yield 50% **4**; m.p. = 90–91°C (Lit. [1]: 91–92°C). —d: NaOMe in MeOH, RT, 1 h; yield 91% **5**; m.p. = 85–87°C. —e: 3 equiv. C<sub>6</sub>H<sub>5</sub>-CHO and 1 equiv. ZnCl<sub>2</sub> in toluene, RT, 16 h; yield 89% **7**, m.p. = 114–115°C from petroleum ether (40–60°C)/ethyl acetate = 50:1.

We allowed the α,β-unsaturated C<sub>16</sub>-aldehyde **3** to react with the α-carbanion of the protected glycine **2** (Scheme 1), since good results had already been achieved in this reaction with simple aldehydes<sup>[6]</sup>. The *erythro*-configured, unsaturated β-hydroxy-α-amino acid **6** was formed exclusively.

The structure of **6** was confirmed by reduction with LiAlH<sub>4</sub> to the D,L-sphingosine **1** (90%) and conversion of the latter into the triacetyl derivative **4**<sup>[1]</sup>. Moreover, cleavage of the *O*-acetyl groups to give **5** and subsequent reaction with benzaldehyde afforded a 1,3-dioxane derivative **7**; the *trans* arrangement of H<sup>2</sup> and H<sup>3</sup>, as is expected for the *erythro*-configuration, is demonstrated in the <sup>1</sup>H-NMR spectrum by the typical coupling constant of 8.9 Hz for

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