

Synthesis and reactivity of *cis*-dichloro(enamine)(amine)platinum(II) complexes

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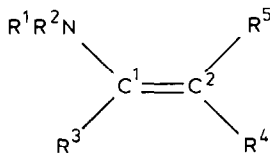
Abstract

The reaction of Zeise's dimer, *trans*- μ -dichlorobis(ethylene)platinum(II) chloride, with a variety of alkyl-substituted enamines led to complexes of the type *cis*-[Pt(C(2)-enamine)(amine)Cl₂], where the enamine ligand is coordinated to the platinum(II) center through its nucleophilic carbon atom (C(2)) and the amine ligand is derived from the parent enamine. Analogous palladium complexes were prepared. The complexes were characterized by elemental analysis, NMR (¹H, ¹³C), and IR spectroscopy.

Addition of 1 equiv. Ph₃P to *cis*-[Pt(CH₃CHCH=NEt₂)(Et₂NH)Cl₂] resulted in substitution of the enamine ligand by Ph₃P. When 2 equiv. Ph₃P were added, both the enamine and amine ligands were replaced. Hydrolysis of *cis*-[Pt(CH₂CHCH=NEt₂)(Et₂NH)Cl₂] in dilute acetic acid resulted in formation of *cis*-[Pt(Et₂NH)₂Cl₂], through enamine hydrolysis. Possible mechanisms for these reactions and for the formation of the complexes are discussed.

Introduction

Enamines, or α,β -unsaturated amines, contain several potential binding sites to platinum, including both the nucleophilic C(2) and N atoms and the π -system of the carbon-carbon double bond. Examples of the above coordination modes have been documented for metal complexes of enamines and enamine analogs [1–7].



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In preliminary studies performed in this laboratory on the reaction between Zeise's dimer, *trans*- μ -dichlorobis(ethylene)platinum(II) chloride, and 1-pyrrolidino-1-butene [8], it was observed that coordination of the enamine to platinum occurred through the nucleophilic carbon atom, C(2). The complex formed also contained a pair of *cis*-chloride ligands, as well as a coordinated amine, which apparently originated from the enamine by hydrolysis.

In this paper we report on the synthesis of a range of platinum(II) and palladium(II) enamine complexes of the general structure, *cis*-[M(C(2)-enamine)-(amine)Cl₂] (M = Pt, Pd), and investigate the reactivity of these compounds toward nucleophilic substitution and hydrolysis. Finally, we address questions on the mechanism of formation of the complexes, specifically on the origin of the coordinated amine.

Experimental

Materials and methods

Potassium tetrachloroplatinate was purchased from Johnson–Matthey and converted to Zeise's salt by a previously reported procedure [9]. Zeise's salt was

Table 1
Analytical data for *cis*-[M(C(2)-enamine)(amine)Cl₂] complexes

Complex	Enamine	Amine	Metal	Analysis (Found (calcd.) (%))		
				C	H	N
1	1-Piperidino-2-ethyl-1-butene	Piperdine	Pt	36.04 (36.06)	6.09 (6.33)	5.04 (5.40)
2	1-Pyrrolidino-1-cyclopentene	Pyrrolidine	Pt	32.74 (32.98)	5.12 (5.07)	5.70 (5.92)
3	1-Pyrrolidino-1-cyclohexene	Pyrrolidine	Pt	33.05 (33.50)	5.41 (5.34)	5.75 (5.75)
4	1-Diethylamino-1-propene	Diethylamine	Pt	28.81 (29.27)	5.87 (5.76)	5.79 (6.20)
5	1-Diethylamino-1-cyclohexene	Diethylamine	Pt	34.94 (34.21)	6.27 (6.10)	5.52 (5.70)
6	3-Diethylamino-2-pentene	Diethylamine	Pt	33.28 (33.26)	4.33 (4.26)	5.98 (5.97)
7	1-Pyrrolidino-1-butene	Pyrrolidine	Pt	31.04 (31.10)	5.27 (5.00)	5.92 (6.08)
8	1-Diisopropylamino-1-butene	Diisopropylamine	Pt	36.54 (36.92)	7.29 (6.73)	4.73 (5.38)
9	1-Diethylamino-1-butene	Diethylamine	Pt	31.07 (30.97)	6.09 (6.02)	5.83 (6.02)
10	2-Diethylamino-3-methyl-2-butene	Diethylamine	Pt	32.51 (32.57)	6.70 (6.56)	6.11 (6.13)
11	1-Diethylamino-1-propene	Diethylamine	Pd	36.39 (36.42)	7.27 (7.17)	7.61 (7.73)
12	1-Pyrrolidino-1-butene	Pyrrolidine	Pd	38.59 (38.70)	5.74 (6.45)	7.65 (7.53)
13	2-Diethylamino-3-methyl-2-butene	Diethylamine	Pd	39.32 (39.95)	7.22 (7.68)	7.49 (7.17)

Table 2
Selected spectroscopic data for enamine complexes

Complex	$\delta(\text{H}(2))$ (ppm) ^a (R ⁴ = H)	$J(^{195}\text{Pt}-^1\text{H}(2))$ (Hz) (R ⁴ = H)	$\delta(\text{H}(1))$ (ppm) ^a (R ³ = H)	$J(^{195}\text{Pt}-^1\text{H}(1))$ (Hz) (R ³ = H)	$\nu(\text{M}-\text{Cl})$ (cm ⁻¹)
1	—	—	7.99(s)	56	282, 318
2	4.68(t)	104	—	—	295, 340
3	5.39(t)	115	—	—	268, 330
4	4.10(m)	88	7.34(d)	37	290, 330
5	4.85(t)	75	—	—	287, 323
6	4.68(q)	63	—	—	299, 320
7	3.92(m)	91	7.55(d)	38	280, 323
8	4.50(m)	87	7.43(d)	37	299, 316
9	4.98(m)	82	7.29(d)	33	—
10	—	—	—	—	287, 322
11	3.90(m)	—	7.8(d)	—	290, 330
12	3.50(m)	—	7.5(d)	—	280, 323
13	—	—	—	—	287, 322

^a Relative to TMS in CDCl₃ solution.

converted to Zeise's dimer by dissolution in ethanolic hydrochloric acid followed by filtration and removal of the solvent [10]. Palladium(II) chloride (Alfa) was converted to [Pd(C₂H₄)Cl₂]₂ by standard procedures [11]. The enamines employed were prepared using either the method of Stork et al. [12] (1-diethylamino-1-propene, 3-diethylamino-2-pentene, 1-pyrrolidino-1-butene, 1-diisopropylamino-1-butene, and 1-diethylamino-1-butene) or White and Weingarten [13] (1-piperidino-2-ethyl-1-butene, 1-pyrrolidino-1-cyclopentene, 1-pyrrolidino-1-cyclohexene, 1-diethylamino-1-cyclohexene, and 2-diethylamino-3-methyl-2-butene). Diethyl ether was distilled from sodium/benzophenone ketyl before use. Toluene was distilled from calcium hydride. Aldehydes and ketones were purchased from Aldrich and distilled before use. Amines were distilled and dried over potassium hydroxide. Triphenylphosphine was recrystallized from 95% ethanol before use. Deuterated solvents were purchased from Aldrich and MSD Isotopes. NMR spectra were obtained on a Bruker WM250 spectrometer, in either CDCl₃ or (C₂D₅)₂O, as specified, with TMS as an internal reference at 0 ppm. ¹³C spectra were obtained under conditions of broad band decoupling. Infrared spectra were recorded on a Nicolet 6000 or a Beckman IR20A spectrometer from KBr sample pellets. GC/MS experiments were performed on a Finnigan MAT 4610 GC/MS. Elemental analyses were performed by Integral Microanalytical Laboratories or by Robertson Labora-

Table 3
Selected ¹³C NMR data for enamine complexes

Complex	$\delta(\text{C}(2))$ (ppm) ^a	$J(^{195}\text{Pt}-^{13}\text{C}(2))$ (Hz)	$\delta(\text{C}(1))$ (ppm) ^a	$J(^{195}\text{Pt}-^{13}\text{C}(1))$ (Hz)
4	27.48	338	158.27	41
7	37.05	359	154.52	46

^a Relative to TMS in CDCl₃ solution.

tory. Molecular weights (osmometry) were determined by Schwarzkopf Microanalytical Laboratory. Elemental analyses are given in Table 1. Spectroscopic data are given in Tables 2 and 3.

Reactions of enamines with Zeise's dimer

The general method of preparation of these complexes has been described in previous publications [8,17].

Zeise's dimer (1 mmol) was suspended in 50 ml of dry, distilled diethyl ether under N_2 . The appropriate enamine (4 mmol) was added via syringe to the stirred suspension. The dimer dissolved completely at this point, and the solution color went from orange to yellow. A small amount of product was formed as a yellow precipitate during reaction, and was removed by filtration. The filtrate was stored at $0^\circ C$ for 1–2 days to yield a crystalline product. After repeated filtrate concentration and product crystallization, yields of 90–95% were obtained. Satisfactory elemental analyses were obtained for all complexes (Table 1).

The same products formed when toluene was used in place of diethyl ether as the solvent, and when Zeise's salt (2 mmol) was used in place of Zeise's dimer.

Synthesis of palladium-enamine complexes

The procedure used was identical to that used for synthesis of the platinum complexes except that $[Pd(C_2H_4)Cl_2]_2$ was used instead of Zeise's dimer. The enamines used in these reactions were 1-diethylamino-1-propene, 1-pyrrolidino-1-butene, and 2-diethylamino-3-methyl-2-butene. Yields of 70–80% were achieved in each case. Satisfactory elemental analyses were obtained for all complexes (Table 1).

Reaction of 1-diethylamino-1-propene with Zeise's dimer in a sealed NMR tube

Zeise's dimer (1 mmol) was dissolved in diethyl ether- d_{10} (0.5 ml) in an NMR tube sealed with a serum cap. To this solution was added 1-diethyl-amino-1-propene (4 mmol) via syringe. The reaction was allowed to progress for 15 min, and then an NMR spectrum (1H) was obtained. Both the enamine complex, *cis*- $[Pt(CH_3CHCH=NEt_2)(Et_2NH)Cl_2]$, and free propanal were observed in the NMR spectrum in approximately equal concentrations.

Reactions of cis-[Pt(CH₃CHCH=NEt₂)(Et₂NH)Cl₂] with triphenylphosphine

The complex, *cis*- $[Pt(CH_3CHCH=NEt_2)(Et_2NH)Cl_2]$ was dissolved in diethyl ether under N_2 and one equivalent of triphenylphosphine was added. After one hour of stirring, the product, *cis*- $[Pt(Et_2NH)(Ph_3P)Cl_2]$, precipitated from solution and was collected in 70% yield. Analysis Found: C, 43.00; H, 4.33; N, 2.32; Cl, 11.66. $C_{22}H_{26}NCl_2Pt$ calcd.: C, 43.93; H, 4.36; N, 2.33; Cl, 11.79%. 1H NMR ($CDCl_3$): δ 1.2 (t, 3H), 3.5 (q, 2H), 7.1–7.8 ppm (m). The reaction was repeated with a reactant ratio (Ph_3P/Pt) of 2/1 and *cis*- $[Pt(Ph_3P)_2Cl_2]$ was obtained. Analysis Found: C, 53.75; H, 3.80; Cl, 8.87. $C_{36}H_{30}P_2Cl_2Pt$ calcd.: C, 54.69; H, 3.82; Cl, 8.97%.

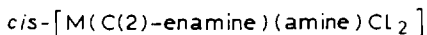
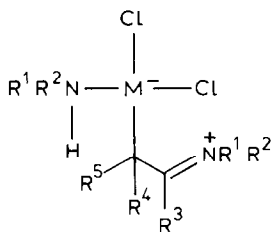
Acid hydrolysis of cis-[Pt(CH₃CHCH=NEt₂)(Et₂NH)Cl₂]

The complex, *cis*- $[Pt(CH_3CHCH=NEt_2)(Et_2NH)Cl_2]$ (1 mmol), was dissolved in dilute (0.01 M) acetic acid (5 ml) and stirred for 2–3 h with gentle heating. The resulting solution was neutralized with $NaHCO_3$, filtered, and concentrated. The

platinum-amine complex, $cis\text{-}[\text{Pt}(\text{Et}_2\text{NH})_2\text{Cl}_2]$, as identified through NMR and IR spectroscopy, was obtained as a precipitate during concentration of the solution. ^1H NMR (CDCl_3): δ 1.6 (t, 3H); 3.2 ppm (q, 2H).

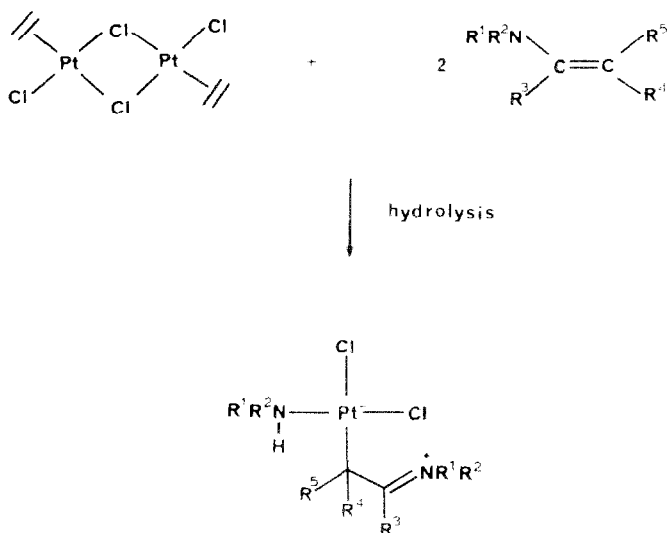
Results and discussion

The reactions of enamines with Zeise's dimer, Zeise's salt, and $[\text{Pd}(\text{C}_2\text{H}_4)\text{Cl}_2]_2$ led to complexes containing both a coordinated enamine and an amine derived from the parent enamine. This reaction, which was initially reported by Kunin and Brown [8], using 1-pyrrolidino-1-butene and Zeise's dimer, has now been found to be general for a variety of enamines (Scheme 1). The complexes prepared are given in Table 1. The molecular weights of representative members of the series show that the complexes are monomers in solution [14]. The spectroscopic data (Tables 2, 3) support a structure of square planar coordination about the platinum(II) center. The IR data show that two coordination sites are occupied by a pair of *cis*-chloride atoms, and the NMR data demonstrate that the remaining positions contain an enamine coordinated through its nucleophilic carbon atom (C(2)) and an amine which originates from hydrolysis of an enamine molecule (discussed below). A representative structure for these complexes is:



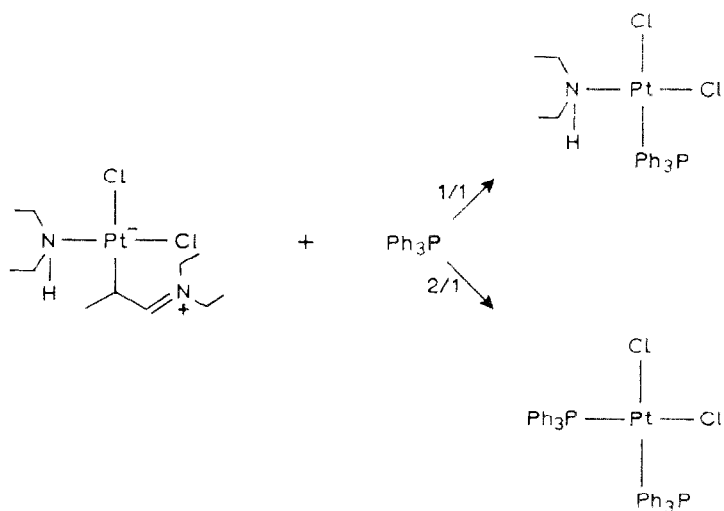
Spectroscopic data for the palladium complexes (Table 2) are consistent with those of the platinum complexes and suggest a structure of $cis\text{-}[\text{Pd}(\text{C}(2)\text{-enamine})(\text{amine})\text{Cl}_2]$ for these complexes.

In order to investigate the reactivity of these complexes, some general reactions were performed. The reaction of $cis\text{-}[\text{Pt}(\text{CH}_3\text{CHCH}=\text{NEt}_2)(\text{Et}_2\text{NH})\text{Cl}_2]$ with triphenylphosphine, which has a high nucleophilicity toward platinum, was performed with $\text{Ph}_3\text{P}/\text{Pt}$ ratios of 1/1 and 2/1. With a 1/1 ratio, the enamine ligand was displaced by a triphenylphosphine ligand, giving the complex, $cis\text{-}[\text{Pt}(\text{Et}_2\text{NH})(\text{Ph}_3\text{P})\text{Cl}_2]$. With a 2/1 ratio, both the enamine and amine ligands were substituted, yielding $cis\text{-}[\text{Pt}(\text{Ph}_3\text{P})_2\text{Cl}_2]$ (Scheme 2). The enamine was shown to be the most labile ligand in the complex. The amine ligand was the next substituted, rather than the chloride ligand *trans* to Ph_3P , a ligand known to have strong *trans*-labilizing ability. This is most likely due to the greater ability of the amine over chloride to act as a leaving group in nonpolar diethyl ether solution.



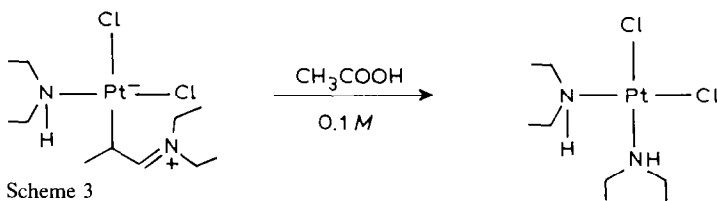
Scheme 1

As free enamines are easily hydrolyzed back to their aldehyde and amine precursors, the acid-catalyzed hydrolysis of *cis*-[Pt(CH₃CHCH=NEt₂)(Et₂NH)Cl₂] was attempted in order to determine whether coordination to platinum affects the susceptibility of the enamine to hydrolysis. Upon hydrolysis of the complex in dilute acetic acid, a bis-amine complex, *cis*-[Pt(Et₂NH)₂Cl₂], was obtained (Scheme 3). The second coordinated amine appears to originate from hydrolysis of the enamine in the original complex. Hydrolysis may occur while the enamine remains coordinated intact to the platinum complex, with the amine liberated during hydrolysis



Scheme 2

ultimately displacing the platinum-carbon bond, or the platinum-carbon bond may first be cleaved, with enamine hydrolysis and amine coordination to platinum occurring subsequently. In either case, the resulting complex contains an amine coordinated in place of the original enamine, giving the observed bis-amine complex, *cis*-[Pt(Et₂NH)₂Cl₂].



Scheme 3

Certain questions on the mechanism of formation of the platinum-enamine complexes remain, e.g. where the coordinated amine in the complex arises from, as no free amine was present in the original reaction mixture.

The first step in the mechanism probably involves a bridge-splitting of Zeise's dimer. In this step, two incoming enamine ligands would open the chloro-bridged dimer into two *cis*-monomers, and coordinate to platinum through their C(2) atoms. This reaction is common in systems containing Zeise's dimer and nucleophiles [15,16].

The next series of steps in the mechanism involve displacement of ethylene from the platinum monomer and coordination of diethylamine at this site. The loss of ethylene was demonstrated in GC/MS experiments where, after trapping the gases given off with Br₂/CCl₄, brominated ethylene derivatives were detected. The diethylamine in the complex was shown to arise from hydrolysis of an enamine, as both the resulting complex and free propanal (in a 1/1 ratio) are observed in the reaction mixture when the reaction of Zeise's dimer with 1-diethylamino-1-propene is performed in a sealed NMR tube. Although solvents and reagents were dried before use, conditions were apparently not stringent enough to eliminate the amount of water required to affect hydrolysis. Preliminary experiments conducted under vacuum line conditions indicate that in the absence of trace water, an unidentified thermally labile species forms and rapidly decomposes. Hydrolysis could occur either on a free or coordinated enamine. It is unlikely that hydrolysis of a non-coordinated enamine occurs, as the enamines proved to be stable in the diethyl ether solution, as shown by NMR. The next step most likely involves displacement of ethylene by a second mole of enamine (C(2)-coordinated). This would result in formation of a complex with a high electron density on platinum, with the instability of this complex promoting hydrolysis of the coordinated enamine. This would occur by a mechanism similar to the acid hydrolysis discussed above. As an alternative, it is possible that the second incoming mol of enamine displaces ethylene and binds to platinum through its amine nitrogen, and that this species then undergoes hydrolysis. Other mechanistic routes could also be considered. Studies to fully elucidate this mechanism have yet to be undertaken.

In summary, both the structure and certain aspects of the reactivity of the complexes formed from the reactions of enamines with Zeise's dimer have been investigated. The complexes contain a carbon-bound enamine which is reactive toward nucleophilic substitution and acid hydrolysis. The amine ligand present in the platinum coordination sphere is postulated to arise from hydrolysis of a

coordinated enamine. The system has shown to be potentially rich in chemistry at both metal and ligand sites.

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