Stable platinum(II) complexed α-aminoethers derived from benzimidazole and benzoxazole

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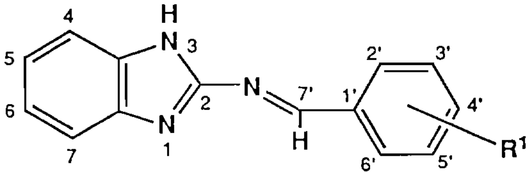
(Received July 5, 1991)

Abstract

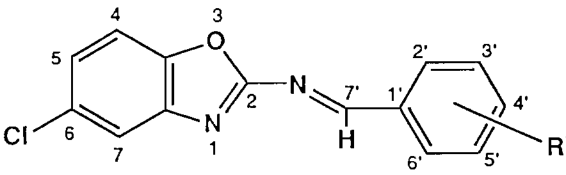
A series of Schiff base compounds derived from 2-aminobenzimidazole and 2-aminobenzoxazole react with Zeise's salt in CH_2Cl_2/ROH ($R=CH_3$, CH_2CH_3, $CH(CH_3)_2$, $CH_2CH_2OCH_3$) to form a series of relatively stable α-aminoether complexes with coordination to Pt(II) via the heterocyclic sp^2 nitrogen. The complexes, *trans*-$PtCl_2(C_2H_4)\{2\text{-}N\text{-}(CH(OR)C_6H_4R^1)$benzimidazole$\}$ (**4**) ($R^1=3\text{-}NO_2$, $R=CH_3$, CH_2CH_3, $CH(CH_3)_2$; $R^1=4\text{-}Cl$, $R=CH_3$) and *trans*-$PtCl_2(C_2H_4)\{2\text{-}N\text{-}(CH(OR)C_6H_4R^1)$benzoxazole$\}$ (**5**) ($R^1=3\text{-}NO_2$, $R=CH_3$, CH_2CH_3, $CH_2CH_2OCH_3$; $R^1=4\text{-}Cl$, $4\text{-}OCH_3$, 4-H, $R=CH_3$) arise through initial coordination of the heterocyclic sp^2 nitrogen followed by attack of ROH on the pendant 2-*N*-benzylidene moiety at the Schiff base carbon. It is suggested that withdrawal of electron density through complexation facilitates alcohol attack. In the absence of complexation the reaction can be 20–30 times slower. A Pd(II) phosphine complex can achieve the same result. ^{1}H NMR spectroscopy, and specifically the chemical shift of the '$CH{=}N$' moiety, provides an indication of the polarization due to complexation. The structure of one complex, **5c**, $R^1=3\text{-}NO_2$, $R=CH_2CH_2OCH_3$, was determined by X-ray diffraction. A prismatic crystal belonging to the space group $P\bar{1}$ with the following characteristics: $a=10.024(3)$, $b=11.242(9)$, $c=13.158(3)$ Å, $\alpha=96.07(3)$, $\beta=107.01(2)$, $\gamma=109.52(3)°$, $V=1302$ Å^3, $Z=2$, was used to determine the structure, which was refined to $R=0.044$.

Introduction

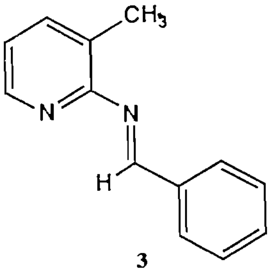
In the course of our studies on the interactions of C–H bonds with Pt(II) [1–4] we became interested in the benzimidazole and benzoxazole ligands **1** and **2** and their relative reactivity when compared to **3**.



1: $R^1=3\text{-}NO_2$ (**a**), 4-Cl (**b**)



2: $R^1=3\text{-}NO_2$ (**a**), 4-Cl (**b**), $4\text{-}OCH_3$ (**c**), H (**d**)



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Although these ligands react with Rh(I) complexes to afford cyclometallated oxidative addition products arising from imine C–H attack [5], the ligands **1** and **2** did not react as hoped with the dinuclear phosphine complexes, *sym,trans*-$[Pt(\mu\text{-}Cl)Cl(PR_3)]_2$ as does **3** and other pyridine related complexes [1–3]. In the hope of facilitating coordination of the heterocyclic nitrogen, N^1, the compounds **1** and **2** were reacted with Zeise's salt. Somewhat surprisingly, this reaction lead to the preparation and isolation of a series of stable α-aminoether derivatives **4** and **5**. We report here on this reaction along with the solid state molecular structure of one member of type **5**. Pre-

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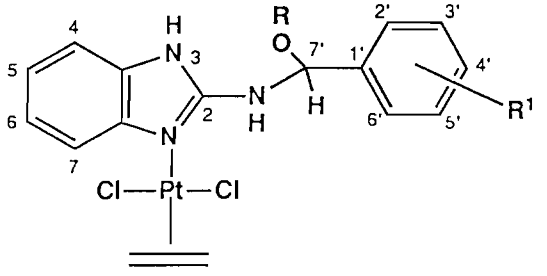
liminary results for **5** have been communicated earlier [6].

Results and discussion

Preparation and characterization

$$K[PtCl_3(C_2H_4)] + \mathbf{1}\ (\text{or}\ \mathbf{2}) \xrightarrow[\text{ROH}]{\text{CH}_2\text{Cl}_2} \mathbf{4}(\text{or}\ \mathbf{5}) + KCl \qquad (1)$$



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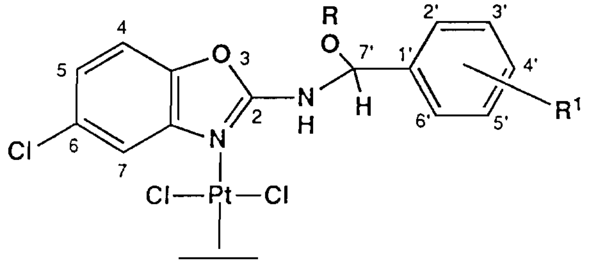
	R¹	R
a	3-NO_2	CH_3
b	3-NO_2	CH_2CH_3
c	3-NO_2	$CH(CH_3)_2$
d	4-Cl	CH_3



5

	R¹	R
a	3-NO_2	CH_3
b	3-NO_2	CH_2CH_3
c	3-NO_2	$CH_2CH_2OCH_3$
d	4-Cl	CH_3
e	4-OCH_3	CH_3
f	H	CH_3

In eqn. (1) we show the chemistry leading to the α-aminoethers **4** and **5**. In contrast to our previous chemistry with dinuclear phosphine complexes the imidazole (or oxazole) sp^2 nitrogen does indeed complex and this is followed by a second step in which the alcohol (originally methanol, in which Zeise's salt is soluble) attacks the pendant Schiff base to afford the α-aminoether moiety. The complexes **4** and **5** are isolable with typical yields in the order of 80–95%. The complexes were characterized by microanalyses, IR, ^1H and ^{13}C NMR, and, in one case, **5c**, by an X-ray diffraction study. Selected analytical and spectroscopic data are shown in Tables 1–4. The α-aminoethers **4** and **5** are readily recognized through their ^1H and ^{13}C NMR spectra in that these reveal characteristic absorptions for H-7′ and C-7′ (*c*. 5.71–6.13 ppm and *c*. 81.8–86.3 ppm, respectively). The form of H-7′ is characteristic for our platinum complexes in that it appears as a doublet due to coupling with the adjacent N–H proton (which normally appears in the aromatic region). Figure 1 shows a ^1H COSY spectrum and indicates the cross peaks associated with this spin–spin coupling. A 2-D ^{13}C, ^1H-correlation spectrum confirms that the C_2H_4 ligand has its ^{13}C signal at the same position as $CDCl_3$ and is consequently obscured by solvent.

TABLE 1. Selected ^1H and ^{13}C NMR data for the ligands

Compound	R¹	δ			
		H-7′	C-7′	H-7	C-7
1a	3-NO_2	9.86		[a]	
1b	4-Cl	9.51		[a]	
2a	3-NO_2	9.45	167.24	7.73	120.27
2b	4-Cl	9.31	168.65	7.68	119.95
2c	4-OCH_3	9.3	169.31	7.645	114.89
2d	H	9.37		7.69	

[a] H-7 is covered under a broad signal together with H-3 and H-4.

TABLE 2. Selected ^1H NMR data for the complexes **4**–**7**

Compound	R¹	δ			J(Pt, H) (Hz)	δ
		H-7′	RO	C_2H_4		H-7
4a	3-NO_2	5.79	3.62[a]	4.95	58.7	7.94
4b	3-NO_2	5.88	[b]	4.95	58.7	7.94
4c	3-NO_2	5.95	[c]	4.95	58.1	7.94
4d	4-Cl	5.71	3.50[a]	4.91	58.1	7.96
5a	3-NO_2	6.13	3.64[a]	4.91	61.5	7.93
5b	3-NO_2	6.25	[d]	4.88	62.2	7.88
5c	3-NO_2	6.36	[e]	4.92	61.7	7.93
5d	4-Cl	6.02	3.54[a]	4.90	62.5	7.90
5e	4-OCH_3	5.985	3.50[a]	4.89	62.2	7.88
5f	H	6.04	3.54[a]	4.89	62.9	7.87
6a	3-NO_2	6.25[f]	3.61[a]			7.29
6b	4-Cl	6.11[f]	3.53[a]			7.22
7a[g]	3-NO_2	9.70		5.0	64.2	8.18
7b	4-Cl	9.56		5.01	63.8	8.13

[a] $R = CH_3$. [b] $R = CH_2CH_3$ (3.77 CH_2CH_3, 1.39 CH_2CH_3). [c] $R = CH(CH_3)_2$ (4.27 $CH(CH_3)_2$, 1.40, 1.34 $CH(CH_3)_2$). [d] $R = CH_2CH_3$ (3.73 CH_2CH_3, 1.35 CH_2CH_3). [e] $R = CH_2CH_2OCH_3$ (4.07, 3.41 $CH_2CH_2OCH_3$, 3.66 $CH_2CH_2OCH_3$). [f] Broad singlet. [g] In CD_2Cl_2.

TABLE 3. Selected ^{13}C NMR data for **4** and **5**

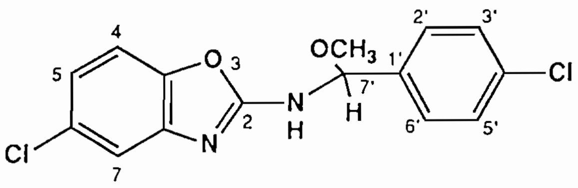
Compound	R^1	δ			
		C-7′	RO	C-7	C_2H_4
4a	3-NO_2	85.37	55.48[a]	117.67	77.45
4b	3-NO_2	83.91	[b]	117.65	77.54
4c	3-NO_2	81.76	[c]	117.70	77.58
5a	3-NO_2	85.47	56.97[a]	118.69	77.45
5b	3-NO_2	84.08	[d]	118.59	77.27
5c	3-NO_2	84.72	[e]	118.61	77.21
5d	4-Cl	85.72	56.28[a]	118.32	77.44
5e	4-OCH_3	86.32	56.07[a]	114.57	77.0

[a] $R=CH_3$. [b] $R=CH_2CH_3$ (65.35 $\mathit{C}H_2CH_3$, 15.10 $CH_2\mathit{C}H_3$). [c] $R=CH(CH_3)_2$ (70.75 $\mathit{C}H(CH_3)_2$, 23.37, 21.31 $CH(\mathit{C}H_3)_2$). [d] $R=CH_2CH_3$ (65.35 $\mathit{C}H_2CH_3$, 15.10 $CH_2\mathit{C}H_3$). [e] $R=CH_2CH_2OCH_3$ (71.99, 68.96 $\mathit{C}H_2\mathit{C}H_2OCH_3$, 56.49 $CH_2CH_2O\mathit{C}H_3$).

Relative kinetics and role of the metal

α-Aminoethers are well known, useful, synthetic intermediates [9, 10]. The uncoordinated α-aminoethers corresponding to **4** and **5** (i) are susceptible to hydrolysis (if one can prepare them, see 'experimental') and (ii) do not rapidly form from **1** or **2** plus alcohol in the absence of Zeise's salt. Our complexes **4a–d** and **5a–f** are stable for hours in solution with only minor amounts (<5%) of hydrolysis as detected by ^1H NMR. Consequently, we have enhanced the reactivity of **2** and **3** relative to attack by alcohol and stabilized the products **4** and **5**, relative to uncomplexed α-aminoether.

As the preparative work was carried out using the alcohol as co-solvent, we have used ^1H NMR to monitor the development of **5d** using 1.1, 3.0 and 5.0 equiv. of CH_3OH in different experiments and observe *c.* 35, 70 and 100% conversion after 2 h at probe temperature (*c.* 293 K). Consequently, although it is not necessary to use the CH_3OH as co-solvent, a significant excess is required to drive the reaction to completion under mild conditions. With CH_3OH as co-solvent conversion to **5d** is complete within 10 min or less.



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The development of uncomplexed α-aminoether (**6**), via the reaction of **2** with CH_3OH, can be monitored by ^1H NMR under identical reaction conditions. Interestingly, we observe no **6** after 10 min; *c.* 21% after 1 h; *c.* 43% after 2 h and finally 90% after 4–5 h. Summing our preparative experience: the use of Zeise's salt leads to a 20–30 fold acceleration of the alcohol attack. Perhaps not unexpected, is the observation that 5 mol% Zeise's salt catalyses the formation of **6** (81% in 1 h).

In an attempt to elucidate the rate determining step, two equivalents of **2** and one of Zeise's dimer, $[Pt(\mu\text{-}Cl)Cl(C_2H_4)]_2$ were reacted in CD_2Cl_2. The products **7** were formed immediately, although they are not very soluble. As with **4** and **5**, **7** is shown to complex on the heterocyclic nitrogen by the absence of the expected [11, 12] large ^3J(Pt, H) coupling to the imine proton (and the X-ray structure which follows). Complex **7a** reacts quantitatively with CD_3OD to give the deuterated analog of **5a** within

TABLE 4. Microanalytical and IR data[a]

Compound	Anal. calc. (found) (%)			N–H	Pt–Cl
	C	H	N		
2a	55.74 (55.79)	2.67 (2.81)	13.93 (13.88)		
2b	57.76 (57.86)	2.77 (2.82)	9.62 (9.77)		
2c	62.78 (62.78)	3.84 (3.79)	9.77 (9.75)		
4a	34.47 (34.25)	3.06 (3.26)	9.46 (9.42)	3365, 3320	341
4b	35.65 (35.37)	3.32 (3.35)	9.24 (9.26)	3390, 3360	340
4c	36.78 (36.66)	3.57 (3.60)	9.03 (8.99)	3355	334
4d	35.10 (34.82)	3.12 (3.09)	7.22 (7.16)		
5a	32.53 (32.56)	2.57 (2.80)	6.69 (6.30)	3319	347
5b	33.69 (33.25)	2.83 (2.81)	6.55 (6.45)		
5c	33.97 (33.53)	3.00 (3.00)	6.25 (6.09)		
5d[b]	33.08 (32.95)	2.61 (2.69)	4.54 (4.57)	3333	339
5e	35.28 (34.67)	3.13 (2.97)	4.57 (4.82)		
10	54.71 (54.37)	3.67 (3.69)	3.83 (4.19)		

[a] In cm^{-1}, as CsI pellets. [b] Cl; 22.97 (22.71).

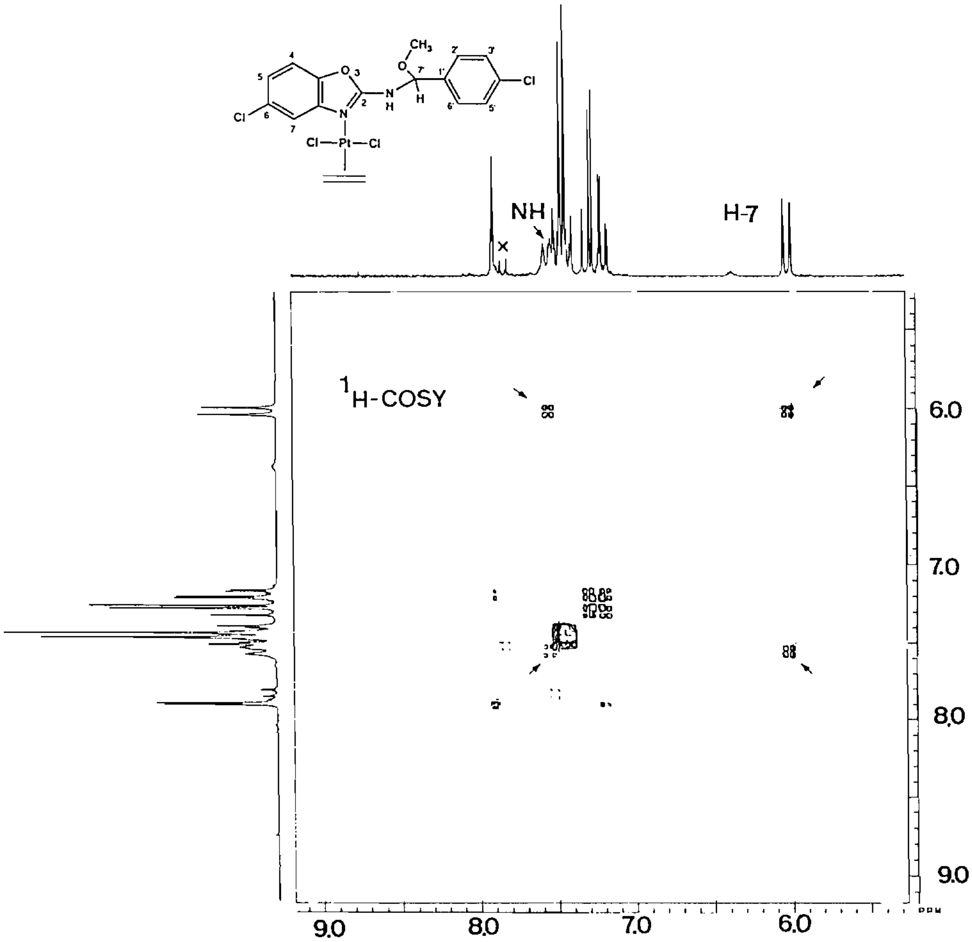
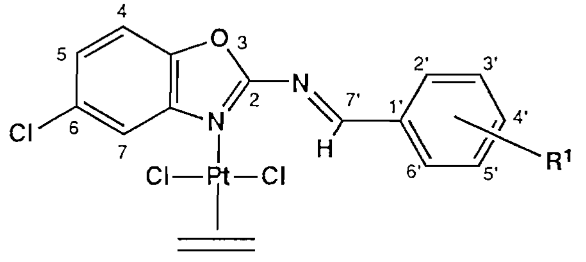


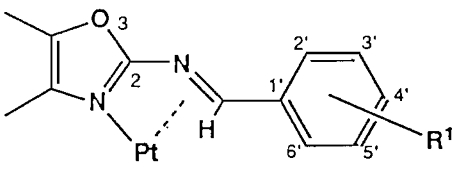
Fig. 1. ^{1}H COSY spectrum for **5d**.



7: $R^1 = 3\text{-}NO_2$ (**a**), 4-Cl (**b**)

5 min. Although we can only draw qualitative conclusions, the dependence of reaction rate on CH_3OH concentration, combined with our observations for **7**, and the general speed with which Zeise's salt reacts with nitrogen nucleophiles [13–15], suggests that **7** is formed relatively rapidly and **5** (or **4**) presumably more slowly.

What role does the Pt(II) play in accelerating the attack of ROH at C-7'? One can imagine at least two contributing factors, which we show in **8** and **9**, which might enhance the electrophilicity at C-7'. In **8** we imply a five-coordinate Pt(II) as a consequence of a weak π-imine interaction, whereas in **9**, there is a polarization due to donation from N^1 to Pt(II). The ground-state structures of **7**, and specifically their ^{1}H spectra, are suggestive that a polarized form such as **9** may be important. The imine proton in the 3-NO_2 and 4-Cl uncomplexed



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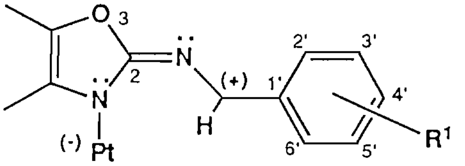

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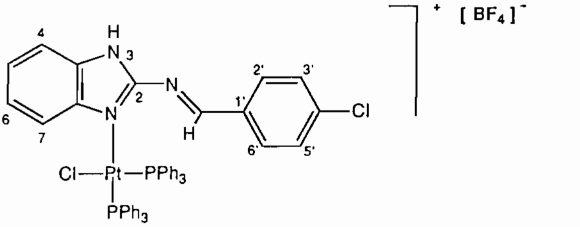
ligands appear at $\delta = 9.45$ and 9.31, respectively; whereas in **7** these protons appear at 9.70 and 9.55, respectively. Moreover, the H-6′ proton *ortho* to C-7′ also shifts downfield on complexation of N^1 ($\Delta\delta$ *c.* 0.12 for **2b**) and as arene coordination is unlikely, some form of electron flow from the imine seems reasonable. In addition to general structural data for bulky heterocyclics coordinated to Pt(II) [1–3, 16–18], the low field shift of the arene proton, H-7, of the heterocycle, suggests that our heterocycle is nearly perpendicular to the coordination plane [1]. However, the absence of a spin–spin coupling from the imine H-7′ to Pt, mitigates against **8** as a significant contributor to the ground state*. We note that in **9** an electron withdrawing substituent, R^1, should enhance the electrophilicity at C-7′, thereby encouraging attack by alcohol. Conversely, a 4-OCH_3 substituent would decrease the amount of positive charge on C-7′ and also stabilize an intermediate arising from protonation of the aminoether oxygen followed by alcohol dissociation. Indeed we find that **5e** is more sensitive to hydrolysis than either **5a** or **5d**, although this observation need not be related to the relative importance of either **8** or **9**.



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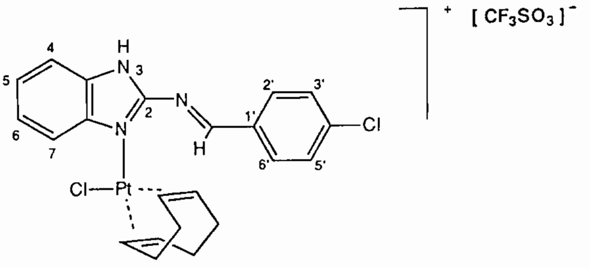

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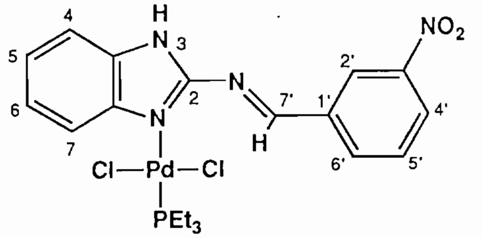
The cationic complexes $[PtCl(\mathbf{1b})(PPh_3)_2]BF_4$ (**10**) and $[PtCl(\mathbf{1b})(1{,}5\text{-}COD)]CF_3SO_3$ (**11**) were prepared in the hope that the formal positive charge on platinum would accelerate the attack of alcohol at C-7′. Neither of these complexes react with methanol to afford analogous α-aminoethers, although both contain coordinated **1b**. Obviously, it is not sufficient just to coordinate the ligand **1b** and we note that δH-7′ for **10** (9.20) and **11** (9.12) are both to high field of **1a** (9.61). It would seem that a combination of electronic and possibly steric effects must be tuned to bring about the correct environment at C-7′, and this brings us to the use of different metals and electrophiles.

As shown in eqn. (3), *trans*-$[PdCl_2(\mathbf{1a})(PEt_3)]$ (**12**), δH-7′ = 10.56, reacts in CH_3OH, to afford the α-aminoether complex **13**, in 72% yield.

$$sym\text{-}trans\text{-}[Pd(\mu\text{-}Cl)Cl(PEt_3)]_2 + \mathbf{1a} \longrightarrow \mathbf{12} \qquad (2)$$

$$\mathbf{12} \xrightarrow[\text{MeOH}]{60\ ^\circ\text{C}} \mathbf{13} \qquad (3)$$



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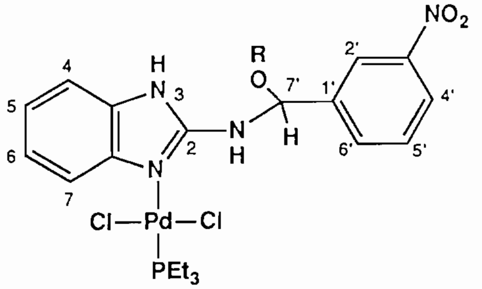

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Although the *sym-trans*-Pd(II) complex (eqn. (2)) is a suitable alternative to Zeise's salt our experience with $PdCl_2(PhCN)_2$, $Au(CF_3SO_3)(PPh_3)$, $Ag(CF_3SO_3)$, $SnCl_2$ (anhydrous) and CF_3SO_3H revealed extensive hydrolysis products under conditions which smoothly afforded **4** and **5** starting from Zeise's salt. Indeed only with $Ag(CF_3SO_3)$ were we able to detect any significant amount of α-aminoether in solution. We interpret these experiments to mean that, in the presence of small amounts of water, the metal center chosen must readily coordinate **1** or **2**, and be soft enough not to coordinate water and thereby facilitate hydrolysis of the Schiff base. Moreover, after ligand coordination the metal center must be capable of polarizing and/or coordinating the Schiff base (in the sense of **8** and **9**). It would seem that Zeise's salt (and Zeise's dimer) as well as the Pd(II) phosphine complex **12**, possess the correct combination of characteristics, and possibly the ^1H chemical shift of H-7′ may provide a hint as to whether the boundary conditions are fulfilled.

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*See ref. 5b for comparison of a Pt(II) coordinated benzimidazole with that of ligand coordinated to Pt(II) with reference to possible coupling constants to platinum.

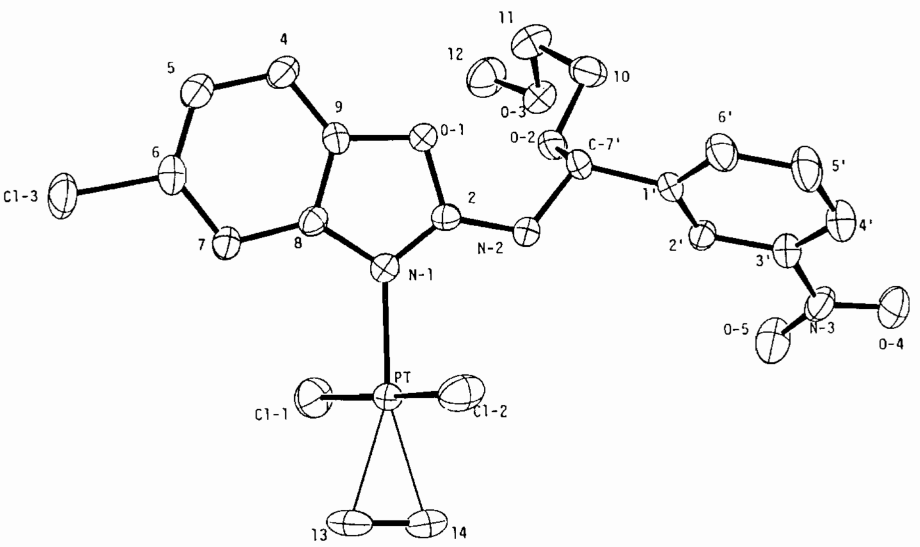

Fig. 2. ORTEP plot for **5c**.

Before closing this section we note the following: (i) removal of the α-aminoether from either **4** or **5** is readily accomplished by adding two equivalents of PPh_3 to afford the sparingly soluble *cis*-$PtCl_2(PPh_3)_2$ which may be filtered off, thereby affecting a clean separation of the metal from the newly formed α-aminoether; however, the α-aminoether is now more susceptible to hydrolysis;

(ii) in some few cases we have made analogous α-aminoether complexes starting from benzothiazole (with $R^1 = 3\text{-}NO_2$) and $[Pd(\mu\text{-}Cl)Cl(PEt_3)]_2$;

(iii) reaction of **2a** with Zeise's salt and an excess of optically active $HOCH_2CH(CH_3)CO_2CH_3$ revealed a single diastereomer in the proton spectrum of the mixture suggesting selective attack of the alcohol on one face of the imine.

X-ray structure of 5c

In view of the various questions concerning the role of the platinum in this α-aminoether chemistry we have determined [6] the solid-state structure of **5c** which arises from attack of ethylene glycol monomethyl ether, on coordinated oxazole **2a**. An ORTEP view of the molecule is shown in Fig. 2, and a list of selected bond lengths and bond angles is given in Table 5.

The local coordination geometry is distorted square planar with *trans* Pt–Cl bonds. Both the C_2H_4 ligand and the plane of the heterocyclic ring are almost perpendicular to the coordination plane defined by the metal, two halogens and nitrogen atom. A $CH_3OCH_2CH_2O$ fragment is connected to the Schiff base carbon, C-7', as a consequence of the attack of alcohol on the imine moiety.

TABLE 5. Selected bond lengths (Å) and bond angles (°) for **5c**

Pt–Cl(1)	2.295(2)	Cl(1)–Pt–Cl(2)	178.32(8)
Pt–Cl(2)	2.286(2)	Cl(1)–Pt–N(1)	90.2(2)
Pt–N(1)	2.062(5)	Cl(1)–Pt–C(13)	91.0(3)
Pt–C(13)	2.155(8)	Cl(1)–Pt–C(14)	90.2(3)
Pt–C(14)	2.160(8)	Cl(2)–Pt–N(1)	88.8(2)
Pt–C(2)	3.057(6)	Cl(2)–Pt–C(13)	89.5(3)
Pt–C(8)	3.067(6)	Cl(2)–Pt–C(14)	91.2(3)
Cl(1)–C(13)	3.174(10)	Pt–N(1)–C(2)	129.8(4)
Cl(1)–C(14)	3.156(9)	Pt–N(1)–C(8)	124.0(4)
Cl(1)–N(1)	3.090(6)	C(2)–N(1)–C(8)	105.5(5)
Cl(2)–C(13)	3.129(10)	N(1)–C(2)–N(2)	129.1(6)
Cl(2)–C(14)	3.178(10)	O(1)–C(2)–N(2)	117.3(6)
Cl(2)–N(1)	3.045(6)	O(2)–C(7')–N(2)	106.3(5)
N(1)–C(2)	1.295(8)	N(2)–C(7')–C(1')	112.3(5)
N(1)–C(8)	1.393(8)	N(1)–C(8)–C(7)	131.6(6)
N(2)–C(2)	1.331(8)	O(1)–C(9)–C(4)	128.2(6)
N(2)–C(7')	1.452(8)	C(7')–O(2)–C(10)	114.3(5)
C(1')–C(7')	1.503(8)		
O(2)–C(7')	1.404(8)		
O(2)–C(10)	1.459(9)		
C(13)–C(14)	1.441(13)		
N(2)–O(3')[a]	2.886(7)		

[a] The prime notation refers to the atom generated by the symmetry operation $1-x$, $-y$, $-z$.

The Pt–Cl separations, 2.295(2) and 2.286(2) Å, are normal for *trans* chloride ligands in square planar complexes [16, 18, 19–21], as are the Pt–C separations, 2.155(8) and 2.160(8) Å, for the ethylene ligand [22–24]. The Pt–N distance, at 2.062(5) Å is relatively short [24], but not unexpected [23, 25, 26] and suggests that there are no steric problems hindering nitrogen coordination. When opposite to a ligand of larger *trans* influence, e.g. trialkyl phosphine [1, 2, 27–29],

sp^2 nitrogen coordinated to Pt(II) has Pt–N separations in the range 2.14–2.21 Å. The bond angles at platinum are typical for this type of complex and do not deviate from the *c.* 90 and 180° angles in any special way.

We turn now to the question of whether our structure can afford a hint as to the relative stability of our complexes. Initially, we considered the possibility of some form of intra- (or inter-) molecular hydrogen bond, e.g. NH coordinated to Cl as a potential stabilizing influence; however, the packing distances do not support this latter hypothesis. There is only one short contact, suggestive of an intermolecular hydrogen bond between N(2) and O(3′), 2.886(7) Å. Further, there are no especially short contacts from the α-aminoether moiety to the Pt(II). Interestingly, the O(2)–C(10) bond length, 1.404(8) Å, is short relative to the O(2)–C(17) separation of 1.459(9) Å. C–O distances in ethers are usually [29] of the order of 1.43 Å. This shortish bond may arise as a consequence of the presence of the electronegative m-$NO_2C_6H_4$ combined with the amino-nitrogen both attached to C(10), and may be related to the stability observed in solution. The N(2)–C(10) separation of 1.452(8) Å is close to what is normally expected [30] for a C–N single bond, 1.47 Å, but considerably longer than that observed for the N(2)–C(2) bond length of 1.331(8) Å. This latter C–N value is longer than those found for the C=N in benzylidene aniline derivatives [31], 1.237(3)–1.281(12) Å, thereby suggesting partial double bond character between C(2) and N(2). This, in turn, lends some support to the possible validity of a resonance structure related to **9**. The structural data do not allow us to definitely assign the observed hydrolysis resistance to these bonding effects, i.e. a relatively strong O(2)–C(10) bond; however, they are very suggestive.

Experimental

Instrumentation and measurements

NMR spectra were measured on WM-250 and AC-200 Bruker spectrometers as $CDCl_3$ solutions (unless otherwise specified). IR spectra were measured as CsI pellets using a Perkin-Elmer 883 infrared spectrometer. Microanalyses were carried out in the analytical laboratory of the ETH, Zurich.

2-Aminobenzimidazole and -oxazole were purchased from Fluka AG. Unless otherwise specified reactions were carried out under an N_2 atmosphere. Since the reactions involving **1** (or **2**), Zeise's salt and alcohol were carried out as suspensions (**1** and **2** are only moderately soluble and KCl precipitates during the reaction), the extent of the reaction was determined by (i) filtration of KCl, (ii) concentrating the CH_2Cl_2/CH_3OH to dryness and (iii) dissolving the solid in $CDCl_3$ followed by ^1H NMR analysis. Using Zeise's dimer to prepare **7** also resulted in partial precipitation of products from CD_2Cl_2 solution as they formed. This method of determining the extent of reaction leads to qualitative results only since (i) evaporation leads to a preferential increase in CH_3OH concentration and (ii) it assumes the reaction is not reversible. For the reactions with CH_2Cl_2/CH_3OH, 1:1, we have a substantial excess of CH_3OH in any case and measurements on the pure substances suggest that the back reactions for **4** and **5** are very slow, relative to our work-up and measurement time.

Preparation of the ligands 1 and 2

All of the ligands were prepared in an identical fashion. For **1a**: a suspension of 3-nitrobenzaldehyde (5.20 g, 39.0 mmol) and 2-aminobenzimidazole (5.19 g, 39.0 mmol) in 50 ml toluene was heated in a Dean-Stark trap until no additional formation of water was detected. The solid which remains suspended was filtered and washed with hexane. Drying affords product (9.9 g, 95%). An alternative work-up involved suspending the crude solid in hot ethanol, filtration and subsequent washing with ether. Microanalytical and NMR data are given in the Tables.

Preparation of 4

These were all prepared as described for **4a**. To a solution of **1a** (217 mg, 0.81 mmol) in 20 ml CH_2Cl_2 was added a solution of $K[PtCl_3(C_2H_4)]$ (300 mg, 0.81 mmol) in 20 ml CH_3OH and the resulting mixture stirred for 2 h at room temperature. Filtration of KCl was followed by removal of the solvents *in vacuo* and recrystallization from methylene chloride/hexane to afford the product (390 mg, 81%).

Preparation of 5e

The use of Zeise's salt in the preparation of **5e** gave only a 13% yield; consequently, an analogous reaction using Zeise's dimer was carried out. Ligand **2c** (28.1 mg, 0.0879 mmol) and $[Pt(\mu\text{-}Cl)Cl(C_2H_4)]_2$ (28.78 mg, 0.049 mmol) were placed in a flask containing 3 ml CH_2Cl_2 and 3 ml CH_3OH and then stirred for 15 min. Filtration followed by removal of the solvents *in vacuo* afforded an essentially quantitative conversion to **5e** as a yellow solid.

Preparation of 13

A suspension of *trans*-$PdCl_2$(**1a**)(PEt_3) (**12**) (122 mg, 0.22 mmol) prepared by treating the palladium dimer with 2 equiv. of **1a** in CH_2Cl_2 and RX from methylene chloride/hexane, was heated in 15 ml

CH_3OH for 2 h. Removal of solvent *in vacuo* was followed by RX from methylene chloride/hexane to afford the product (101 mg, 72%).

Crystallography

Crystals suitable for X-ray diffraction of compound **5c** were obtained by crystallization from methylene chloride/hexane and are air stable.

A prismatic crystal was mounted on a glass fiber at a random orientation on an Enraf-Nonius CAD4 diffractometer and used for the unit cell and space group determination as well as for the data collection. Unit cell dimensions were obtained by least-squares fit of the 2θ values of 25 high order reflections ($9.0 < \theta < 14.0$) using the CAD4 centering routines. Selected crystallographic and other relevant data are listed in Table 6; see also 'Supplementary material'.

Data were measured with variable scan speed to ensure constant statistical precision on the collected intensities. Three standard reflections were used to check the stability of the crystal and of the experimental conditions and were measured every hour; no significant variation was detected. The orientation of the crystal was checked by measuring three reflections every 300 measurements. Data have been corrected for Lorentz and polarization factors and for decay, using the data reduction programs of the CAD4-SPD package [32]. An empirical adsorption correction was applied by using azimuthal (Ψ) scans of three 'high-χ' angle reflections ($84° < \chi < 88°$; $7.6° < \theta < 15.4°$). Transmission factors were in the range 0.619–0.998. The standard deviations of intensities were calculated in term of statistics alone, while those on F_0 were calculated as reported in Table 6. Intensities were considered as observed if $|F_0 2| > 2.0\sigma |F_2|$. A $F_0 = 0.0$ was given to those reflections having negative net intensities.

TABLE 6. Experimental data for the X-ray diffraction study of **5c**

Chemical formula	$C_{19}H_{20}Cl_3N_3O_5Pt$
Molecular weight	671.823
Space group	$P\bar{1}$ (No. 2)
a (Å)	10.024(3)
b (Å)	11.242(9)
c (Å)	13.158(3)
α (°)	96.07(3)
β (°)	107.01(2)
γ (°C)	109.52(3)
Z	2
V (Å^3)	1302(3)
D_{calc} (g cm^{-3})	1.713
μ (cm^{-1})	63.69
T (°C)	22
λ (Å)	0.71069 (graphite monochromated, Mo K$\bar{\alpha}$)
Transmission coefficient	0.998–0.619
R[a]	0.044
R_w[b]	0.052

[a] $R = \Sigma||F_o| - 1/k|F_c||/\Sigma|F_o|$. [b] $R_w = [\Sigma w(|F_o| - 1/k|F_c|)^2/\Sigma w|F_o|^2]^{1/2}$ where $w = [\sigma^2(F_o)]^{-1}$ and $\sigma(F_o) = [\sigma^2(F_o{}^2 + f^2(F_o{}^2)^2]^{1/2}/2F_o$ with $f = 0.045$.

TABLE 7. Final atomic coordinates and isotropic thermal parameters for **5c**[a]

Atom	x	y	z	B (Å^2)
Pt	0.10726(4)	0.23228(3)	0.25833(3)	3.398(7)
Cl1	−0.1181(3)	0.0912(3)	0.1297(3)	5.82(8)
Cl2	0.3281(3)	0.3731(3)	0.3900(3)	5.85(8)
Cl3	−0.3570(3)	0.1271(3)	0.4816(2)	6.30(8)
O1	−0.0345(6)	0.5409(6)	0.3114(5)	3.4(1)
O2	−0.0269(6)	0.6130(6)	0.0937(6)	3.7(2)
O3	−0.2680(7)	0.5828(7)	−0.1033(6)	4.9(2)
O4	0.4825(9)	0.8025(9)	−0.1047(7)	6.8(2)
O5	0.3125(9)	0.6147(9)	−0.1257(6)	6.2(2)
N1	0.0074(7)	0.3606(7)	0.2848(6)	3.4(2)
N2	0.1234(7)	0.5392(7)	0.2163(6)	3.6(2)
N3	0.3900(8)	0.7250(9)	−0.0756(7)	4.7(2)
C1′	0.2442(9)	0.7323(8)	0.1543(7)	3.3(2)
C2	0.0356(9)	0.4767(8)	0.2682(7)	3.1(2)
C2′	0.2553(9)	0.6936(9)	0.0562(8)	3.4(2)
C3′	0.377(1)	0.7705(9)	0.0317(8)	3.7(2)
C4	−0.211(1)	0.4746(9)	0.4126(8)	4.0(2)
C4′	0.484(1)	0.883(1)	0.0986(9)	5.1(3)
C5′	0.469(1)	0.921(1)	0.197(1)	5.9(3)
C5	−0.284(1)	0.371(1)	0.4501(8)	4.4(2)
C6′	0.349(1)	0.846(1)	0.2232(9)	4.7(3)
C6	−0.260(1)	0.256(1)	0.4333(8)	3.9(2)
C7′	0.110(1)	0.6550(8)	0.1821(8)	3.6(2)
C7	−0.165(1)	0.2367(9)	0.3806(8)	3.7(2)
C8	−0.0916(9)	0.3437(8)	0.3426(7)	3.1(2)
C9	−0.1180(9)	0.4556(8)	0.3606(7)	3.2(2)
C10	−0.074(1)	0.717(1)	0.0610(9)	4.8(3)
C11	−0.243(1)	0.659(1)	−0.0027(9)	4.8(3)
C12	−0.427(1)	0.517(1)	−0.164(1)	6.4(4)
C13	0.187(1)	0.077(1)	0.280(1)	6.2(3)
C14	0.227(1)	0.134(1)	0.194(1)	6.1(3)

[a] Anisotropically refined atoms are given in the form of the isotropic equivalent thermal parameter defined as: $4/3[a^2B(1,1) + b^2B(2,2) + c^2B(3,3) + ab(\cos\gamma)B(1,2) + ac(\cos\beta)B(1,3) + bc(\cos\alpha)B(2,3)]$.

The structure was solved by a combination of Patterson and Fourier methods and refined by full matrix least-squares (the function minimized was $[\Sigma w(F_0 - 1/k|F_c|)^2]$) with $w = [\sigma^2(F_0)]^{-1}$. No extinction correction was applied.

The scattering factors used, corrected for the real and imaginary parts of the anomalous dispersion, were taken from the literature [33]. Anisotropic temperature factors were used for all but the hydrogen atoms.

The contribution of the hydrogen atoms in their calculated positions (C–H = 0.95 Å, $B = 5.0$ Å^2) was taken into account but not refined.

Upon convergence (no parameter shift $>0.4\sigma(p)$) the Fourier difference map showed no significant feature. All calculations were carried out by using the SPD crystallographic package [32]. Final atomic coordinates and thermal factors are given in Table 7.

Supplementary material

Experimental data for the X-ray diffraction study (Table SI, 2 pages), anisotropic thermal parameters (Table SII, 2 pages), extended list of bond lengths and angles (Table SIII, 3 pages) and torsion angles (Table SIV, 1 page) are available from the authors on request. F_0/F_c values (36 pages) have already been deposited (see ref. 6).

Acknowledgements

We thank the ETH Zürich, the Swiss National Science Foundation and the Italian CNR for support as well as Johnson Matthey for the loan of precious metals.

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