Unusual Dehydrogenation of a Diethylenetriamine Ligand to a Schiff Base Ligand in the Co-ordination Sphere of Platinum(IV)

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Trans,mer-[(OH)$_2$(dien)Pt(*N*-3-1mec)](ClO$_4$)$_2$, (**2**), (dien = diethylenetriamine, $C_4H_{13}N_3$; 1mec = 1-methylcytosine, $C_5H_7N_3O$) is, on warming in H_2O, pH *ca.* 2—6, converted to several products, including the corresponding *sym-fac, cis*-isomer (**4**) and a Pt^{II} compound [($C_4H_{11}N_3$)Pt(*N*-3-1mec)](ClO$_4$)$_2$, (**3**), which contains the tridentate Schiff base ligand NH$_2$–CH$_2$–CH=N–CH$_2$–CH$_2$–NH$_2$.

Diethylenetriamine has been widely applied in co-ordination chemistry.[1] It usually behaves as a tridentate and innocent ligand, although exceptions are known.[2] We herewith report on an unexpected and unusual dehydrogenation of dien co-ordinated to a Pt^{IV} leading to *N*-[2-aminoethylidene]-1,2-diaminoethane which, to our knowledge, has not previously been observed. Formally *mer,trans*-[(OH)$_2$(dien)Pt(*N*-3-1mec)](ClO$_4$)$_2$ (**2**) reacts to give (**3**) as depicted in Scheme 1.

In a parallel reaction, (**2**) is also converted to an isomer (**4**) in which the dien ligand is *fac* as opposed to *mer* in (**2**).† Minor

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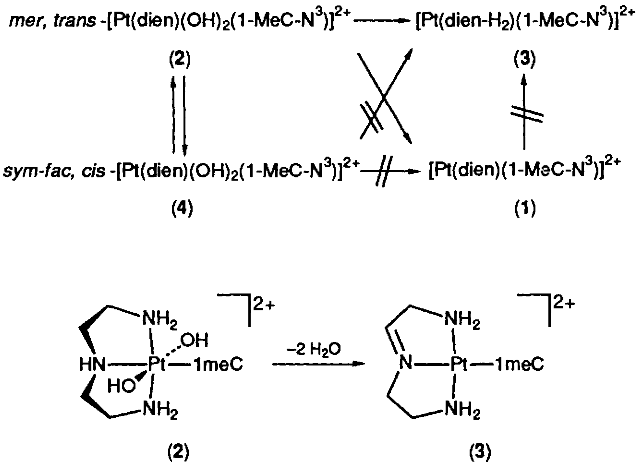
† The *mer* orientation of the dien ligand in (**2**) was unambiguously established by comparing the dien resonance pattern with that of a related nucleobase complex of known *X*-ray structure.[3]



identified products are $[(\text{dien})\text{Pt}(N\text{-3-1mec})]^{2+}$, (**1**),[‡] and 1mec. We discovered these reactions while studying metal (Pt) migration processes on the model nucleobase 1-methylcytosine. With *trans,trans,trans*-$[\text{Pt}(\text{NH}_3)_2(\text{OH})_2(\text{1mec})_2]^{2+}$, we had observed Pt^{IV} migration from *N*-3 to *N*-4. This process took place *via* a *N*-3, *N*-4 chelate intermediate and occurred in a sequential elimination and addition of H_2O.[4,5] In contrast (**2**),[‡] obtained from $[(\text{dien})\text{Pt}(N\text{-3-1mec})]\,(\text{ClO}_4)_2$, (**1**),[‡] on oxidation with H_2O_2, showed completely different behaviour. According to ^{1}H NMR spectroscopy, two major new products, (**3**)[‡] and (**4**)[‡], are formed on heating (70 °C) an aqueous solution of (**2**). Typically, 50% of (**2**) is converted within 24 h to (**3**) (25%), (**4**) (10—15%), (**1**) (1—6%), and 1mec (1—10%), depending on the pH. After 4 days, (**3**) represents the major component (60%) of the mixture. Both (**3**) and (**4**) were isolated on a preparative scale. As concluded from the ^{1}H NMR spectrum[§] of isolated (**4**) and confirmed by preliminary *X*-ray data, (**4**) is *sym-fac,cis*-$[(\text{dien})(\text{OH})_2\text{Pt}(N\text{-3-1mec})]^{2+}$. Neither (**1**) nor (**4**) appear to be intermediates between (**2**) and (**3**) as concluded from the solution behaviour of isolated (**1**) and (**4**), respectively.

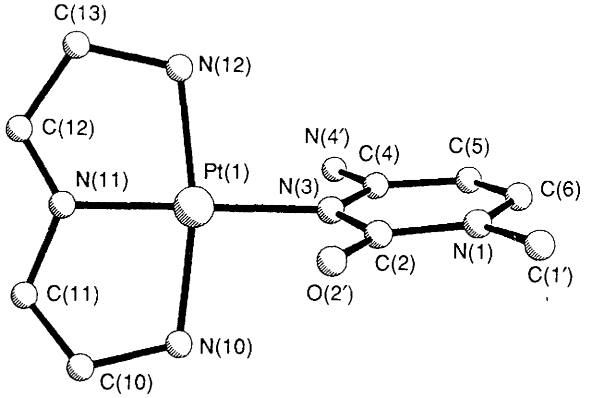


Figure 1. View of the cation of $[(\text{C}_4\text{H}_{11}\text{N}_3)\text{Pt}(N\text{-3-1mec})](\text{ClO}_4)_2$ (**3**) and the atom numbering scheme. Pt(1), N(3), N(10), N(11), N(12) are in the plane.

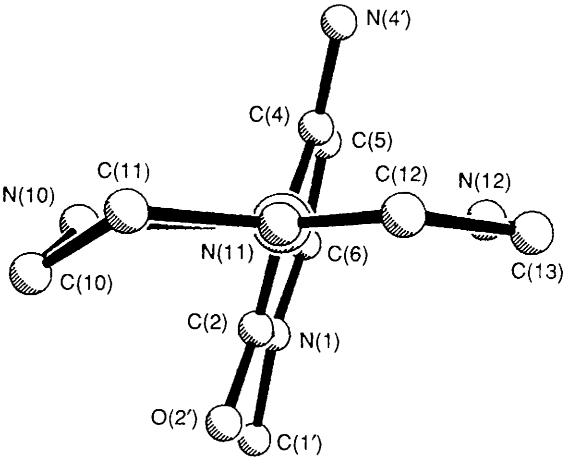


Figure 2. The cation of (**3**) as viewed along the N(11), Pt(1), N(3) vector, demonstrating the nearly planar Pt(1), N(11), C(12), C(13), N(12) chelate ring.

The crystal structure of (**3**)[¶] has been determined. Figures 1 and 2 illustrate the cation of (**3**). Figure 1 appears to be almost the same as a $[(\text{dien})\text{Pt}^{\text{II}}\text{L}]$ compound. However, a closer look at structural details and in particular the side view of the cation (Figure 2) shows that the original dien ligand has been converted to a Schiff base ligand. In $[(\text{dien})\text{Pt}^{\text{II}}\text{L}]$ compounds, the two carbons adjacent to the bridgehead N atom are dislocated from the PtN_3 plane by 0.5—0.8 Å;[3,6] in the case of (**3**) only a single CH_2 group [C(10)], which is not adjacent to the bridgehead N, is substantially out of the plane (0.45 Å) of the Schiff base ligand. All other atoms are within *ca.* 0.1 Å of the PtN_4 plane. This change is caused by the introduction of a double bond [1.30(3) Å] between N(11) and C(12). The N(11)–C(11) bond length [1.47(3) Å] is in the normal range for a C–N single bond. Angles about N(11) are 121(1)° [Pt–N(11)–C(12)], 112(1)° [Pt–N(11)–C(11)], and 126(2)° [C(11)–N(11)–C(12)] and are consistent with a nearly planar environment for N(11). In the ^{1}H NMR spectrum (D_2O, pD 4.8, 0.06 M) of (**3**), the proton at C(12) occurs at 8.16 ppm with characteristic ^{195}Pt satellites of ^3J 100 Hz, visible even at 300 MHz. The COSY spectrum shows this proton to correlate with two of the three CH_2 resonances centred at 4.20 and 3.78 ppm. The third CH_2 set at 3.21 does not couple with the 8.16 ppm peak. The 1mec resonances occur at positions typical of Pt^{II} compounds containing the ligand bound *via* N(3) [7.61 ppm, H(6), d, ^3J *ca.* 7.3 Hz; 6.04, H(5), d; 3.42 ppm (CH_3), s]. The ^{13}C NMR resonance of C(12) of (**3**) in D_2O, pD 4.8 is observed at 177.4 ppm (^{195}Pt satellites, ^2J *ca.* 76 Hz) and was identified by a DEPT experiment.

The reaction (**2**) → (**3**) formally represents a condensation

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[‡] Compound (**1**) was prepared from $[(\text{dien})\text{PtI}]\text{I}$, AgClO_4, and 1mec in 93% yield. Compound (**2**) was obtained in 60% yield by treating (**1**) with H_2O_2 as previously described.[4] Compounds (**3**) and (**4**) were isolated by fractional crystallization of a warmed sample of (**2**) (3—5 d, 70 °C, HNO_3, pH *ca.* 2) in the sequence (**3**), (**2**), and (**4**). Isolated yields after recrystallisation from water were 15% each. Satisfactory elemental analyses (C, H, and N) were obtained for (**1**), (**2**), and (**3**). Based on the Cl content and its behaviour in water, (**4**) crystallises as (**4**) · 0.5 HClO_4 when isolated at pH *ca.* 2.

[§] ^{195}Pt-^{1}H(5) coupling constant (^4J *ca.* 9 Hz) indicated a Pt^{IV} oxidation state for (**4**).

[¶] *Crystal data*: $\text{C}_9\text{H}_{18}\text{N}_6\text{O}_9\text{PtCl}_2$, $M = 620.3$, orthorhombic, space group *Pbca*, $a = 19.820(3)$, $b = 15.085(3)$, $c = 12.215(2)$ Å, $U = 3652.1$ Å^3, $Z = 8$, $D_m = 2.26$, $D_c = 2.256$ g cm^{-3}, $\lambda = 0.71069$ Å. Crystal size 0.1 × 0.1 × 0.05 mm. Data were collected at room temperature $2 \leqslant \theta \leqslant 25°$. Lorentz, polarisation, and empirical absorption corrections were applied. 3215 Independent reflections were obtained and 2837 reflections with $F_o \geqslant 2\sigma(F_o)$ were used for the calculations. The structure was solved by the Patterson method. Refinement using anisotropic temperature factors for Pt and the two Cl atoms led to $R = 0.083$, $R_{wF} = 0.083$. Hydrogen atoms were ignored. Atomic co-ordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue 1.

reaction, consisting of a reductive elimination at the metal centre and a simultaneous oxidation of the dien ligand. In addition, both reductive elimination [giving (**1**)], nucleobase displacement (giving 1mec), and an isomerization reaction [giving (**4**)] take place. While the isomerization process (**2**) → (**4**) can be rationalized by assuming a ring-opening of the dien ligand and a penta-co-ordinate intermediate, the mechanism of the conversion (**2**) → (**3**) remains to be established.

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