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AN *sp*^{2} YLIDE CARBON-TO-METAL BONDING: X-RAY MOLECULAR STRUCTURE OF $[Pt^{II}(NH_2CH_2CH_2NH_2)(C_5H_4NC(O)CNC_5H_3(CH_3)_2\text{-}3,5)]ClO_4 \cdot 2H_2O$

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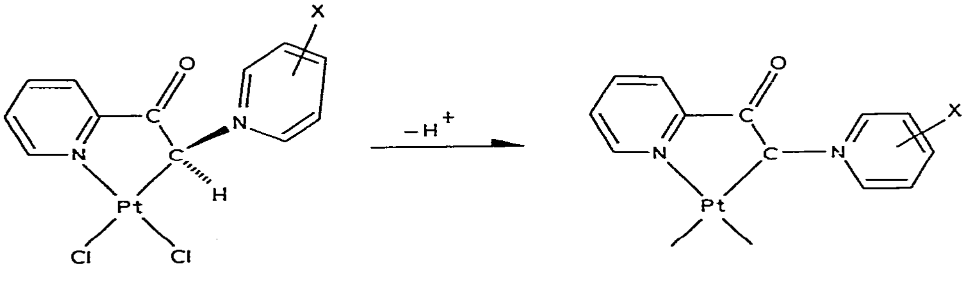
Summary

An X-ray structure analysis for the title complex obtained by the reaction of $Pt^{II}Cl_2(C_5H_4NC(O)\bar{C}H\overset{+}{N}C_5H_3(CH_3)_2\text{-}3,5)$ with ethylenediamine in water has revealed the presence of an ylide carbon atom which is coordinated to the platinum(II) ion with an *sp*^{2} configuration.

Ylide carbon atoms are well known to bond with metal ions forming a four-coordinate configuration. However, the bonding scheme that the ylide carbon atom ligating metal ions is three-coordinate has been reported only for limited phosphorus ylide-metal complexes [1–4]. Substituted pyridinium phenacylides and 2-pyridylcarbonylmethylides react with dichlorobis(dimethylsulfide)platinum(II) to form complexes having the ylide carbon-to-metal bond [5,6]. Elimination of ylide protons from platinum(II)-ylide complexes I is expected to afford a new type of ylide-metal complexes in which ylide carbon atoms attached to platinum are three-coordinate (eq. 1).



(1)

X = H, 4-CH_3, 3,5-$(CH_3)_2$, and 4-C_6H_5

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To a suspension of dichloro(3,5-dimethylpyridinium 2-pyridylcarbonylmethylide)platinum(II) [6] (0.14 g, 0.28 mmol) in water (20 cm^3) was added ethylenediamine (0.13 g, 2.2 mmol) and the mixture stirred for 1 h. The solids were dissolved, the solution turning red. After addition of $NaClO_4 \cdot H_2O$ (0.062 g, 0.44 mmol) the solution was concentrated to 50% of the volume under reduced pressure and heating (ca. 40°C). It was allowed to stand overnight to give red needles (0.070 g). This compound was formulated as $[Pt(NH_2CH_2CH_2NH_2)(C_5H_4NC(O)CNC_5H_3(CH_3)_2\text{-}3,5)]ClO_4 \cdot 2H_2O$ (II) on the basis of elemental analysis and spectroscopic characterization. In order to decide on the configuration of the three-coordinate ylide carbon attached to the metal ion, we have determined the crystal and molecular structure of II by X-ray diffraction.

Red needles of II crystallized in the monoclinic space group $P2_1/n$; a 19.032(3), b 7.923(1), c 14.590(2) Å; $\beta = 102.31(1)°$; V 2149.6(5) Å^3; $Z = 4$, D_c 1.903(5) g cm^{-3}, D_m (flotation) 1.91 g cm^{-3}. Intensity data were collected on a computer-controlled diffractometer using graphite-monochromatized Mo-K_α radiation. The structure was solved by the heavy-atom method and refined by the block-diagonal least-squares procedure to a current conventional R value of 5.2% for 3301 observed reflections ($|F_0| > 3\sigma(F)$). Anisotropic thermal vibrations were assumed for the non-hydrogen atoms. The hydrogen atoms were not included in the refinement.

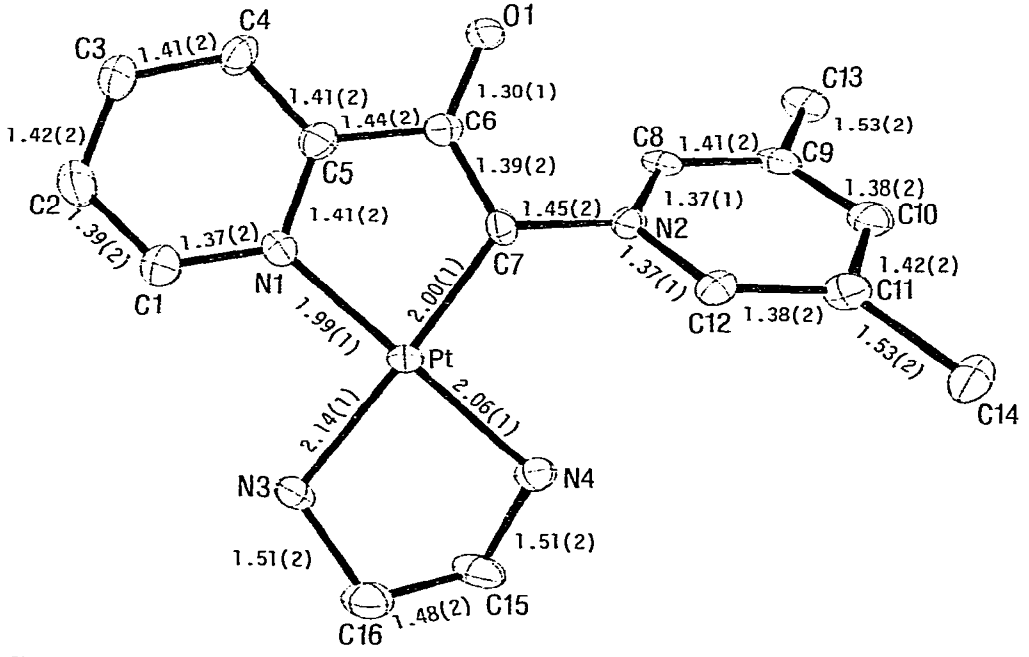

Fig. 1. View of the molecular structure of the cation moiety $[Pt(NH_2CH_2CH_2NH_2)(C_5H_4NC(O)CNC_5H_3(CH_3)_2\text{-}3,5)]^+$. ORTEP drawing [11] with 20% probability ellipsoids. Bond lengths (Å) are shown with e.s.d.'s in parentheses. Relevant bond angles (°) are: N(1)–Pt–C(7), 80.0(5); N(1)–Pt–N(3), 97.5(4); N(3)–Pt–N(4), 82.1(4); N(4)–Pt–C(7), 100.4(5); Pt–N(1)–C(5), 115.4(9); Pt–C(7)–C(6), 117.4(9); Pt–C(7)–N(2), 126.0(8); Pt–N(3)–C(16), 109.0(8); Pt–N(4)–C(15), 109.3(9); N(2)–C(7)–C(6), 116.7(10); C(5)–C(6)–O(1), 118.5(12); C(5)–C(6)–C(7), 112.3(10); C(7)–C(6)–O(1), 129.3(12).

The crystal structure consists of discrete cation moieties (Fig. 1) and perchlorate ions including two water molecules of crystallization. No unusual intermolecular contact was found. The platinum atom assumes a square-planar geometry with N(1), N(3), N(4), and C(7) within ±0.04 Å. Pt, N(2), C(7), C(6), and O(1) are also coplanar within ±0.01 Å: the ylide carbon atom, C(7), coordinated to platinum adopts an sp^2 configuration. This mode of ylide-metal attachment is the first example for nitrogen ylide-metal complexes, although only limited phosphorus ylide-metal complexes [3,4] containing three-coordinate ylide carbon atoms were well characterized by X-ray crystallographic studies.

The Pt–C(7) distance (2.00(1) Å) is close to Pt–C (sp^2 and carbenoid) (2.13–1.95 Å) [7,8]. The present complex does not show a remarkable shortening of the ylide–metal bond found in $(\eta^5\text{-}C_5H_5)_2ClZrCHP(C_6H_5)_3$ [3] and $(\eta^5\text{-}C_5H_5)_3UCHP(CH_3)_2(C_6H_5)$ [4]. Delocalization of electrons on the ylide carbon atom to the carbonyl group seems to cause the lengthening of C(6)–O(1) (1.30(1) Å) and rather short C(6)–C(7) distances (1.39(2) Å). This is similar for 2-pyridylcarbonylmethylide-metal complexes [9,10] in which coordination through the pyridyl nitrogen and carbonyl oxygen atoms is assumed. The 3,5-dimethylpyridinium ring is twisted by 47° from the C(7)–C(6)–C(5)–N(1)–Pt plane, which can be explained by steric hindrance between the C(12)-hydrogen and N(4)-hydrogen atoms. Moreover, this steric repulsion seems to cause the significantly large bond angle of Pt–C(7)–N(2) (126.0(8)°) compared with that of C(6)–C(7)–N(2) (116.7(10)°).

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