Synthesis, structures and catalytic properties of palladacycles derived from N,N-dimethylaminomethylferrocene

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ABSTRACT

Cyclopalladated complexes with a N,N-dimethylaminomethylferrocenyl (dmaf) backbone and three pyridine co-ligands, $[Pd\{(\eta^5\text{-}C_5H_5)Fe[(\eta^5\text{-}C_5H_3)CH_2NMe_2]\}Cl(R\text{-}Py)]$ (**2**: R = 4-H; **3**: R = 4-cyano; **4**: 4-N,N-dimethylamino) have been synthesized and characterized. The single crystal X-ray diffraction analyses show that the palladium(II) in both **3** or **4** is coordinated in a distorted square planar geometry with the two nitrogen atoms trans to each other. The three palladacyles were shown to greatly catalyze the methanolysis of the P=S containing pesticide parathion but showed different accelerations. It was found that the replacement of phenyl by ferrocenyl in the palladacycle backbone of **2** lowers the kinetic $_s^s pKa$ of the Pd-(HOCH_3) required for activity by almost 2 units.

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Phosphorothionate triesters comprise a family of compounds that are widely used as agricultural pesticides and have potent insecticidal and acaricidal properties while maintaining lower levels of toxicity toward mammals [1,2]. On the one hand, they greatly promote crop production, but on the other hand, the environmental accumulation of these toxic compounds presents potential ecological and health concerns. Moreover, these pesticides are chemically related to G- and V-type nerve agents [3]. For these reasons, developing an efficient chemical and biological decomposition strategy is highly desired. Despite many attempts including catalytic hydrolytic and oxidative process [4–6], however, decomposing these materials with the required efficiency and safety has remained largely unsuccessful. For practical applicability for the decomposition of organic phosphate pesticides and related chemical warfare agents, valuable decontamination methods are expected to occur at relatively neutral pH and room temperatures and to convert the toxic starting materials into far less toxic products completely at a rapid rate, e.g. $t_{1/2}$ values of less than a few minutes. Recently it was shown that some C,N-ortho cyclometalated palladium and platinum complexes can effectively catalyze the hydrolysis of phosphorothionates [7–10]. More recently, we have shown that a palladated complex containing the N,N-dimethylaminomethylphenyl ligand, namely Pd(dmba)-(py)(OTf), also promotes the methanolysis of phosphorothionates and shows greater catalytic efficacy in terms of reaction rate rela-

tive to the hydrolytic process [11]. The advantages of the catalytic methanolysis of phosphorothionates include higher solubility of both substrates and catalysts and non-inhibition of catalysis because of neutral, but less toxic, phosphorothionate products resulted from the process.

To develop more efficient catalysts and further understand the catalytic mechanism, we tried to incorporate a ferrocenyl group in the palladacyle and to investigate the effect on catalyst efficiency that would be provided by the high electron density on cyclopentadienyl rings. In this communication, we report on the structures and catalytic properties of the three palladacycles **2–4** containing N,N-dimethylaminomethylferrocenyl ligand (see Scheme 1).

Palladacycles **2–4** were synthesized in yields above 70% by the reaction with pyridine or substituted pyridines in benzene at room temperature from dimer compound **1**, which was prepared according to the literature method [12]. These were fully characterized by IR, ^1H NMR, and elemental analysis [13]. Complex **2** was first prepared by Komatsu et al. [14] and its crystal structure was also reported [15].

The IR spectra of **3** and **4** showed bands at ca. 3070 cm^{-1} that are characteristic of the ferrocenyl C–H stretching. The bands due to the C=N stretching of the pyridine ligands appear at 1604.5 and 1618.7 cm^{-1}, respectively, which are shifted to lower frequencies due to the coordination to the metal. Complex **3** also showed the band from the cyano group at 2233.5 cm^{-1}.

The NMR data support the formation of a Pd–C bond. The resonances due to the ferrocenyl fragments appear as four singlets of relative intensities 5:1:1:1. It is noted that the signal from the

Scheme 1.

R =H, 2; R =CN, 3; R = N(CH₃)₂, 4
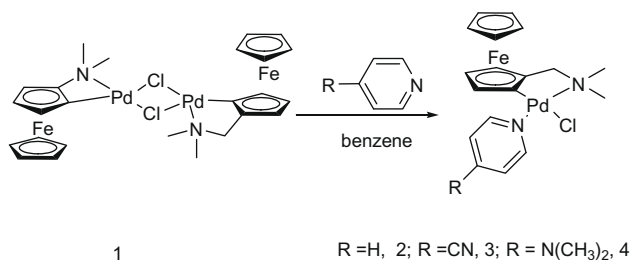
proton adjacent to the metalated carbon atom (H⁵) of **3** and **4** shifted to high-field at 3.25 and 3.04 ppm, respectively, which can be attributed to the ring current of the pyridine rings in a *cis*-arrangement to the metalated carbon atom [16]. This also indicates that the two nitrogen atoms from pyridine and amine moieties are a *trans* position. Thus the palladium coordination geometry of **3** and **4** in solutions is the same as those in crystal structures (see below).

Single crystals suitable for diffraction measurements were prepared by diffusing n-hexanes into a dichloromethane solution of the complex at room temperature. General views of palladacycles **3** and **4** are shown in Figs. 1 and 2, with the most important bond lengths and angles being given in the figure captions. Data collection details are given in Ref. [17].

It can be seen that the palladium atom displays the expected approximate square-planar coordination resulting from being bound to a chlorine, the two nitrogens from the pyridine and amine moieties and the carbon atom of the ferrocenyl unit. The two nitrogen atoms are positioned *trans* to one another in the two compounds. The C(1)–Pd(1)–Cl(1) and N(1)–Pd–N(2) angles are 172.45(6)° and 175.00(6)° for complex **3** and 178.01(6)° and 175.29(6)° for complex **4**. The Pd(1)–C(1), Pd(1)–Cl(1), and Pd(1)–N(1) bond lengths in **3** and **4** are almost in the same range as that seen for complex **2** and those in the palladacycles with *N,N*-dimethylbenzylamine and acetophenone oxime ligands [11]. Compared to the Pd–N1 bond length (2.170(10) Å) in [Pd{(η⁵-C₅H₅)Fe[(η⁵-C₅H₃)CH₂NMe₂]}Cl(PPh₃)] [18], those in **3** (2.0973(16) Å) and **4** (2.1158(17) Å) are shorter due to the weak *trans* effect of the pyridine relative to triphenylphosphine ligand. It is of note that the Pd(1)–N(2) bond lengths (2.0317(16) Å in **3**

and (2.0396(17) Å in **4**) are almost the same as that in **2** [15] indicating they are not greatly affected by the substituents on pyridine rings, no matter whether it is an electron-withdrawing cyano group in **3** or an electron-donating group *N,N*-dimethylamino moiety in **4**.

The metallacycle in complex **3** is practically planar and its mean plane forms an angle of 2.54° with the plane of the C₅H₃ ring. The dihedral angle between the pyridine and palladacyle plane consisting of Pd(1)–C(1)–C(10)–C(11)–N(1) is 56.14°. In complex **4**, the Pd atom shows a displacement equaling 0.076 Å from the mean plane of the metalacycle indicating that the coordination sphere is slightly distorted. The dihedral angle between the pyridine plane and the palladacyle plane in **4** is 57.11° and the dihedral angle between the palladacycle plane and the C₅H₃ ring is 17.79°. The average bond distances of Fe–C for substituted ring and unsubstituted ring are 2.052 and 2.04 Å in **3** while those in **4** are 2.053 and 2.048 Å. However, the Fe–C bond distances for the ring-carbon substituted by the CH₂–NMe₂ groups are the longest (2.0770(10) Å in **3** and 2.083(2) Å in **4**).

In preliminary experiments to determine the catalytic activity of **2–4** for the methanolysis of P=S pesticides, we investigated the methanolysis of parathion (O,O-diethyl O-(4-nitrophenyl)-phosphorothioate) under buffered condition (triethylamine, ^s_spH 10.80 [19], room temperature). The kinetics of the reaction were monitored by observing the rate of appearance of 4-nitrophenol at 320 nm and 25 °C using a Cary300 UV/visible spectrophotometer (Scheme 2) [20]. At [Pd] = 1×10^{-5} mol dm⁻³, the observed first-order rate constants for the complete methanolysis of parathion (2.0×10^{-5} mol dm⁻³) with **2–4** are 3.93×10^{-4}, 7.01×10^{-3} and 6.5×10^{-5} s⁻¹, respectively. Compared to the methoxide-catalyzed background reaction at the same ^s_spH of 10.8, which is calculated to be 1.02×10^{-8} s⁻¹ [21], palladacycles **2–4** at a concentration of 10^{-5} mol dm⁻³ afforded accelerations of 3.85×10^4, 6.87×10^5, and 6.37×10^3-fold, respectively. Thus, the three palladacycles can greatly accelerate the methanolysis of parathion but have different accelerations. The complex containing electron-withdrawing group cyano (**3**) is much more active (about 100-fold) than the complex containing the electron-donating *N,N*-dimethylamino group on co-ligand pyridine (**4**).

The concentration dependence of k_{obs}^{max} on [**2**] was measured under the same buffer condition, which shows linearity over the concentration range studied, and indicates that the kinetically

Fig. 2. Molecular structure of complex **4** showing the atom numbering. Displacement parameters are shown at the 50% level. Selected bond lengths (Å) and bond angles (°): Pd(1)–C(1) 1.967(2); Pd(1)–N(1) 2.1158(17); Pd(1)–N(2) 2.0396(17); Pd(1)–Cl(1) 2.4189(5); C(1)–Pd(1)–N(1) 83.07(7); C(1)–Pd(1)–N(2) 92.28(7); N(1)–Pd(1)–N(2) 175.29(6); C(1)–Pd(1)–Cl(1) 178.01(6); N(1)–Pd(1)–Cl(1) 94.98(5); N(2)–Pd(1)–Cl(1) 89.71(5).
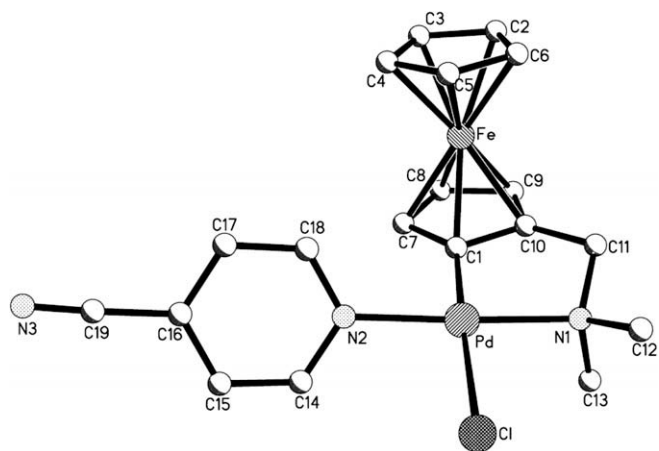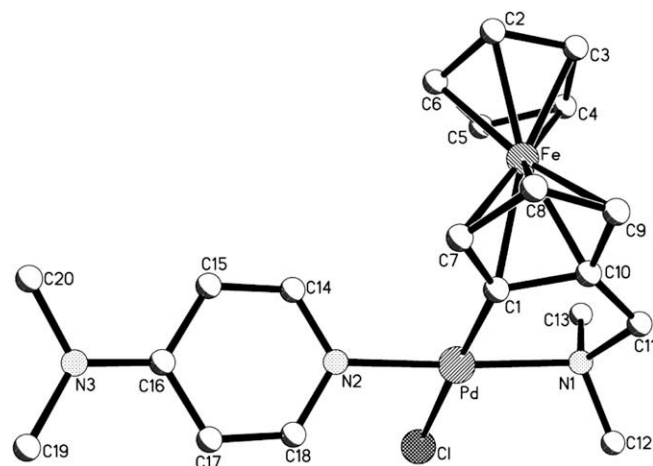

Fig. 1. Molecular structure of complex **3** showing the atom numbering. Displacement parameters are shown at the 50% level. Selected bond distances (Å) and bond angles (°): Pd(1)–C(1) 1.9747(19); Pd(1)–N(1) 2.0973(16); Pd(1)–N(2) 2.0317(16); Pd(1)–Cl(1) 2.4160(5); C(1)–Pd(1)–N(1) 82.34(7); C(1)–Pd(1)–N(2) 92.82(7); N(1)–Pd(1)–N(2) 175.00(6); C(1)–Pd(1)–Cl(1) 172.45(6); N(1)–Pd(1)–Cl(1) 94.84(4); N(2)–Pd(1)–Cl(1) 90.83(5).