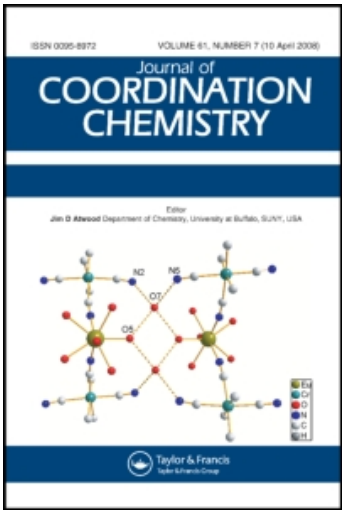

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(*S*)-4-*tert*-Butyl-2-phenyl-2-oxazoline derived palladacycles as efficient catalysts for the decomposition of P=S pesticides

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(*S*)-4-*tert*-Butyl-2-phenyl-2-oxazoline derived palladacycles as efficient catalysts for the decomposition of P=S pesticides#

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Three palladacycles with *N*,*N*-*trans* coordination, (*S*)-{2-[2-(4-*tert*-butyl)oxazolinyl]phenyl-C^1,N}(4-R-pyridine)(aqua)$_n$palladium(II) triflate (R = CF_3, $n = 1$, **1**; R = H, $n = 0$, **2**; R = NMe_2, $n = 1$, **3**), have been prepared from the respective chloride precursors and were characterized with IR and ^{1}H-NMR and elemental analyses. The crystal structures of **2** and a pincer complex (*S*,*S*)-{2,6-bis[2-(4-*iso*-propyl)oxazolinyl]phenyl-N,C^1,N}bromo-palladium(II) hydrate (**5**) were determined. For methanolysis of P=S pesticides, it was found that *ortho*-palladated complexes **1–3** effectively catalyzed the reaction; however, the pincer complex **4** with triflate counterion was much less active. Relative to the methoxide-promoted background reaction at ^s_spH 10.80, 1 mmol L^{-1} of palladacycles **1–3** can accelerate the methanolysis by 8.7×10^9, 1.5×10^9, and 1.0×10^8-fold, respectively. For racemic P=S pesticides, such as letophos and EPN, it proved that there is no clear chiral discrimination during the catalysis. The reaction mechanism of the catalytic methanolysis was discussed according to the experimental results.

Keywords: Palladacycle; Methanolysis; Pesticide; Kinetic

1. Introduction

Thiophosphoric acid esters comprise a family of compounds that are usually used as agricultural pesticides because of their high insecticidal and acaricidal properties but much lower mammalian toxicity than their P=O counterparts [1, 2]. With an annual world production of hundred thousands of tons, their widespread use and environmental accumulation are becoming an ecological and health threat. Finding green catalytic processes for efficient degradation of these chemicals has spurred much attention. Many efforts have been directed to catalytic or enzymatic hydrolysis and oxidation of these chemicals [3–9], but their efficiency including reaction speed and completeness of the degradation still needs to be greatly improved.

Recently, we demonstrated that *ortho*-palladated complex, Pd(dmba)(py)(OTf) (dmba = *N*,*N*-dimethylbenzylamine) [10], effectively catalyzed the methanolysis of

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#Dedicated to Prof. Rudi van Eldik on the occasion of his 65th birthday.

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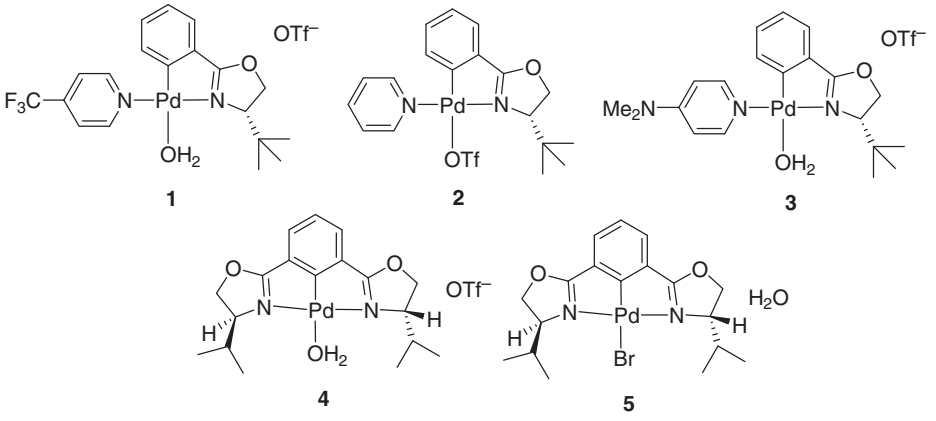


Scheme 1. Chemical structures of palladacycles.

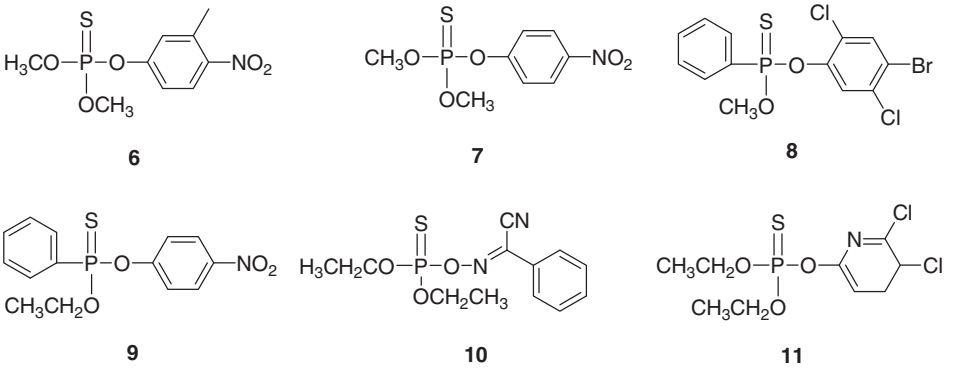
phosphorothionates. The advantages of a catalytic alcoholysis method over hydrolysis include greater substrate solubility in the alcohol medium, greatly increased reaction rates probably attributable to a lower dielectric constant/polarity medium effect that also gives enhanced M^{x+}: substrate pre-equilibrium complexation and the fact that the products are also neutral OP compounds that are non-inhibitory since they bind to the metal catalyst with a similar strength as the starting OP materials [11, 12].

To further investigate the system and develop more efficient catalysts, we have prepared palladacycles **1–3** derived from (*S*)-4-*tert*-butyl-2-phenyl-2-oxazoline ligands as well as pincer palladacycles **4** and **5** (scheme 1) by considering that pincer complexes are widely applied in catalysis [13–15]. The reason for incorporation of the chiral ligand in palladacycles is to explore the possibility of asymmetric methanolysis since some pesticides are racemic mixtures. Basicity effects of the co-coordinated pyridine ligands in the catalysis were also investigated. We report here their synthesis, characterization, crystal structures, and some kinetic studies of their catalytic methanolysis of certain P=S pesticides (scheme 2).

2. Experimental

2.1. *Materials and methods*

Methanol (99.8% anhydrous), sodium methoxide (0.5 mol dm^{-3} solution in methanol) and silver triflate (AgOTf) were purchased from Aldrich and used without purification. $HClO_4$ (70% aqueous solution) was purchased from BDH. Fenitrothion (**6**, *O*,*O*-dimethyl *O*-(3-methyl-4-nitrophenyl) phosphorothioate), methyl-parathion (**7**, *O*,*O*-dimethyl *O*-(4-nitrophenyl) phosphorothioate), letophos (**8**, *O*-4-bromo-2,5-dichlorophenyl *O*-methyl phenylphosphonothioate), and EPN (**9**, *O*-ethyl *O*-4-nitrophenylphenylphosphonothioate) were purchased from Chem. Service Inc.; phoxim (**10**, α-[[(diethoxyphosphinthioyl)oxy]-imino]benzene-acetonitrile) and



Scheme 2. Chemical structures of pesticides investigated.

chlorpyrifos (**11**, *O*,*O*-diethyl-*O*-[3,5,6-trichloro-2-pyridyl]-phosphorothiate) are gifts obtained from Beijing Yoloo Pesticide Company Ltd., China.

Caution: All the phosphorus substrates described herein are acetylcholinesterase inhibitors; compounds **6–10** have oral LD_{50} values of 250, 6, 43, and 8, 82,300 mg kg^{-1}, respectively in rats [16].

^{1}H- and ^{31}P-NMR spectra were determined at 400 and 161.97 MHz using a Bruker Avance-400 NMR spectrometer. In $CDCl_3$, ^{1}H-NMR spectra were referenced to the $CHCl_3$ peak at 7.26 ppm. ^{31}P-{1H}-NMR spectra were referenced to an external standard of 70% phosphoric acid in water, and upfield chemical shifts are negative. Elemental analyses were performed on an Elementar Vario El instrument. IR spectra were obtained as KBr pellets using a Nicolet 380 FT-IR spectrometer. Melting points were measured on a Fisher–John melting point apparatus.

2.2. *Preparation of palladacycles 1–4*

2.2.1. General procedure for 1–3. To a solution of (*S*)-chloro{2-[2-(4-*tert*-butyl)oxazolinyl]-phenyl-*C*,*N*}(4-R-pyridine)palladium(II) (R=CF_3, H, and NMe_2) [17] (0.30 mmol) in dichloromethane (20 mL) solid AgOTf (93.0 mg, 0.36 mmol, 1.2 eq) was added. The mixture was stirred at room temperature for 3 h and then filtered through celite. The celite was washed with another 20 mL of dichloromethane and the combined organics stripped of solvent by rotary evaporation under reduced pressure. The solid residue was recrystallized from a mixture of hexanes and dichloromethane to afford the desired product.

(*S*)-{2-[2-(4-*tert*-butyl)oxazolinyl]phenyl-C^1,N}(trifluoromethylpyridine)(aqua)-palladium(II) triflate, **1**. Yield: 75%, m.p.: 185°C.

IR (KBr, cm^{-1}): 3420(br), 2967(m), 1629(vs), 1488(m), 1422(m), 1327(vs), 1253(vs), 1170(vs), 1145(vs), 1029(vs), 921(m), 840(m), 734(m), 679(m), and 637(m). ^{1}H-NMR (ppm, 400 MHz, $CDCl_3$): δ 9.18 (d, J = 8.0 Hz, $H^{2'}$ and $H^{6'}$ on py), 7.75 (d, J = 8.0 Hz, $H^{3'}$ and $H^{5'}$ on py), 7.26 (d, J = 8.0 Hz, H^3 on phenyl), 7.10 and 6.99 (m, H^4 and H^5 on phenyl), 6.01 (d, J = 8 Hz, H^6 on phenyl), 4.73 (dd, J = 9.0 Hz, 3.0 Hz, OCH), 4.64 (t, J = 8.0 Hz, NCH), 4.08 (J = 9.0 Hz, 3.0 Hz, OCH), 1.73 (br, aqua), and

0.97 (s, $C(CH_3)_3$). ^{19}F-NMR (ppm, 376.45 MHz, $CDCl_3$): δ −67.73 (CF_3-py), and −81.1 ($CF_3SO_3^-$). Anal. Calcd for $C_{20}H_{22}F_6N_2O_5PdS$ (Fw: 622.87): C 38.57%, H 3.56%, N 4.50%. Found: C 38.22%, H 3.53%, N 4.43%.

(*S*)-{2-[2-(4-*tert*-butyl)oxazolinyl]phenyl-C^1,N}(pyridine)palladium(II) triflate, **2**. Yield: 79%, m.p.: 220°C (decom.).

IR (KBr, cm^{-1}): 2961(m), 1625(vs), 1574(m), 1454(m), 1409(m), 1309(vs), 1235(vs), 1204(s), 1015(vs), 921(s), 736(m), 694(m), and 637(m). ^{1}H-NMR (ppm, 400 MHz, $CDCl_3$): δ 8.90 (d, $J = 8.0$ Hz, $H^{2'}$, $H^{6'}$ on py), 7.94 (m, $H^{4'}$ on py), 7.49 (t, $J = 6.0$ Hz, $H^{3'}$, $H^{5'}$ on py), 7.23 (d, $J = 8.0$ Hz, H^3 on phenyl) and 7.07 (m, H^4 on phenyl), 6.98 (m, H^5 on phenyl), 6.10 (d, $J = 8.0$ Hz, H^6 on phenyl), 4.76 (dd, $J = 9.0$ Hz, 3.0 Hz, OCH), 4.58 (t, $J = 9.0$ Hz, NCH), 4.17 (dd, $J = 9.0$ Hz and 3.0 Hz, NCH), 1.04 (s, $C(CH_3)_3$). ^{19}F-NMR (ppm, 376.45 MHz, $CDCl_3$): δ −81.1 ($CF_3SO_3^-$). Anal. Calcd for $C_{19}H_{21}F_3N_2O_4PdS$ (Fw: 536.84): C 42.51%, H 3.94%, N 5.22%. Found: C 42.61%, H 4.14%, N 5.11%.

(*S*)-{2-[2-(4-*tert*-butyl)oxazolinyl]phenyl-C^1,N}(*N*,*N*-dimethylaminopyridine)-(aqua) palladium(II), **3**. Yield: 59%, m.p.: 210°C (decom.).

IR (KBr, cm^{-1}): 3420(br), 2960(m), 1624(vs), 1541(s),(m), 1398(s), 1302(vs), 1266(vs), 1224(vs), 1207(vs), 1025(s), 921(m), 817(m), 735(m), 679(m), and 634(m). ^{1}H-NMR (ppm, 400 MHz, $CDCl_3$): δ 8.33 (d, $J = 6.5$ Hz, $H^{2'}$ and $H^{6'}$ on py), 7.22 (m, H^3 on phenyl) and 7.02 (m, H^4 and H^5 on phenyl), 6.50 (d, $J = 6.5$ Hz, $H^{3'}$ and $H^{5'}$ on py), 6.43 (m, H^6 on phenyl), 4.70 (dd, $J = 8.0$ Hz, 2.5 Hz, OCH), 4.55 (t, $J = 8.0$ Hz, NCH), 4.12 (dd, $J = 8$ Hz, 2.5 Hz, OCH), 3.05 (s, 6H), 1.92 (br, aqua), and 1.06 (s, 9H). Anal. Calcd for $C_{21}H_{28}F_3N_3O_5PdS$ (Fw: 597.94): C 42.18%, H 4.72%, N 7.03%. Found: C 42.39%, H 4.62%, N 7.15%.

(*S*,*S*)-{2,6-Bis[2-(4′-*iso*-propyl)-oxazolinyl)]phenyl}aquapalladium(II) triflate (**4**)

Palladacycle **4** was prepared according to the literature method by using (*S,S*)-{2, 6-bis[2-(4′-*iso*-propyl)-oxazolinyl)]phenyl}bromopalladium(II) hydrate (**5**) as starting material and characterized by ^{1}H-NMR and elemental analysis [18]. The crystal structure of **5** has been determined.

2.3. *X-ray crystal structure determination*

Crystals of **2** and **5** suitable for diffraction measurements were prepared by slow diffusion of *n*-hexanes into dichloromethane solutions of the corresponding palladacycles. A single crystal of each was mounted on a glass fiber with grease and cooled to −93°C in a stream of nitrogen gas controlled with a Cryostream Controller 700. Data collection was performed on a Bruker SMART CCD 1000 X-ray diffractometer with graphite-monochromated Mo-Kα radiation ($\lambda = 0.71073$ Å), operating at 50 kV and 30 mA over 2θ ranges of 4.34–50.00° and 3.66–49.98° for **2** and **5**, respectively. No significant decay was observed during data collection.

Data were processed using the Bruker AXS Crystal Structure Analysis Package, version 5.10 [19]. Neutral atom scattering factors were taken from Cromer and Waber [20]. The raw intensity data were integrated using SAINT-Plus; absorption corrections were applied using SADABS [21].

The structural data for the data collection and refinement for palladacycles **2** and **5** are given in table 1. Selected bond lengths, bond angles, and torsional angles for the two

Table 1. Experimental data for the X-ray diffraction study on **2** and **5**.

Complex	**2**	**5**
Empirical formula	$C_{19}H_{21}F_3N_2O4PdS$	$C_{18}H_{25}BrN_2O_3Pd$
Formula weight	536.84	503.71
Temperature (K)	180(2)	180(2)
Wavelength (Å)	0.71073	0.71073
Space group	*P* 2(1)2(1)2(1)	*P* 2(1)2(1)2(1)
Unit cell dimensions (Å, °)		
a	10.0169(6)	14.4320(10)
b	10.5770(6)	5.9361(4)
c	20.1993(11)	11.1156(8)
α	90	90
β	90	90
γ	90	90
Volume (Å^3), *Z*	2140.1(2), 4	952.27(11), 2
Calculated density (g cm^{-3})	1.666	1.757
Absorption coefficient, (mm^{-1})	1.018	3.091
F(000)	1080	504
Crystal size (mm^3)	$0.35 \times 0.20 \times 0.10$	$0.30 \times 0.25 \times 0.20$
θ range for data collection (°)	2.17–25.00	1.83–24.99
Limiting indices	$-11 \le h \le 11$; $-12 \le k \le 12$; $-21 \le l \le 24$	$-17 \le h \le 16$; $-6 \le k \le 7$; $-13 \le l \le 13$
Reflections collected	12,667	5462
Independent reflections	3763 [R(int) = 0.0178]	1665 [R(int) = 0.0175]
Data/restraints/parameters	3763/2/365	1655/1/166
Goodness-of-fit on F^2	1.000	1.060
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0186$, $wR_2 = 0.0489$	$R_1 = 0.0177$, $wR_2 = 0.0464$
Largest difference peak and hole (e Å^{-3})	0.313 and −0.277	0.381 and −0.345

complexes are presented in table 2. ORTEP diagrams for **2** and **5** at the 50% probability level are given in figures 1 and 2, respectively.

2.4. *Kinetic methods*

The $CH_3OH_2^+$ concentration was determined using a Denver Ultrabasic pH meter calibrated with standard aqueous buffers (pH 4.00 and 10.00). Values of ^s_spH were calculated by subtracting a correction constant of −2.24 from the experimental meter reading as reported by Bosch *et al*. [22–24].

For designation of pH in non-aqueous solvents we use the forms recommended by the IUPAC, *Compendium of Analytical Nomenclature*. *Definitive Rules 1997* 3rd Edn, Blackwell, Oxford, UK (1998). The term ^s_spH designates that "pH" is measured in, and referenced to, the same solvent, which in this case is methanol. Since the autoprotolysis constant of methanol is $10^{-16.77}$, neutral ^s_spH is 8.4 for methanol.

2.4.1. Kinetics on methanolysis of 6. The kinetics of methanolysis of fenitrothion **6** promoted by **1–4** were monitored by observing the rate of appearance of 3-methyl-4-nitrophenol at 318 nm or 3-methyl-4-nitrophenolate at 404 nm using a Varian Cary 300 UV-Vis spectrophotometer. All reactions were followed to at least three half-times at 25 ± 0.1°C under buffered conditions. Buffers were prepared from *N*-methylmorpholine (^s_sp*K*a = 8.23), trimethylamine (^s_sp*K*a = 9.60), triethylamine (^s_sp*K*a = 10.78), and 2,2,6,6-tetramethylpiperidine (^s_sp*K*a = 11.86). The total [buffer] varied between 1 and

Table 2. Selected bond lengths (Å), angles (°), and torsion angles (°) for **2** and **5**.

2		**5**	
Pd(1)–C(2)	1.978(2)	Pd(1)–C(1)	1.943(4)
Pd(1)–O(2)	2.1789(18)	Pd(1)–Br(1)	2.5190(5)
Pd(1)–N(1)	2.0301(17)	Pd(1)–N(1)	2.068(2)
Pd(1)–N(2)	2.0386(18)	Pd(1)–N(1)$^{\#1}$	2.068(2)
C(2)–Pd(1)–N(1)	81.60(9)	C(1)–Pd(1)–N(1)	78.89(7)
C(2)–Pd(1)–N(2)	92.69(10)	C(1)–Pd(1)–N(1)$^{\#1}$	78.89(7)
N(1)–Pd(1)–N(2)	172.22(9)	N(1)–Pd(1)–N(1)$^{\#1}$	157.77(13)
C(2)–Pd(1)–O(2)	175.72(9)	C(1)–Pd(1)–Br(1)	180.0
N(2)–Pd(1)–O(2)	91.20(7)	N(1)–Pd(1)–Br(1)	101.11(7)
N(1)–Pd(1)–O(2)	94.36(7)	N(1)$^{\#1}$–Pd(1)–Br(1)	101.11(7)

#1: $-x$, $-y-2$, z.

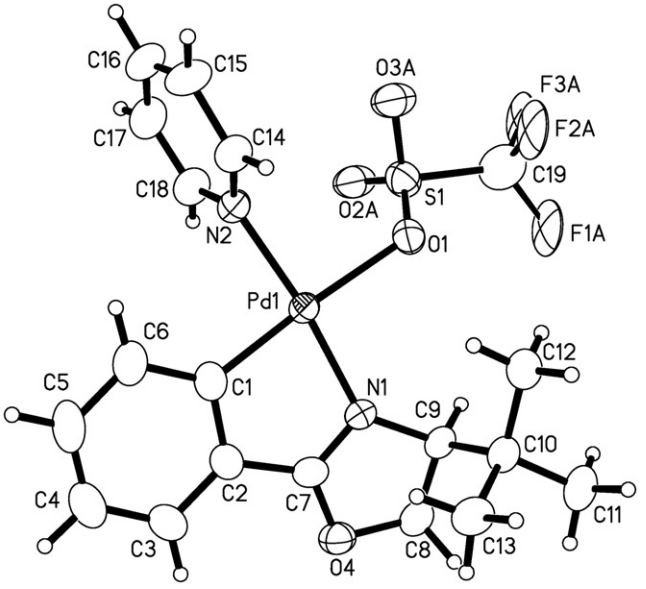


Figure 1. ORTEP presentation of the molecular structure of **2**. Displacement ellipsoids for non-H atoms are shown at the 50% probability level and hydrogens are represented by circles of arbitrary size.

3×10^{-3} mol dm^{-3} and the buffers were partially neutralized with 70% $HClO_4$. To avoid any chloride contamination from the glass electrode that might affect the metal ion reactions duplicate solutions were prepared, one for $^{s}_{s}$pH measurements, and the second portion being used for kinetics. In all cases, $^{s}_{s}$pH values measured before and after reaction were consistent within 0.1 unit.

The pseudo-first-order rate constants (k_{obs}) were evaluated by fitting absorbance *versus* time traces to a standard exponential model. Stock solutions of palladium complexes **1–4** were prepared in pure methanol at 2×10^{-3} mol dm^{-3}. In order to determine the kinetic order in [Pd], a series of kinetic runs was undertaken at $^{s}_{s}$pH 10.80, (triethylamine buffer) using 2.84×10^{-5} mol dm^{-3} fenitrothion **6** in the presence of varying [Pd] from $(0.4 \times 10^{-5}$ to 8×10^{-5} mol dm^{-3}. The pseudo-first-order rate constants (k^{obs}_{max}) were obtained by extrapolating to [buffer] = 0.0 mol dm^{-3}. The k_{obs}

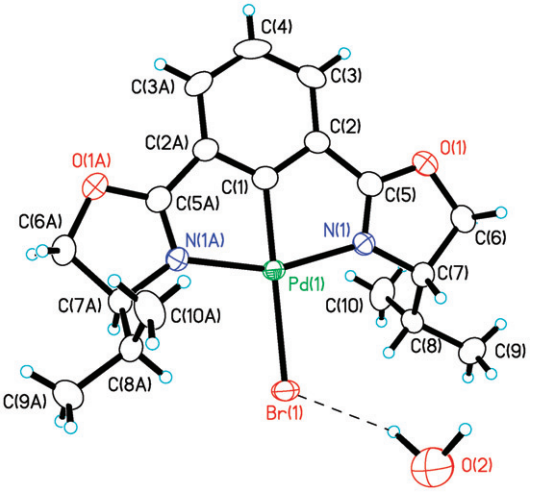


Figure 2. ORTEP presentation of the molecular structure of **5**. Displacement ellipsoids for non-H atoms are shown at the 50% probability level and hydrogens are represented by circles of arbitrary size.

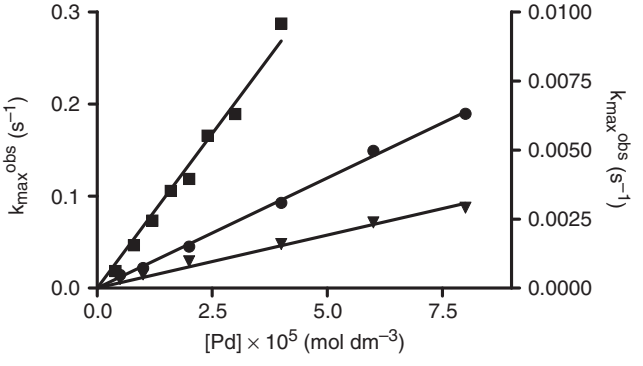


Figure 3. A plot of k_{max} *vs.* [Pd] of palladacycles **1–3** for methanolysis of **6** [2.84×10^{-5} mol dm^{-3}] at 25°C, buffer triethylamine (1–3) × 10^{-3} mol dm^{-3}, extrapolated to zero [buffer], $^{s}_{s}$pH 10.80. k_{max} of **1** (■) and **2** (▼) corresponds to left *Y*-axis and that of **3** (●) corresponds to right *Y*-axis. Maximal second-order rate constant (k_2^{max}) for catalyzed reaction from the gradients of the plots.

versus [Pd] plots gave straight lines (figure 3), the gradients of which were taken as the second-order catalytic rate constant (k_2^{obs}) and listed in table 3.

The $^{s}_{s}$pH dependence of the catalytic rate constant was determined by obtaining the k_{max}^{obs} rate constants for methanolysis of 2.84×10^{-5} mol dm^{-3} of **6** between $^{s}_{s}$pH 9.08 and 12.2 in the presence of a single concentration of **1–3** (2.0×10^{-5} mol dm^{-3}). The k_2^{obs} second-order rate constants are obtained as $k_{max}^{obs}/(2 \times 10^{-5}$ mol $dm^{-3})$ and are plotted in figure 4. The data of the kinetic experiments can be found in "Supplementary material", named as suppl-kinetic-data.pdf.

2.4.2. Turnover experiments. To demonstrate that palladacycles were truly catalytic, turnover experiments of the methanolysis of an excess of substrates **6–11** (scheme 3) relative to palladacycles were investigated in triethylamine buffer at $^{s}_{s}$pH

Table 3. Second-order rate constants (k_2^{obs}) from concentration dependence at ${}^{s}_{s}pH$ 10.80, and the maximum second-order rate constants from fits to equation (2) of the ${}^{s}_{s}pH/k_2$ kinetic data for methanolysis of **6** catalyzed by palladacycles **1–3** at $[Pd] = 2.0 \times 10^{-5}$ mol dm^{-3}, $[\mathbf{6}] = 2.84 \times 10^{-5}$ mol dm^{-3}, and 25°C.

Palladacycles	k_2^{obs} (mol^{-1} dm^3 s^{-1})	k_2^{max} (mol^{-1} dm^3 s^{-1})	pK_a
1	$(6.7 \pm 0.2) \times 10^3$	$(7.5 \pm 0.8) \times 10^3$	10.78 ± 0.08
2	$(1.15 \pm 0.04) \times 10^3$	$(4.2 \pm 0.2) \times 10^3$	11.00 ± 0.03
3	$(0.080 \pm 0.001) \times 10^3$	$(0.36 \pm 0.11) \times 10^3$	11.0 ± 0.2
MeO$^-$	7.2×10^{-4}		

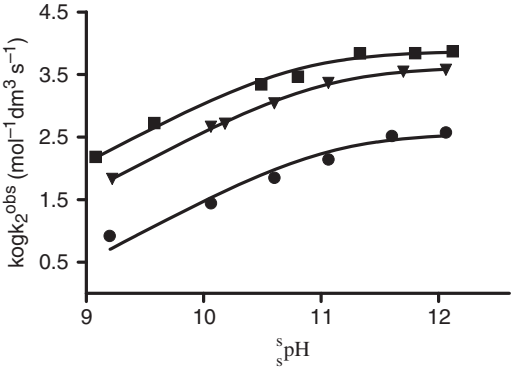
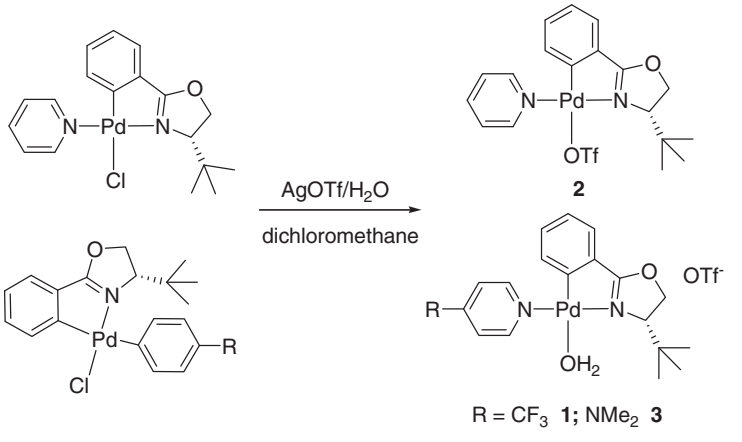


Figure 4. Plot of log k_2^{obs} *vs.* ${}^{s}_{s}pH$ for methanolysis of **6** at $[\mathbf{6}] = 2.84 \times 10^{-5}$ mol dm^{-3}, catalyzed by palladacycles **1** (■), **2** (▼), **3** (●), ($[Pd] = 2.0 \times 10^{-5}$ mol dm^{-3}) at 25°C. k_2^{max} and kinetic ${}^{s}_{s}pK_a$ values were obtained according to the literature method [10].



Scheme 3. Preparation of palladacycles.

10.80 using a Varian Cary 300 UV-Vis spectrophotometer and confirmed by ^{31}P-NMR spectroscopy.

In most cases, intensity *versus* time data adhered to good first-order behavior for at least three half-times, and standard fitting of the data to an exponential model yielded the pseudo-first-order rate constants given in table 4 along with the turnover numbers.

Table 4. Turnover conditional rate constants for methanolysis of different phosphorothioate esters catalyzed by **1** (8.2×10^{-6} mol dm^{-3}) at 1 mmol L^{-1} TEA, $^{s}_{s}$pH 10.80, 25°C.

Phosphorothioate esters/(mol dm^{-3})		TON	k^{obs} (s^{-1})	k_2^{obs} (dm^3 mol^{-1} s^{-1})	^{31}P-NMR (ppm)	
					Substrate	Product
6	1.45×10^{-4}	17.7	9.6×10^{-4}	117	66.05	73.11
7	4.8×10^{-4}	58.5	4.0×10^{-3}	487	65.95	73.14
8	1.6×10^{-4}	19.5	1.02×10^{-2}	1243	85.37	88.57
9	1.6×10^{-4}	19.5	1.03×10^{-2}	1256	88.85	90.92
10	4.8×10^{-4}	58.5	2.2×10^{-3}	268	68.45	69.54
11	1.6×10^{-4}	19.5	2.8×10^{-4}	34.1	61.16	69.54

TEA, tetraethylammonium chloride and TON, turnover numbers.

3. Results and discussion

3.1. *Syntheses of 1–3*

Syntheses of the palladacycles were straightforward, exchange of counterion from chloride to triflate with silver triflate gave good yields of the desired compounds (scheme 3). Three new palladacycles were characterized by IR, ^{1}H-NMR, and elemental analysis. Palladacycles containing aqua and triflate ligands or counterion have attracted much attention due to their high catalytic activities and rich structure variety [25–29].

The presence of water in **1** and **3** were confirmed by IR spectra, which showed a broad peak at 3400 cm^{-1}. The C=N stretching bands at 1629, 1625, and 1624 cm^{-1} for **1–3**, respectively, redshift compared to 1654 cm^{-1} of the free oxazoline ligand supporting coordination of the oxazoline ring.

The upfield shift of H^6 results from shielding of pyridine ring, which is at the *trans* position to nitrogen in the palladacycle ligand and non-planar to phenyl ring [30]. H^6 of the palladacycle ring is shifted upfield to δ 6.01, 6.10, and 6.43 ppm, respectively, for **1–3**. Thus, ^{1}H-NMR spectra of **1–3** show typical features of *N*,*N*-*trans* conformation in solution. For the three complexes, CH_2 of the oxazoline moiety shows two double–double splittings with spin–spin coupling constants of 8.0–9.0 and 2.5–3.0 Hz, which indicates conformation of oxazoline ring in λ(S) configuration [31].

3.2. *Description of crystal structures of 2 and 5*

The structure of **2** (figure 1) is similar to its chloride precursor [17]. The palladium displays the expected square planar coordination with pyridine and oxazoline nitrogens *trans* to one another. The dihedral angles between pyridine ring and palladacycle ring is 75.75°. The dihedral angle between the planes {C(1)Pd(1)N(1)} and {N(2)Pd(1)(O1)} is 5.61°, with a maximum displacement of Pd of 0.049 Å. The Pd–C and Pd–N bond lengths in **2** fall within the range of values reported for other cyclopalladated derivatives of *N*,*N*-dimethylbenzylamine and oxazoline [10, 31].

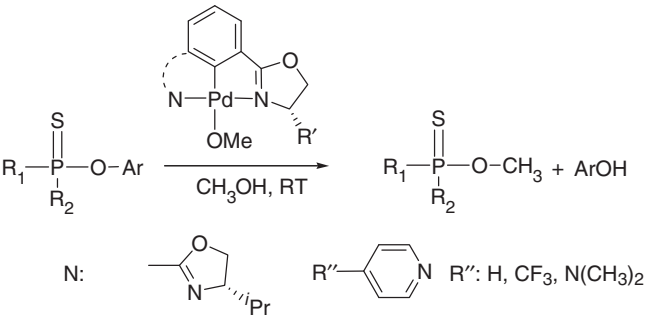
For **5** (figure 2), the palladium is bound to two mutually *trans* oxazoline moieties, the phenyl carbon (*via* C(1)) and bromide. The geometry around palladium is a slightly distorted square-planar coordination sphere with C(1)–Pd–Br(1) and N(1)–Pd–N(1)$^{\#}$ angles being 180° and 157.77(13)°, respectively. The five-membered metallacycles are

symmetrically puckered in the same direction, with Pd(1)–N(1)–C(5)–C(2) torsion angle of 0.5(3)°. The bond lengths and angles (table 2) are in good agreement with those in (*S*,*S*)-{2,6-bis[2-(4-*iso*-propyl)oxazolinyl]phenyl-N,C^1,N}chloropalladium(II) hydrate [25] and (*S*,*S*)-{2,6-bis[2-(4-*iso*-propyl)oxazolinyl]phenyl-N,C^1,N}aquapalladium(II) triflate [18]. The bromide is hydrogen-bonded to water with water–oxygen to bromide distance of 3.468(2) Å.

3.3. *Methanolysis of 6 catalyzed by 1–4*

3.3.1. Preliminary experiments. Before we studied the concentration and pH dependences of the catalytic methanolysis of P=S pesticides in buffered solution (scheme 4), we first screened the activities of the above-mentioned palladacycles at $^{s}_{s}$pH 10.80, $[\mathbf{6}] = 2.84 \times 10^{-5}\,\mathrm{mol\,L^{-1}}$ and $[\mathrm{Pd}] = 2 \times 10^{-5}\,\mathrm{mol\,L^{-1}}$. It was found that k_{obs} with **2** is $2.25\,\mathrm{min^{-1}}$, while that of **4** is $0.0228\,\mathrm{min^{-1}}$, i.e., about 100 times slower than that of **2**. Thus, the pincer system is not highly proficient at promoting methanolysis of **6**, and further kinetic work was focused on the *ortho*-palladated compounds **1–3**. Second, we tried to use palladacycles **1–3** for asymmetric methanolysis of chiral thiophosphates. It was immediately found that the absorbance *versus* time traces for methanolysis of the racemic thiophosphates, letophos **8** and EPN **9**, promoted by **2** are strictly first order, showing no evidence of two independent first-order curves with different rate constants, and therefore no evidence of kinetically significant chiral discrimination under the experimental conditions.

3.3.2. Dependence of the kinetic values for methanolysis of 6 on 1–3 and $^{s}_{s}$pH. On the basis of our previous studies [10], the concentration dependences on palladacycles **1–3** for the methanolysis of fenitrothion were measured at $^{s}_{s}$pH 10.80 (triethylamine buffer) with the k^{obs}_{max} values being plotted in figure 3. The plots are linear with no upward or downward curvature, indicative of kinetically active monomeric **1–3** without evidence of any appreciable amount of dimer at these low concentrations. The linearity of the concentration dependences is different from their chloride precursors, which showed downward curvature at higher concentration due to inhibition of chloride [17].



R_1: alkoxyl; R_2: alkoxyl or phenyl; Ar: substituted aryl; R′: -^{i}Pr/^{t}Bu;

Scheme 4. Catalytic methanolysis of pesticides with palladacycles.

The second-order rate constants (k_2^{obs}) are evaluated as the gradients of the linear plots and are listed in table 3. The activities of palladacycles **1–3** varied with basicities of the co-ligand pyridines. Palladacycle **1**, which contains the electron withdrawing 4-trifluoromethylpyridine ligand, is the most active complex in the series. The k_2 of **1** is 5.8 and 83.8 times higher than that of palladacycles **2** and **3**, respectively.

The pseudo-first-order rate constants (k_{max}^{obs}) for methanolysis of **6** promoted by a 2.0×10^{-5} mol dm^{-3} solution of **1–3** at different $^{s}_{s}$pH values between $^{s}_{s}$pH 9.08 and 12.22 were determined. The corresponding second-order rate constants for **1–3** are obtained as $k_{max}^{obs}/(2 \times 10^{-5}\,mol\,dm^{-3})$ and are plotted in figure 4. The appearance of the plot suggests a catalytic process where a basic form of the catalyst is active. Following the literature method [10], the k_2^{max} and kinetic $^{s}_{s}pK_a$ value can be obtained and are listed in table 3.

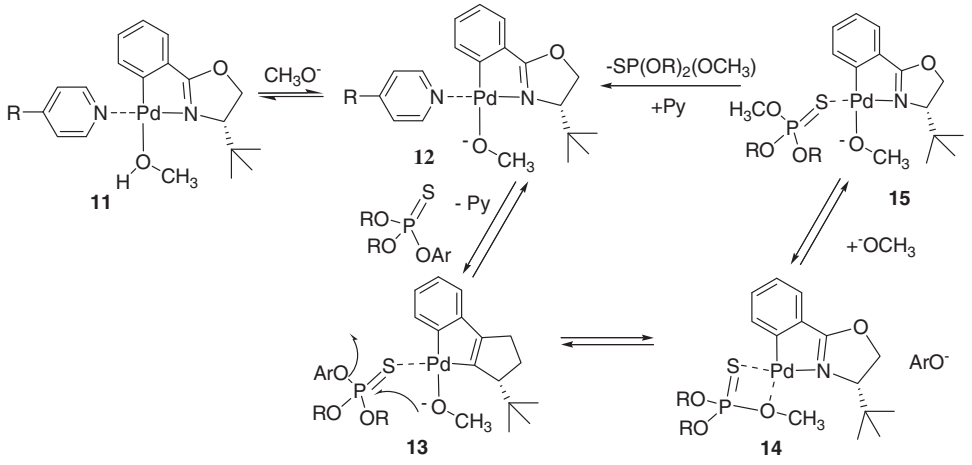
Relative to the background reaction, each palladacycle **1–3** is much more active than methoxide ion for promoting methanolysis of fenitrothion **6**. This can be discussed from two aspects. First, we compared the catalytic efficiency, i.e., k_2 value of the reaction. It can be seen that the k_2 values of **1–3** are 9.3×10^6, 1.6×10^6, and 0.11×10^6-fold higher than that of methoxide which is 7.2×10^{-4} mol dm^{-3} s^{-1} [32]. Secondly, we compared the reaction half-times at $^{s}_{s}$pH 10.80 in the presence or absence of the palladacycles. The computed half-life times in the presence of 1 mmol dm^{-3} of **1–3** are 0.10, 0.60, and 8.7 s, respectively, compared to the background methoxide-promoted reaction which has a half-life time of 9.0×10^8 s, the accelerations achieved by palladacycles **1–3** are 9.0×10^9, 1.5×10^9, and 1.0×10^8-fold, respectively.

3.4. *Turnover experiments*

The methanolysis of six P=S pesticides (shown in scheme 2) catalyzed by **1** under turnover conditions was investigated spectroscopically under buffered conditions (1–2 mmol L^{-1} triethylamine, $^{s}_{s}$pH 10.80, and ambient temperature) in methanol. The conditional rate constants determined are given in table 4. Complete methanolysis of these thiophosphates under turnover conditions has been confirmed by ^{1}H- and ^{31}P-NMR. Palladacycles **1–3** are very effective catalytic systems for decomposition of various pesticides, capable of forming non-toxic, methoxylated products under turnover conditions with good first-order kinetics.

3.5. *Postulated reaction mechanism*

A proposed mechanism for the reaction which is consistent with the experimental data obtained and previous studies [10, 17, 33] is given in scheme 5. The results suggest that palladacycles **1–3**, when introduced into methanol solution, exist predominantly as mono-methanol complex **11**. The catalytically active form is generated by the ionization of a Pd-bound methanol to form **12** having a macroscopic $^{s}_{s}pK_a$ of ~10.90. The required substitution of pyridine with P=S substrate to form the highly catalytically active species **13** can be deduced from the different activities of palladacycles **1–3**. While palladacycle **1**, containing the weakly coordinated trifluoromethylpyridine ligand, showed higher activity due to the ready dissociation of the weakly coordinating pyridine, palladacycle **3**, bearing a strongly coordinated 4-(*N*,*N*-dimethylamino)pyridine gave somewhat poorer activity, and the non-dissociable pincer **4** gave even poorer activity.



Scheme 5. Postulated possible reaction mechanism.

The required substitution of pyridine with the P=S-containing substrate to form the kinetically competent species is suggested to arise from a typical bimolecular association of the pesticide with the palladacycle to form a five-coordinate associative complex or transient (not shown) from which expulsion of the pyridine occurs to give **13**. Once formed, **13** reacts *via* intramolecular delivery of the *cis*-coordinated methoxide to the adjacent P=S unit to form **14**. Whether the P=S–OAr cleavage reaction from **13** to form **14** involves a stepwise mechanism, through a five-coordinate phosphorane intermediate, or concerted displacement of the leaving group from P cannot be ascertained on the basis of the available evidence. Turnover of the catalyst requires displacement of the P=S product from **15** to regenerate **12**, again probably through an associative process with methoxide.

4. Conclusion

Three new palladacycles **1–3** derived from (*S*)-4-*tert*-butyl-2-phenyl-2-oxazoline have been synthesized and characterized with IR, ^{1}H-NMR, and elemental analysis. Complex **2** and a pincer complex **5** were also characterized by X-ray single crystal structure analyses. Palladacycles **1–3** have been successfully applied in the catalytic methanolysis of P=S pesticides. The most effective catalysts for methanolysis of thiophosphates are the *ortho*-palladacycles containing weakly coordinating monodentate ligands. The pincer palladacycles and the *ortho*-palladacycles containing strongly binding monodentate ligands are far less active. There is no chiral discrimination during the methanolysis under the experimental conditions. To achieve asymmetric methanolysis by imputing chiral nitrogen ligands in the palladacycle system and to create reusable polymer-bound or silica-supported catalyst are under investigation.

Supplementary material

CCDC-710463 (for **2**) and CCDC-763345 (for **5**) contain the supplementary crystallographic data for this article. These data can be obtained free of charge from the Cambridge Crystallographic Data Center *via* www.ccdc.cam.ac.uk/data_request/cif

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