FULL PAPER

Dalton
www.rsc.org/dalton

Stoichiometric reactions of methylparathion with a palladium aryl oxime metallacycle

Mieock Kim and François P. Gabbaï*
Chemistry Department, Texas A&M University, 3255 TAMU, College Station, TX 77843-3255, USA

Received 27th July 2004, Accepted 3rd September 2004
First published as an Advance Article on the web 21st September 2004

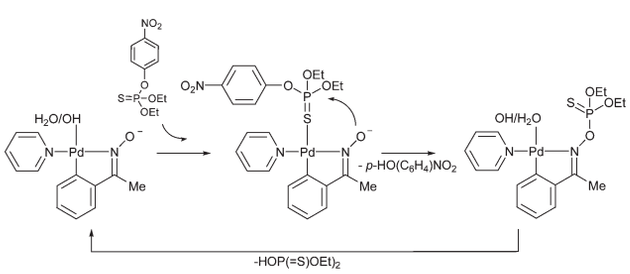
The reaction of $[Pd_3(OAc)_6]$ with (*E*)-acetophenone oxime and pyridine in $CHCl_3$ under reflux affords the metallacycle [Pd(OAc){*C*,*N*-($C_6H_4C(CH_3)$=NOH)-2}(py)] (**1**) as a yellow air-stable complex. The same reaction carried out at room temperature in the absence of pyridine affords the trinuclear oximato complex [Pd(μ-(*E*)-*ON*=$C(CH_3)$Ph)(μ-OAc)]$_3$ (**2**), which can be converted into **1** upon heating in the presence of pyridine. As indicated by ^{1}H and ^{31}P NMR spectroscopy, complex **1** reacts with methylparathion in acetone-d_6–D_2O solutions to afford [Pd(*S*P(=O)$(OCH_3)_2$){*C*,*N*-($C_6H_4C(CH_3)$=NOH)-2}(py)] (**3**) and [Pd(μ-*S*P(=O)$(OCH_3)_2$){*C*,*N*-($C_6H_4C(CH_3)$=NOH)-2}]$_2$ (**4**) as well as free *p*-nitrophenol. Compounds **1**–**4** have been characterized by single-crystal X-ray analysis, NMR and EA. Compounds **1** and **3** are mononuclear complexes with the acetate and dimethylthiophosphate ligand, respectively, *trans* from the phenyl group. Compound **2** is a trinuclear complex whose structure can be derived from that of $[Pd_3(OAc)_6]$ by replacing three of the acetate ligands on one side of Pd_3 plane by three N,O-coordinated oximate ligands. Complex **4** is a dinuclear complex in which the two square-planar palladium moieties are linked by the sulfur atoms of the bridging dimethylthiophosphate ligands.

Introduction

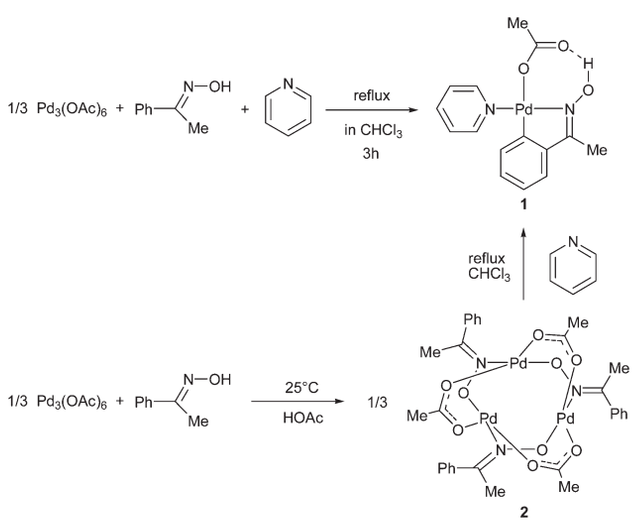
Organophosphorus esters that act as acetylcholine esterase inhibitors are used as pesticides and chemical warfare agents.[1] Owing to the obvious adverse natures of these chemicals,[2,3] a great deal of effort has been devoted to the development of methods that allow for their neutralization.[4] In this regard, hydrolysis reactions that produce non-toxic phosphate or phosphonate anions have received an increasing amount of attention. In the case of parathion (*O*,*O*-diethyl *O*-*p*-nitrophenyl thiophosphate), a pesticide whose environmental presence is generating growing concerns,[5] the hydrolysis reaction results in the release of *p*-nitrophenol and formation of the corresponding thiophosphate diester which is non-toxic. This hydrolysis is remarkably slow and takes up to several months at neutral pH.[6] In the presence of Lewis-acidic transition metal catalysts, the rate of this reaction increases. While coordination complexes typically display a marginal activity,[7–10] recent reports suggest that organometallic catalysts can be remarkably active.[11,12] In particular, the group of Ryabov has investigated several cyclometallated palladium and platinum aryl oxime complexes ([MCl{*C*,*N*-($C_6H_4C(CH_3)$=NOH)-2}(L)], M = Pd or Pt, L = DMSO or pyridine) that greatly accelerate the hydrolysis of parathion.[12] Although no reaction intermediates have been isolated, it has been proposed that the activity of such catalysts results from the coordination of parathion at the metal center followed by an intramolecular nucleophilic attack by the neighboring oximate (Scheme 1). Regeneration of the catalysts is proposed to occur by hydrolysis of the phosphorylated oximate. As part of our general interest in the metal-mediated hydrolysis of organophosphorus esters, we have decided to visit the stoichiometric reactions that occur between cyclometallated palladium aryl oxime complexes and methylparathion (*O*,*O*-dimethyl *O*-*p*-nitrophenyl thiophosphate). In this paper, we report the synthesis of the palladium aryl oxime derivative [Pd(OAc){*C*,*N*-($C_6H_4C(CH_3)$=NOH)-2}(py)] (**1**) and the products of its stoichiometric reaction with methylparathion.

Results and discussion

The palladium aryl oxime metallacycle [Pd(OAc){*C*,*N*-($C_6H_4C(CH_3)$=NOH)-2}(py)] (**1**) is obtained in one step by reaction of $[Pd_3(OAc)_6]$ with (*E*)-acetophenone oxime and pyridine in $CHCl_3$ under reflux for 3 h (Scheme 2). Compound **1** is a yellow air-stable complex which can be recrystallized from benzene. It has been characterized by NMR, elemental analysis and X-ray analysis (Fig. 1). As expected for a cyclopalladated complex, the ^{1}H NMR spectrum of **1** shows an upfield shift of the proton resonance of the *ortho*-palladated ring.[13,14] Compound **1** crystallizes in the monoclinic $P2_1/c$ space group. The palladium atom displays the expected square planar coordination with the pyridine and oxime nitrogen atoms positioned *trans* to one another. The five-membered palladacycle ring of **1** is slightly



Scheme 1



Scheme 2

DOI: 10.1039/b411313f

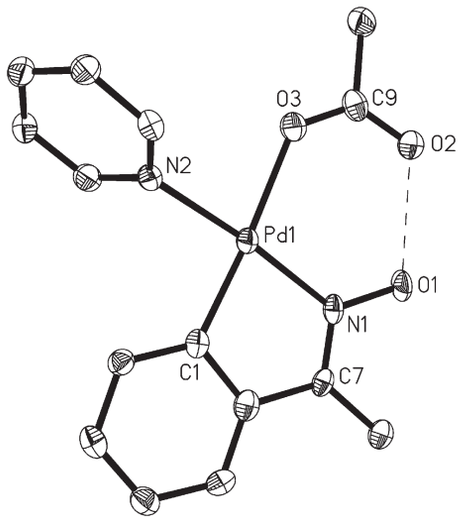


Fig. 1 Structure of complex **1** in the crystal. Selected bond lengths (Å) and angles (°). Pd(1)–C(1) 1.974(6), Pd(1)–N(1) 2.018(5), Pd(1)–N(2) 2.048(5), Pd(1)–O(3) 2.145(4); C(1)–Pd(1)–N(1) 80.3(2), C(1)–Pd(1)–N(2) 94.4(2), N(1)–Pd(1)–N(2) 174.7(2), C(1)–Pd(1)–O(3) 175.9(2), N(1)–Pd(1)–O(3) 103.79(19), N(2)–Pd(1)–O(3) 81.48(18).

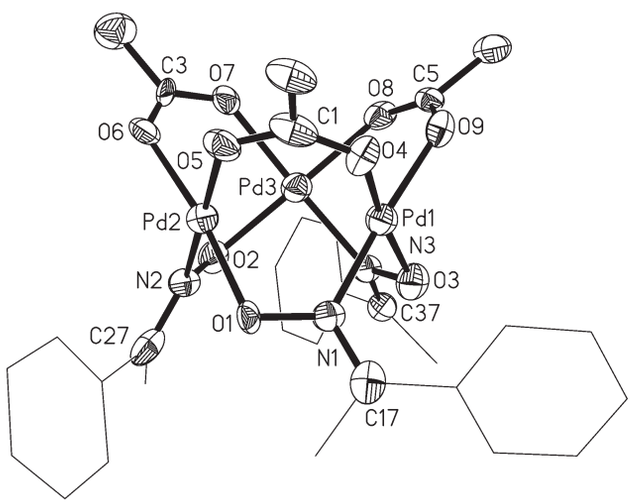
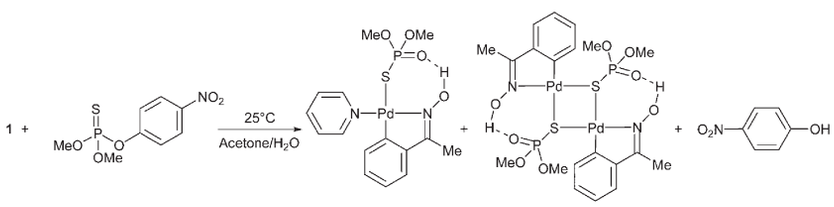


Fig. 2 Structure of complex **2** in the crystal. Selected bond lengths (Å) and angles (°). Pd(1)–O(4) 1.996(8), Pd(1)–N(1) 2.002(10), Pd(1)–O(3) 2.004(8), Pd(1)–O(9) 2.021(8), Pd(1)–Pd(3) 3.0146(15), Pd(1)–Pd(2) 3.0327(15), Pd(2)–Pd(3) 3.0712(17); O(4)–Pd(1)–N(1) 89.3(4), O(4)–Pd(1)–O(3) 172.0(3), N(1)–Pd(1)–O(3) 90.7(4), O(4)–Pd(1)–O(9) 90.0(3), N(1)–Pd(1)–O(9) 175.7(4), O(3)–Pd(1)–O(9) 89.4(3), Pd(3)–Pd(1)–Pd(2) 61.04(4), Pd(1)–Pd(2)–Pd(3) 59.19(3), Pd(1)–Pd(3)–Pd(2) 59.77(3).

strained (bond angle of C(1)–Pd–N(1) is 80.3°). The Pd–C(1) bond length of 1.974(6) Å is typical of Pd–C(sp^2) bonds of compounds featuring a square-planar palladium bound to a co-planar aryl ring.[15] Altogether, this structure is similar to that of [PdCl{*C*,*N*-($C_6H_4C(CH_3)$=NOH)-2}(py)].[14] The acetate ligand is terminally ligated through one of its oxygen atoms. As indicated by the O(1)–O(2) distance of 2.512 Å, the non-coordinated carbonyl oxygen atom of the acetate ligand (O(2)) is hydrogen bonded to the protonated oxime functionality.

In the course of these investigations, we were able to isolate the trinuclear oximato complex [Pd(μ-(*E*)-*ON*=$C(CH_3)$Ph)(μ-OAc)]$_3$ (**2**) which is formed in the reaction of [$Pd_3(OAc)_6$] with (*E*)-acetophenone oxime in $CHCl_3$ at room temperature (Scheme 2). This compound can be converted into **1** upon reflux in $CHCl_3$ in the presence of pyridine. Compound **2** has been characterized by NMR, elemental analysis and X-ray analysis (Fig. 2). This derivative crystallizes with two molecule of interstitial benzene in the asymmetric unit. It features a trinuclear structure similar to that observed for [$Pd_3(OAc)_6$][16] and the related oximate complex [Pd(μ-(*Z*)-*ON*=C^{i}PrPh)$_2$]$_3$.[17] The structure of **2** can be derived from that of [$Pd_3(OAc)_6$] by replacement of three of the acetate ligands on one side of Pd_3 plane by three N,O-coordinated oximate ligands. The resulting Pd–N (av. 1.99 Å) and Pd–O (av. 2.00 Å) are similar to those observed in the structure of [Pd(μ-(*Z*)-*ON*=C^{i}PrPh)$_2$]$_3$.[17]

Complex **1** promptly reacts with methylparathion in acetone-d_6–D_2O solution. While methylparathion is stable for several weeks in these aqueous solvent mixtures, addition of **1** results in the rapid production of *p*-nitrophenol as shown by ^{1}H NMR spectroscopy (Scheme 3). This reaction is also accompanied by the appearance of two phosphorus containing products, namely, [Pd(*S*P(=O)$(OCH_3)_2$){*C*,*N*-($C_6H_4C(CH_3)$=NOH)-2}(py)] (**3**) and [Pd(μ-*S*P(=O)$(OCH_3)_2$){*C*,*N*-($C_6H_4C(CH_3)$=NOH)-2}]$_2$ (**4**) which give rise to ^{31}P NMR signals at 53 and 29 ppm, respectively. Both of these signals are upfield from the ^{31}P resonance of methylparathion which appears at 66 ppm[18] and do not correspond to the thiosphosphoric acid HSP(=O)$(OMe)_2$ derivative whose ^{31}P resonance appears at 65 ppm.[19] Upon longer reaction time, the signal corresponding to methylparathion at 67 ppm ultimately disappears to afford **3** and **4** in a 9 : 1 ratio. Compounds **3** and **4** simultaneously crystallize from the reaction mixture which complicated their isolation in a pure form. Single crystals could however be separated on the basis of their colors and were characterized by NMR and X-ray analysis. Complex **3** (Fig. 3) is a mononuclear yellow complex which crystallizes in the monoclinic space group *C*2/*c*. Its structure can be derived from that of **1** by substitution of the acetate ligand with a sulfur-bound dimethylthiophosphate ligand which originates from the hydrolyzed methylparathion. The resulting Pd–S bond of 2.461(1) Å is similar to that of the cyclometallated palladium dithiolate complex [Pd{*C*,*N*-$N(Me)_2CH_2C_6H_4$-2}{*S*,*S*-$S_2P(OPr^n)_2$}] (2.458(2) Å).[20] The P–S bond length of 1.982(1) Å is intermediate between double bond (1.94 Å) and single bond (2.09 Å) values. All other structural parameters are almost identical to those found in **1**. As in **1**, the oxime functionality is protonated and hydrogen bonded to the phosphoryl oxygen atom O(2) (O(1)···O(2) = 2.615 Å). Complex **4** (Fig. 4) is a dinuclear orange complex which crystallizes in the monoclinic space group $P2_1/c$. The two square-planar palladium moieties are linked by the sulfur atoms of the bridging dimethylthiophosphate ligands. The Pd–S distances of 2.327(1) and 2.473 (1) Å are comparable to those observed in related complexes such as [Pd_2((*t*-BuNH)$_2$P(=O)S)$_4$] (av. Pd–S = 2.34 Å) which also features bridging thiophosphate groups.[21] The Pd–S distance of 2.473(1) Å *trans* to the carbon atom of the cyclometallated ligand is slightly longer than that of 2.327(1) Å *trans* to the Pd–N bond due to the *trans* influence originating from the orthometallated phenyl ligand.[10,22] As in **3**, the O(1A)···O(2) distance of 2.662 Å indicate that presence of a hydrogen bond between the protonated oxime functionality and the phosphoryl oxygen atom. All other structural parameters are almost identical to those found in **1**.



Scheme 3

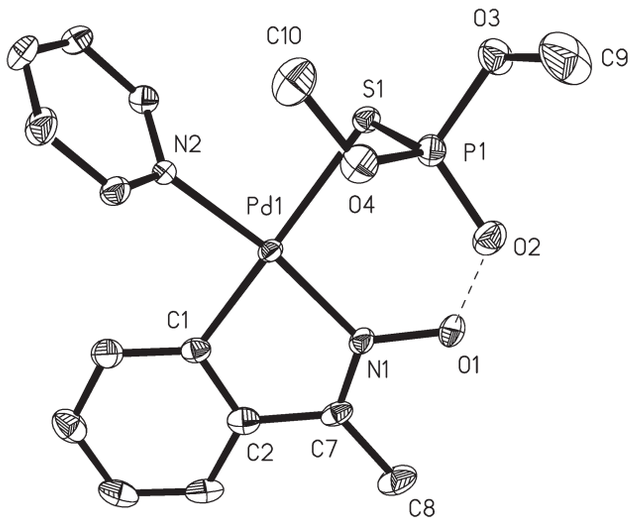


Fig. 3 Structure of complex **3** in the crystal. Selected bond lengths (Å) and angles (°). Pd(1)–C(1) 1.995(3), Pd(1)–N(1) 2.017(3), Pd(1)–N(2) 2.038(3), Pd(1)–S(1) 2.4609(10), S(1)–P(1) 1.982(1); C(1)–Pd(1)–N(1) 79.88(12), C(1)–Pd(1)–N(2) 93.62(12), N(1)–Pd(1)–N(2) 170.58(11), C(1)–Pd(1)–S(1) 172.81(9), N(1)–Pd(1)–S(1) 99.54(8), N(2)–Pd(1)–S(1) 87.76(8), P(1)–S(1)–Pd(1) 96.46(5).

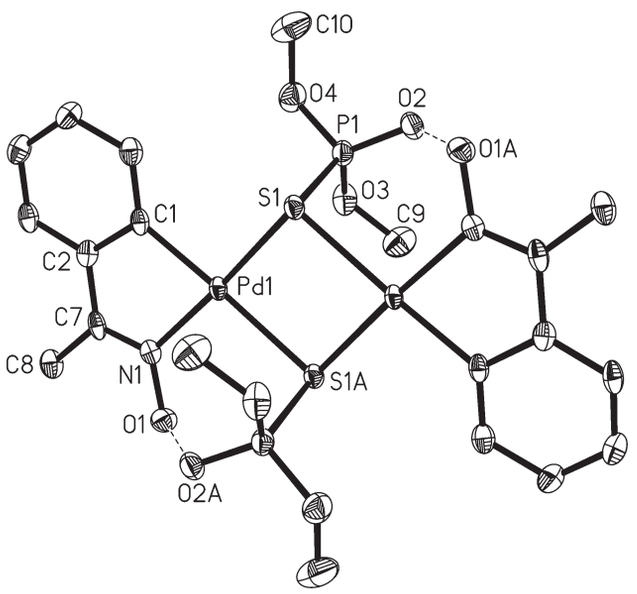


Fig. 4 Structure of complex **4** in the crystal. Selected bond lengths (Å) and angles (°). Pd(1)–C(1) 2.003(4), Pd(1)–N(1) 2.029(3), Pd(1)–S(1) 2.3268(10), Pd(1)–S(1A) 2.4727(10), S(1)–P(1) 2.061(1); C(1)–Pd(1)–N(1) 79.57(14) C(1)–Pd(1)–S(1) 97.44(11), N(1)–Pd(1)–S(1) 176.53(9), C(1)–Pd(1)–S(1A) 177.96(11), S(1)–Pd(1)–S(1A) 84.47(4).

Conclusion

The reaction of the palladium aryl oxime complex **1** with methylparathion leads to the formation of isolable palladium thiophosphate compounds. The formation of these compounds reflects the thiophilic character of palladium and possibly accounts for the ability of such complexes to promote the hydrolysis of methylparathion. These findings suggest that thiophosphate complexes such as **3** are possible intermediates in the catalyzed hydrolysis of methylparathion by cyclometallated palladium aryl oxime complexes.

Experimental

General considerations

CAUTION: *Methylparathion is highly toxic and should be handled in a well-ventilated fume hood.* Solvents were dried by standard method. All NMR studies were carried out on Inova 300 or 500 MHz NMR spectrometer (300 or 500 MHz for ^{1}H, 75.4 or 125.7 MHz for ^{13}C, 121.4 MHz for ^{31}P NMR). 85% H_3PO_4 was used as an external standard for the solution ^{31}P NMR spectra. The proton and carbon signals of the deuterated solvent were used as internal standard for the ^{1}H and ^{13}C NMR spectra, respectively. Elemental analyses were performed by Atlantic Microlab Inc. at Norcross, GA 30091. Melting points were measured on a Laboratory Devices Mel-Temp apparatus and were not corrected. The methylparathion solution was provided by A/S CHEMINOVA, LEMVIG, DK-7620, Denmark as a gift. (*E*)-Acetophenone oxime was synthesized by the reaction of acetophenone with hydroxylamine hydrochloride in EtOH–pyridine as described in the literature.[23]

[Pd(OAc){*C*,*N*-($C_6H_4C(CH_3)$=NOH)-2}(py)] (1)

Method 1. Acetophenone oxime (0.14 ml, 1 mmol) and pyridine (0.16 ml, 2 mmol) were added to a solution of palladium acetate (224 mg, 1 mmol) in $CHCl_3$ (15 ml). The resulting orange–red solution was refluxed for 3 h. Following addition of water (10 ml), the product was extracted with chloroform (3 × 15 ml). Evaporation of the solvents yielded a yellow oil which was dissolved in benzene. Slow evaporation of the solvent led to the formation of bright yellow crystals of **1** (360 mg, 95%); mp 163 °C. Anal. $C_{15}H_{16}N_2O_3Pd$ requires C 47.57, H 4.26. Found: C 47.47, H 4.34%. ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.79 [2H, d, *J*(HH) 7.5 Hz, NC_5H_5], 7.94 [1H, t, *J*(HH) 7.5 Hz, NC_5H_5], 7.47 [2H, t, *J*(HH) 7.5 Hz, NC_5H_5], 7.05 [1H, d, *J*(HH) 7.0 Hz], 7.01 [1H, t, *J*(HH) 7.0 Hz] and 6.77 [1H, t, *J*(HH) 7.0 Hz] (H-arom, H_3–H_5 of Pd–$C_6H_4C(CH_3)$=NOH), 6.15 [1H, d, *J*(HH) 7.0 Hz, H_6 of Pd–$C_6H_4C(CH_3)$=NOH], 2.24 [3H, s, CO_2CH_3], 1.89 [3H, s, NCH_3]. ^{13}C NMR (75.4 MHz, $CDCl_3$): δ 180.7 [CO_2CH_3], 164.7 [Pd–$C_6H_4C(CH_3)$=NOH], 152.9, 151.3, 145.3, 138.8, 132.5, 127.7, 125.7, 125.0, and 124.8 [Pd–$C_6H_4C(CH_3)$=NOH and NC_5H_5], 24.6 [CO_2CH_3], 11.4 [$C_6H_4C(CH_3)$=NOH].

Method 2. Pyridine (0.08 ml, 1.0 mmol) was added to a solution of **2** (270 mg, 0.3 mmol) in $CHCl_3$ (15 ml). The resulting orange–red solution was refluxed for 3 h. Following addition of water (10 ml), the product was extracted with chloroform (3 × 15 ml). Evaporation of the solvents yielded a yellow oil which was dissolved in benzene. Slow evaporation of the solvent led to the formation of bright yellow crystals of **1** (327 mg, 96%).

[Pd(μ-(*E*)–ON=$C(CH_3)$Ph)(μ-OAc)]$_3$ (2)

A suspension of palladium acetate (224 mg, 1 mmol) in acetic acid (6 ml) was added to a solution of acetophenone oxime (0.14 ml, 1 mmol). Stirring the resulting solution overnight at room temperature resulted in precipitation of orange microcrystals of **2** (270 mg, 90%) which were collected by filtration and washed with H_2O and *n*-hexane. Anal. $C_{30}H_{33}N_3O_9Pd_3$ requires C 40.09, H 3.70. Found: C 40.15, H 3.73%. ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.09 [2H, d, *J*(HH) 7.0 Hz, $N(CH_3)C_6H_5$], 7.60 [2H, t, 2H, *J*(HH) 7.0 Hz, $N(CH_3)C_6H_5$], 7.50 [1H, t, *J*(HH) 7.0 Hz, $N(CH_3)C_6H_5$], 2.04 [3H, s, CO_2CH_3], 2.02 [3H, s, N=$C(CH_3)C_6H_5$]. ^{13}C NMR (75.4 MHz, $CDCl_3$): δ 184.0 [CO_2CH_3], 158.6 [N=$C(CH_3)C_6H_5$], 137.5, 129.7, 128.6 and 127.3 [N=$C(CH_3)C_6H_5$], 23.2 [CO_2CH_3], 18.1 [$N(CH_3)C_6H_5$].

Reaction of 1 with methylparathion: formation of [Pd(SP(=O)-$(OCH_3)_2$){*C*,*N*-($C_6H_4C(CH_3)$=NOH)-2}(py)] (3) and [Pd(μ-SP(=O)$(OCH_3)_2$){*C*,*N*-($C_6H_4C(CH_3)$=NOH)-2}]$_2$ (4)

A 80 wt% solution of methylparathion in xylenes (362 mg, 1.1 mmol) was added to a solution of complex **1** (380 mg, 1 mmol) in acetone (10 ml) and water (0.5 mL). After 24 h, the integrated ^{31}P NMR spectrum of the mixture indicated complete consumption of methyl parathion and formation of **3** and **4** in a 9 : 1 ratio. Evaporation of the volatiles afforded an oily residue which was dissolved in $CHCl_3$ (40 mL), washed with

Table 1 Crystal data, data collection, and structure refinement for complexes **1**–**4**

Crystal data	**1**	**2**·2C_6H_6	**3**	**4**
Formula	$C_{15}H_{16}N_2O_3Pd$	$C_{42}H_{45}N_3O_9Pd_3$	$C_{15}H_{19}N_2O_4PPdS$	$C_{10}H_{14}NO_4PPdS$
M_r	378.70	1055.01	460.75	381.65
Crystal size/mm	0.45 × 0.20 × 0.20	0.18 × 0.06 × 0.06	0.86 × 0.27 × 0.06	0.25 × 0.17 × 0.14
Crystal system	Monoclinic	Monoclinic	Monoclinic	Monoclinic
Space group	$P2_1/c$	$P2_1/c$	$C2/c$	$P2_1/c$
a/Å	11.848(3)	10.207(3)	13.240(4)	7.6851(12)
b/Å	17.343(4)	16.621(5)	15.252(5)	18.574(3)
c/Å	7.1257(16)	24.231(7)	17.807(6)	9.4072(16)
β/°	99.488(4)	94.142(5)	94.532(8)	101.870(3)
V/Å^3	1444.2(6)	4100(2)	3585(2)	1314.1(4)
Z	4	4	8	4
D_c/g cm^{-3}	1.742	1.709	1.707	1.929
μ(Mo-Kα)/mm^{-1}	1.296	1.360	1.262	1.697
F(000)/e	760	2112	1856	760
Data collection				
T/K	110(2)	110(2)	110(2)	110(2)
Scan mode	ω	ω	ω	ω
hkl range	−13 to 13, −19 to 19, −8 to 8	−11 to 11, −18 to 18, −17 to 26	−14 to 8, −15 to 16, −19 to 10	−4 to 8, −20 to 10, −9 to 10
Measured refl.	9772	20737	3150	3696
Unique refl. [R_{int}]	2271 [0.0367]	5903 [0.0957]	2133 [0.0247]	1709 [0.0340]
Refl. used for refinement	2271	5903	2133	1709
Absorption correction	Empirical	Empirical	None	None
T_{min}/T_{max}	0.8344/0.6768	0.7931/0.6922		
Refinement				
Refined parameters	190	478	217	167
$R1$,[a] $wR2$[b] [$I > 2\sigma(I)$]	0.0468, 0.1032	0.0645, 0.1288	0.0237, 0.0657	0.0248, 0.0629
$\rho_{max/min}$/e Å^{-3}	2.147/−0.884	1.781/−0.636	0.362/−0.319	0.545 and −0.648

[a] $R1 = (F_o - F_c)/F_o$. [b] $wR2 = \{[w(F_o^2 - F_c^2)^2]/[w(F_o^2)^2]\}^{1/2}$; $w = 1/[\sigma^2(F_o^2) + (ap)^2 + bp]$; $p = (F_o^2 + 2F_c^2)/3$; a = 0.055 (**1**), 0.03 (**2**), 0.04 (**3**), 0.0361 (**4**); b = 15 (**1**), 0 (**2**), 4 (**3**), 0.9441 (**4**).

H_2O and concentrated to 5 mL. Small yellow crystals of **3** and orange crystals of **4** coated by a dark oily residue formed upon standing. Compounds **3** and **4** were obtained as a mixture such that a satisfactory elemental analysis could not be obtained.

3. ^{1}H NMR (300 MHz, acetone-d_6): δ 8.89 [2H, d, J(HH) 7.2 Hz, NC_5H_5], 7.70 [2H, t, J(HH) 7.2 Hz, NC_5H_5], 7.24 [1H, d, J(HH) 7.2 Hz, NC_5H_5], 6.7–7.1 [3H, m, H-arom, H_3–H_5 of Pd–C_6H_4C(CH_3)=NOH], 5.93 [2H, d, J(HH) 7.2 Hz, H_6 of Pd–C_6H_4C(CH_3)=NOH], 3.61 [6H, d, J(HP) 12.6 Hz, CH_3OP], 2.29 [3H, s, Pd–C_6H_4C(CH_3)=NOH]. ^{13}C NMR (75.4 MHz, $CDCl_3$): δ 162.5 [Pd–C_6H_4C(CH_3)=NOH], 153.0, 152.5, 143.7, 138.1, 130.5, 128.5, 125.2, 124.3 and 123.6 [Pd–C_6H_4C(CH_3)=NOH and NC_5H_5], 54.4 [d, J(HP) 2.6, P–OCH_3) 10.6 [s, Pd–C_6H_4C(CH_3)=NOH)]. ^{31}P NMR (121.4 MHz, acetone-d_6): δ 53.6 [s].

4. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.0–7.4 [8H, m, H-arom Pd–C_6H_4C(CH_3)=NOH], 4.00 (12H, d, J(HP) 12.5 Hz, CH_3OP), 2.30 [s, 3H, Pd–C_6H_4C(CH_3)=NOH]. ^{31}P NMR (121.4 MHz, acetone-d_6): δ 29.3 [s]. A satisfactory ^{13}C spectrum could not be obtained because of insufficient sample.

Crystallography

Crystal data, data collection, and structure refinement for complexes **1**–**4** are provided in Table 1.

CCDC reference numbers 245836–245839.

See http://www.rsc.org/suppdata/dt/b4/b411313f/ for crystallographic data in CIF or other electronic format.

Acknowledgements

Support from the US Army Medical Research and Material Command as well as the Korea Science and Engineering Foundation (Grant to M. K.) is gratefully acknowledged. We thank A/S CHEMINOVA for providing us with methylparathion.

References

1 *Pesticides remediation in soils and water*, ed. P. C. Keaney and T. Roberts, Wiley, New York, 1998.
2 H. A. Alegria and T. J. Shaw, *Environ. Sci. Technol.*, 1999, **33**, 850–856.
3 R. J. Gilliom, J. E. Barbash, D. W. Kolpin and S. J. Larson, *Environ. Sci. Technol. A, Pages*, 1999, **33**, 164A–169A.
4 (*a*) H. Morales-Rojas and R. A. Moss, *Chem. Rev.*, 2002, **102**, 2497–2521; (*b*) Y. C. Yang, J. A. Baker and J. R. Ward, *Chem. Rev.*, 1992, **92**, 1729–1743.
5 R. Reichman, Y. Mahrer and R. Wallach, *Environ. Sci. Technol.*, 2000, **34**, 1321–1330.
6 S. B. Lartiges and P. P. Garrigues, *Environ. Sci. Technol.*, 1995, **29**, 1246–1254.
7 J. A. A. Ketellaar, H. R. Gersmann and M. Beck, *Nature*, 1956, **177**, 392–393.
8 (*a*) M. Zeinali and A. Torrents, *Environ. Sci. Technol.*, 1998, **32**, 2338–2342; (*b*) J. M. Smolen and A. T. Stone, *Environ. Sci. Technol.*, 1997, **31**, 1664–1673; (*c*) H. B. Wan, M. K. Wong and C. Y. Mok, *Pestic. Sci.*, 1994, **42**, 93–99.
9 (*a*) C. M. Hartshorn, A. Singh and E. L. Chang, *J. Mater. Chem.*, 2002, **12**, 602–605; (*b*) R. A. Moss and H. Morales-Rojas, *Langmuir*, 2000, **16**, 6485–6491; (*c*) F. M. Menger, L. H. Gan, E. Johnson and D. H. Durst, *J. Am. Chem. Soc.*, 1987, **109**, 2800–2803; (*d*) J. R. Morrow and W. C. Trogler, *Inorg. Chem.*, 1989, **28**, 2330–2333; (*e*) R. A. Moss, P. K. Gong and H. Morales-Rojas, *Org. Lett.*, 2002, **4**, 1835–1838; (*f*) R. W. Hay, T. Clifford, D. T. Richens and P. Lightfoot, *Polyhedron*, 2000, **19**, 1485–1492.
10 P. Hendry and A. M. Sargeson, *Aust. J. Chem.*, 1986, **39**, 1177–1186.
11 L. Y. Kuo and N. M. Perera, *Inorg. Chem.*, 2000, **39**, 2103–2106.
12 G. M. Kazankov, V. S. Sergeeva, E. N. Efremenko, L. Alexandrova, S. D. Varfolomeev and A. D. Ryabov, *Angew. Chem., Int. Ed.*, 2000, **39**, 3117–3119.
13 H. Onoue, K. Minami and K. Nakagawa, *Bull. Chem. Soc. Jpn.*, 1970, **43**, 3480–3485.
14 A. D. Raybov, G. M. Kazankov, A. K. Yatsimirsky, L. G. Kuz'mina, O. Y. Burtseva, N. V. Dvortsova and V. A. Polyako, *Inorg. Chem.*, 1992, **31**, 3083–3090.

15 Yu. Struchkov, A. S. Batsanov and Yu. L. Slovokhotov, *Sov. Sci. Rev. B.: Chem.*, 1987, **10**, 386.
16 A. C. Skapski and M. L. Smart, *J. Chem. Soc. D.*, 1970, 658.
17 A. G. Constable, W. S. McDonald, L. C. Sawkins and B. L. Shaw, *Chem. Commun.*, 1978, 1061–1062.
18 T. Kuivalainen, J. El-Bahrauoui, R. Uggla, R. Kostiainer and M. R. Sundberg, *J. Am. Chem. Soc.*, 2000, **122**, 8073–8074.
19 (*a*) The chemical ^{31}P shift of dimethylthiophosphate salt has been previously reported: M. Mahajna, G. B. Quistad and J. E. Casida, *Chem. Res. Toxicol.*, 1997, **10**, 64–69; (*b*) P. C. J. Jamer, H. C. P. F. Roelen, H. van den Elst, G. A. van der Marel and J. H. van Boom, *Tetrahedron Lett.*, 1989, **30**, 6757–6760.
20 S. Narayan, V. K. Jain and R. J. Butcher, *J. Organomet. Chem.*, 1997, **549**, 73–80.
21 O. J. Scherer, K. Forstinger, J. Kaub and W. S. Sheldrick, *Chem. Ber.*, 1986, **119**, 2731–2747.
22 Y. Qin, S. Selvaratnam, J. J. Vittal and P.-H. Leung, *Organometallics*, 2002, **21**, 5301–5306.
23 (*a*) M. A. Bigdeli, Mir. M. A. Nikje, S. Jafari and M. M. Heravi, *J. Chem. Res. (S)*, 2002, 20–21; (*b*) J.-M. Coustard, J.-C. Jacquesy and B. Violeau, *Tetrahedron Lett.*, 1992, **33**, 8085–8086; (*c*) B. S. Furniss, A. J. Hannaford, P. W. G. Smith and A. R. Tatchell, *Vogel's textbook of practical organic chemistry*, Longmans, London, 5th edn., 1996, p. 1259.