The chemistry of phosphorodiselenoates: structure, catalysis and formation of Se-esters†

Bijay Sarkar,[a] Chiang-Shiang Fang,[a] Lee-Yan You,[a] Ju-Chun Wang[b]
and C. W. Liu*[a]

Received (in Montpellier, France) 31st July 2008, Accepted 27th October 2008
First published as an Advance Article on the web 11th December 2008
DOI: 10.1039/b813267d

Though metal complexes of dialkyl diselenophosphate ligands $[Se_2P(OR)_2]^-$ (dsep) have been reported in several occasions, the solid-state structure of isolated dsep ligands is still unknown. Herein the ammonium salt of the dsep ligand, $NH_4Se_2P(O^iPr)_2$, is structurally characterized and N–H···Se type of H-bonding interactions are revealed. In addition, the $NH_4Se_2P(OR)_2$ ligands serve as an ammonia source in the Fe powder catalyzed condensation of acetone with ammonia to form 2,2,6,6-tetramethyl-4-oxopiperidinium salts of the dsep ligand, $[\{H_2N(CH_2)_2(CMe_2)_2CO\}\{Se_2P(OR)_2\}]$ (**1a** = ^{i}Pr, **1b** = Et) of which **1b** is structurally characterized. Novel syntheses of Se-esters of *O*,*O*′-dialkylphosporodiselenoic acid, **2**, **3**, **4**, **5**, **6**, **7**, directly from the ammonium salts have been achieved. The reactions, where one of the Se atoms of the dsep unit acts as the nucleophilic center, include Michael addition, epoxide ring opening addition, acylation and α-alkynation.

Introduction

The first report of metal complexes containing diselenophosphate $[\{Se_2P(OR)_2\}]^-$ ligands (abbreviated as dsep) was published by Zingaro *et al.* in 1968.[1] More recent innovations for the use of dsep ligands in coordination chemistry lies in the synthesis of multi-metallic cluster compounds.[2] Surprisingly no structure of free dialkyl diselenophosphate ligands $[(RO)_2PSe_2]^-$ or their salts is known mainly because of their thermally unstable nature. In addition, they are highly susceptible to aerial oxidation and thus Ibers *et al.* were able to achieve the structural characterization of only two oxidized forms the dsep ligand, $[(EtO)_2P(Se)Se]_2Se$ and $[(^iPrO)_2P(Se)Se]_2$.[3] In sharp contrast the structures of diselenophosphinate $[R_2PSe_2]^-$ (R = ^{t}Bu, Ph, ^{i}Pr) ligands were structurally characterized as their triethylammonium salts by O'Brien's group only in 2007.[4] Woollins' group has also reported a dimeric compound $[CH_2(PhPSe_2)_2]^{2-}$,[5] as a potassium salt which contains a diselenophosphinate moiety, and a sodium complex of $[Ph_2PSe_2]^-$ containing an uncoordinated $[Ph_2PSe_2]^-$ ligand.[6] Also Grobe *et.al.* published the structure of a zwitterionic species, $[\{(^iPr)_2NC\}_2P_2Se_2]$, which has a non-coordinated $R_2PSe_2^-$ unit.[7] It should be noted that the structure of free diselenophosphonate $[(R)(OR)PSe_2]^-$ or its salts is still unknown.[8]

On the other hand, the involvement of the ammonium salt of any dsep ligand as the source of ammonia in the formation of 4-oxopiperidinium rings is still unknown. However, the synthesis of 2,2,6,6-tetramethyl-4-oxopiperidine or its salts with various anions is commonly achieved by the condensation reaction of acetone with ammonia or ammonium donor substrates in the presence of catalysts.[9] These catalysts include Lewis acids, protonic acids, active halogen compounds (*viz.* sulfonyl halides, sulfuryl halides, *N*-haloamides, *N*-haloimides, β-haloesters, α-haloketones, α-halohydroxy compounds), and aluminosilicates containing calcium *etc.* Only in few instances, researchers have reported the solid-state structures of 4-oxopiperidinium salts with bulky anions such as $[HPO_3CH_2CONEt_2]^-$ and $[(C_6F_5)_2PO_2]^-$.[10] Yamamoto *et al.* reported that the synthesis of a palladium complex in the presence of NH_4PF_6 in acetone resulted in the formation of 4-oxopiperidinium ring and it was co-crystallized with the palladium compound having a formula of $[\{Pd(1,8\text{-dpmn})(XylNC)_2\}\{HN(CH_2)_2(CMe_2)_2CO\}_2](PF_6)_4$ (1,8-dpnm = 1,8-bis[(diphenylphosphino)methyl]naphthalene, XylNC = xylyl isocyanide).[11]

The discovery that the dinucleotide containing phosphoroseleno moiety may have antiviral properties[12] as well as the incorporation of phosphoroselenoate in DNA strands[13] has increased the importance for the study of the phosphoroselenium–carbon bond formation, which would aid the introduction of a different functionality on a phosphoroselenium unit. Although a handful of Se-glycosylations by the formation of Se–C bonds were reported mostly by the nucleophillic attack of a phosphoroselenium (PSe^-) unit on glycosyl bromide/anhydride,[14] yet commonly the P–Se–C unit forms *via* isomerization of a P(Se)C unit. For example, Rachon and his co-workers reported the formation of Se-esters by isomerization of *O*-alkoxalyl-monoselenophosphates.[15] While concentrating on *O*,*O*′-dialkyl diselenophosphate $[(RO)_2PSe_2]^-$, only few examples were reported in the 1970s in which they have been used as the nucleophile to attack alkyl halides to form Se-esters of phosphorodiselenoic acids.[16a–f] Recently

---

[a] *Department of Chemistry, National Dong Hwa University, 97401 Hualien, Taiwan*
[b] *Department of Chemistry, Soochow University, Taipei, 111 Taiwan, R. O. C. E-mail: chenwei@mail.ndhu.edu.tw*

† Electronic supplementary information (ESI) available: Synthesis and characterization data for compounds **1–7**. CCDC reference numbers 706306 and 706307. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/b813267d

Woollins' group reported a similar reaction where an amine salt of bisdiselenophosphonic acid reacted with CH_3I to produce *Se*,*Se*-dialkyldiesters of general formula $[PhP(Se)(SeCH_3)O(CH_2)_nO(SeCH_3)(Se)PPh]$.[16g] Murai reported the successful introduction of different functional groups on the Se atom of diselenoic acid ($RCSe_2H$)[17] and phosphinoselenothioic acid $[R_2P(S)SeH]$[18] to form Se-esters of these acids. As yet, no further progress in the introduction of other functional groups on the Se of the phosphorodiselenoic acid has been achieved except the aforementioned examples.

Herein, we report the structure of isopropyl homologue of dsep, $NH_4Se_2P(O^iPr)_2$ (**i**), along with the ability of $NH_4Se_2P(OR)_2$ to involve itself in the catalytic condensation of acetone in the presence of Fe powder to form 2,2,6,6-tetramethyl-4-oxopiperidinium salts of the ligand. The structure of the 4-oxopiperidinium salt of ethyl homologue $[\{H_2N(CH_2)_2(CMe_2)_2CO\}\{Se_2P(OEt)_2\}]$, **1b** is also characterized. The syntheses of Se-esters of *O*,*O′*-dialkylphosphorodiselenoic acid, **2**–**7** by nucleophilic substitution/addition of ammonium salts of dsep towards different types of electrophiles are also reported.

Results and discussion

Although the syntheses of ammonium salts of dsep ligands[19] and their metal complexes[2] were reported earlier, none of the free dsep ligands were structurally characterized. Herein the isopropyl homologue $NH_4[Se_2P(O^iPr)_2]$, (**i**) was unequivocally corroborated by single-crystal X-ray crystallography. It crystallizes in the monoclinic $P2_1/n$ space group and the asymmetric unit contains a solvated chloroform molecule. Selected bond lengths and angles are presented in Table 1. The P atom is attached to two Se and two O atoms in a distorted tetrahedral geometry. The O1–P1–O2 angle of 99.33(11)° is the smallest among the bond angles around the P atom whereas the angle Se1–P1–Se2 (117.28(4)°) is the largest. The two P–Se distances are unequal 2.1415(8), 2.1248(8) Å and are slightly shorter than the P–Se distances [2.159(8) and 2.139(7) Å] reported for $(HNEt_3)(Ph_2PSe_2)$.[4] The ammonium cation forms H-bonds with four selenium atoms from three, adjacent anionic $[Se_2P(O^iPr)_2]^-$ units to form a 1D supramolecular array along the *a* axis (Fig. 1). The observed H-bonding parameters, presented in Table 2, are well within the reported Se···H bonding limit.[20]

Table 1 Selected bond lengths (Å) and angles (°) in **i** and **1b** with esds in the parenthesis

i			
Se(1)–P(1)	2.1415(8)	Se(2)–P(1)	2.1248(8)
P(1)–O(1)	1.593(2)	P(1)–O(2)	1.597(2)
O(1)–C(1)	1.462(4)	O(2)–C(4)	1.474(4)
O(1)–P(1)–O(2)	99.33(11)	O(1)–P(1)–Se(2)	111.23(9)
O(2)–P(1)–Se(2)	113.10(9)	O(1)–P(1)–Se(1)	110.01(9)
O(2)–P(1)–Se(1)	104.23(8)	Se(2)–P(1)–Se(1)	117.28(4)
1b			
Se(1)–P(1)	2.1281(15)	Se(2)–P(1)	2.1123(14)
P(1)–O(1)	1.597(4)	P(1)–O(2)	1.570(4)
O(1)–C(1)	1.431(7)	O(2)–C(3)	1.418(8)
N(1)–C(9)	1.527(6)	N(1)–C(5)	1.528(6)
O(3)–C(7)	1.209(7)	O3′–C7′	1.263(18)
O(2)–P(1)–O(1)	96.7(2)	O(2)–P(1)–Se(2)	112.20(17)
O(1)–P(1)–Se(2)	113.61(16)	O(2)–P(1)–Se(1)	109.58(17)
O(1)–P(1)–Se(1)	105.49(16)	Se(2)–P(1)–Se(1)	117.17(6)
C(9)–N(1)–C(5)	121.0(4)	N(1)–C(9)–C(13)	105.4(4)
N(1)–C(9)–C(8)	107.7(4)	N(1)–C(9)–C(12)	108.6(4)
N(1)–C(5)–C(6)	107.1(4)	C(5)–C(6)–C(7)	111.2(4)
C(7)–C(8)–C(9)	110.9(4)	O(3)–C(7)–C(8)	122.5(7)
O(3)–C(7)–C(6)	122.2(6)	C(6)–C(7)–C(8)	115.3(5)

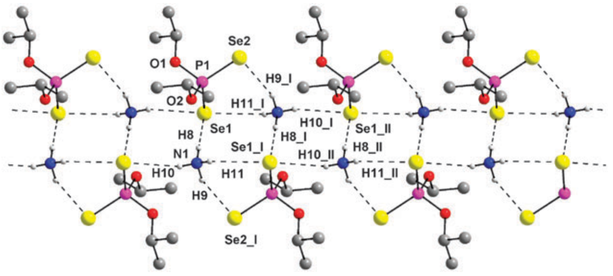


Fig. 1 H-Bonded supramolecular array of cations and anions in (**i**) along the *a* axis. Interactions with solvated $CHCl_3$ were not taken into consideration (symmetry code for I = 2 − *x*, 1 − *y*, 2 − *z*; II = 1 + *x*, *y*, *z*).

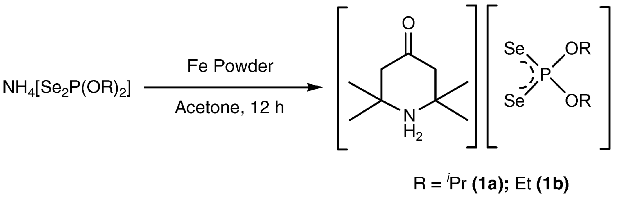
Use of $NH_4Se_2P(OR)_2$ ligands as NH_3 source in catalytic pathways

Unlike Yamamoto *et al.* who reported the formation of 2,2,6,6-tetramethyl-4-oxopiperidinium hexafluorophosphate salt during the synthesis of a palladium complex in acetone and co-crystallized with the Pd complex formulated as $[\{Pd(1,8\text{-}dpmn)(XylNC)_2\}\{HN(CH_2)_2(CMe_2)_2CO\}_2](PF_6)_4$,[11] the 2,2,6,6-tetramethyl-4-oxopiperidinium salts of the of dsep ligand [isopropyl (**1a**) and ethyl (**1b**) homologue] are isolated as white solids in 58 and 69% yield, respectively, when the ammonium salts of dsep ligand $NH_4Se_2P(OR)_2$ (R = ^{i}Pr, Et) were stirred in acetone for 12 h in the presence of a catalytic amount (22 mol%) of iron powder at room temperature (Scheme 1). Presumably the 4-oxopiperidinium cation is produced from the condensation of acetone with NH_3 generated from the ammonium cation of the ligand in the presence of iron powder. It is to be noted that the use of some iron salts (*viz.* $FeCl_3$) does not produce 4-oxopiperidinium salts of the dsep ligand. In addition to the resonance frequency of ethyl (or isopropyl) protons of the dsep ligand, methylene and methyl protons of the oxopiperidinium ring can also be observed in ^1H NMR spectrum of **1a**, **1b** (see ESI†). ^{31}P NMR spectra show a single resonance at 81.5 ppm with a pair of Se satellites (J_{PSe} = 741 Hz) for **1a** while a single peak is observed at 86.7 ppm (J_{PSe} = 759 Hz) for **1b**. Although both the 0.5 and 1.3 ppm upfield shift for **1a** and **1b** compared to their ammonium salts is insignificant, the increment in the ^{31}P–^{77}Se coupling constant value ~21 and 39 Hz for **1a** and **1b**, respectively, compared to their precursor (J_{PSe} = 720 Hz)[19] does suggest that the P–Se bond order has increased in the oxopiperidinium salt. Indeed there is lesser amount of H-bonding interactions observed in the solid-state structure of **1b** compared to the ammonium salt of the dsep (**i**).

Single-crystal X-ray diffraction of **1b** was performed and a perspective view is presented in Fig. 2(a). Selected bond

Table 2 Hydrogen-bonding parameters for **i** and **1b**

D–H···A	D–H/Å	H···A/Å	D···A/Å	D–H···A/°	Symmetry operation for A
i					
N1–H8···Se1	0.92(5)	2.58(5)	3.502(5)	177(5)	*x*, *y*, *z*
N1–H9···Se2	1.01(6)	2.46(6)	3.392(4)	154(4)	2 − *x*, 1 − *y*, 2 − *z*
N1–H10···Se1	0.88(5)	2.65(6)	3.500(4)	162(4)	1 − *x*, 1 − *y*, 2 − *z*
N1–H11···Se1	0.81(5)	2.83(6)	3.483(4)	139(5)	2 − *x*, 1 − *y*, 2 − *z*
1b					
N1–H1D···Se1	0.90	2.56	3.454(5)	172	*x*, *y*, *z*
N1–H1A···Se1	0.90	2.73	3.598(6)	163	−0.5 + *x*, 0.5 − *y*, −0.5 + *z*



Scheme 1

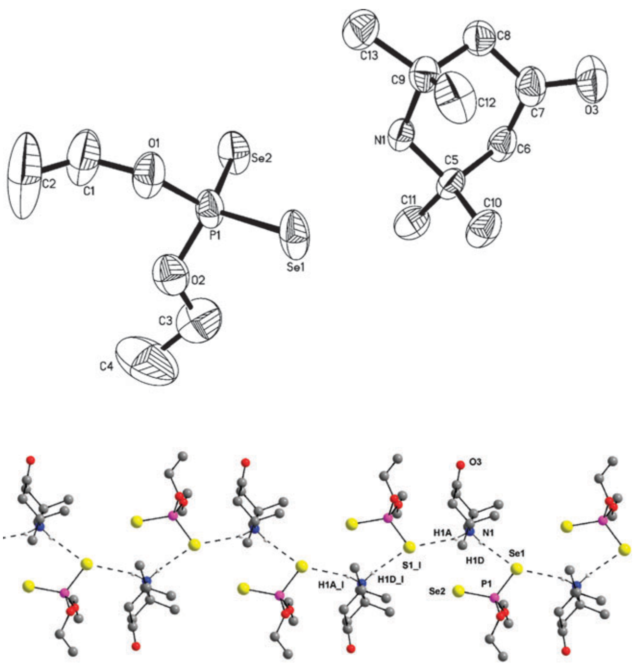


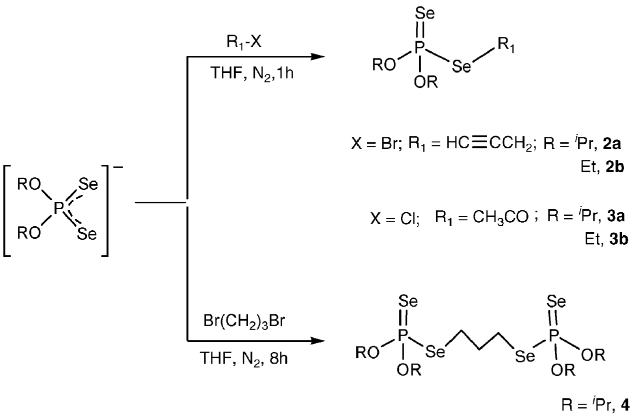
Fig. 2 (a) Perspective view of compound **1b** (30% probability); (b) 1D array of cations and anions in **1b** (symmetry code for I = −0.5 + *x*, 0.5−*y*, −0.5 + *z*).

lengths and angles are presented in Table 1. The monoanionic, diselenophosphate unit contains a P atom attached to two Se and two O atoms in a distorted tetrahedral manner. The largest angle around P atom (Se2–P1–Se1) is 117.17(6)° while the smallest (O2–P1–O1) is 96.7(2)°. The N atom of the oxopiperidinium ring, which is in chair conformation, is slightly closer to the Se1 atom of the anionic unit as evident from non-bonding distances of Se1···N (3.454(5) Å) compared to Se2···N (3.589(4) Å). Se1 of the diselenophosphate unit forms H-bonding with two hydrogen atoms (H1A and H1D) on N atoms of neighboring oxopiperidinium cations in the crystal lattice. The H-bonding leads to the formation of a one-dimensional supramolecular array as shown in Fig. 2(b). The Se···H distances (Table 2) are within the reported range.[20] The H-bonding of Se1 to two cationic units, resulted in a slightly larger P1–Se1 bond length of 2.1281(15) than that of P1–Se2, 2.1123(14) Å, and these lengths are in between P–Se single and double bonds.[3,21]

Phosphorodiselenoic acid as nucleophile

The two, almost equal P–Se bond lengths observed in the ammonium salt of *O*,*O*′-dialkylphosphorodiselenoic acid suggest that the negative charge is delocalized over the entire PSe_2 unit. Thus solution-state ^{31}P NMR exhibits only one set of Se satellites flanked around the singlet peak originated from ^{31}P–^{77}Se coupling by two equivalent Se atoms. When the ammonium salt, $NH_4Se_2P(OR)_2$, was stirred with an equimolar amount of alkynyl bromide or acetyl chloride in THF at room temperature under N_2 atmosphere (Scheme 2), one of the Se atoms acts as a nucleophile and attacks on the electrophilic carbon center to form an Se-ester of phosphorodiselenoic acid. The degeneracy of two Se attached to a P atom is lifted and thus both P–Se and P=Se bonds exist in the products. The ^{31}P NMR spectra of the Se-esters show two pairs of Se satellites flanked around a singlet peak. Also the ^{77}Se NMR spectrum of the product shows two doublets compared to only one doublet in the precursor. For comparison, the chemical shifts and coupling constants of compounds **2**–**7** in ^{31}P and ^{77}Se NMR spectra are summarized in Table 3.

For example, reaction of propargyl bromide with isopropyl homologues of phosphorodiselenoic acid salt (**i**) is completed within an hour to produce **2a** in 79% yield. Unlike its precursor, $NH_4Se_2P(O^iPr)_2$, which displays only one set of selenium satellites, **2a** shows two pairs of Se satellites in the ^{31}P NMR spectrum at 77.7 ppm with coupling constants ($^1J_{PSe}$)



Scheme 2

Table 3 $^{31}P\{^1H\}$, $^{77}Se\{^1H\}$ and ^{13}C NMR data (δ in ppm, J in Hz), mass and yield of compounds **2–7**

Compound	Yield (%)	^{31}P NMR[ac]	^{77}Se NMR[bc]	^{13}C NMR[cd]	Mass (m/z)
2a	79.0	77.7 (891.4, 469.9)	418.8 (469.4) −88.4 (891.6)	16.3 (3.8)	385.09 $[M + K]^+$
2b	77.1	82.9 (896.6, 478.7)	388.0 (478.6) −93.7 (896.9)	15.9 (4.0)	318.04 $[M]^+$
3a	76.7	66.6 (889.1, 466.6)	729.7 (466.6) −40.3 (889.7)	193.5 (5.8)	389.30 $[M + K]^+$
3b	82.9	72.0 (896.2, 473.1)	690.8 (474.5) −44.3 (897.9)	192.6 (5.9)	322.10 $[M]^+$
4	88.0	79.7 (884.9, 480.7)	352.7 (480.7) −90.1 (885.1)	31.4 (3.9)	680.36 $[M + Na]^+$
5a	48.8	78.4 (879.8, 490.9)	422.3 (490.6) −70.6 (880.6)	58.5 (4.2)	429.24 $[M + Na]^+$
5b	38.8	83.6 (886.5, 500.1)	379.4 (503.7) −75.3 (887.2)	58.4 (3.8)	379.04 $[M + H]^+$
6	29.8	80.5 (882.7, 477.7)	377.9 (477.9) −93.5 (882.6)	44.2 (2.4)	379.22 $[M + H]^+$
7a	66.1	82.2 (894.3, 418.1)	412.8 (418.3) −82.4 (894.2)	119.3 (6.3)	445.27 $[M + K]^+$
7b	80.1	88.3 (900.9, 422.6)	497.7 (422.3) −111.1 (904.0)	119.6 (6.4)	401.41 $[M + Na]^+$

[a] Coupling constants calculated from the selenium satellites in ^{31}P NMR. [b] Coupling constants of the doublet peaks in ^{77}Se NMR. [c] J values are in parentheses. [d] Only the chemical shift of the carbons attached to Se (Se–C) are presented.

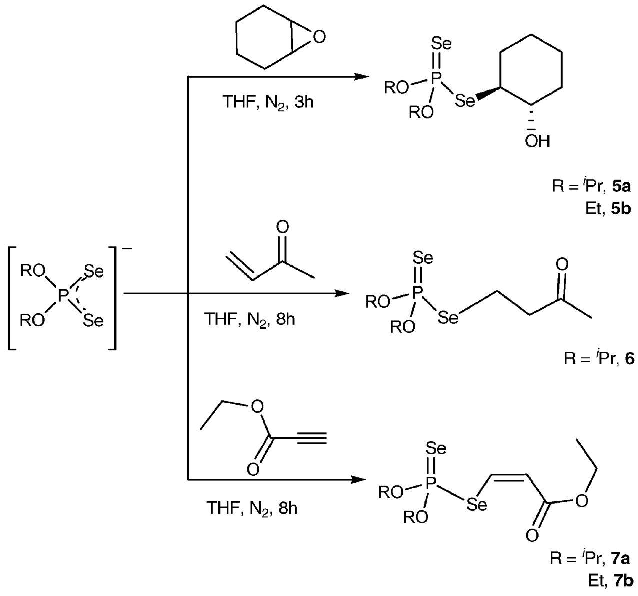
891.4 and 469.9 Hz. This confirms the simultaneous existence of both P–Se single and double bonds in compound **2a**. Alternately, this indicates that two Se atoms are no longer equivalent as the degeneracy of the two selenium–phosphorus bonds in phosphorodiselenoic acid salt is destroyed by the formation of one Se–C bond and also that the delocalized π-electrons in the precursor are now localized only on one phosphorus–selenium bond in **2a**. A similar phenomenon is observed also for the ethyl homologue **2b**. The ^{77}Se NMR spectrum of **2a**, **2b** also displays two doublet peaks attributable to two, nonequivalent Se coupled by the phosphorus nuclei. P–Se coupling constants obtained from ^{31}P and ^{77}Se NMR spectra are comparable for all the compounds (Table 3).

In addition, the formation of the compounds **2a**, **2b** is confirmed by MALDI-TOF mass spectrometry as the compounds showed m/z peaks at 385.09 and 318.04, respectively, which correspond to $[M + K]^+$ and M^+ (Table 3) where M represents the molecular weight of the compounds. Microanalysis data of **2a** also match with the calculated value. However, a good microanalysis result for the ethyl homologue **2b** could not be obtained due to its highly unstable nature. In addition the ^{13}C NMR spectra of compounds **2a**, **2b** show doublet peaks for the C atom attached to Se. For example **2a** shows a doublet peak at 16.3 ($^2J_{CP}$ = 3.8 Hz) arising from the two-bond coupling of ^{13}C nuclei by ^{31}P nuclei. This phenomenon also confirms the formation of the Se–C bonds. This phenomenon is observed throughout the series of compounds, **2–7** and listed in Table 3. On the other hand, the protons on the carbon adjacent to the Se ($SeCH_2C{\equiv}CH$) show doublet of doublet peaks at 3.53 ($^3J_{PH}$ = 12.9, $^4J_{HH}$ = 2.7) and at 3.47 ppm ($^3J_{PH}$ = 12.9 Hz, $^4J_{HH}$ = 2.7 Hz) for **2a** and **2b**, respectively, due to three-bond coupling by ^{31}P and four-bond coupling to acetylenic proton, which are also reminiscent of the formation of the Se-ester compounds.

Stirring acetyl chloride with equimolar ammonium salt of isopropyl and ethyl homologues of dsep resulted in acetyl Se-ester **3a** and **3b** in 76.7 and 82.9% yield, respectively (Scheme 2). In a similar manner as discussed above, ^{31}P NMR resonance frequencies of **3a** and **3b** also show singlet peaks with two sets of Se satellites (Table 3). It can be noted that the larger coupling constants (*e.g.* 889.1 ppm for **3a**) should have originated from coupling by ^{77}Se double bonded to phosphorus whereas the smaller value of coupling constant (say 466.6 ppm for **3a**) corresponds to selenium–phosphorus single bond coupling. The ^{77}Se NMR spectrum also exhibits two sets of doublets for **3a** and **3b** (Table 3). It is interesting to note that the Se atoms of dsep forming Se–C bonds, resonate with a lower value of coupling constant as it would have originated from phosphorus–selenium single bond coupling. Thus the Se atom resonating at 729.7 ppm (J_{SeP} = 466.6 Hz) for **3a** corresponds to the acylated selenium atom.

Stirring 1,3-dibromopropane with two equivalents of $NH_4Se_2P(O^iPr)_2$ in THF at room temperature resulted in a disubstituted product $[(O^iPr)_2P(Se)Se(CH_2)_3SeP(Se)(O^iPr)_2]$, **4** as a colorless oil which was well characterized by multinuclear NMR and MALDI-TOF mass spectrometry (Scheme 2, Table 3). In ^{31}P NMR spectroscopy it also shows a singlet flanked with two pairs of selenium satellites and the ^{77}Se NMR spectrum shows two doublet peaks (Table 3). This suggests that both diselenophosphate units in the disubstituted product are equivalent in solution state. In the ^{1}H NMR spectrum the Se–C*H* proton showed a multiplet due to the simultaneous coupling of phosphorus and proton nuclei on the adjacent carbon.

On the other hand, the epoxide ring-opening reactions by the nucleophilic attack of phosphorodiselenoate on cyclohexene oxide has never been reported even though Murai reported a similar reaction with a phosphinoselenothioic acid.[18b] The reaction of the ammonium salt of phosphorodiselenoic acid with cyclohexene oxide resulted in *Se*-(2-hydroxycyclohexyl) esters **5a** and **5b** in 48.8 and 38.8% yield, respectively. A singlet peak in ^{31}P NMR spectrum and two



Scheme 3

doublet peaks in ^{77}Se NMR spectrum confirm only a single stereoisomer has been formed for **5a** and **5b**. Because the reaction was performed in aprotic solvent, a S$_N$2 pathway is expected to yield the product containing a hydroxyl group *trans* to the selenium atom.

Although Murai *et al.* reported phosphinoselenothioic acid as the nucleophile to react with α,β-unsaturated ketone in a Michael type addition reaction,[18b] yet there is no report where phosphorodiselenoic acid or its salts are used to perform a similar reaction. Only the isopropyl homologue $NH_4[Se_2P(O^iPr)_2]$ is reacted with methyl vinyl ketone successfully resulting in *Se*-(butan-2-one) ester **6** (Scheme 3). Pure compound **6** was isolated in 29.8% yield only after the purification of the crude product on a preparative TLC. ^{1}H NMR of **6** does not show resonances around 6 ppm corresponding to the vinyl proton which confirms the absence of the olefin moiety in the product. We could not characterize its ethyl homologue due to the thermal instability of the product.

However, similar type of reactions were carried out using ethyl propiolate with both the isopropyl and ethyl homologs of dsep to afford **7a**, **7b** in 66 and 80% yield, respectively (Scheme 3). The ^{1}H NMR spectra of **7a**, **7b** both display a doublet of doublet peaks for the proton on the carbon (α-C) bonded to selenium which is reminiscent of the coupling by both adjacent protons and P atom. However, the proton on the β-carbon (Se–CH═C*H*) is coupled only to a single proton on the α-carbon and its ^{1}H NMR spectrum exhibits a coupling constant of 9.51 Hz at 6.45 ppm for **7a** and 9.54 Hz at 6.48 ppm for **7b**, which is more likely to be a coupling to the adjacent *cis*-proton.[22] This suggests the probable conformation about the double bond is *Z*. Compounds **7a** and **7b** also display a very small doublet peak centered at 6.26 ($^3J_{HH}$ = 15.9 Hz) and 6.29 ($^3J_{HH}$ = 15.9 Hz) ppm, respectively. The larger coupling constant indicates that the *E*-isomer also was produced as a minor product but the integration ratios suggest that only 8% and 2% might have been formed in the case of **7a** and **7b**, respectively. This result is in good agreement with Murai's work with phosphinoselenothioic acids where his group obtained the *Z*-isomer as the major product.[18b]

^{13}C NMR spectra of all the compounds **2**–**7** show doublet peaks for the carbon atom attached to Se due to the ^{31}P–^{13}C coupling. The ^{13}C NMR of the carbon atoms attached to the Se in compounds **2**–**7** are listed in the Table 3. All the Se atoms attached to carbon in compounds **2**–**7** show downfielded resonances whereas the other Se atom (P═Se) show highly upfielded shift with negative values (Table 3) in ^{77}Se NMR spectra.

In Murai's work the phosphinoselenothioic acid was generated from its ammonium salt first which was eventually allowed to react with the epoxide or α,β-unsaturated ketone to achieve the epoxide ring opening addition or Michael type addition.[18b] In sharp contrast, we could be able to run the reactions listed in Scheme 3 directly from the ammonium salt of the phosphorodiselenoic acid to obtain compounds **5**–**7**.

Conclusion

In conclusion, the first structural report of $NH_4Se_2P(O^iPr)_2$ is achieved along with a 1D chain produced *via* the H-bonding between the NH moieties and Se atoms of the dsep ligand. We also demonstrated the formation of 4-oxopiperidinium cationic ring *via* the iron powder catalyzed condensation of acetone in presence of ammonium salts of dsep ligands, which presumably acted as the source of NH_3. The structural elucidation of $[\{H_2N(CH_2)_2(CMe_2)_2CO\}\{Se_2P(OEt)_2\}]$ could enable us to demonstrate the H-bonding interactions of cationic oxopiperidinium and anionic dsep ligand in the solid state. Also in this report we have demonstrated the successful formation of selenium-ester directly by the reaction of ammonium salts of the *O*,*O*′-dialkylphosphorodiselenoic acid with a variety of electrophiles *via* different nucleophillic substitution/addition pathways and all of the new compounds have been well characterized despite their highly unstable nature. These include the first report of Michael-type addition and ring opening reaction of epoxide by a phosphorodiselenoate.

Experimental

All the solvents *viz*. acetone, dichloromethane, THF were purchased from Mallinckrodt Chemicals and purified before use following standard procedures.[23] All other reagent grade chemicals were purchased from Aldrich and used without further purification. Elemental analyses were done using a Heraeus VarioEL-III CNH analyzer. Multinuclear (^{1}H, ^{13}C, ^{31}P and ^{77}Se) NMR spectra were recorded with a Bruker Advance DPX300 FT-NMR spectrometer. The ^{31}P{^{1}H} and ^{77}Se{^{1}H} NMR spectra were referenced externally against 85% H_3PO_4 (δ = 0 ppm) and PhSeSePh (δ = 463 ppm), respectively. Syntheses of the compounds $NH_4Se_2P(OR)_2$ (where R = ^{i}Pr (**i**); Et (**ii**)) were reported earlier.[19] Spectroscopic data including NMR, IR and Mass of the compounds **1**, **2**, **3**, **4**, **5**, **6**, **7** are listed in ESI.†

Syntheses

$[\{H_2N(CH_2)_2(CMe_2)_2CO\}\{Se_2P(OR)_2\}]$, 1a, 1b. The reaction was carried out simply by stirring dsep ligand in the presence of 22 mol% of Fe powder in acetone at room temperature. In a typical reaction, to a solution of $NH_4[Se_2P(O^iPr)_2]$ (1.3 g, 4 mmol) in 50 mL acetone in a Schlenk flask, Fe powder (0.05 g, 0.90 mmol) was added at room temperature under N_2 and stirred for 12 h. It was then filtered through Celite and evaporated under reduced pressure using a vacuum pump. The solid residue was then washed with hexane and dissolved in ether to filter it again through Celite. Finally it was dried under reduced pressure to obtain the product $[\{H_2N(CH_2)_2(CMe_2)_2CO\}\{Se_2P(O^iPr)_2\}]$ (**1a**) as a white solid.

$[\{H_2N(CH_2)_2(CMe_2)_2CO\}\{Se_2P(O^iPr)_2\}]$, 1a. Yield: 1.08 g (58.7%). Anal. Calc. for $C_{15}H_{32}NO_3PSe_2$: C 38.9; H 6.96; N 3.02, Found: C 39.0; H 6.99; N 2.97%.

$[\{H_2N(CH_2)_2(CMe_2)_2CO\}\{Se_2P(OEt)_2\}]$, 1b. Yield: 1.22 g (69.3%). Anal. Calc. for $C_{13}H_{28}NO_3PSe_2$: C 35.8; H 6.44; N 3.22. Found: C 35.9; H 6.48; N 3.25%.

$[CH{\equiv}CCH_2SeP(Se)(OR)_2]$, 2a, 2b. In general, alkynylation of dsep ligand was carried out by stirring it with an equimolar amount of propargyl bromide in THF at room temperature. In a typical experiment, to a 20 mL THF solution of $NH_4Se_2P(O^iPr)_2$ (0.30 g, 0.93 mmol) propargyl bromide (80% solution in toluene) (100 µL, 0.93 mmol) was added and the mixture was stirred at room temperature for 1 h under nitrogen atmosphere. The solution was filtered to remove NH_4Br. The filtrate was evaporated under vacuum to obtain $HC{\equiv}CCH_2SeP(Se)(O^iPr)_2$ (**2a**) as a yellowish green oil.

$[HC{\equiv}CCH_2SeP(Se)(O^iPr)_2]$, 2a. Yield: 0.37 g (79.0%). Anal. Calc. for $C_9H_{17}O_3PSe_2$: C, 31.23; H, 4.95. Found: C, 31.06; H, 4.67%.

$[HC{\equiv}CCH_2SeP(Se)(OEt)_2]$, 2b. A similar procedure described above was adopted except that $(NH_4)Se_2P(OEt)_2$ was used instead of $(NH_4)Se_2P(O^iPr)_2$. Yield: 0.33 g (77.1%).

$[CH_3C(O)SeP(Se)(OR)_2]$, 3a, 3b. A suspension of $(NH_4)Se_2P(OR)_2$ in THF was stirred with acetyl chloride at room temperature under an inert atmosphere to obtain the products as pale green oils. In a typical experiment, to a suspension of $NH_4Se_2P(O^iPr)_2$ (0.44 g, 1.35 mmol) in 20 mL THF was added acetyl chloride (100 µL, 1.38 mmol) and the mixture was stirred at room temperature for 1 h under a nitrogen atmosphere. The reaction mixture was then evaporated to dryness at room temperature using vacuum. The residue was dissolved in 20 mL CH_2Cl_2 and filtered to remove the salt formed. The filtrate was evaporated under vacuum to obtain $CH_3C(O)SeP(Se)(O^iPr)_2$ (**3a**) as a greenish yellow oil.

$[CH_3C(O)SeP(Se)(O^iPr)_2]$, 3a. Yield: 0.37 g (76.7%). Anal. Calc. for $C_8H_{17}O_3PSe_2{\cdot}CH_2Cl_2$: C, 24.80; H, 4.40. Found: C, 24.81; H, 4.75%.

$[CH_3C(O)SeP(Se)(OEt)_2]$, 3b. Yield: 0.38 g (82.9%).

$[(^iPrO)_2P(Se)Se(CH_2)_3SeP(Se)(O^iPr)_2]$, 4. 1,3-Dibromopropane (25 µL, 0.25 mmol) was added to a 10 mL THF solution of $[(NH_4)Se_2P(O^iPr)_2]$ (0.16 g, 0.50 mmol) in a Schlenk flask and stirred for 8 h under N_2 atmosphere. The reaction mixture was filtered to remove the salt formed during the reaction. The solvent was evaporated under vacuum at room temperature to obtain the product as a colorless oil. Yield: 0.14 g (88.0%); Anal. Calc. for $C_{15}H_{34}O_4P_2Se_4$: C, 27.45; H, 5.22; Found: C, 27.76; H, 5.17%.

$[1,2\text{-}(OH)C_6H_{10}\{SeP(Se)(OR)_2\}]$, 5a, 5b. The synthesis was carried out by stirring dsep ligand $NH_4Se_2P(OR)_2$ in THF with cyclohexene oxide at room temperature under nitrogen atmosphere. In a typical reaction, to a suspension of $NH_4Se_2P(O^iPr)_2$ (0.40 g, 1.23 mmol) in 20 mL of THF was added cyclohexene oxide (100 µl, 1.38 mmol) and the mixture was stirred at room temperature for 3 h under a nitrogen atmosphere. Then the reaction mixture was evaporated to dryness. The resulting solution was vacuum-dried to obtain $1,\ 2\text{-}(OH)C_6H_{10}\{SeP(Se)(O^iPr)_2\}$ (**5a**) as a pale green oil.

$[1,2\text{-}(OH)C_6H_{10}\{SeP(Se)(O^iPr)_2\}]$, 5a. Yield: 0.24 g (48.8%). Anal. Calc. for $C_{12}H_{25}O_3PSe_2$: C, 35.48; H, 6.20; Found: C, 35.65; H, 6.17%.

$[1,\ 2\text{-}(OH)C_6H_{10}\{SeP(Se)(OEt)_2\}]$, 5b. Similar reaction carried out with $(NH_4)Se_2P(OEt)_2$ instead of $NH_4Se_2P(O^iPr)_2$. The reaction was continued for 6 h. Yield: 0.18 g (38.8%).

$[CH_3COCH_2CH_2SeP(Se)(O^iPr)_2]$, 6. To a solution of $NH_4Se_2P(O^iPr)_2$ (0.44 g, 1.35 mmol) in 20 mL of THF was added but-3-en-2-one (100 µl, 1.35 mmol) and stirred at room temperature for 8 h under nitrogen atmosphere. Then the solvent and the excess of but-3-en-2-one were removed under vacuum. The compound was isolated by preparative TLC by using 5% ethyl acetate in hexane. After running the solvent TLC plate four spots were isolated and the second spot from the top was the desired compound. After cutting the silica gel from the TLC plate, CH_2Cl_2 was added to dissolve it and filtered to isolate the product, to obtain a greenish yellow oil. Yield: 0.15 g (29.8%). Anal. Calc. for $C_{10}H_{21}O_3PSe_2{\cdot}0.5CH_2Cl_2$: C, 30.53; H, 5.37; Found: C, 30.70; H, 5.43%.

$[EtO_2CCH{=}CHSeP(Se)(OR)_2]$, 7a, 7b. Michael addition type reactions of $NH_4Se_2P(OR)_2$ on ethyl propiolate were carried out by stirring the reactants at room temperature in THF under N_2 atmosphere. In a typical reaction, to a suspension of $NH_4Se_2P(O^iPr)_2$ (0.40 g, 1.23 mmol) in 20 mL of THF, was added ethyl propiolate (130 µl, 1.24 mmol) and the mixture was stirred at room temperature for 8 h under a nitrogen atmosphere. Then the reaction mixture was evaporated to dryness at room temperature under vacuum to obtain the product $EtO_2CCH{=}CHSeP(Se)(O^iPr)_2$ (**7a**) as a yellowish green oil.

$[EtO_2CCH{=}CHSeP(Se)(O^iPr)_2]$, 7a. Yield: 0.33 g (66.1%).

$[EtO_2CCH{=}CHSeP(Se)(OEt)_2]$, 7b. The product was obtained in a similar reaction as described before while $NH_4Se_2P(OEt)_2$ was used instead of $(NH_4)Se_2P(O^iPr)_2$. Yield:

Table 4 Crystallographic data for $NH_4[Se_2P(O^iPr)_2]$ (**i**) and $[\{(CH_3)_2C_5H_4NO\}\{Se_2P(OEt)_2\}]$ (**1b**)

	i·$CHCl_3$	**1b**
Formula	$C_7H_{19}Cl_3NO_2PSe_2$	$C_{13}H_{28}NO_3PSe_2$
M_r	444.47	435.25
Crystal symmetry	Monoclinic	Monoclinic
Space group	$P2_1/n$	$P2_1/n$
a/Å	6.8693(5)	7.9318(13)
b/Å	14.9715(12)	22.409(4)
c/Å	17.3393(15)	11.2624(18)
β/°	100.082(3)	102.172(3)
V/Å^3	1755.7(2)	1956.8(5)
Z	4	4
T/K	223(2)	298(2)
D_c/g cm^{-3}	1.682	1.477
μ/mm^{-1}	4.748	3.866
Reflection collected	8954	20173
Independent reflections	4033	3353
R_{int}	0.0295	0.0353
Data/restraints/parameters	4033/0/169	3353/3/188
Final R indices $[I > 2\sigma(I)]^{ab}$	$R1 = 0.0364$	$R1 = 0.0464$
	$wR2 = 0.0888$	$wR2 = 0.0862$
R indices (all data)	$R1 = 0.0538$	$R1 = 0.0664$
	$wR2 = 0.0937$	$wR2 = 0.0937$
GOF	1.046	1.034
$\Delta\rho_{max}$/e Å^{-3}	0.778	0.647
$\Delta\rho_{min}$/e Å^{-3}	−0.504	−0.520

[a] $R1 = \sum|F_o| - |F_c|/\sum|F_o|$. [b] $wR2 = \{\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]\}^{1/2}$.

0.37 g (80.1%). Anal. Calc. for $C_9H_{17}O_4PSe_2$: C, 28.59; H, 4.53; Found: C 28.80; H 4.53%.

Crystal structure determination of i·$CHCl_3$ and 1b

Single crystals suitable for X-ray crystallography for **i** and **1b** were obtained by the slow evaporation of the chloroform solution of the compound. They were mounted on the tip of glass fiber with epoxy resin and the data were collected on APEX II CCD diffractometer using graphite-monochromated Mo-Kα radiation (λ = 0.71073 Å). Data reduction was performed with *SAINT*,[24] which corrects for Lorentz and polarization effects. A multi-scan absorption correction based on SADABS was applied. The structure was solved by the use of direct methods, and refinement was performed by the least-squares methods on F^2 with the SHELXL-97 package,[25] incorporated in SHELXTL/PC V5.10.[26] Both ammonium hydrogens and chloroform hydrogen of **i** were located and refined isotropically. Other H-atoms were allowed to ride in idealized positions. The C=O group on the oxopiperidinium ring of **1b** is unequally disordered over two orientations. The site occupancy factors were refined to 0.860(4) for the major orientation and to 0.140(4) for minor orientation. In the minor component, the C=O distance as well as the displacement parameters were set to the same values as those found in the major component and the distances of C7′–C10 and C7′–C12 were fixed at 1.55 Å. The crystallographic data are presented in Table 4.

Acknowledgements

We thank the National Science Council of Taiwan (NSC 97-2113-M-259-007-MY3) for the financial support. An anonymous reviewer's comment on the crystallographic part is also acknowledged.

References

1 V. Krishnan and R. A. Zingaro, *Inorg. Chem.*, 1969, **8**, 2337.
2 (*a*) Representative examples: C. W. Liu, C.-S. Fang, C.-W. Chuang, T. S. Lobana, B.-J. Liaw and J.-C. Wang, *J. Organomet. Chem.*, 2007, **692**, 1726; (*b*) C. W. Liu, H.-C. Chen, J.-C. Wang and T.-C. Keng, *Angew. Chem., Int. Ed.*, 2001, **40**, 2342; (*c*) T. S. Lobana, J.-C. Wang and C. W. Liu, *Coord. Chem. Rev.*, 2007, **251**, 91.
3 V. Bereau and J. A. Ibers, *Acta Crystallogr., Sect. C: Cryst. Struct. Commun.*, 2000, **56**, 584.
4 C. Q. Hguyen, M. Afzaal, M. A. Malik, M. Helliwell, J. Raftery and P. O'Brien, *J. Organomet. Chem.*, 2007, **692**, 2669.
5 P. Kilian, P. Bhattacharyya, A. M. Z. Slawin and J. D. Woollins, *Eur. J. Inorg. Chem.*, 2003, 1461.
6 M. J. Pilkington, A. M. Z. Slawin, D. J. Williams and J. D. Woollins, *Polyhedron*, 1991, **10**, 2641.
7 J. Grobe, D. Le Van, T. Pohlmeyer, F. Immel, H. Pucknat, B. Krebs, J. Kuchinke and M. Lage, *Tetrahedron*, 2000, **56**, 27.
8 Cambridge Structure Database: Version 5.29, July 2008.
9 (*a*) I. Orban, H. Lind, H. Brunetti, J. Rody and M. Rasberger, *US Pat.*, 3959295, 1976; (*b*) S. L. Suib, R. E. Malz, Jr and Y.-C. Son, *US Pat.*, 6646127, 2003; (*c*) W. H. De Camp, I. V. Micovic and S. W. Pelletier, *Cryst. Struct. Commun.*, 1974, **3**, 427; (*d*) P. C. Effendy, C. J. Junk, L. M. Kepert, T. C. Louis, B. W. Skelton and A. H. White, *Z. Anorg. Allg. Chem.*, 2006, **632**, 1312.
10 (*a*) G. S. Conary, D. J. McCabe, L. J. Caudle, E. N. Duesler and R. T. Paine, *Inorg. Chim. Acta*, 1993, **207**, 213; (*b*) C. F. Campana, K. W. Oliver, S. J. Rettig, R. C. Thompson, J. Trotter and S. Xia, *Acta Crystallogr., Sect. C: Cryst. Struct. Commun.*, 1998, **54**, 99.
11 Y. Yamamoto, Y. Fukui, K. Matsubara, H. Takeshima, F. Miyauchi, T. Tanase and G. Yamamoto, *J. Chem. Soc., Dalton Trans.*, 2001, 1773.
12 L. A. Woźniak, M. Sochacki, H. Mitsuya, S. Kageyama and W. J. Stec, *Bioorg. Med. Chem. Lett.*, 1994, **4**, 1033.
13 Y. Xu and E. T. Kool, *J. Am. Chem. Soc.*, 2000, **122**, 9040.
14 (*a*) M. Michalska, I. Orlich-Krezel and J. Michalski, *Tetrahedron*, 1978, **34**, 2821; (*b*) J. Borowiecka, *Heteroat. Chem.*, 2000, **11**, 292; (*c*) K. Misiura, D. Szymanowicz and W. J. Stec, *Collect. Czech. Chem. Commun.*, 1996, **61**, S101; (*d*) M. Michalska, J. Borowiecka, P. Lipka and T. Rokita-Trygubowicz, *J. Chem. Soc., Perkin Trans. 1*, 1989, **9**, 1619; (*e*) M. Michalska, J. Michalski and I. Orlich-Krezel, *Pol. J. Chem.*, 1979, **53**, 253; (*f*) M. Michalska, J. Michalski and I. Orlich, *Bull. Acad. Pol. Sci., Ser. Sci. Chim.*, 1974, **22**, 1053; (*g*) P. Lipka and M. Michalska, *Carbohydr. Res.*, 1983, **113**, 317; (*h*) W. Kudelska, *Heteroat. Chem.*, 1999, **10**, 259.
15 J. Rachon, G. Cholewinski and D. Witt, *Chem. Commun.*, 2005, 2692.
16 (*a*) R. D. Korak and N. I. Zemlyanskii, *Zh. Obshch. Khim.*, 1971, **41**, 1211; (*b*) N. I. Zemlyanskii and R. D. Gorak, *Zh. Obshch. Khim.*, 1971, **41**, 2446; (*c*) N. I. Zemlyanskii, R. D. Gorak and Y. I. Kolodii, *Ukr. Khim. Zh.*, 1973, **39**, 68; (*d*) N. L. Zemlyanskii, Y. G. Melńik, V. V. Turkevich, I. P. Makota and A. S. Koretskii, *Ser. Khim.*, 1975, **17**, 65; (*e*) Y. I. Melńik, Y. I. Kolodii and N. I. Zemlyanskii, *Zh. Obshch. Khim.*, 1977, **47**, 305; (*f*) Y. I. Melńik, D. I. Prots, Y. I. Kolodii and V. M. Slavich, *Zh. Obshch. Khim.*, 1986, **560**, 1059; (*g*) G. Hua, Y. Li, A. M. Z. Slawin and J. D. Woollins, *Tetrahedron*, 2008, **640**, 5442.
17 K. Tani, T. Murai and S. Kato, *J. Am. Chem. Soc.*, 2002, **124**, 5960.
18 (*a*) T. Murai, T. Kimura, A. Miwa, D. Kurachi and S. Kato, *Chem. Lett.*, 2002, **31**, 914; (*b*) T. Kimura, T. Murai, A. Miwa, D. Kurachi, H. Yoshikawa and S. Kato, *J. Org. Chem.*, 2005, **70**, 5611.
19 (*a*) C. W. Liu, I.-J. Shang, C.-M. Hung, J.-C. Wang and T.-C. Keng, *J. Chem. Soc., Dalton Trans.*, 2002, 1974; (*b*) C. W. Liu, T. S. Lobana, J.-L. Xiao, H.-Y. Liu, B.-J. Liaw, C.-M. Hung and Z. Lin, *Organometallics*, 2005, **24**, 4072.
20 T. Okamura, K. Taniuchi, K. Lee, H. Yamamoto, N. Ueyama and A. Nakamura, *Inorg. Chem.*, 2006, **45**, 9374.

21 B. K. Santra, J.-L. Chen, B. Sarkar and C. W. Liu, *Dalton Trans.*, 2008, 2270.

22 R. M. Silverstein, F. X. Webster and D. Kiemle, *Spectrometric Identification of Organic Compounds*, Wiley, New York, 7th edn, 2005.

23 D. D. Perrin, W. L. F. Armarego and D. R. Perrin, *Purification of Laboratory Chemicals*, Pergamon Press, Oxford, 2nd edn, 1980.

24 SAINT V4.043: Software for the CCD Detector System; Bruker Analytical X-ray System: Madison, WI, 1995.

25 G. M. Sheldrick, *SHELXL-97: Program for the Refinement of Crystal Structure*, University of Göttingen, Göttingen, Germany, 1997.

26 SHELXL 5.10 (PC version): Program Library for Structure Solution and Molecular Graphics, Bruker Analytical X-ray Systems, Madison, WI, 1998.