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The Chemistry of Phosphorodiselenoates: Structure, Catalysis and Formation of Se-esters

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Synthesis and characterization data for compounds 1~7

Genaral Synthesis of [{$H_2N(CH_2)_2(CMe_2)_2CO$}{$Se_2P(OR)_2$}], 1a-b: 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 fask, 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 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 get the product [{$H_2N(CH_2)_2(CMe_2)_2CO$}{$Se_2P(O^iPr)_2$}] (**1a**) as white solid.

[{$H_2N(CH_2)_2(CMe_2)_2CO$}{$Se_2P(O^iPr)_2$}], (1a): Yield: 1.08g (58.7%). Mp. 101 °C (decomp.). Anal calcd 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 %. ^1H NMR (300 MHz, $(CD_3)_2CO$, δ, ppm): 4.80(m, 2H, $OC\mathit{H}(CH_3)_2$), 3.78(s, br, NH_2), 2.77(s, 4H, CH_2), 1.59 (s, 12H, CH_3), 1.21 (d, 6Hz, 12H,

$OCH(CH_3)_2$). ^{31}P NMR (121.49 MHz, $(CD_3)_2CO$, δ, ppm): 81.5 (J_{PSe}= 741 Hz). FAB-MS (m/z): 464.7 $[M+H]^+$

$[\{H_2N(CH_2)_2(CMe_2)_2CO\}\{Se_2P(OEt)_2\}]$, (1b): Yield: 1.22 g (69.3%). Mp. 152°C (decomp.). Anal calcd 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%. ^{1}H NMR (300 MHz, $(CD_3)_2CO$, δ, ppm): 4.05(m, 4H, $-OCH_2CH_3$), 2.77(s, 4H, $-CH_2-$), 1.63 (s, 12H, $-C(CH_3)_2$), 1.3(t, $^3J_{HH}$ = 14Hz, 6H, $-OCH_2CH_3$); ^{31}P NMR (121.49 MHz, $(CD_3)_2CO$, δ, ppm): 86.7 (J_{PSe} = 759Hz).

General synthesis of $[CH{\equiv}CCH_2SeP(Se)(OR)_2]$, 2a-b.

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

$HC{\equiv}CCH_2SeP(Se)(O^iPr)_2$ (2a). Yield: 0.37g (79.0%). Anal. Calcd for $C_9H_{17}O_3PSe_2$: C, 31.23; H, 4.95. Found: C, 31.06; H, 4.67; IR (KBr, cm^{-1}): 3290 (ν_{CH}), 2107($\nu_{C\equiv C}$). ^{1}H NMR (300 MHz, $CDCl_3$, δ, ppm): 4.87(m, 2H, $-CH(CH_3)_2$), 3.53 (dd, $^3J_{PH}$ = 12.9, $^4J_{HH}$ = 2.7, 2H, $-SeCH_2C{\equiv}CH$), 2.28 (t, $^4J_{HH}$ = 2.7, 1H, $-CH_2C{\equiv}CH$), 1.37 (d, $^3J_{HH}$ =

6.3 Hz, 6H, -CH(CH_3)$_2$) ; ^{13}C NMR (75.5 MHz, CDCl$_3$, δ, ppm): 79.7 (d, J_{CP} = 6.4 Hz), 74.4 (d, J_{CP} = 6.4 Hz), 72.8, 23.6 (d, J_{CP} = 9.3 Hz), 16.3 (d, J_{CP} = 3.8 Hz); ^{31}P NMR (121.5 MHz, CDCl$_3$, δ, ppm): 77.7 (J_{PSe} = 891.4, 469.9 Hz); ^{77}Se NMR (57.2 MHz, CDCl$_3$, δ, ppm): 418.8 (d, J_{SeP} = 469.4 Hz), -88.4 (J_{SeP} = 891.6 Hz). MALDI-TOF : 385.09 [M+K$^+$].

HC≡CCH$_2$SeP(Se)(OEt)$_2$ (2b). A similar procedure described above was adopted except that (NH$_4$)Se$_2$P(OEt)$_2$ was used instead of (NH$_4$)Se$_2$P(O^{i}Pr)$_2$. Yield: 0.33g (77.1%). IR (KBr, cm^{-1}): 3310(ν_{CH}), 2212($\nu_{C\equiv C}$).. ^{1}H NMR (300 MHz, CDCl$_3$, δ, ppm): 4.21 (m, 4H, -OCH_2CH$_3$), 3.47 (dd, $^3J_{PH}$ = 12.9 Hz, $^4J_{HH}$ = 2.7 Hz, 2H, -SeCH_2C≡CH), 2.30 (t, $^4J_{HH}$ = 2.7 Hz, 1H, -CH$_2$C≡CH), 1.39 (t, $^3J_{HH}$ = 7.1 Hz, 6H, -OCH$_2$CH_3) ; ^{13}C NMR (75.5 MHz, CDCl$_3$, δ, ppm): 79.8 (d, J_{CP} = 5.3 Hz), 72.6, 64.6 (d, J_{CP} = 5.2 Hz), 15.9 (d, J_{CP} = 4.0Hz), 15.7 (d, J_{CP} = 8.7 Hz); ^{31}P NMR (121.5 MHz, CDCl$_3$, δ, ppm): 82.9 (J_{PSe} = 896.6, 478.9 Hz); ^{77}Se NMR (57.2 MHz, CDCl$_3$, δ, ppm): 388.02 (d, J_{SeP} = 478.6 Hz), -93.7 (d, J_{SeP} = 896.9 Hz). MALDI-TOF: 318.04[M$^+$].

General procedure for synthesis of [CH$_3$C(O)SeP(Se)(OR)$_2$], 3.

A suspension of (NH$_4$)Se$_2$P(OR)$_2$ in THF was stirred with acetyl chloride at room temperature under inert atmosphere to obtain the products as pale green oils. In a typical experiment, to a suspension of NH$_4$Se$_2$P(O^{i}Pr)$_2$ (0.44g, 1.35mmol) in 20 mL THF was added acetyl chloride (100μL, 1.38mmol) and the mixture was stirred at room temperature for 1h 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 get rid of 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: 0.37g (76.71%). Anal. Calcd for $C_8H_{17}O_3PSe_2{\cdot}CH_2Cl_2$: C, 24.80; H, 4.40. Found: C, 24.81; H, 4.75.; ^{1}H NMR (300 MHz, $CDCl_3$, δ, ppm): 4.98 (m, 2H, $-CH(CH_3)_2$), 2.51 (d, $^4J_{HP}$ = 2.1 Hz, 3H, CH_3CO-), 1.36 (t, $^3J_{HH}$ = 6.3 Hz, 6H, $-CH(CH_3)_2$); ^{13}C NMR (75.48 MHz, $CDCl_3$, δ, ppm): 193.5 (d, J_{CP} = 5.8 Hz), 75.2 (d, J_{CP} = 6.4 Hz), 36.3, 23.7 (d, J_{CP} = 4.5 Hz), 23.2 (d, J_{CP} = 5.1 Hz); ^{31}P NMR (121.49 MHz, $CDCl_3$, δ, ppm): 66.6 (J_{PSe} = 889.1, 466.6 Hz); ^{77}Se NMR (57.24MHz, $CDCl_3$, δ, ppm): 729.7 (d, J_{SeP} = 466.6 Hz), -40.3 (d, J_{SeP} = 889.7Hz). MALDI-TOF: 389.30 [$M+K^+$]. IR (KBr, cm^{-1}): 1736 (ν_{CO}).

$CH_3C(O)SeP(Se)(OEt)_2$ (3b). Yield: 0.38g (82.9%). ^{1}H NMR (300 MHz, $CDCl_3$, δ, ppm): 4.26 (m, 4H,$-OCH_2CH_3$), 2.52 (d, $^3J_{PH}$ = 2.0 Hz, 3H, CH_3CO-), 1.40 (t, $^3J_{H\text{-}H}$ = 7.1 Hz, 6H, $-OCH_2CH_3$) ; ^{13}C NMR (75.5 MHz, $CDCl_3$, δ, ppm): 192.6 (d, J_{CP} = 5.9 Hz), 65.3 (d, J_{CP} = 5.6 Hz), 36.4, 15.7 (d, J_{CP} = 8.48 Hz); ^{31}P NMR (121.5 MHz, $CDCl_3$, δ, ppm): 72.0 (J_{PSe} = 896.2, 473.1 Hz); ^{77}Se NMR (57.2 MHz, $CDCl_3$, δ, ppm): 690.8 (d, J_{SeP} = 474.5 Hz), -44.3 (d, J_{SeP} = 897.9 Hz). MALDI-TOF: 322.109 [M^+], IR (KBr, cm^{-1}): 1726 (ν_{CO}).

Synthesis of [(^{i}PrO)$_2$P(Se)Se(CH$_2$)$_3$SeP(Se)(O^{i}Pr)$_2$], 4. 1,3-Dibromopropane (25 μL, 0.25 mmol) was added to a 10 mL THF solution of [(NH$_4$)Se$_2$P(O^{i}Pr)$_2$] (0.16 g, 0.50mmol) in a Schlenk flask and stirred for 8h under N$_2$ atmosphere. The reaction mixture was filtered to get rid of the salt formed during the reaction. The solvent was evaporated under vacuum at room temperature to obtain the product as colorless oil. Yield: 0.14g (88 %); Anal. Calcd for $C_{15}H_{34}O_4P_2Se_4$: C, 27.45; H, 5.22; Found ; C, 27.76; H, 5.17; ^{1}H NMR (300 MHz, CDCl$_3$, δ, ppm): 4.84 (m, 4H, -OC*H*-), 3.00 (m, 4H, Se-C*H*$_2$-CH$_2$-C*H*$_2$-Se), 2.25 (m, 2H, -CH$_2$C*H*$_2$CH$_2$-), 1.34 (d, $^3J_{HH}$ = 6.3 Hz, 24H); ^{13}C NMR (75.5 MHz, CDCl$_3$, δ, ppm): 74.4 (d, J_{CP}= 7.1 Hz), 31.4 (d, J =3.9Hz), 31.2, 23.5 (d, J_{CP} = 21.5 Hz); ^{31}P NMR (121.5 MHz, CDCl$_3$, δ, ppm): 79.7 (J_{PSe} = 884.9, 480.7Hz); ^{77}Se NMR (57.2 MHz, CDCl$_3$, δ, ppm): 352.7 (d, J_{SeP} = 480.7Hz), -90.1 (d, J_{SeP} = 885.1 Hz),; MALDI-TOF MS: 680.36 [M+Na$^+$].

General synthesis of [1,2-(OH)C$_6$H$_{10}${SeP(Se)(OR)$_2$}], 5a-b.

The synthesis was carried out by stirring dsep ligand NH$_4$Se$_2$P(OR)$_2$ in THF with cyclohexene oxide at room temperature under nitrogen atmosphere. In a typical reaction, to a suspension of NH$_4$Se$_2$P(O^{i}Pr)$_2$ (0.40g, 1.23 mmol) in 20 mL of THF was added cyclohexene oxide (100μl, 1.38mmol) and the mixture was stirred at room temperature for 3h under a nitrogen atmosphere. Then the reaction mixture was evaporated to dryness. The resulting solution was vacuum-dried to obtain 1, 2-(OH)C_6H_{10}{SeP(Se)(O^{i}Pr)$_2$} (5**a**) as a pale green oil.

[1,2-(OH)C_6H_{10}{SeP(Se)(O^{i}Pr)$_2$}], 5a. Yield: 0.24g (48.8%). Anal. Calcd for $C_{12}H_{25}O_3PSe_2$: C, 35.48; H, 6.20; Found: C, 35.65; H, 6.17; IR (KBr, cm^{-1}): 3400 (br, ν_{CH}); ^{1}H NMR (300 MHz, $CDCl_3$, δ, ppm): 4.82 (m, 2H, -OC*H*(CH_3)$_2$), 3.52 (m, 1H, -CH_2C*H*(OH)CH-), 3.19 (m, 1H, -CH_2C*H*(Se)CH-), 2.68 (s, 1H, -CHO*H*), 2.04-2.27 (m, 2H, cyclohexane ring), 1.63-1.69 (m, 3H, cyclohexane ring), 1.29 (m, 15H, -CH_3 + cyclohexane); ^{13}C NMR (75.5 MHz, $CDCl_3$, δ, ppm): 74.7 (d, J_{CP} = 7.5 Hz), 73.4 (d, J_{CP} = 3.5 Hz), 58.5 (d, J_{CP} = 4.2 Hz), 34.9, 33.7 (d, J_{CP} = 4.6 Hz), 26.9, 24.1, 23.6 (d, J_{CP} = 19.7 Hz); ^{31}P NMR (121.5 MHz, $CDCl_3$, δ, ppm): 78.6 (J_{PSe} = 879.8, 490.9); ^{77}Se NMR (57.2 MHz, $CDCl_3$, δ, ppm): 422.3 (J_{SeP} = 490.6), -70.6 (J_{SeP} = 880.6). MALDI-TOF: 429.24 [M+Na$^+$].

[1, 2-(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^{i}Pr)$_2$. The reaction was continued for 6 hours. Yield: 0.18g (38.8%). IR (KBr, cm^{-1}): 3400 (br ν_{CH}); ^{1}H NMR (300 MHz, $CDCl_3$, δ, ppm): 4.11 (m, 4H, -OC*H*$_2$$CH_3$), 3.48 (m, 1H, -CH_2C*H*(OH)CH-), 3.33 (m, 1H, -CH_2C*H*(Se)CH-), 3.04-3.15 (m, 2H, cyclohexane ring), 1.49-2.42 (m, 7H, cyclohexane ring), 1.29 (m, 12H, -CH_2C*H*$_3$); ^{13}C NMR (75.5 MHz, $CDCl_3$, δ, ppm): 73.1 (d, J_{CP} = 3.6 Hz), 64.8 (d, J_{CP} = 9.1 Hz), 58.4 (d, J_{CP} = 3.8 Hz), 35.0, 34.1 (d, J_{CP}

= 16.2 Hz), 26.8, 24.1, 15.6 (d, J_{CP} = 8.7 Hz); ^{31}P NMR (121.5 MHz, $CDCl_3$, δ, ppm): 83.8 (J_{PSe} =886.5, 500.1 Hz); ^{77}Se NMR (57.2 MHz, $CDCl_3$, δ, ppm):): 379.4 (d, J_{SeP} = 503.7 Hz), -75.3 (d, J_{SeP} = 887.2Hz). MALDI-TOF: 379.04 [M+H$^+$].

Synthesis of [$CH_3COCH_2CH_2SeP(Se)(O^iPr)_2$], 6. To a solution of $NH_4Se_2P(O^iPr)_2$ (0.44g, 1.35mmol) in 20 mL of THF was added but-3-en-2-one (100μl, 1.35 mmol) and stirred at room temperature for 8h 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% EA in hexane. After running the solvent TLC plate showed 4 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 greenish yellow oil.

[$CH_3COCH_2CH_2SeP(Se)(O^iPr)_2$], 6. Yield: 0.15g (29.8%). Anal. Calcd. 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. IR (KBr, cm^{-1}): 1718 (ν_{CO}). ^{1}H NMR (300 MHz, $CDCl_3$, δ, ppm): 4.84 (m, 2H, -C*H*(CH_3)$_2$), 3.06(m, 4H, $CH_3COCH_2CH_2$-), 2.16(s, 3H, $CH_3COCH_2CH_2$-), 1.35 (m, 6H, -CH(CH_3)$_2$); ^{13}C NMR (75.5 MHz, $CDCl_3$, δ, ppm): 206.8, 74.4 (d, J_{CP} = 7.2 Hz), 44.2 (d, J_{CP} = 2.4 Hz), 30.0, 24.2 (d, J_{CP} = 3.8 Hz), 23.6 (d, J_{CP} = 4.3 Hz); ^{31}P NMR (121.5 MHz, $CDCl_3$, δ, ppm): δ 80.5 (J_{PSe} = 884.7, 448.4 Hz); ^{77}Se NMR (57.2 MHz, $CDCl_3$, δ, ppm): 377.9 (d, J_{SeP} = 477.9 Hz), -93.5 (d, J_{SeP} = 882.6 Hz). MALDI-TOF: 379.22 [M+H]$^+$.

General synthesis of [$EtO_2CCH=CHSeP(Se)(OR)_2$], 7a-b.

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 $NH_4Se_2P(O^iPr)_2$ (0.40g, 1.23mmol) in 20 mL of THF, was added ethyl propiolate (130µl, 1.24mmol) and the mixture was stirred at room temperature for 8h under 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: 0.33g (66.1%). ^{1}H NMR (300 MHz, $CDCl_3$, δ, ppm): 7.79 (dd, $^3J_{HH}$ = 9.48 Hz, $^3J_{PH}$ = 17.79 Hz, 1H, -SeC*H*=CHCO), 6.45(d, 0.92 H, $^3J_{HH}$ = 9.51Hz, -SeCH=C*H*CO), 6.26 (d, $^3J_{HH}$ = 15.85 Hz, 0.08H, -SeCH=C*H*CO), 4.80 (m, 2H,-C*H*(CH_3)$_2$), 4.18 (m, 2H, CH_3CH_2O-), 1.3 (m, 12H, -CH(CH_3)$_2$); ^{13}C NMR (75.5 MHz, $CDCl_3$, δ, ppm): 166.8, 144.5, 119.3 (d, J_{CP} = 6.3 Hz), 74.7 (d, J_{CP} = 6.3 Hz), 60.8 (d, J_{CP} = 13.3 Hz), 23.5(d, J_{CP} = 24.2 Hz), 14.3; ^{31}P NMR (121.5 MHz, $CDCl_3$, δ, ppm): 82.3 (J_{PSe} = 894.3, 418.1 Hz); ^{77}Se NMR (57.2 MHz, $CDCl_3$, δ, ppm): 412.8 (d, J_{SeP}= 418.3 Hz), -82.4 (d, J_{SeP} = 894.2 Hz). IR (KBr, cm^{-1}): 1716 (ν_{CO}). MALDI-TOF: 445.27 [M+K$^+$].

[$EtO_2CCH=CHSeP(Se)(OEt)_2$], 7b. The product obtained in a similar reaction as described before while $NH_4Se_2P(OEt)_2$ was used instead of $(NH_4)Se_2P(O^iPr)_2$. The reaction was completed in 8h. Yield: 0.37g (80.1%). Anal. Calcd for $C_9H_{17}O_4PSe_2$: C, 28.59; H, 4.53; Found: C 28.80; H 4.53. ^{1}H NMR (300 MHz, $CDCl_3$, δ, ppm): 7.78 (dd, $^3J_{HH}$ = 9.54 Hz, $^3J_{PH}$ = 17.64 Hz, 1H, -SeC*H*=CHCO), 6.48(d, J_{HH} = 9.54 Hz, 0.98 H, -SeCH=C*H*CO), 6.28 (d, $^3J_{HH}$ = 15.90 Hz, 0.02 H, -SeCH=C*H*CO), 4.25-4.03 (m, 4H, -POCH_2CH$_3$, -CO$_2$CH_2CH$_3$),), 1.34 (t, $^3J_{HH}$ =7.11Hz, 6H, -POCH$_2$CH_3), 1.28 (t, $^3J_{HH}$ = 7.14 Hz, 3H, -CO$_2$CH$_2$CH_3); ^{13}C NMR (75.5 MHz, $CDCl_3$, δ, ppm): 166.7, 144.1, 119.6 (d, J_{CP} = 6.4 Hz), 64.9 (d, J_{CP} = 5.6 Hz), 60.9, 15.6(d, J_{CP} = 8.4 Hz), 14.3; ^{31}P NMR (121.5 MHz, $CDCl_3$, δ, ppm): 88.6 (J_{PSe} = 900.9, 422.6 Hz); ^{77}Se NMR (57.2 MHz, $CDCl_3$, δ, ppm): 497.7 (d, J_{SeP} = 422.3 Hz), -111.1 (d, J_{SeP} = 904.0 Hz). IR (KBr, cm^{-1}): 1726 (ν_{CO}). MALDI-TOF: 401.41 [M+Na]$^+$.