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ORIGINAL PAPER

A Facile Synthesis and Crystallographic Analysis of Seven Trityl Phosphorus Compounds and Two Nickel(II) Phosphine Side-Products

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Abstract The syntheses and X-ray analyses of triphenylmethyl (trityl=Tr) phosphorus compounds are reported and the structural similarities, differences and ^{31}P chemical shifts compared. A series of seven trityl-substituted phosphorus-containing compounds have been characterized by single crystal X-ray diffraction. Ph_3CPPh_2, **1**, a bulky P(III) compound crystallizes in the triclinic space group $P\bar{1}$, $a = 7.5624(6)$ Å, $b = 9.5470(8)$ Å, $c = 16.9722(14)$ Å, $\alpha = 83.4720(10)°$, $\beta = 80.541(2)°$, $\gamma = 68.1580(10)°$, the borane complex of **1**, **2**, $Ph_3CPPh_2(BH_3)$ crystallizes as monoclinic colorless crystals, $P2_1/c$, $a = 10.0972(12)$ Å, $b = 9.6955(12)$ Å, $c = 25.197(3)$ Å, $\beta = 90.258(2)°$. The analogous methyl substituted, **3**, $Ph_3CPMe_2(BH_3)$ is monoclinic, C_2/c, $a = 15.628(3)$ Å, $b = 12.770(3)$ Å, $c = 18.406(4)$ Å, $\beta = 103.968(3)°$. Compounds **4**–**7** are trityl substituted P(V) compounds: $Ph_3CP(Ph)(O)(OH)$, **4**, crystallizes in the triclinic space group $P\bar{1}$, $a = 8.9847(18)$ Å, $b = 9.7443(19)$ Å, $c = 12.786(3)$ Å, $\alpha = 72.045(3)°$, $\beta = 72.031(3)°$, $\gamma = 78.769(3)°$. Esterification of **4** affords TrCP(O)(Ph)OBn **5**, space group, $P2_1/c$, $a = 7.9196(5)$ Å, $b = 31.701(2)$ Å, $c = 19.8062(13)$ Å, $\beta = 99.7750(10)°$. A phosphonate diester was also characterized, $Ph_3CP(O)(OEt)_2$, **6**, triclinic, $P\bar{1}$, $a = 7.9521(17)$ Å, $b = 9.2205(19)$ Å, $c = 14.471(3)$ Å, $\alpha = 85.906(4)°$, $\beta = 83.031(4)°$, $\gamma = 68.283(4)°$. Treatment of the trityl *H*-phosphinic acid, $Ph_3CPO_2H_2$, with elemental selenium yields yellow crystals of **7**, $[Ph_3CP(O)(OH)Se]_2$, $P2_1/c$, $a = 9.0603(4)$ Å, $b = 22.3652(11)$ Å, $c = 16.9134(7)$ Å, $\beta = 107.035(2)°$. In our efforts to isolate a nickel-phosphine complex, two Ni(II) complexes were crystallographically analyzed, $[Ni(OP(H)Ph_2)_6]_2BF_4^-$ **8** and **9**. Complex **8** with an uncoordinated BF_4^- ion crystallizes as yellow orthorhombic crystals, Pbca, $a = 18.8247(12)$ Å, $b = 18.5518(12)$ Å, $c = 21.0976(14)$ Å, while crystals of **9** are trigonal, $R\bar{3}c$, $a = b = 13.1545(12)$ Å, $c = 68.461(9)$ Å.

Keywords Trityl · Phosphorus compounds · Selenophosphonic acid

Introduction

Triphenylmethyl (trityl, Tr) compounds have generated interest as they can be used for hydride abstraction, oxidative cleavage, and more recently for the stabilization of transition metal clusters [1–4]. Furthermore, trityl-containing phosphorus species are well documented [5–8] but limited structural data has been reported. We recently reported the synthesis and characterization of phosphonothioic and boranophosphonic acids supported by the trityl group, namely $Ph_3CP(S)(OH)_2$, $(Ph_3CP(O)(BH_3^-)(OH)]LH^+$ (L = Lewis base) [9]. These were both conveniently synthesized in high yields from trityl *H*-phosphinic acid ($Ph_3CPO_2H_2$). Additionally, $TrPO_2H_2$ and $TrPO_3H_2$ were also characterized by X-ray diffraction. The study provided the very first structurally characterized examples of both phosphonothioate and boranophosphonate compounds. In continuing with our investigations in this area, we wished to examine how alteration of the phosphorus substituents affected structural parameters and ^{31}P chemical shifts. The advantage of a trityl moiety is the crystallinity of the derived compounds, and therefore a unique opportunity to compare structural features directly in the same series. To this end, we prepared and characterized Ph_3CPPh_2 **1**, $Ph_3CP(BH_3)(Ph)_2$ **2**, $Ph_3CP(BH_3)(Me)_2$ **3**, $Ph_3CP(O)(OH)Ph$ **4**, $Ph_3CP(O)(OBn)(Ph)$ **5**,

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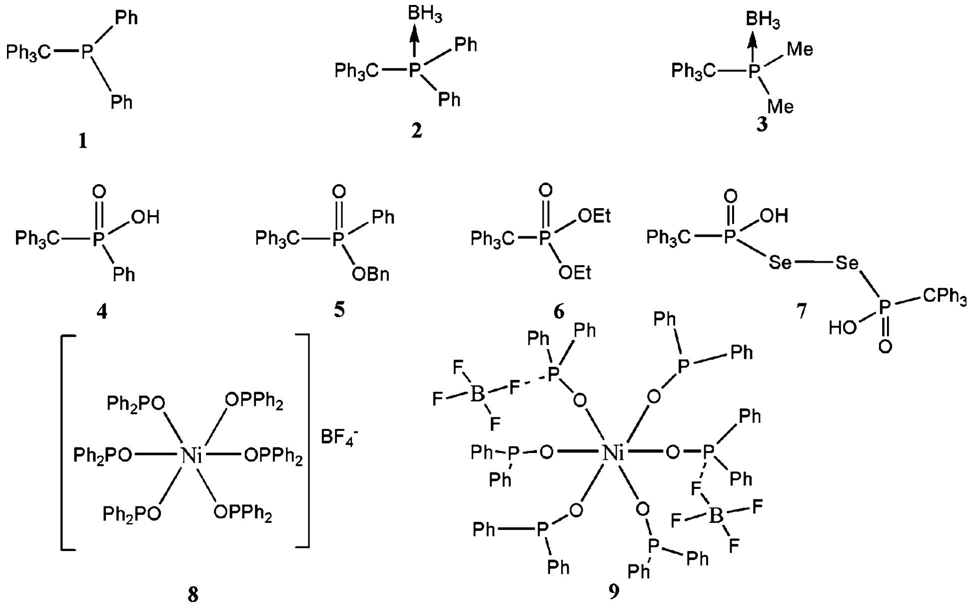


Fig. 1 Summary of the trityl phosphorus compounds prepared and characterized

$Ph_3CP(O)(OEt)_2$ **6**, and $[Ph_3CP(O)(OH)Se]_2$, **7** (Fig. 1). In our attempts to isolate transition metal–trityl phosphine complexes, two cationic complexes were isolated of the formula, $[Ni(OP(H)Ph_2)_6]_2BF_4^-$ **8** and **9** that differ in their anion incorporation. In **8**, the anion is separated from the cation center, while in complex **9**, incorporation of three bridged fluorine atoms, affords a contact cation–anion structure.

Experimental

All chemicals were purchased from Aldrich or Acros and used as received. Melting points were preformed on a Meltemp apparatus under ambient conditions, and the melting points are not corrected. Crystal data were collected with a Bruker SMART 1000 diffractometer using graphite monochromated molybdenum radiation ($\lambda = 0.7107$ Å). Crystals were attached to glass fibers using paratone oil and data were collected at −60 °C. The data were processed using SAINT and corrected for absorption [10, 11]. Structures were solved by direct methods using the SHELXS-97 program and refined via full-matrix least squares [10, 11]. Crystal data for all compounds is given in Table 2. High resolution mass spectrometry was provided by University of North Carolina, electrospray ionization.

Synthesis of **1**, Diphenyl Tritylphosphine

Procedure To a yellow stirring CH_2Cl_2 (25 mL) suspension of triphenylcarbenium tetrafluoroborate (2.5 g, 7.6 mmol) in a Schlenk flask was added diphenylphosphine (1.3 mL, 7.6 mmol) neat via syringe. The reaction immediately turned clear and colorless and was allowed to stir overnight, after which time a white precipitate had developed. Approximately 25 mL of DI water, which had been previously degassed via purging with nitrogen gas for approximately 1 hour, was then added rapidly via cannula, followed by the addition of a threefold excess of NEt_3 (3.2 mL, 22.8 mmol). The clear and colorless biphasic reaction mixture was allowed to stir overnight, at which time the aqueous layer containing $[Et_3NH][BF_4]$ was removed by syringe. The CH_2Cl_2 was removed in vacuo to yield diphenyl tritylphosphine as a white powder. Crystals were grown at room temperature (rt) from CH_2Cl_2. Isolated yield: 99% Mp: turned pale yellow at 119 °C; became waxy from 131–135 °C; melted 140–144 °C IR (nujol mull, cm^{-1}) 1594, 1155, 973, 742, 699 ^1H NMR (300 MHz, C_6D_6) δ 7.19–7.06 (m, 17H, Ar*H*), 7.04–6.99 (t, 4H, Ar*H*, $^1J = 7.5$ Hz), 6.77–6.72 (t, 4H, Ar*H*, $^1J = 7.6$ Hz) ^{13}C NMR (300 MHz, C_6D_6) δ 94.3, 126.4, 127.8, 127.9, 128.0, 129.0, 129.7, 131.1, 131.2, 134.3, 135.3, 135.5, 135.6 ^{31}P NMR (300 MHz, C_6D_6) δ 27.9 HRMS (EI) calcd. for $C_{31}H_{25}P$, (M + H) 429.1772, found 429.1763.

Synthesis of **2**, Diphenyl Tritylphosphine-Borane

Procedure A toluene solution of diphenyl tritylphosphine (0.4 g, 0.93 mmol) was cooled to −78 °C and 1.0 M BH_3.THF (0.93 mL, 0.93 mmol) was added dropwise to give a clear colorless solution. The cooling bath was removed immediately and the reaction mixture was allowed to stir overnight at rt. Concentration and storage at rt of the toluene solution afforded diphenyl tritylphosphine-borane as colorless needles. Isolated yield: 14% Mp: 146–150 °C, ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.32 (t, 2H, Ar*H*, $^1J = 7.3$ Hz), 7.24–7.19 (m, 5H, Ar*H*), 7.15–7.14 (m, 12H, Ar*H*), 7.10 (d, 1H, Ar*H*, $^1J = 2.6$), 7.07–7.06 (m, 1H, Ar*H*), 6.99 (t, 4H, Ar*H*, $^1J = 8.8$ Hz) ^{13}C NMR (300 MHz, $CDCl_3$) δ 69.6, 125.3, 126.4, 126.5, 126.8, 127.0, 127.3, 127.5, 127.9, 128.4, 128.5, 129.9. 130.95, 131.0, 133.8, 133.9, 140.7, 142.9, ^{11}B NMR (28.88 MHz, $CDCl_3$) δ –32.4 ^{31}P NMR (300 MHz, $CDCl_3$) δ 39.6, IR (nujol mull, cm^{-1}) 3162, 2360, 1154.

Synthesis of **3**, Dimethyl Tritylphosphine-Borane

Procedure PCl_3 (15.5 mL, 177.4 mmol) was added slowly to the trityl *H*-phosphinic acid (5.5 g, 17.7 mmol) previously placed in a flask under N_2 atmosphere, at rt. The reaction mixture was stirred at rt for 1 h, then at reflux for 2 h. After cooling down to rt, the excess of PCl_3 was evaporated in vacuo, affording the tritylphosphonous dichloride as a fluffy solid. The tritylphosphonous dichloride (1.7 g, 5 mmol) was dissolved in distilled THF (16 mL) and the solution placed at −78 °C. CH_3MgCl (C = 3.0 M solution in THF, 6.7 mL, 20 mmol) was added dropwise via syringe and the reaction mixture stirred at rt for 12 h. Then, $BH_3.Me_2S$ (C = 2.0 M in solution in THF, 10 mL, 20 mmol) was added at rt and the mixture stirred for 4 h. The reaction was quenched by addition of deionized water at 0 °C. The aqueous layer was extracted with EtOAc (3×) and the combined organic extracts were washed with brine (1×), dried over $MgSO_4$. After filtration and evaporation, the residue was purified by column chromatography on silica gel (100% toluene), affording **3** as a white powder. Isolated yield: 15%. Crystals suitable for X-ray diffraction were obtained by rt evaporation of the powder in toluene/CH_2Cl_2 (5:1). Mp: 147–149 °C, ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.38–7.2 (m, 15H, Ar*H*), 1.30 (s, 3H, C*H*3), 1.27 (s, 3H, C*H*3) ^{13}C NMR (75.45 MHz, $CDCl_3$) δ 14.20 (d, $^1J_{PC} = 36$ Hz), 59.34 (d, $^1J_{PC} = 25$ Hz), 127.5 (d, $^4J_{PCCCC} = 2$ Hz), 128.3, 130.6 (d, $^9J_{PCCC} = 5$ Hz), 142.3 ^{31}P NMR (121.47 MHz, $CDCl_3$) δ 27.7 (dm, $J_{PB} = 33$ Hz), ^{11}B NMR (28.88 MHz, $CDCl_3$) –32.2 (bs), IR (KBr, cm^{-1}) 2327 (B-H), 701 (P-B).

Synthesis of **4**, Phenyl Tritylphosphinic Acid

Procedure To a solution of phenyl *H*-phosphinic acid (20.14 g, 0.142 mol) in distilled toluene (100 mL) was added BSA (70 mL, 0.284 mmol) dropwise at rt, under N_2 atmosphere. The reaction mixture was stirred at reflux for 1 h 45 min. Then, a solution of trityl chloride (39.58 mg, 0.142 mol) in toluene (100 mL) was added to the reaction mixture and the resulting mixture stirred for an additional 13 h at rt. The reaction was quenched by addition of MeOH and after evaporation of the solvent in vacuo, the residue was washed several times with EtOAc and the precipitate vacuum-filtered, giving **4** as a white powder. Isolated yield: 98%. Single crystals obtained from rt evaporation of a toluene/CH_2Cl_2/MeOH (5:1:1) Mp: 282–284 °C ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.36–7.33 (m, 5H, Ar*H*), 7.28–7.26 (m, 8H, Ar*H*), 7.18–7.11 (m, 3H, Ar*H*), 7.09–7.04 (m, 5H, Ar*H*). ^{13}C NMR (75.45 MHz, $CDCl_3$) δ 63.92 (d, $^1J_{PC} = 94$ Hz), 127.0, 127.6 (d, $^1J_{PC} = 13$ Hz), 127.9, 131.4 (d, $^9J_{PCCC} = 6$ Hz), 131.8, 133.5, 133.8 (d, $^2J_{PCC} = 9$ Hz), 141.3 ^{31}P NMR (121.47 MHz, $CDCl_3$) δ 45.5 (s), IR (KBr, cm^{-1}) 1164 (P=O), 956 (P–OH), HRMS (ES) calcd. for $C_{25}H_{21}O_2P$, (M–H) 383.1201, found 383.1212.

Synthesis of **5**, Phenyl Tritylphosphinic Acid Benzyl Ester

Procedure To a solution of trityl *H*-phenylphosphinic acid (577 mg, 1.5 mmol) in $CHCl_3$ (8 mL), at rt and under N_2 atmosphere, was added benzyl bromide (0.36 mL, 3 mmol). Silver oxide (695 mg, 3 mmol) was added to the reaction mixture in 5 portions (every 30 min) and stirred at reflux. After cooling down to rt, the crude mixture was filtered through celite and the filtrate was then concentrated in vacuo. The residue was purified by column chromatography on silica gel (EtOAc/Hexanes, 2:8 then 1:0), affording **5** as a white powder. Isolated yield: 80%. Single crystals for X-ray analysis were obtained from crystals obtained from: toluene/CH_2Cl_2/MeOH (5:2:1) Mp: 144–145 °C, ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.53–7.44 (m, 6H, Ar*H*), 7.41–7.31 (m, 2H, Ar*H*), 7.29–7.14 (m, 15H, Ar*H*), 7.10–7.04 (m, 2H, Ar*H*), 5.10 (dd, $J_{HP} = 6$ Hz, $J = 12$ Hz, 1H), 4.82 (dd, $J_{HP} = 6$ Hz, J = 12 Hz, 1H). ^{13}C NMR (75.45 MHz, $CDCl_3$) δ 64.6 (d, $^1J_{PC} = 102$ Hz), 66.8 (d, $^2J_{POC} = 7$ Hz), 127.3, 127.9, 128.1 (d, $^1J_{PC} = 85$ Hz), 128.13, 128.2, 129.9, 131.5, (d, $^3J_{PCCC} = 6$ Hz), 132.2 (d, $^4J_{PCCCC} = 3$ Hz), 134.3 (d, $^2J_{PCC} = 9$ Hz), 136.8 (d, $^3J_{POCC} = 7$ Hz), 141.8 (d, $^4J_{PCCCC} = 3$ Hz). ^{31}P NMR (121.47 MHz, $CDCl_3$) δ 43.9 (s), IR (KBr, cm^{-1}) 1214 (P=O), 1006 (P–OH), HRMS (EI) calcd. for $C_{32}H_{27}O_2P$, (M) 474.1749, found 474.1739.

Synthesis of **6**, Trityl phosphonic Acid Diethyl Ester

This compound was prepared according to the literature [12] via the Arbuzov reaction of $(EtO)_3P$ with TrCl in refluxing benzene (75%). Crystals suitable for X-ray diffraction were obtained from CH_2Cl_2/toluene.

Synthesis of **7**, Diseleno Tritylphosphinic Acid

Procedure Under N_2 atmosphere, elemental selenium (257 mg; 3.25 mmol) was added to a solution of trityl

H-phosphinic acid (400 mg; 1.3 mmol) in freshly distilled toluene (10 mL), at rt. Et_3 N (0.55 mL; 3.89 mmol) was then added dropwise to the solution *via* syringe and the reaction mixture was stirred at reflux for 7 h. After this time, the mixture was cooled down to rt and stirred for 10 h, then concentrated in vacuo. The residue was partitioned between $CHCl_3$ and 2 M aqueous HCl. The aqueous layer was extracted with $CHCl_3$ (3×) and the combined organic extracts were dried over $MgSO_4$ and concentrated to afford a yellowish-white powder. MeOH was added to the obtained powder, giving a heterogeneous mixture from which the insoluble solid was separated from the solution by vacuum filtration, affording **7** as a bright yellow powder. Isolated yield: 28%, Mp: 180–190 °C (decomposition) ^1H NMR (300 MHz, DMSO-d_6) δ 7.29–7.20 (m, 15H, Ar*H*), 3.80 (bs, 2H, O*H*) ^{13}C NMR (75.45 MHz, DMSO-d_6) δ 21.69, 125.9, 128.8, 129.6, 138.0 ^{31}P NMR (121.47 MHz, DMSO-d_6) δ 39.0 (s); 38.8 (s), IR (KBr, cm^{-1}) 3415.1 (OH), 1166.0 (P=O), 976.5 (P–OH), HRMS (ES) calcd. for $C_{38}H_{32}O_4P_2Se_2$, (M–H) 769.0059, found 769.0068 Crystals obtained from: toluene.

Synthesis of **8**, $[Ni(OP(H)Ph_2)_6]_2BF_4^-$ (unattached BF_4^-)

Procedure Under a nitrogen atmosphere, a CH_2Cl_2 solution of $[Ph_3CP(H)Ph_2][BF_4]$ (0.30 g, 0.58 mmol) in a Schlenk flask was added rapidly via cannula to a stirring CH_2Cl_2 suspension of $NiCl_2$ (0.091 g, 0.70 mmol) in a Schlenk flask at rt. The cloudy orange reaction mixture was allowed to stir overnight. Extraction of the resulting amber solution into THF and storage at rt afforded colorless crystalline blocks of $[NiOP(H)Ph_2][BF_4]_2$, **8**. Isolated yield: 32% (based on 3:1 $[Ph_3CP(H)Ph_2][BF_4]$:product ratio) Mp: 53–57 °C, ^1H NMR (300 MHz, C_6D_6) δ 8.3 (s, P-*H*), 7.24–7.18 (m, Ar*H*), 6.86–6.67 (m, Ar*H*) ^{13}C NMR (300 MHz, C_6D_6) δ 125.1, 127.9, 127.3, 127.5, 128.5, 129.4, 129.6, 130.7, 143.0 ^{31}P NMR (300 MHz, C_6D_6) δ 18.7 ^{19}F NMR (300 MHz, C_6D_6) δ –71.8, –75.4, IR (nujol mull, cm^{-1}) 3,062, 1,599, 751, 699, 605.

Synthesis of **9**, $[Ni(OP(H)Ph_2)_6]_2BF_4^-$ (attached BF_4)

The same procedure was followed as for **8**, except using 0.17 g (0.33 mmol) $[Ph_3CP(H)Ph_2][BF_4]$ and 0.043 g (0.33 mmol) $NiCl_2$ and also taking rigorous precautions not to introduce air or moisture into the reaction to attempt to obtain the oxygen-free product. Nevertheless, large colorless diamond shaped crystals of the isomeric $[NiOP(H)Ph_2][BF_4]_2$, **9**, were obtained from the THF solution.

Isolated yield: 28% Mp: 51–56 °C ^1H NMR (300 MHz, C_6D_6) δ 8.3 (s, P-*H*), 7.63–7.57 (m, Ar*H*), 7.24–7.17 (m, Ar*H*), 6.87–6.66 (m, Ar*H*) ^{13}C NMR (300 MHz, C_6D_6) δ 125.1, 127.0, 127.2, 128.5, 130.9, 143.0, ^{19}F NMR (300 MHz, C_6D_6) δ –145.5, IR (nujol mull, cm^{-1}) 2725, 1154, 699.

Results and Discussion

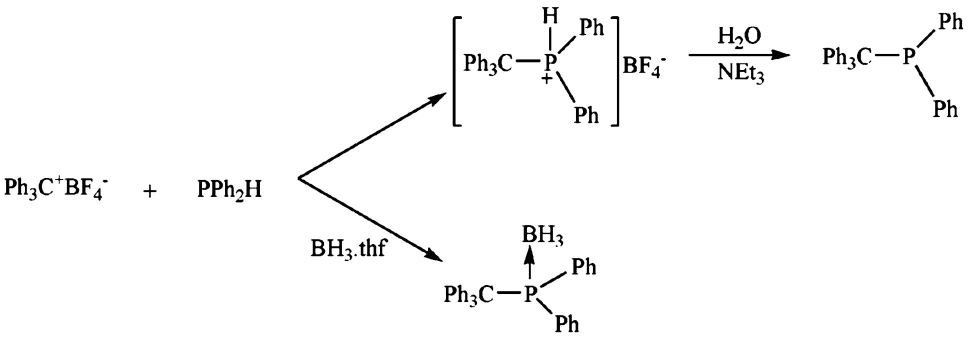
Synthesis and Discussion of the P(III) Compounds **1** and **2**

The reaction of $Ph_3C^+BF_4^-$ with one equivalent of Ph_2PH proceeds cleanly in DCM to afford $Ph_3CP(H)Ph_2$ BF_4^- which is a well known reaction [13] in which the trityl group reacts with the phosphorus lone pair, rather than the hydride of the phosphine so that the quaternized phosphonium ion is formed, Scheme 1.

The neutral molecule, Ph_3CPPh_2 can be isolated in almost quantitative yield (99%) by treatment of $[Ph_3CP(H)Ph_2]BF_4^-$ with triethylamine and water. Crystals of Ph_3CPPh_2 were isolated through concentration of the dichloromethane solution and storage overnight at rt. The solid-state structure of **1**, is depicted in Fig. 2.

Single crystal X-ray analysis revealed that **1** crystallizes in the triclinic space group $P\bar{1}$. Treatment of **1**, with one equivalent of BH_3.thf affords the borane adduct $Ph_3CPPh_2(BH_3)$ **2**, Fig. 3.

As expected the geometry around the P center is trigonal pyramidal in **1** and distorted tetrahedral in **2**. The P–C bond



Scheme 1 Synthesis of Ph_3CPPh_2 and $Ph_3CPPh_2(BH_3)$

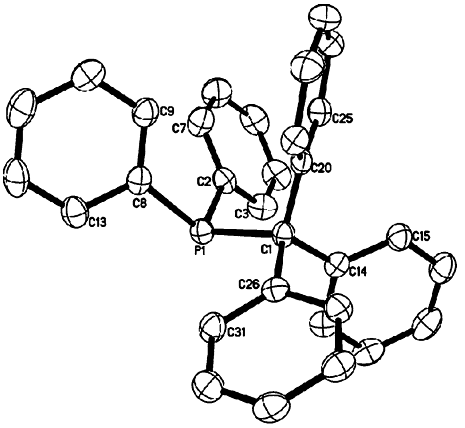


Fig. 2 X-ray crystal structure of Ph_3CPPh_2, **1**. Thermal ellipsoids drawn at 30% probability level. Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (°): P1–C2 1.8368(19), C1–P1–C2 104.23(8), C2–P1–C8 104.30(9)

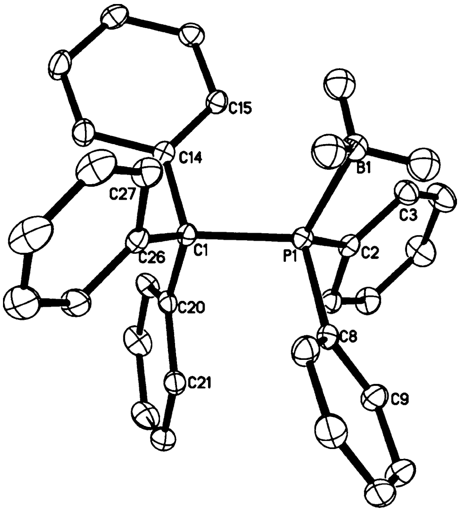


Fig. 3 X-ray crystal structure of $Ph_3CPPh_2(BH_3)$, **2**. Thermal ellipsoids drawn at 30% probability level. Selected bond lengths (Å) and angles (°): P1–C2 1.8302(19), P1–B1 1.939(2), C1–P1–B1 117.49(10)

lengths of 1.9433(19) Å in **1** and 1.9265(19) Å in **2** are at the longer end of documented P–C bonds, but are an indication of the steric congestion around the P center. For example, the sterically congested $[P(^tBu)_4]BF_4$ has a P–C bond distance of 1.924(4) Å [14] and the related cation, tris(*p*-methoxyphenyl)(triphenylmethyl)phosphonium tetrakis(3,5-bis(trifluoromethyl)phenyl)borate a P–C bond length of 1.931(1) Å [15]. The central carbon, C1, displays typical tetrahedral geometry with the three phenyl groups adopting a propeller arrangement. The remaining metric parameters are unexceptional. To compare the effects of the steric congestion around the phosphorus atom, the phenyl groups were substituted for methyl groups. $[Ph_3CPMe_3]^+$ with counter anions of $[B(C_6F_5)_4]^-$ and $[BF_4]^-$ has been reported previously in the literature [16], however, the neutral molecule, Ph_3CPMe_2 has not been reported. Crystals of Ph_3CPMe_2 could not be isolated, however, the borane adduct, $Ph_3CPMe_2(BH_3)$, complex, **3**, Fig. 4 was obtained from a toluene/dichloromethane solution (5:1) and characterized.

Complex **3** was prepared from the reaction of MeMgBr with the well-known $TrPCl_2$ [6], followed by addition of BH_3–Me_2S. Reducing the steric bulk around the phosphorus atom only leads to a slight shortening of the P–C bond to 1.913(2) Å while the P–B bond of 1.803(3) Å is considerably shorter than that observed in **2** at 1.939(2) Å. The P–C bond length in **3**, is longer than that of 1.887(4) Å observed in $[Ph_3CPMe_3]^+$ [16], attributed to the removal of electron density from the P-center by the coordinated borane. Infrared spectroscopy of **2** and **3** exhibit stretches of 2,370 and 2,327 cm^{-1} respectively, corresponding to B–H stretches and absorption at 654 cm^{-1} for **3** associated with the P–B stretch [17]. ^{31}P chemical shifts of **1** and **3** are similar, recorded at 27.9 for **1** and 27.7 for **3**, while complex **2** has a slightly more downfield shift at 39.6 ppm. The ^{31}P NMR of **1** confirms the solid-state structural assignment of the neutral phosphine as can be compared with the doublet observed at 13.6 ppm for $[Ph_3CP(H)Ph_2]BF_4^-$ [13, 18].

P(V) Trityl Complexes

In order to compare structural parameters between P(III) and P(V) and to extend our examination of trityl

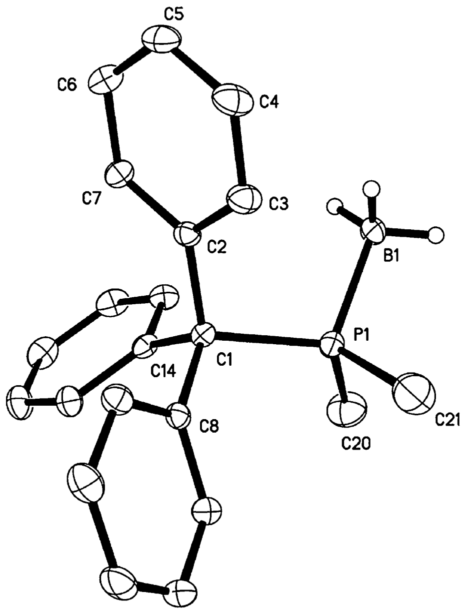
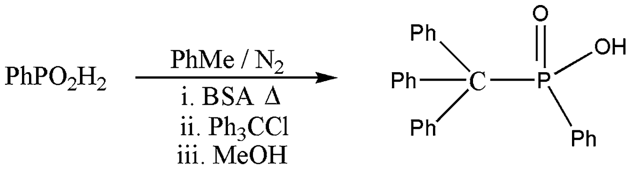


Fig. 4 Crystal structure of $Ph_3CPMe_2(BH_3)$ **3**. Thermal ellipsoids drawn at 30% probability, hydrogen atoms are omitted for clarity except on the boron atom. Selected bond lengths (Å) and angles (°): P1–C21 1.854(3), P1–C20 1.858(3), P1–B1 1.803(3), C1–P1–B1 108.14(11)



BSA = N-O bis(trimethylsilyl)acetamide

Scheme 2 Synthesis of phosphinic acid **4**

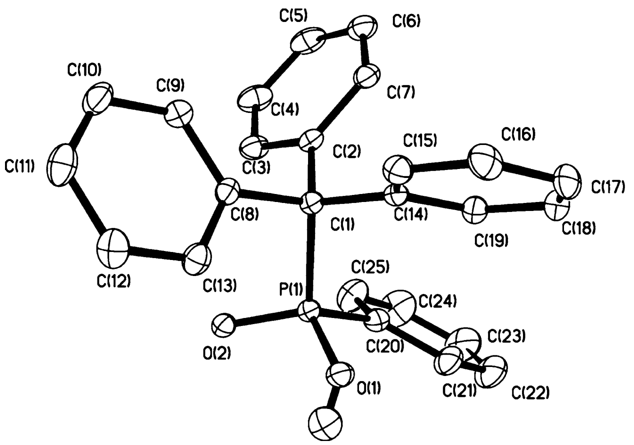


Fig. 5 Solid-state analysis of phenyl tritylphosphinic acid **4**. Thermal ellipsoids drawn at 30% probability, hydrogen atoms are omitted for clarity, excluding O(1), the protonated oxygen atom

phosphorus compounds, compound **4**, phenyl tritylphosphinic acid was prepared from phenyl *H*-phosphinic acid, BSA and Ph_3CCl, Scheme 2, Fig. 5.

Phenyl tritylphosphinic acid, **4**, crystallizes as triclinic colorless crystals, space group $P\bar{1}$. The change in the oxidation state from (III) to (V) causes a shortening of the P-C bond length to 1.8748(19) Å. The pentavalent phosphorus species, **4**–**7** exhibit common trigonal bipyramidal geometry at the P atom with P–O bonds of 1.5398(14) Å (P1–O1) and (P1–O2) 1.5106(14) Å that are as expected. The hydrogen atom on the protonated oxygen atom was located using the electron density difference map and confirmed by spectroscopic techniques.

Treatment of phenyl tritylphosphinic acid with benzyl bromide and silver oxide, following purification by column chromatography afforded the corresponding ester; phenyl tritylphosphinic benzyl ester, in 80% yield, Fig. 6.

The benzyl group has found considerable use in organic chemistry as a protective group [19] as can be easily removed under neutral conditions via hydrogenolysis. A survey of the CCDC [20] revealed that, to the best of our knowledge **5** is the first structurally characterized example of a benzyl ester of a phosphinic acid. Compound **5** crystallizes in the monoclinic space group, $P2_1/c$ and within the asymmetric unit are found two crystallographically independent molecules—that have slightly different bond lengths and angles, for example: P–C 1.8753(19)/1.8769(18) Å, P1–O1 1.4752(14), P2–O3 1.4744(14) Å.

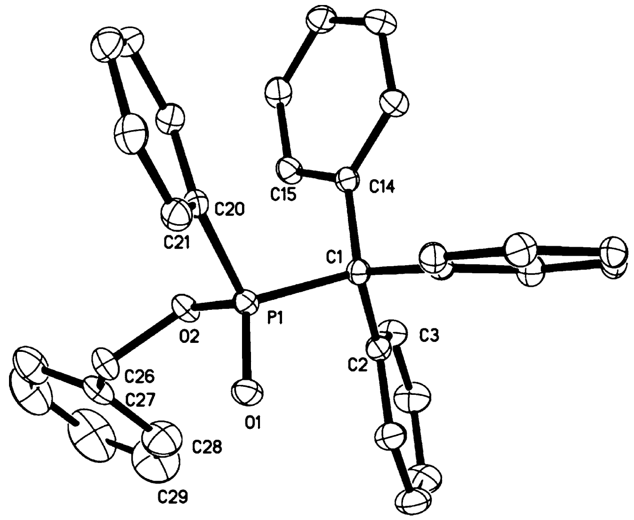


Fig. 6 X-ray crystal structure of phenyl tritylphosphinic benzyl ester, **5**

For comparison, compound **6**, the phosphonate diester, $Ph_3CP(O)(OEt)_2$, of $TrPO_3H_2$ was synthesized via the Arbuzov reaction of $(EtO)_3P$ with TrCl in refluxing benzene. Colorless crystals suitable for X-ray diffraction obtained from a mixture of CH_2Cl_2/PhMe, Fig. 7. The structural parameters of **6** are similar to those exhibited in **5**. The P1–O1 bond length of 1.4671(14) Å is indicative of a P=O bond while the phosphonate ester bonds differ slightly, P1–O2 1.5770(14) and P1–O3 1.5813(14) Å.

Following our previous isolation of the phosphonothioic acid, $Ph_3CP(S)(OH)_2$ [9], it seemed a logical extension to prepare the selenium and tellurium analogues, although selenophosphonic acids have been less well researched [21, 22]. The reaction of trityl *H*-phosphinic acid with elemental selenium afforded yellow crystals of **7** in 28% yield, Fig. 8.

Complex **7** crystallizes in the monoclinic space group, $P2_1/c$, and interestingly rather than forming the terminally bonded P=Se complex, a dimeric structure with a Se–Se single bond was formed. The Se–Se distance of 2.3326(6) Å can be compared with that of 2.34 Å which is the sum of the covalent radii [23], and is comparable with the structurally similar bis(diisopropoxy-seleno phosphinoyl) diselenide, that has a Se–Se bond length of 2.351(6) Å [21, 24]. As expected the diselenide has a *trans* PSe–SeP conformation. The ^{31}P NMR exhibits two chemical shift at 39 and 38 ppm, although it is possible that in solution there is equilibrium between the monomeric and dimeric form exists, mass spectrometry analysis on **7** shows a peak associated with the dimeric parent ion, (769). Dimerization of selenols RSeH is not unusual in air [25, 26].

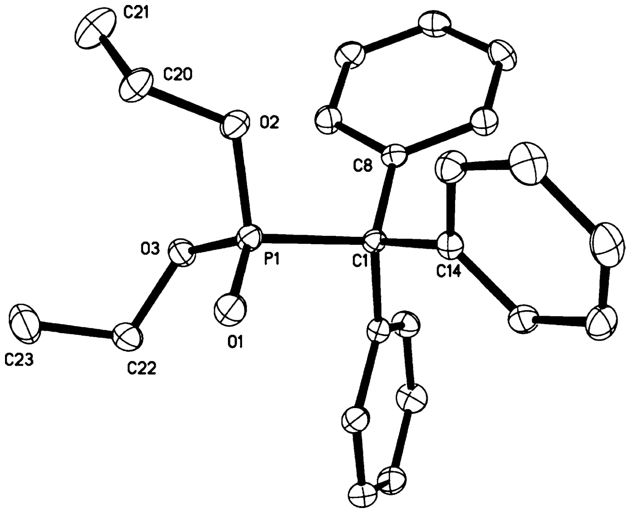


Fig. 7 X-ray crystal structure of $TrPO(OEt)_2$. **6**

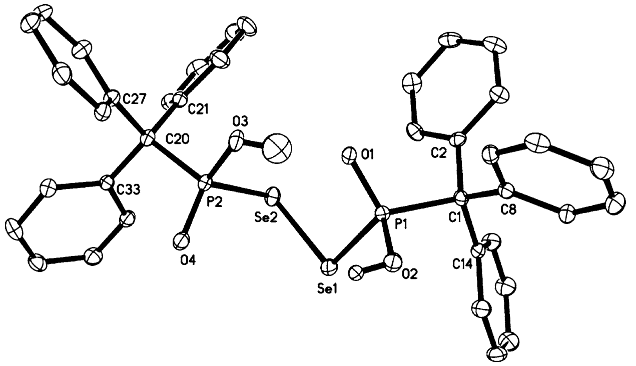


Fig. 8 Crystal structure of **7**. Thermal ellipsoids at 30% probability and hydrogen atoms except on oxygen atoms, O2 and O3 are removed for clarity. Selected bond lengths (Å) and angles (°): Se1-P1 2.2686(11), Se1–Se2 2.3326(6), Se2–P2 2.2717(11), P1–O1 1.495(3), P1–O2 1.559(3), P2–O3 1.547(3), P2–O4 1.492(3), P2–Se2–Se1 97.64(3), P1–Se1–Se2 101.65(3)

Comparison of the structural parameters of **5** and **7**, Table 1, show minimal differences with comparable P–C and P–O bond lengths. Phosphinic acids are well known to form dimers or species that are connected by hydrogen bonding [27–29]. Surprisingly, in **4**–**7**, despite the protonated oxygen atoms adjacent to P=O bonds, no hydrogen bonding is observed. Nevertheless, examination of the packing diagram of **7** shows that the molecules arrange themselves so that the protonated oxygen atom aligns with a P=O group from an adjacent molecule, however, the distance is too far for a hydrogen bonding interaction.

Discussion of the Nickel Complexes, **8** and **9**

Trialkyl phosphines with bulky substituents are highly useful ligands to support palladium-catalysis in various cross coupling reactions [30]. The advantages of a variable ligand backbone are demonstrated by the enormous success of the Buchwald—biphenyl based phosphines [31, 32]. Moreover, nickel(II) complexes are active catalysts for a wide variety of reactions, in particular the SHOP (Shell higher olefin process) process which utilizes $[NiL_4]$ where L = phosphine or phosphite[33–36]. Nickel phosphine complexes are generally synthesized from labile Ni[0] complexes by reduction of an appropriate Ni(II) complex, $NiCl_2L_2$ (L = phosphine) can be prepared by displacement of water from $NiCl_2.6H_2O$ by the corresponding phosphine [37]. We assumed that this approach could be harnessed for coordination of the trityl phosphine to a nickel center. In this vein, the reactions of $NiCl_2$ with 'in-situ' generated trityl phosphine (Ph_3CPPh_2) were performed. Complexes **8** and **9** were isolated in moderate and low yields, Fig. 9.

Following the solid-state analysis, it is apparent that rather than reacting with the neutral phosphine, the Ni–Cl bonds have been cleaved by the Ph_3C^+ group, and the hydrolyzed Ph_2PO fragment has coordinated to the metal center. The outcome of these reactions is not too unexpected since the P–C bond of Ph_3C–P is relatively unstable due to the significant stability of the corresponding trityl cation (Ph_3C^+) [38]. In complexes **8** and **9**, the nickel atoms adopt octahedral geometry, as expected with Ni(II) complexes [39, 40] with all of the six coordination sites occupied by oxygen atoms from the $OPPh_2$ fragment.

In complex **8**, the asymmetric unit consists of three $OPPh_2$ fragments coordinated to the Ni(II) center, which is at half occupancy, and one BF_4^- counterion, with each atom at full occupancy, to balance the one-half of the +2 charge. The complete structure of the isomeric complex **9**, in contrast, contains two BF_4^- anions to balance the Ni(II) center, the boron atom of the former being at one-third occupancy and

Table 1 A comparison of pertinent bond lengths and angles in compounds **1**–**7**

Bond/Angle	1	2	3	4	5	6	7
P–C(trityl)	1.9433(19)	1.9265(19)	1.913(2)	1.8748(19)	1.8753(19)	1.8616(18)	1.876(4)
C1–P1–R1	105.57(8)	107.91(8)	113.79(12)	113.93(9)	111.84(8)	113.49(8)	111.89(17)
P1–O1	n/a	n/a	n/a	1.5398(14)	1.4752(14)	1.4671(14)	1.495(3)
P1–O2	n/a	n/a	n/a	1.5106(14)	1.5913(13)	1.5770(14)	1.559(3)
^{31}P NMR (δ ppm)	27.9	39.6	27.7 (dm $J_{P–B}$ 33 Hz)	45.5	43.9	27.0	39.0 (20%), 38 (80%)

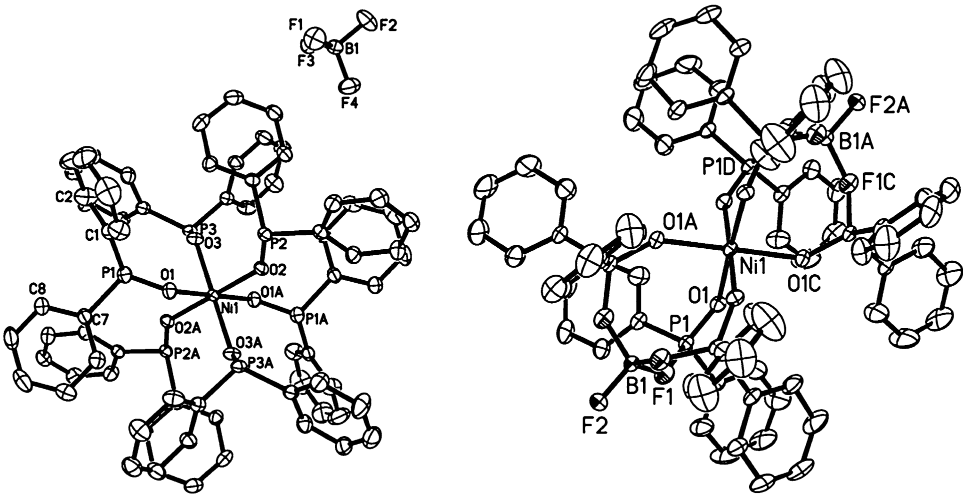


Fig. 9 X-ray crystal structures of the nickel complexes **8** (left) and **9** (right). Selected bond lengths (Å) and angles (°): Complex **8**: Ni1–O1 2.052(5), P1–O1 1.514(5), O1–Ni1–O1 180.0(4), Complex **9**: Ni1–O1 2.058(2), P1–O1 1.480(2), O1–Ni1–O1a 91.29(8)

the latter being at one-sixth occupancy in the asymmetric unit. More intriguingly, three out of four of the fluorine atoms of each of the BF_4^- counterions in **9** are bridging, such that each of the six P atoms is ligated to a doubly bonded oxygen atom, two phenyl groups and with an interaction of 1.548(2) Å to a fluorine atom from the BF_4^- ion. The P–F, and P–O distances compare well with one of only two similarly reported structures [41–44], namely, (η6-*p*-cymene)[diphenylphosphinofluorido)trifluoroborato-κ2P,F](diphenylphosphinoylfluorido)trifluoroborato-κO] ruthenium(II), that has a P–F distance of 1.554(4) Å and a P=O distance of 1.478(4) Å.

Because in the overall structures of both complexes the Ni(II) charge is counteracted by the presence of two BF_4^- ions, each of the $OPPh_2$ fragments must necessarily be neutral. Furthermore, the P–O distances for **8** and **9** of 1.514(5) and 1.480(2) Å respectively are within the range for documented PO bonds [9, 45, 46]. Therefore, each

Table 2 Crystal data and data collection summary for complexes **1**–**9**

Compound	$TrPPh_2$ **1**	$TrP(BH_3)Ph_2$ **2**	$TrP(BH_3)Me_2$ **3**
Chemical formula	$C_{31}H_{25}P$	$C_{31}H_{28}PB$	$C_{21}H_{24}PB$
Formula weight	428.48	442.31	318.18
Crystal system	Triclinic	Monoclinic	Monoclinic
Space group	$P\overline{1}$	$P2_1/c$	C2/c
T(K)	213(2)	213(2)	91(2)
a (Å)	7.5624(6)	10.0972(12)	15.628(3)
b (Å)	9.5470(8)	9.6955(12)	12.770(3)
c (Å)	16.9722(14)	25.197(3)	18.406(4)
α (°)	83.4720(10)	90	90
β (°)	80.541(2)	90.258(2)	103.968(3)
γ (°)	68.1580(10)	90	90
V ($Å^3$)	1120.08(16)	2466.7(5)	3564.7(13)
Z	2	4	8
Reflections collected	5755	12097	14813
Independent reflections	3965	4471	3217
Data/restraints/parameter ratio	3965/0/289	4471/0/310	3217/0/208
R int	0.0171	0.0337	0.0617
D calc (Mg/m^3)	1.270	1.191	1.186
F(000)	452	936	1360
R indices (all data)	R1 0.0541, wR2 = 0.1075	R1 = 0.0632, wR2 = 0.1014	R1 = 0.0630, wR2 = 0.1448
Final R indices [$I > 2\sigma(I)$]	R1 = 0.0389, wR2 = 0.0940	R1 = 0.0380, wR2 = 0.0846	R1 = 0.0462, wR2 = 0.1326
Largest difference peak and hole (e $Å^{-3}$)	0.469 and −0.352	0.336 and −0.354	0.549 and −0.337

Table 2 continued

Compound	TrP(O)(OH)Ph **4**	TrCP(O)(Ph)OBn **5**	TrP(O)(OEt)$_2$ **6**
Chemical formula	$C_{25}H_{21}PO_2$	$C_{32}H_{27}O_2P$	$C_{23}H_{25}O_3P$
Formula weight	384.39	474.51	380.40
Crystal system	Triclinic	Monoclinic	Triclinic
Space group	$P\bar{1}$	$P2_1/c$	$P\bar{1}$
T(K)	91(2)	213(2)	213(2)
a (Å)	8.9847(18)	7.9196(5)	7.9521(17)
b (Å)	9.7443(19)	31.701(2)	9.2205(19)
c (Å)	12.786(3)	19.8062(13)	14.471(3)
α (°)	72.045(3)	90	85.906(4)
β (°)	72.031(3)	99.7750(10)	83.031(4)
γ (°)	78.769(3)	90	68.283(4)
V (Å^3)	1006.8(3)	4900.3(6)	978.0(4)
Z	2	8	2
Reflections collected	8639	47552	5687
Independent reflections	3626	9881	4305
Data/restraints/parameters	3627/0/253	9881/0/631	4305/0/246
R int	0.1037	0.0418	0.0174
D calc (Mg/m^3)	1.268	1.286	1.292
F(000)	404	2000	404
R indices (all data)	R1 = 0.0662, wR2 = 0.1370	R1 = 0.0651, wR2 = 0.1125	R1 = 0.0632, wR2 = 0.1203
Final R indices [$I > 2\sigma(I)$]	R1 = 0.0540, wR2 = 0.1250	R1 = 0.0413, wR2 = 0.0942	R1 = 0.0457, wR2 = 0.1086
Largest difference peak and hole (e Å^{-3})	0.446 and −0.444	0.349 and −0.374	0.446 and −0.343
Compound	[TrP(O)(OH)Se]$_2$ **7**	[Ni(OPPh$_2$)$_6$]2BF$_4$, **8**	[Ni(OPPh$_2$)$_6$]BF$_4$, **9**
Chemical formula	$C_{38}H_{32}O_4P_2Se$	$C_{72}H_{66}B_2F_8NiO_6P_6$[a]	$C_{72}H_{66}B_2F_8NiO_6P_6$[a]
Formula weight	772.50	1445.40	1445.40
Crystal system	Monoclinic	Orthorhombic	Trigonal
Space group	$P2_1/c$	Pbca	R-3c
T(K)	213(2)	213(2)	213(2)
a (Å)	9.0603(4)	18.8247(12)	13.1545(12)
b (Å)	22.3652(11)	18.5518(12)	13.1545(12)
c (Å)	16.9134(7)	21.0976(14)	68.461(9)
α (°)	90	90	90
β (°)	107.035(2)	90	90
γ (°)	90	90	120
V (Å^3)	3276.9(3)	7368.0(8)	10259.4(19)
Z	4	4	6
Reflections collected	19005	38423	16165
Independent reflections	7769	6649	2081
Data/restraints/parameters	7769/2/423	6649/2/438	2081/0/144
R int	0.0422	0.0980	1.036
D calc (Mg/m^3)	1.566	1.301	1.398
F(000)	1560	2976	4439
R indices (all data)	R1 = 0.0864 wR2 = 0.1416	R1 = 0.1491, wR2 = 0.2780	R1 = 0.0706, wR2 = 0.1284
Final R indices [$I > 2\sigma(I)$]	R1 = 0.0474, wR2 = 0.1180	R1 = 0.0764, wR2 = 0.2006	R1 = 0.0408, wR2 = 0.1055
Largest difference peak and hole (e Å^{-3})	1.757 and −0.631	2.254 and –0.861	0.322 and −0.385

[a] Formula includes hydrogen atoms on the phosphorus centers

phosphorus atom is deemed to have an attached hydrogen atom. Indeed in complex **8**, peaks corresponding to hydrogen atoms could be located on all three P atoms in the asymmetric unit, but the refinement for only two of these would converge. Likewise, in complex **9**, the peak corresponding to the hydrogen on the one P in the asymmetric unit could be located but could not be successfully refined. Complex **8** contains solvent accessible voids which are calculated by PLATON [47] to be 811.8 Å^3, which per unit cell is 7368 Å^3, this is likely to be disordered THF molecules, the solvent that the reaction was performed in and from which crystals were obtained Table 2.

Conclusion

A series of trityl supported P(III) and P(V) complexes have been synthesized and fully characterized through single crystal X-ray analysis, NMR, IR and mass spectrometry. Comparison of the structural features of **1**–**7** reveal that P–C bond length decreases as the phosphorus oxidation state increases from +3 to +5 arising from less electronic repulsion. As a result, ^{31}P chemical shifts become shifted downfield.

Given the importance of both the trityl group and phosphorus compounds in a multitude of synthetic and biological applications the structural and spectroscopic data will be a useful database for reference and comparison.

Supplementary Information

CCDC 686581—686589 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via (please use the link below) by e mailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK, Fax: +44-1223-336033. www.ccdc.cam.ac.uk/data_request/cif.

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