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Aroylspirophosphoranes bearing two naphth-1,8-diyl-8-oxy groups: synthesis, crystal structure, and $n_p(O_{apical}) \rightarrow \pi^*(C{=}O)$ charge transfer interaction

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ABSTRACT

The reactions of aroyl chlorides with the lithium phosphoranide generated from bis(naphth-1,8-diyl-8-oxy)phosphorane **1** afforded aroylspirophosphoranes **3a**–**f**. The *p*-anisoyl- and *p*-*tert*-butylbenzoylphosphoranes **3a** and **3b** bearing an electron-donating aryl group were stable to moisture on silica gel. The crystal structures of *p*-anisoyl-, *p*-*tert*-butylbenzoyl-, benzoyl-, and *p*-fluorobenzoylphosphorane (**3a**, **3b**, **3d**, and **3e**) elucidated by X-ray structural analysis suggested effective intramolecular $n_p(O_{apical}) \rightarrow \pi^*(C{=}O)$ charge transfer stabilization to be operative.

1. Introduction

Pentacoordinate phosphorus compounds, 10-P-5[1] phosphoranes, have been under active investigation, since the phosphorane is a representative hypervalent compound[2] and has been considered to be a key model compound for elucidating the reaction mechanism of biological processes such as phosphoryl transfer and hydrolysis of phosphates.[3] Stable phosphoranes usually assume trigonal bipyramidal (TBP) structures in which there are two distinctive sites, the apical and the equatorial sites. A fundamental feature of the phosphorane is its stereochemical non-rigidity, that is, the facile inter-exchange of substituents at the apical and equatorial sites in a TBP structure without bond cleavage, which has been explained by the Berry pseudorotation (BPR) process.[4,5] The equatorial bonds can be described as sp^2 hybrid orbitals of the P atom. The apical bond can be explained with the concept of the three-center four-electron (3c-4e) bond, in which the electrons are delocalized into the apical substituents to relieve the electron density of the central atom.[2,6] Thus, electronegative substituents are preferred in the apical sites, a phenomenon leading to the concept of apicophilicity.[2,7] The apical bond is weaker than the equatorial bond if the substituents at the apical and equatorial sites are identical.

Experimental[8] and theoretical[9] apicophilicity scales do not necessarily follow the electronegativity scale and the apicophilicity of a substituent must be attributed to the combined influence of multiple factors. For instance, it has been determined experimentally for modified Martin spirophosphoranes that the acetyl group is less apicophilic (more equatophilic) than the methoxy group although they have similar electronegativity.[8j] This result has been interpreted as a stereoelectronic effect involving the acyl group in the equatorial position and the two oxygen atoms in the apical positions, with intramolecular $n_p(O_{apical}) \rightarrow \pi^*(C{=}O)$ charge transfer contributing to stabilization (Fig. 1).[10] For effective $n \rightarrow \pi^*$ interaction in acylphosphoranes, the acyl group orients to have its π acceptor orbital parallel to the apical bond, or in other words, the acyl carbonyl group tends to be coplanar with the equatorial plane.[9a,b,d,10]

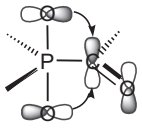

Fig. 1. Intramolecular $n_p(O_{apical}) \rightarrow \pi^*(C{=}O)$ charge transfer stabilization in the acylphosphoranes bearing apical oxygen atoms.

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Acylphosphoranes can also be considered as model compounds for pentacoordinate phosphorus intermediates in the hydrolysis reaction of triesters of phosphonoformic acid (PFA), which have been synthesized as prodrugs of PFA showing antiviral activity against most retro-viruses.[11] The rate acceleration observed in the base-catalyzed hydrolysis of the PFA triesters via P–O bond cleavage[11d] has been explained by the involvement of $n\rightarrow\pi^*$ stabilization in the pentacoordinate intermediates.[10] Although several acylphosphoranes have previously been synthesized,[8j,12] the $n\rightarrow\pi^*$ interaction has not been clearly demonstrated from their structural aspects. It is worth noting that the average torsion angle of the carbonyl group from the equatorial plane in a Martin acetylspirophosphorane was shown to be 17.8° by X-ray structural analysis (Fig. 2),[8j] where the deviation from the ideal angle of 0° for efficient $n\rightarrow\pi^*$ interaction was attributed to the bulkiness of the trifluoromethyl groups of the Martin ligands.

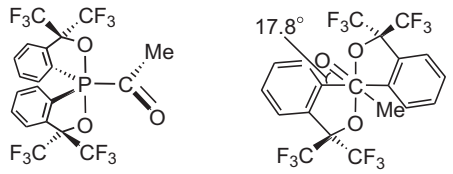


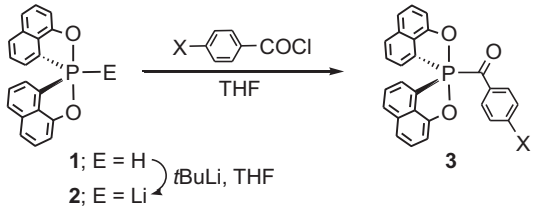
Fig. 2. Torsion angle of the carbonyl group from the equatorial plane in a Martin acetylspirophosphorane.

By utilizing bis(naphth-1,8-diyl-8-oxy)phosphorane **1**, we have succeeded in the syntheses of sterically congested phosphoranido complexes.[13] It has also been found in the Horner–Wadsworth–Emmons-type (HWE) reaction that the phosphorane reagent derived from **1** was more reactive than the corresponding reagent of the Martin phosphorane system.[14] The naphth-1,8-diyl-8-oxy group derived from 1-naphthol is a flat bidentate, which is much less sterically demanding than the Martin ligand. Thus, one could anticipate that the carbonyl group in acylspirophosphoranes bearing two naphth-1,8-diyl-8-oxy groups would be essentially coplanar with the equatorial plane. Herein, we report on the syntheses of aroylspirophosphoranes **3**, and on the X-ray crystal structural analyses of **3a**, **3b**, **3d**·0.5CH_3CN, and **3e** bearing a *p*-anisoyl, a *p*-*tert*-butylbenzoyl, a benzoyl, and a *p*-flurorobenzoyl group, respectively.

2. Results and discussion

2.1. Synthesis

The reaction of the lithium phosphoranide **2** generated from bis(8-oxy-1-naphthyl)hydrophosphorane **1** with aroyl chlorides, benzoyl chloride or *p*-substituted benzoyl chlorides, gave air-stable aroylspirophosphoranes **3** (Scheme 1, Table 1). In the case of **3a** and **3b**, in which the benzoyl substituents X were electron-donating ($\sigma^{15}<0$), purification of the crude mixtures could be carried out by silica gel chromatography to give the products in good yields. On



a) X = OMe, **b**) X = *t*Bu, **c**) X = SMe, **d**) X = H, **e**) X = F, **f**) X = CN

Scheme 1.

Table 1
Syntheses of aroylspirophosphoranes **3a**–**f**

	X	σ[a]	Yield[b]/%	$^1J_{CP}$[c]/Hz	ν_{CO}[d]/cm^{-1}
3a	OMe	−0.27	82	173.0	1649
3b	*t*-Bu	−0.20	67	173.2	1655
3c	SMe	0.00	53	174.4	1649
3d	H	0.00	44	174.6	1660
3e	F	0.06	24	176.4	1655
3f	CN	0.66	29	180.6	1668

[a] Hammett substituent constant from Ref. 15.
[b] Isolated yield.
[c] Coupling constant between phosphorus and the directly bonded carbonyl carbon observed by ^{13}C NMR ($CDCl_3$, 151 MHz).
[d] Frequency of the carbonyl absorption observed by IR (KBr).

the other hand phosphoranes **3c**–**f**, in which benzoyl substituents X were not electron-donating ($\sigma\geq0$), slowly hydrolyzed on silica gel to give hydrophosphorane **1**. Thus, phosphoranes **3c**–**f** were obtained in lower yields by purification with PTLC (CH_2Cl_2/hexane 1:1) followed by recrystallization.

Although aroylphosphoranes **3** were stable in anhydrous organic solvents, dichloromethane, chloroform, benzene, tetrahydrofuran, acetonitrile, MeOH, EtOH, or *i*PrOH, at room temperature, they slowly hydrolyzed upon long exposure to moisture to give hydrophosphorane **1**. ^1H and ^{13}C NMR ($CDCl_3$) spectroscopic analyses suggested that the two naphthyl groups were spectroscopically equivalent due to fast rotation around the carbonyl carbon–phosphorus bond on the NMR time scale. Although the ^{31}P NMR chemical shift (δ −38.6 to −39.3) of the phosphoranes and the ^{13}C NMR chemical shift of the carbonyl carbons (δ 191.3–193.0) do not significantly vary with the benzoyl substituents X, the $^1J_{CP}$ value for the carbonyl carbon increases as the σ value of X increases. The frequency (1660 cm^{-1}) for carbonyl absorption in the IR spectrum of benzoylphosphorane **3d** is nearly identical to that (1659 cm^{-1}) of bis(pinacolate) benzoylphosphorane.[12c] The frequencies (1649–1668 cm^{-1}) of ν_{CO} in the series of aroylphosphoranes **3** are higher than those of aroyldiphenylphosphanes (1643–1652 cm^{-1})[16] and dialkyl aroylphosphonates (1639–1655 cm^{-1}).[16c,17] These results imply that the $n_p(O_{apical})\rightarrow\pi^*(C{=}O)$ interaction in the aroylphosphorane is weaker than the $n_p(P)\rightarrow\pi^*(C{=}O)$ and $n_p(O_{P=O})\rightarrow\pi^*(C{=}O)$ interactions in the aroylphosphane and aroylphosphonate, respectively.

2.2. X-ray crystal structural analysis

The crystal structures of aroylspirophosphoranes **3a**, **3b**, **3d**·0.5CH_3CN, and **3e** could be elucidated by X-ray crystal structural analyses. ORTEP drawings [overview and side view along the P–C(carbonyl) axis] are shown in Fig. 3. Selected bond lengths, bond angles, and dihedral angles are listed in Table 2, along with the corresponding data of methylphosphorane **4**[13a,b,18] (Scheme 2, Fig. 4) also bearing two naphth-1,8-diyl-8-oxy groups. For all of the compounds, the geometry around the hypervalent phosphorus atom is trigonal bipyramidal (TBP) structure with the two oxygen atoms in the apical positions and the sum of the equatorial angles is 360°, which is the ideal value for TBP structures.

The presence of intramolecular $n_p(O_{apical})\rightarrow\pi^*(C{=}O)$ charge transfer interactions in the solid states of **3a**, **3b**, **3d**, and **3e** is highly suggestive by the conformation of the aroyl groups and the unusual distortion of the solid state structures of the spirophosphorane from ideal TBP structure. As for the former, the carbonyl groups are nearly coplanar with the equatorial plane in spite of steric repulsion between the aryl groups at the carbonyl carbon and the naphth-1,8-diyl-8-oxy groups. The repulsion is evident from the equatorial C1–P1–C21 angles (123.30°–130.55°), which are much larger than the ideal equatorial angle of 120° and the other two equatorial angles (112.65°–122.49°) of **3a**, **3b**, **3d**, and **3e**. The torsion angles

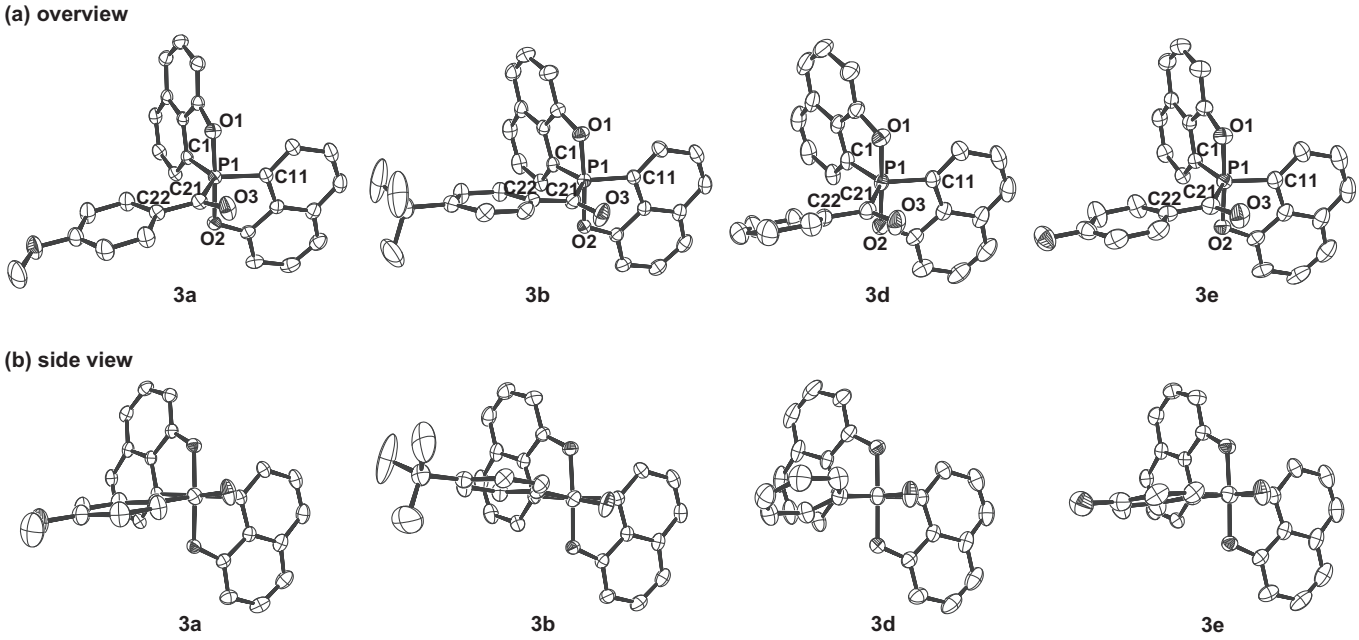
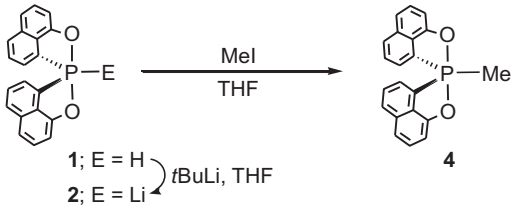


Fig. 3. ORTEP diagrams of **3a**, **3b**, **3d**·0.5CH_3CN, and **3e** showing the thermal ellipsoids at the 30% probability level. All hydrogens and CH_3CN molecule are omitted for clarity.

Table 2
Selected structural parameters for aroylspirophosphoranes **3b**, **3c**, **3e**, **3f**, and methylphosphorane **4**

	3a	3b	3d	3e	4
Bond lengths/Å					
P1–O1	1.7597(12)	1.7763(13)	1.7751(18)	1.7606(15)	1.791(2)
P1–O2	1.7863(12)	1.7619(14)	1.7692(18)	1.7781(14)	1.803(2)
P1–C1	1.8100(19)	1.8066(16)	1.801(3)	1.8044(14)	1.814(3)
P1–C11	1.8009(17)	1.7977(18)	1.792(3)	1.794(3)	1.811(3)
P1–C21	1.8760(18)	1.873(2)	1.863(4)	1.8687(18)	1.804(3)
Bond angles/°					
O1–P1–O2	175.13(6)	174.40(8)	175.17(11)	173.04(8)	179.2(1)
O1–P1–C1	89.35(7)	88.77(7)	89.34(11)	89.34(7)	88.6(1)
O1–P1–C21	87.98(7)	85.92(8)	86.43(11)	86.05(8)	89.9(1)
O2–P1–C11	89.29(7)	89.85(7)	89.66(11)	89.84(9)	88.4(1)
O2–P1–C21	87.42(7)	89.18(8)	88.78(11)	87.39(8)	90.6(1)
C1–P1–C11	115.98(8)	118.27(9)	122.49(13)	116.97(9)	121.6(2)
C1–P1–C21	130.55(8)	129.06(9)	123.30(13)	130.04(10)	117.8(1)
C11–P1–C21	113.47(9)	112.65(8)	114.19(12)	113.00(8)	120.6(2)
Torsion angles/°					
C1–P1–C21–O3	170.98(10)	172.42(11)	174.47(17)	−174.72(11)	
C1–P1–C21–C22	−9.79(17)	−9.95(18)	−3.1(3)	4.9(2)	
C11–P1–C21–O3	−9.94(14)	−9.29(15)	−3.9(3)	4.69(17)	
C11–P1–C21–C22	169.29(11)	168.35(12)	178.48(17)	−175.67(13)	
Average torsion angle[a]	9.87	9.62	3.5	4.8	

[a] Average torsion angle from the equatorial plane.



Scheme 2.

(3.5°–9.9°) of the carbonyl groups from the equatorial plane are much smaller than that of the reported Martin acetylspirophosphorane (Fig. 2).[8j] This difference can be attributed to the difference in steric demands between the flat naphth-1,8-diyl-8-oxy group and the bulky Martin ligand. It is also notable that the aryl group on the aroyl carbon is coplanar to the carbonyl group, which can be rationalized by the π-conjugation of the aryl group with the carbonyl group.

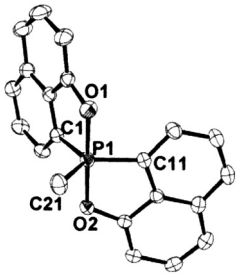


Fig. 4. ORTEP diagram of **4** showing thermal ellipsoids at the 30% probability level. All hydrogens are omitted for clarity.

As for the latter, generally, distortion of the TBP geometry about the phosphorus atom of spirophosphoranes except for several metallaphosphoranes[13a,b,d,19] is along the Berry pseudorotation coordinate with the monodentate equatorial group as the pivot.[4,20] According to this preference, the O1–P1–C21 angles and the O2–P1–C21 angles of **3a**, **3b**, **3d**, and **3e** should be larger than the ideal angle of 90°. However, these angles (85.92°–89.18°) are smaller than 90°, while the structure of methylphosphorane **4** was quite ordinary. Thus, it is reasonable to assume that the unusual inclination of the apical bond toward the monodentate carbonyl group is induced by intramolecular $n \rightarrow \pi^*$ interaction (Fig. 1). The shorter apical P–O bonds (1.760–1.786 Å) of the aroylphosphoranes compared with those (1.791–1.803 Å) of methylphosphorane **4** can also be rationalized to be a consequence of such interactions.

3. Conclusions

The reaction of the lithium phosphoranide **2** generated from bis(8-oxy-1-naphthyl)hydrophosphorane **1** with aroyl chlorides afforded air-stable aroylspirophosphoranes **3**. Phosphoranes **3** hydrolyzed upon long exposure to moisture but were stable in anhydrous solutions. Intramolecular $n_p(O_{apical}) \rightarrow \pi^*(C{=}O)$ charge

transfer interactions are highly suggested according to the X-ray structural analyses of **3a**, **3b**, **3d**, and **3e**. In the crystal structure, the carbonyl groups are essentially coplanar with the equatorial plane and the apical bond is titled toward the presumably interacting carbonyl group, a distortion opposite of what is usually observed for spirophosphoranes with TBP geometry. Since novel phosphoranes **3** can be considered to be analogues of pentacoordinate phosphorus intermediates in the hydrolysis reaction of triesters of PFA, which are potentially useful as antiviral drugs, it can be said that we have provided experimental structural support for the theoretically proposed stereoelectronic effect in this reaction.[11]

4. Experimental section

4.1. General

All reactions were carried out under a nitrogen atmosphere. Hydrophosphorane **1** was prepared according to a published procedure.[21] Dry solvents used in the reactions and recrystallization were purchased from Wako Pure Chemical Industries, Ltd. Preparative thin layer chromatography (PTLC) was carried out on plates coated with Merck silica gel 60 GF_{254}.

Melting points were measured with a Yanaco micro melting point apparatus and are uncorrected. ^1H (600 MHz), ^{13}C (151 MHz), and ^{31}P (243 MHz) NMR spectra were recorded on a Brucker AVANCE-II (600 MHz) spectrometer. Elemental analyses were performed on a Perkin–Elmer 2400 CHN elemental analyzer. IR spectra were recorded on a JASCO FT/IR-610 spectrometer. High-resolution mass spectra (HRMS) were measured on a Thermo Scientific Exactive Plus FTMS using atmospheric-pressure chemical ionization (APCI).

4.2. Aroylspirophosphoranes 3

*4.2.1. 2-(4′-Methoxybenzoyl)-2,2′λ^5-spirobi[2H-naphth[1,8-cd]-1,2-oxaphosphole] (**3a**).* To a solution of **1** (100 mg, 0.316 mmol) in 20 mL of THF was added dropwise *t*-BuLi (1.55 M *n*-pentane solution, 0.22 mL, 0.34 mmol) at room temperature. The solution was stirred for 10 min and then 4-methoxybenzoyl chloride (0.044 mL, 0.32 mmol) was added. The reaction mixture was stirred at room temperature for 30 min and then the solvents were removed under reduced pressure. Purification of the residue was carried out by PTLC (CH_2Cl_2) to give **3a** as pale yellow powder. Yield 117 mg (82%); mp 259–261 °C. Anal. Calcd for $C_{28}H_{19}O_4P$: C 74.66, H 4.25. Found: C 74.82, H 4.25; ^1H NMR ($CDCl_3$, 600 MHz) δ=8.30 (ddd, *J*=12.0, 7.2, and 0.6 Hz, 2H), 8.03 (dd, *J*=7.8 and 2.4 Hz, 2H), 7.82 (d, *J*=9.0 Hz, 2H), 7.66 (ddd, *J*=8.4, 7.2, and 6.6 Hz, 2H), 7.47 (dd, *J*=8.4 and 7.8 Hz, 2H), 7.37 (dd, *J*=8.4 and 1.8 Hz, 2H), 6.96 (d, *J*=7.2 Hz, 2H), 6.76 (dd, *J*=9.0 and 1.8 Hz, 2H), 3.76 (s, 3H); ^{13}C NMR ($CDCl_3$, 151 MHz) δ=191.3 (d, *J*=173.0 Hz), 164.3, 156.4, 133.2 (d, *J*=8.2 Hz), 132.2 (d, *J*=14.0 Hz), 131.9 (d, *J*=1.8 Hz), 131.5 (d, *J*=4.2 Hz), 129.5, 129.3, 128.4 (d, *J*=16.5 Hz), 128.0 (d, *J*=76.9 Hz), 124.3 (d, *J*=148.7 Hz), 116.7, 114.3, 105.3, 55.5; ^{31}P NMR ($CDCl_3$, 162 MHz) δ=−38.7; IR (KBr, cm^{-1}) ν=3060, 2958, 2837, 1649, 1626, 1591, 1508, 1489, 1454, 1419, 1369, 1340, 1323, 1309, 1269, 1250, 1236, 1215, 1205, 1163, 1147, 1105, 1041, 1028, 962, 935, 839–754; HRMS (APCI): $[M+H]^+$, found 451.1099. $C_{28}H_{20}O_4P$ requires 451.1094.

*4.2.2. 2-(4′-tert-Butylbenzoyl)-2,2′λ^5-spirobi[2H-naphth[1,8-cd]-1,2-oxaphosphole] (**3b**).* To a solution of **1** (100 mg, 0.316 mmol) in 20 mL of THF was added dropwise *t*-BuLi (1.59 M *n*-pentane solution, 0.22 mL, 0.35 mmol) at room temperature. The solution was stirred for 10 min and then 4-*tert*-butylbenzoyl chloride (0.63 mL, 0.35 mmol) was added. The reaction mixture was stirred at room temperature for 30 min and then the solvents were removed under reduced pressure. Purification of the residue was carried out by PTLC (CH_2Cl_2/hexane 1:1) to give **3b** as yellow powder. Yield 101 mg (67%); mp 250–252 °C. Anal. Calcd for $C_{31}H_{25}O_3P$: C 78.14, H 5.29. Found: C 78.04, H 5.31; ^1H NMR ($CDCl_3$, 600 MHz) δ=8.30 (dd, *J*=12.0 and 7.2 Hz, 2H), 8.02 (dd, *J*=8.4 and 3.0 Hz, 2H), 7.79 (d, *J*=8.4 Hz, 2H), 7.66 (dt, *J*=7.2 and 6.6 Hz, 2H), 7.47 (t, *J*=8.4 Hz, 2H), 7.37 (dd, *J*=8.4 and 1.8 Hz, 2H), 7.30 (dd, *J*=8.4 and 1.8 Hz, 2H), 6.96 (d, *J*=7.8 Hz, 2H), 1.23 (s, 9H); ^{13}C NMR ($CDCl_3$, 151 MHz) δ=192.3 (d, *J*=173.2 Hz), 158.0, 156.3, 133.2 (d, *J*=8.3 Hz), 132.5 (d, *J*=74.7 Hz), 132.2 (d, *J*=14.3 Hz), 131.5 (d, *J*=4.4 Hz), 129.6, 129.5, 129.3, 128.5 (d, *J*=16.5 Hz), 126.0, 124.2 (d, *J*=149.0 Hz), 116.8, 105.4, 35.2, 30.9; ^{31}P NMR ($CDCl_3$, 162 MHz) δ=−38.6; IR (KBr, cm^{-1}) ν=3053, 2962, 2868, 1655, 1626, 1601, 1576, 1491, 1454, 1419, 1408, 1367, 1340, 1248, 1205, 1182, 1147, 1101, 1043, 1016, 960, 935, 920, 845–754; HRMS (APCI): $[M+H]^+$, found 477.1620. $C_{31}H_{26}O_3P$ requires 477.1614.

*4.2.3. 2-(4′-Methylthiobenzoyl)-2,2′λ^5-spirobi[2H-naphth[1,8-cd]-1,2-oxaphosphole] (**3c**).* To a solution of **1** (100 mg, 0.316 mmol) in 20 mL of THF was added dropwise *t*-BuLi (1.59 M *n*-pentane solution, 0.22 mL, 0.35 mmol) at room temperature. The solution was stirred for 10 min and then a solution of 4-methylthiobenzoyl chloride (64.9 mg, 0.348 mmol) in 5 mL of THF was added. The reaction mixture was stirred at room temperature for 30 min and then the solvents were removed under reduced pressure. Purification of the residue was carried out by PTLC (CH_2Cl_2/hexane 1:1) followed by recrystallization from CH_2Cl_2/hexane to give **3c** as yellow crystals. Yield 77.8 mg (53%); mp 248–250 °C. Anal. Calcd for $C_{28}H_{19}O_3PS$: C 72.09, H 4.11. Found: C 72.35, H 4.15; ^1H NMR ($CDCl_3$, 600 MHz) δ=8.30 (dd, *J*=12.0 and 7.2 Hz, 2H), 8.03 (dd, *J*=7.8 and 2.4 Hz, 2H), 7.73 (d, *J*=8.4 Hz, 2H), 7.66 (q, *J*=7.2 Hz, 2H), 7.47 (t, *J*=8.4 Hz, 2H), 7.37 (dd, *J*=8.4 and 1.8 Hz, 2H), 7.07 (dd, *J*=8.4 and 1.2 Hz, 2H), 6.96 (d, *J*=7.2 Hz, 2H), 2.40 (s, 3H); ^{13}C NMR ($CDCl_3$, 151 MHz) δ=191.9 (d, *J*=174.4 Hz), 156.3, 147.6, 133.3 (d, *J*=8.3 Hz), 132.2 (d, *J*=14.2 Hz), 131.6 (d, *J*=4.2 Hz), 131.3 (d, *J*=75.5 Hz), 129.8, 129.5, 129.3, 128.5 (d, *J*=16.4 Hz), 125.1, 124.1 (d, *J*=149.3 Hz), 116.8, 105.4, 14.5; ^{31}P NMR ($CDCl_3$, 162 MHz) δ=−38.8; IR (KBr, cm^{-1}) ν=3051, 2922, 1649, 1626, 1581, 1549, 1489, 1454, 1419, 1400, 1369, 1340, 1325, 1250, 1232, 1213, 1182, 1146, 1105, 1090, 1043, 1016, 953, 933, 916, 818–727; HRMS (APCI): $[M+H]^+$, found 467.0873. $C_{28}H_{20}O_3PS$ requires 467.0865.

*4.2.4. 2-Benzoyl-2,2′λ^5-spirobi[2H-naphth[1,8-cd]-1,2-oxaphosphole] (**3d**).* To a solution of **1** (100 mg, 0.316 mmol) in 20 mL of THF was added dropwise *t*-BuLi (1.59 M *n*-pentane solution, 0.22 mL, 0.35 mmol) at room temperature. The solution was stirred for 10 min and then benzoyl chloride (0.040 mL, 0.35 mmol) was added. The reaction mixture was stirred at room temperature for 30 min and then the solvents were removed under reduced pressure. Purification of the residue was carried out by PTLC (CH_2Cl_2/hexane 1:1) followed by recrystallization from CH_2Cl_2/hexane to give **3d** as pale yellow crystals. Yield 58.0 mg (44%); mp 214–215 °C. Anal. Calcd for $C_{27}H_{17}O_3P$: C 77.14, H 4.08. Found: C 77.42, H 4.06; ^1H NMR ($CDCl_3$, 600 MHz) δ=8.31 (dd, *J*=12.0 and 7.2 Hz, 2H), 8.04 (dd, *J*=8.4 and 3.0 Hz, 2H), 7.84 (d, *J*=8.4 Hz, 2H), 7.67 (dt, *J*=7.2 and 6.6 Hz, 2H), 7.49–7.46 (m, 3H), 7.38 (dd, *J*=8.4 and 1.8 Hz, 2H), 7.28 (t, *J*=7.8 Hz, 2H), 6.96 (d, *J*=7.2 Hz, 2H); ^{13}C NMR ($CDCl_3$, 151 MHz) δ=193.0 (d, *J*=174.6 Hz), 156.3, 135.2 (d, *J*=74.0 Hz), 133.9, 133.3 (d, *J*=8.6 Hz), 132.2 (d, *J*=14.2 Hz), 131.6 (d, *J*=4.2 Hz), 129.5, 129.4, 129.3, 128.8, 128.5 (d, *J*=16.5 Hz), 124.0 (d, *J*=149.8Hz), 116.8, 105.4; ^{31}P NMR ($CDCl_3$, 162 MHz) δ=−38.7; IR (KBr, cm^{-1}) ν=3049, 1660, 1626, 1593, 1576, 1491, 1454, 1419, 1367, 1338, 1248, 1219, 1203, 1180, 1147, 1105, 1041, 1018, 999, 962, 931, 804–750; HRMS (APCI): $[M+H]^+$, found 421.0987. $C_{27}H_{18}O_3P$ requires 421.0988.

*4.2.5. 2-(4′-Fluorobenzoyl)-2,2′λ^5-spirobi[2H-naphth[1,8-cd]-1,2-oxaphosphole] (**3e**).* To a solution of **1** (100 mg, 0.316 mmol) in 20 mL of THF was added dropwise *t*-BuLi (1.59 M *n*-pentane

solution, 0.22 mL, 0.35 mmol) at room temperature. The solution was stirred for 10 min and then 4-fluorobenzoyl chloride (0.041 mL, 0.35 mmol) was added. The reaction mixture was stirred at room temperature for 30 min and then the solvents were removed under reduced pressure. Purification of the residue was carried out by PTLC (CH_2Cl_2/hexane 1:1) followed by recrystallization from CH_3CN to give **3e** as yellow crystals. Yield 33.0 mg (24%); mp 185–186 °C; Anal. Calcd for $C_{27}H_{16}FO_3P$: C 73.97, H 3.68. Found: C 73.86, H 3.67; ^{1}H NMR ($CDCl_3$, 600 MHz) δ=8.30 (dd, J=12.6 and 7.2 Hz, 2H), 8.03 (dd, J=8.4 and 3.0 Hz, 2H), 7.86 (dd, J=9.0 and 5.4 Hz, 2H), 7.66 (dt, J=7.8 and 6.6 Hz, 2H), 7.48 (t, J=8.4 Hz, 2H), 7.38 (dd, J=8.4 and 1.8 Hz, 2H), 6.96 (d, J=7.8 Hz, 2H), 6.94 (dd, J=8.4 and 1.8 Hz, 2H); ^{13}C NMR ($CDCl_3$, 151 MHz) δ=191.6 (d, J=176.4 Hz), 166.1 (d, J=257.3 Hz), 156.2, 133.4 (d, J=8.3 Hz), 132.19 (d, J=14.6 Hz), 132.16 (d, J=10.0 Hz), 131.8 (d, J=4.2 Hz), 131.6 (dd, J=75.8 and 2.9 Hz), 129.41 (d, J=23.6 Hz), 129.38, 128.5 (d, J=16.6 Hz), 123.7 (d, J=149.9 Hz), 116.9, 116.2 (d, J=22.2 Hz), 105.5; ^{31}P NMR ($CDCl_3$, 162 MHz) δ=−38.9; IR (KBr, cm^{-1}) ν=3062, 1655, 1626, 1591, 1577, 1502, 1489, 1454, 1410, 1367, 1338, 1250, 1228, 1205, 1153, 1103, 1041, 1018, 1009, 964, 953, 935, 849–735; HRMS (APCI): $[M+H]^+$, found 439.0898. $C_{27}H_{17}FO_3P$ requires 439.0894.

*4.2.6. 2-(4′-Cyanobenzoyl)-2,2′λ^5-spirobi[2H-naphth[1,8-cd]-1,2-oxaphosphole] (**3f**).* To a solution of **1** (100 mg, 0.316 mmol) in 20 mL of THF was added dropwise *t*-BuLi (1.59 M *n*-pentane solution, 0.22 mL, 0.35 mmol) at room temperature. The solution was stirred for 10 min and then a solution of 4-cyanobenzoyl chloride (57.6 mg, 0.348 mmol) in 10 mL of THF was added. The reaction mixture was stirred at room temperature for 30 min and then the solvents were removed under reduced pressure. Purification of the residue was carried out by PTLC (CH_2Cl_2/hexane 1:1) followed by recrystallization from CH_2Cl_2/CH_3CN to give **3f** as yellow crystals. Yield 41.0 mg (29%); mp 199–201 °C. Anal. Calcd for $C_{28}H_{16}NO_3P$: C 75.50, H 3.62, N 3.14. Found: C 75.47, H 3.67, N 3.22; ^{1}H NMR ($CDCl_3$, 600 MHz) δ=8.31 (dd, J=12.6 and 7.2 Hz, 2H), 8.07 (dd, J=7.8 and 3.0 Hz, 2H), 7.89 (d, J=8.4 Hz, 2H), 7.69 (dt, J=7.8 and 6.6 Hz, 2H), 7.57 (dd, J=9.0 and 1.8 Hz, 2H), 7.49 (dd, J=8.4 and 7.2 Hz, 2H), 7.41 (dd, J=8.4 and 2.4 Hz, 2H), 6.97 (d, J=7.8 Hz, 2H); ^{13}C NMR ($CDCl_3$, 151 MHz) δ=192.2 (d, J=180.6 Hz), 155.9, 138.6 (d, J=74.0 Hz), 133.7 (d, J=8.6 Hz), 132.6, 132.2 (d, J=14.5 Hz), 132.0 (d, J=4.2 Hz), 129.5, 129.42, 129.36, 128.6 (d, J=16.6 Hz), 123.0 (d, J=151.0 Hz), 117.6, 117.2, 116.9, 105.6; ^{31}P NMR ($CDCl_3$, 162 MHz) δ=−39.3; IR (KBr, cm^{-1}) ν=3055, 2227, 1668, 1624, 1576, 1491, 1454, 1417, 1406, 1363, 1338, 1290, 1247, 1211, 1172, 1149, 1103, 1043, 1016, 976, 958, 931, 914, 854–754; HRMS (APCI): $[M+H]^+$, found 446.0946. $C_{28}H_{17}NO_3P$ requires 446.0941.

4.3. 2-Methyl-2,2′λ^5-spirobi[2*H*-naphth[1,8-*cd*]-1,2-oxaphosphole] (4)

To a solution of **1** (100 mg, 0.316 mmol) in 20 mL of THF was added dropwise *t*-BuLi (1.59 M *n*-pentane solution, 0.22 mL, 0.35 mmol) at room temperature. The solution was stirred for 10 min and then an excess amount of iodomethane (0.50 mL, 8.0 mmol) was added. After 30 min of stirring at room temperature water (20 mL) was added and the mixture was extracted with Et_2O (50 mL×3). The collected organic layer was dried over $MgSO_4$ and the volatiles were removed under reduced pressure. Purification of the residue was carried out by PTLC (CH_2Cl_2/hexane 1:1) followed by recrystallization from CH_2Cl_2/hexane to give **4** as pale crystals. Yield 87.0 mg (84%); mp 178–180 °C. Anal. Calcd for $C_{21}H_{15}O_2P$: C 76.36, H 4.57. Found: C 76.20, H 4.46; ^{1}H NMR ($CDCl_3$, 600 MHz) δ=8.33 (ddd, J=12.0, 7.2, and 0.6 Hz, 2H), 7.97 (dd, J=7.8 and 2.4 Hz, 2H), 7.61 (ddd, J=7.8, 7.2, and 6.6 Hz, 2H), 7.52 (dd, J=8.4 and 7.2 Hz, 2H), 7.33 (dd, J=8.4 and 2.4 Hz, 2H), 6.96 (d, J=7.2 Hz, 2H), 2.42 (d, J=16.8 Hz, 3H); ^{13}C NMR ($CDCl_3$, 151 MHz) δ=156.1, 133.5 (d, J=8.8 Hz), 132.0 (d, J=14.3 Hz), 130.9 (d, J=4.2 Hz), 129.21 (d, J=25.1 Hz), 129.19, 128.0 (d, J=15.9 Hz), 125.7 (d, J=156.4 Hz), 115.6, 103.9, 22.4 (d, J=124.6 Hz); ^{31}P NMR ($CDCl_3$, 162 MHz) δ=−28.7; IR (KBr, cm^{-1}) ν=3053, 2920, 1626, 1576, 1491, 1456, 1419, 1367, 1338, 1300, 1255, 1207, 1171, 1147, 1113, 1043, 1020, 970, 933, 893, 868, 814–735; HRMS (APCI): $[M+H]^+$, found 331.0884. $C_{21}H_{16}O_2P$ requires 331.0882.

4.4. X-ray structure determination

Yellow crystals of **3a** (plates), **3b** (prisms), **3d**·0.5CH_3CN (prisms), and **3e** (plates) were grown by recrystallization from CH_3CN (for **3a**, **3d**, and **3e**) or CH_2Cl_2/hexane (for **3b**). The diffraction data were measured on a Rigaku AFC-7*R* diffractometer using graphite monochromated Mo Kα radiation (λ=0.71069 Å). The data were collected at 296 K using MSC/AFC diffractometer control software. The structure was solved by direct methods using SIR92. All non-hydrogen atoms were refined anisotropically. All hydrogen atoms were refined using a riding model.

*4.4.1. Crystal/refinement data for **3a**.* $C_{28}H_{19}O_4P$, M=450.43, triclinic, $P\bar{1}$, a=9.9957(9) Å, b=10.738(2) Å, c=11.456(1) Å, α=77.51(1)°, β=65.709(7)°, γ=75.93(1)°, V=1077.7(3) Å^3, Z=2, D_c=1.388 g cm^{-3}, μ(Mo Kα)=1.620 cm^{-1}, F(000)=468.00, 4938 unique reflections, 317 parameters, R_1 ($I>2\sigma(I)$)=0.0381, wR_2 (all data)=0.1099, GOF 1.039.

*4.4.2. Crystal/refinement data for **3b**.* $C_{31}H_{25}O_3P$, M=476.51, triclinic, $P\bar{1}$, a=11.418(3) Å, b=13.401(3) Å, c=8.549(2) Å, α=108.42(2)°, β=97.34(2)°, γ=82.19(2)°, V=1224.6(4) Å^3, Z=2, D_c=1.292 g cm^{-3}, μ(Mo Kα)=1.435 cm^{-1}, F(000)=500.00, 5634 unique reflections, 341 parameters, R_1 ($I>2\sigma(I)$)=0.0474, wR_2 (all data)=0.1581, GOF 1.056.

*4.4.3. Crystal/refinement data for **3d**·0.5CH$_3$CN.* $C_{28}H_{18.5}N_{0.5}O_3P$, M=440.93, monoclinic, $C2/c$, a=32.133(2) Å, b=9.478(2) Å, c=16.083(3) Å, β=114.658(8)°, V=4451(2) Å^3, Z=8, D_c=1.316 g cm^{-3}, μ(Mo Kα)=1.528 cm^{-1}, F(000)=1832.00, 5115 unique reflections, 317 parameters, R_1 ($I>2\sigma(I)$)=0.0478, wR_2 (all data)=0.1540, GOF 0.991.

*4.4.4. Crystal/refinement data for **3e**.* $C_{27}H_{16}FO_3P$, M=438.39, triclinic, $P\bar{1}$, a=10.082(2) Å, b=10.052(2) Å, c=12.415(3) Å, α=80.57(2)°, β=80.76(2)°, γ=59.80(2)°, V=1068.2(4) Å^3, Z=2, D_c=1.363 g cm^{-3}, μ(Mo Kα)=1.645 cm^{-1}, F(000)=452.00, 4888 unique reflections, 305 parameters, R_1 ($I>2\sigma(I)$)=0.0412, wR_2 (all data)=0.1158, GOF 0.993.

CCDC-944085 (**3a**), CCDC-944086 (**3b**), CCDC-944087 (**3d**·0.5CH_3CN), and CCDC-944088 (**3e**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Supplementary data

Copies of ^{1}H NMR and ^{13}C NMR spectra of aroylphosphoranes **3** and methylphosphorane **4**. Supplementary data associated with this article can be found in the online version, at http://dx.doi.org/10.1016/j.tet.2013.08.004. These data include MOL files and InChiKeys of the most important compounds described in this article.

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