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Novel C_1-symmetric dibenzophosphole ligands: application in hydroformylation reactions

Abdelhouad Oukhrib [a,b,c], Laurence Bonnafoux [d], Armen Panossian [d], Sandrine Waifang [a,b], Duc Hanh Nguyen [a,b], Martine Urrutigoity [a,b], Françoise Colobert [d], Maryse Gouygou [a,b,*], Frédéric R. Leroux [d,*]

[a] CNRS, LCC (Laboratoire de Chimie de Coordination), 205, route de Narbonne, 31077 Toulouse, France
[b] Université de Toulouse, UPS, INPT, LCC, 31077 Toulouse, France
[c] Laboratoire de Chimie des substances naturelles, Faculté des Sciences Semlalia, Université Cadi Ayyad, B.P. 2390 Marrakech, Morocco
[d] CNRS-Université de Strasbourg, UMR 7509, SynCat, 25 Rue Becquerel, 67087 Strasbourg Cedex 02, France

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ABSTRACT

A new family of non-symmetrical disubstituted dibenzophospholes possessing different steric and electronic effects have been synthesized and characterized. Their preliminary evaluation in rhodium-catalyzed hydroformylation reactions is presented.

1. Introduction

The design and synthesis of new ligands is the key for the development of transition metal catalyzed processes and requires the fine tuning of steric and electronic properties of the ligands. This is particularly true for phosphine-based ligands, widely used in many catalytic transformations of synthetic relevance. For hydroformylation, one of the most important homogeneous catalytic processes applied on an industrial scale,[1] a large number of phosphorus ligands[2] have been developed and there is a continued interest in the design of new ligands to increase the efficiency and selectivity of this chemical transformation. Among them, phosphole ligands[3] and more specifically dibenzophosphole[4]-based ligands have been successfully used in Rh- and Pt-catalyzed hydroformylation,[5] including in their asymmetric version. The catalytic performances of these ligands, possessing a more electron-withdrawing group than the diphenylphosphino one, are generally improved in terms of activities and selectivities, with respect to the branched aldehyde, when compared to the diphenylphosphino-counterparts. Until now, 5-phenyl-5*H*-dibenzophosphole is the most commonly used compound as monophosphole ligand or as synthetic subunit to elaborated ligands for hydroformylation.[5]

Recently, non-symmetrical mono-, di-, and tetra-substituted dibenzophospholes have become accessible from a methodology based on a transition metal-free aryne cross-coupling.[6]

As part of our continuing interest in the design of phosphole-based ligands for application in catalysis,[7] we report an efficient synthetic method for the preparation of a new family of non-symmetrical disubstituted dibenzophospholes possessing different steric and electronic properties and their effects in the preliminary evaluation of rhodium-catalyzed hydroformylation reactions.

2. Results and discussion

2.1. Synthesis of C_1-symmetric dibenzophospholes

Several structures containing the dibenzo[*b*,*d*]phosphole (or 9-phosphafluorene) motif have been synthesized, either as a byproduct in the synthesis of other phosphorus compounds, or as the desired product itself. The methods to access this motif can be listed as

* Corresponding authors. E-mail addresses: gouygou@lcc-toulouse.fr, maryse.gouygou@lcc-toulouse.fr (M. Gouygou), frederic.leroux@unistra.fr (F.R. Leroux).

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follows: (a) nucleophilic substitution at phosphorus by 2,2′-dilithiobiaryls (intermolecular), or *ortho*-lithiophenyl substituents (intramolecular);[8] (b) nucleophilic aromatic substitution (S_NAr) of primary phosphines onto 2,2′-difluorobiaryls, or intramolecular S_NAr in diaryl-substituted, activated phosphorus intermediates;[9] (c) intramolecular electrophilic aromatic substitution (S_EAr) in diaryl-substituted, activated phosphorus intermediates;[10] (d) palladium-catalyzed intramolecular C–X or C–H phosphination of (2-biaryl) phosphorus compounds;[11] (e) internal palladium-catalyzed reductive cross-coupling of a di(2-bromophenyl)phosphinic acid;[12] (f) transition metal-catalyzed cycloaddition reactions for the construction of the dibenzophosphole core;[13] (g) redox or photochemical radicalar processes;[14] (h) thermal redox-cycloaddition (the McCormack reaction);[15] (i) and more recently, the reaction of (*ortho*-lithiophenyl)phosphine–borane complexes with in situ generated arynes, as a variant of the so-called 'ARYNE coupling' that we developed.[6]

Although the most used method remains the nucleophilic substitution of a 2,2′-dilithiobiaryl onto an electrophilic phosphorus reagent, it has mainly been employed in the case of symmetrical 2,2′-dihalobiaryls. A tentative explanation resides in the difficulty of synthesis of di- or polyhalogenated non-symmetrical biaryls bearing exchangeable halogens in positions 2 and 2′. The ARYNE coupling allowed us to overcome this difficulty and to prepare various functionalized C_1-symmetric 2,2′-dihalobiaryls.[16,17] When treated with *n*-BuLi (2 equiv) then chlorodiphenylphosphine (2 equiv) in toluene at high temperature, we showed that they led to a mixture of diphosphine (major) and dibenzophosphole.[17]

On the other hand, starting from the same 2,2′-dihalobiaryls and using classical reaction conditions for the preparation of phosphafluorenes (double halogen/lithium exchange with *n*-BuLi in THF at −78 °C followed by trapping with 1 equiv of dichlorophenylphosphine) afforded the desired C_1-symmetric dibenzophospholes **3**, **4** in 30–96% yields (Table 1). In order to obtain the dilfluoromethylenedioxy and tetrafluoroethylenedioxy analogues **4b** and **c** in acceptable yields, the use of the 2′-iodinated starting biaryl in lieu of the brominated one, and of 3 equiv of *n*-BuLi were required.[18]

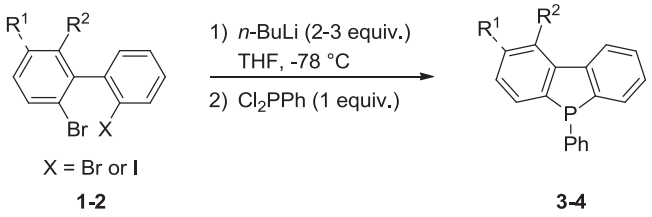


Table 1
Synthesis of non-symmetrical dibenzophosphole ligands

Entry	Biaryl	R^1	R^2	X	Product	Yield (%)
1	**1a**	H	H	Br	**3a**	82
2	**1b**	H	F	Br	**3b**	53
3	**1c**	H	CH_3	Br	**3c**	40
4	**1d**	H	OCH_3	Br	**3d**	49
5	**1e**	H	Cl	Br	**3e**	56
6	**1f**	H	Br	Br	**3f**	37
7	**1g**	H	Ph	Br	**3g**	63
8	**1h**	H	$N(CH_3)_2$	Br	**3h**	39
9	**1i**	H	OCF_3	Br	**3i**	61
10	**2a**	OCH_2O		Br	**4a**	96
11[a]	**2b**	OCF_2O		I	**4b**	30
12[a]	**2c**	OCF_2CF_2O		I	**4c**	45

[a] 3 equiv of *n*-BuLi were used.

Since these dibenzophospholes appeared to be air-sensitive, the workup and purification had to be performed immediately after the end of the reaction and the compounds stored under argon.

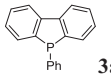
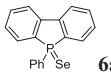
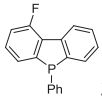
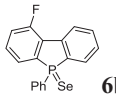
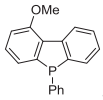
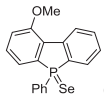
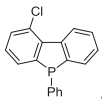
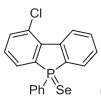
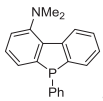
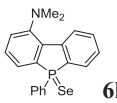
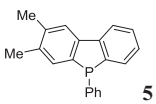
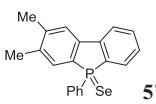
Due to their unsymmetrically substituted biaryl backbone and to the tetrahedral geometry of phosphorus in dibenzophospholes, compounds of Table 1 should exhibit central chirality at phosphorus. On the other hand, no atropogenicity was expected. Indeed the phosphole subunit presents a flat geometry, except in the case of dibenzophospholes bearing unusually widespread substituents, as in phosphafluorenes being part of a helicene structure,[11c] which is not the case here.[19] Consequently, no diastereomeric mixture was expected, which was confirmed by ^1H and ^{31}P NMR analysis, by which a single isomer was detectable at room temperature.

2.2. Hydroformylation reactions

For a preliminary evaluation in hydroformylation, a series of representative dibenzophospholes exhibiting different electronic properties was chosen.

The evaluation of the σ-donor ability[20] was done by measuring the magnitude of $^1J_{P-Se}$[21] in the ^{77}Se isotopomer of the dibenzophosphole selenides quantitatively prepared by reacting the corresponding ligands with elemental selenium in $CDCl_3$ at RT. The $^1J_{P-Se}$ reported in Table 2 shows that **3h** and 2,3-dimethyl-5-phenyl-5*H*-dibenzophosphole **5**[22] are the best σ-donor ligands of our selected series with the smallest value of $^1J_{P-Se}$. **3d** exhibits an intermediate σ-donor ability, similar to **3a**, while **3b** and **e** appear as having the lowest σ-donor ability. The σ-donor power of all these dibenzophosphole ligands is lower than that of PPh_3.

Table 2
^{31}P NMR shifts and ^{31}P–^{77}Se coupling constants for selenides prepared from selected dibenzophosphole ligands and PPh_3

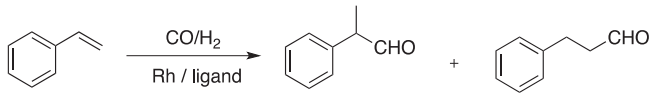
L	Selenide	δ ^{31}P (ppm)	^1J(P–Se) (Hz)
 **3a**	 **6a**	27.64	748
 **3b**	 **6b**	29.23	759
 **3d**	 **6d**	28.40	746
 **3e**	 **6e**	27.76	757
 **3h**	 **6h**	26.96	743
 **5**	 **5'**	27.05	741
PPh_3	$Ph_3P{=}Se$	35.28	730

In the first set of experiments, the catalytic performances of these dibenzophole ligands were explored in Rh-catalyzed hydroformylation reactions of styrene. The reaction was investigated

with the catalyst prepared in situ by adding the ligand to $[Rh(CO)_2(acac)]$ in the presence of syngas CO/H_2[2a] to instantaneously and selectively produce $[Rh(H)(CO)_2L_2]$ providing the active species by dissociation of a CO ligand. The tests were carried out under mild conditions at a temperature of 60 °C and a pressure of 30 bar of syngas CO/H_2 (1:1) using a substrate to rhodium ratio of 1000. For comparison purposes, the hydroformylation of styrene was also conducted with **3a**[23] and PPh_3 in the same conditions since PPh_3 is referred as the standard phosphine for the hydroformylation of terminal olefins.

The first runs (Table 3, entries 1–4) performed with two different ligand to rhodium ratios (2/1 and 4/1)[24] show that the activity and regioselectivity of rhodium catalysts containing **3a** dibenzophosphole ligand are independent of the **3a**/Rh ratios (entries 2, 4) as already observed with 1,2,5-triphenylphosphole.[3j] In contrast, comparative runs 1 and 2 with PPh_3 show that increasing the amount of PPh_3 induces a very low decrease in conversion and a slight increase in regioselectivity, a trend commonly observed in the hydroformylation of terminal alkenes.[3j]

Table 3
Hydroformylation of styrene[a]



Entry	Ligand	Time (h)	Conv. (%)[b]	Aldehydes (%)[b]	*b*/*l*[b]	TOF (min^{-1})[c]
1	PPh_3	6	100	100	90/10	5.6
2	PPh_3[d]	6	98	100	94/6	nd
3	**3a**	6	98	100	91/9	5.9
4	**3a**[d]	6	100	100	92/8	nd
5	**3b**	6	100	100	95/5	5.1
6	**3d**	6	98	100	93/7	5.1
7	**3e**	6	99	100	95/5	4.9
8	**3h**	6	100	100	93/7	5.8
9	**5**	6	100	100	92/8	6.6

[a] Reaction conditions: H_2/CO (1:1)=30 bar; $[Rh(CO)_2(acac)]$/ligand (1:2); S/C=1000, toluene (30 mL), 60 °C.
[b] Conversion, percentage of aldehydes and branched/linear ratio were determined by GC analysis with decane as internal standard.
[c] TOF=turnover frequency defined as mol of aldehyde produced per mol of rhodium per min, determined after 1 h.
[d] Rh/Ligand=1:4, nd: not determined.

Runs 5–9 with ligands **3b**, **d**, **e**, **h** and **5** have been performed with a ligand-to-rhodium ratio of 2. All dibenzophosphole/rhodium catalysts show good activities as evidenced by the satisfactory turnover numbers and turnover frequencies recorded (TON up to 1000, TOF=4.9–5.9 min^{-1}). Dibenzophosphole ligands **3a**, **h** and **5** provide rhodium catalysts that are more active than the one employing Ph_3P (Table 3, entry 1 vs entries 3, 8, and 9). It is interesting to note that there is an influence of the electronic properties of the dibenzophosphole substituents on the catalytic activity as the activity increases with methyl groups, while it decreases with fluoro, chloro or methoxy substituents (Table 3, entries 3, 5–7 and 9).

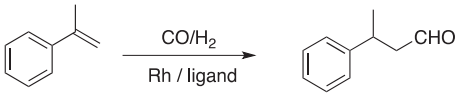
Excellent conversions and chemoselectivities were reached with all of these catalytic systems, which compare quite well with that obtained with PPh_3. As a result, a nearly total conversion of styrene into aldehydes was obtained after 6 h in all cases without formation of hydrogenated products (ethylbenzene, 2-phenylpropanol) (Table 3, entries 3–7).

In addition, high regioselectivities in favor of branched aldehydes were recorded in each case (91–95%). Interestingly, dibenzophosphole ligands **3b**, **d**, **e**, **h**, and **5** provide more selective rhodium catalysts than the one employing Ph_3P (Table 3, entry 1 vs entries 5–9). The electronic properties of the ligand slightly affect the regioselectivity of the reaction as an electron-withdrawing substituent on the dibenzophosphole ring provides the best regioselectivity in favor of the branched isomer (Table 3, entry 5 and 7).

Due to these promising results in terms of activity and regioselectivity, we decided to explore the hydroformylation of a more difficult substrate, such as α-methylstyrene.[25]

Rhodium catalytic systems with dibenzophosphole ligands provide poor active rhodium catalysts under similar conditions, as no conversion was observed at 60 °C under 30 bar of CO/H_2 (1:1) even after 18 h. However, hydroformylation of α-methylstyrene can be carried out if the temperature is raised to 90 °C under a CO/H_2 pressure of 50 bar during 18 h with a ligand-to-rhodium ratio of 4. The more interesting results, summarized in Table 4, show that even under these conditions only moderate conversions were recorded (60–76%, Table 4, entries 2–4). However, high chemoselectivities were observed as hydrogenated products (alkane, alcohol) were not detected. In addition, high regioselectivities were recorded in each case giving exclusively the linear aldehyde as previously reported.[26] It is worth noting that the dibenzophosphole/rhodium catalysts except that with **3d**, show the same performance as the PPh_3–rhodium system for the hydroformylation of α-methylstyrene (Table 4, entry 1).

Table 4
Hydroformylation of α-methylstyrene[a]



Entry	Ligand	Conversion (%)[b]	Linear aldehyde (%)[b]
1	PPh_3	76	100
2	**3a**	76	100
3	**3d**	60	100
4	**3e**	74	100

[a] Reactions conditions: H_2/CO (1:1)=50 bar; $[Rh(CO)_2(acac)]$/ligand (1:4); S/C=1000, toluene (30 mL), 18 h, 90 °C.
[b] Determined by GC analysis with decane as internal standard.

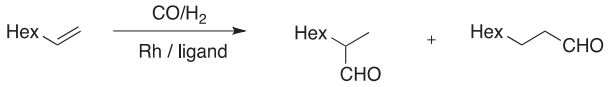
To expand the scope of these Rh-catalysts, we have investigated the hydroformylation of 1-octene, an unactivated alkene, which is also the most frequently used standard substrate beside styrene. The reaction was carried out under the same experimental conditions as described for styrene. The results are summarized in Table 5.

All of the dibenzophosphole ligands gave active catalytic systems in the hydroformylation of octene with excellent conversions over 3 h (93–97%). A comparison of the TOF obtained with dibenzophosphole ligands with the one obtained with PPh_3 evidences the beneficial effect of the dibenzophosphole ligands in the hydroformylation reaction of 1-octene (Table 4, entries 1–8). The catalytic system involving ligand **3e** shows the best activity. At this stage, it is difficult to correlate the activity of Rh-catalysts with the electronic properties of the dibenzophosphole substituents.

The hydroformylation reaction led to the aldehydes as major products with regioselectivities in favor of the linear aldehyde (Table 5, entries 2–10). The small amount of isomerization products (internal alkenes) obtained under these conditions (<12%) suggests a lower β-elimination reaction rate. A comparison of results obtained after 3 h (Table 5, entries 2–7) shows the influence of the electronic properties of the ligands on chemoselectivity and regioselectivity. Ligand **3e** provides the best catalytic system regarding selectivities (98% aldehyde, *b*/*l*=29/71) with a ligand/Rh ratio of 2 (Table 5, entry 4).

On the other hand, increasing the ligand/Rh ratio affects the regioselectivity (Table 5, entries 8–10) in favor of the linear aldehyde. With a ligand/Rh ratio of 4 (Table 5, entry 9), the ligand **3a** provides the most active catalytic system with similar results in

Table 5
Hydroformylation of 1-octene[a]



Entry	Ligand	Ligand/[Rh] ratio	Time (h)	Conversion (%)[b]	Isomerization products (%)[b]	Aldehydes (%)[b]	*b*/*l*[b]	TON[c]	TOF (min^{-1})[d]
1	PPh_3	2	3	80	11	89	31/69	710	1.7
2	**3a**	2	3	96	6	94	34/66	902	7.1
3	**3b**	2	3	96	8	92	30/70	883	7.0
4	**3d**	2	3	93	6	94	33/67	875	6.5
5	**3e**	2	3	97	2	98	29/71	950	7.2
6	**3h**	2	3	96	12	88	29/71	844	6.3
7	**5**	2	3	96	10.5	89.5	31/69	860	7.0
8	**3a**	2	6	98	1.5	98.5	39/61	965	7.0
9	**3a**	4	6	100	1	99	28/72	999	nd
10	**3a**	8	6	94	1	99	27/73	930	nd

[a] Reactions conditions: H_2/CO (1:1)=30 bar; S/C=1000, toluene (30 mL), 60 °C.
[b] Determined by GC analysis with decane as internal standard.
[c] TON=turnover number defined as mol of aldehyde produced per mol of rhodium.
[d] TOF=turnover frequency defined as mol of aldehyde produced per mol of rhodium per min, determined after 1 h. nd: not determined.

terms of selectivities (99% aldehyde, *b*/*l*=28/72) to the ligand **3e** used with a ligand/Rh ratio of 2.

3. Conclusions

C_1-Symmetric 2,2′-dihalobiaryls obtained by ARYNE coupling were converted into the corresponding dibenzophospholes by double halogen/metal exchange followed by trapping with dichlorophenylphosphine. These new monodentate non-symmetrical dibenzophosphole ligands provide efficient rhodium catalysts for the hydroformylation of styrene, α-methylstyrene, and 1-octene as substrates. Good activities were recorded for unhindered substrates, and good to excellent chemo- and regioselectivities were observed for styrene and α-methylstyrene. A correlation between the electronic properties of the substituents on the dibenzophosphole unit and the catalytic activities and/or selectivities could be observed. These results open the way for a fine-tuning of the catalyst properties.

4. Experimental section

4.1. General considerations

The syntheses of ligands were performed in dry and degassed solvents under an argon atmosphere. *n*-BuLi was purchased as a hexanes solution, and titrated before use using Gilman's double titration method. The starting biaryls were prepared according to Ref. 17.

4.2. General procedure for the synthesis of dibenzophosphole ligands

At −78 °C, a solution of *n*-butyllithium (2.0 mmol, 2 equiv) in hexanes (1.1 mL) was added slowly to a solution of the 2,2′-dihalobiaryl (1.0 mmol) in tetrahydrofuran (2 mL). After 30 min, a solution of dichlorophenylphosphine (0.18 g, 0.14 mL, 1.0 mmol, 1 equiv) in toluene (1 mL) was added slowly. After 15 min, the reaction mixture was allowed to reach 25 °C and was treated with a saturated aqueous solution of ammonium chloride (15 mL). The mixture was extracted with ethyl acetate (3×15 mL), and the combined organic layers were dried over sodium sulfate. Evaporation of the solvent followed by column chromatography on silica gel using cyclohexane as the eluent gave the corresponding dibenzophosphole. All analytical data were identical to those previously reported.[17]

*4.2.1. 1-Fluoro-5-phenyl-5H-dibenzophosphole (**3b**).* Colorless crystals (53%). Mp 99–102 °C. ^{31}P NMR (161 MHz, $CDCl_3$): δ (ppm)=−5.4. ^1H NMR ($CDCl_3$, 300 MHz): δ (ppm)=8.26 (d, *J*=8.1 Hz, 1H), 7.69 (t, *J*=6.7 Hz, 1H), 7.5–7.4 (m, 2H), 7.4–7.2 (m, 7H), 7.15 (dd, *J*=12.0, 1.1 Hz, 1H). ^{13}C NMR (75 MHz, $CDCl_3$): δ (ppm)=161.43, 158.1, 145.7 (dd, *J*=4.3, 2.6 Hz), 142.2 (d, *J*=2.7 Hz), 141.3 (dd, *J*=4.7, 1.8 Hz), 135.7 (d, *J*=19.1 Hz), 132.9, 132.7, 130.2 (d, *J*=22.2 Hz), 129.6, 129.1, 128.8–128.6 (m, 3C), 127.6 (dd, *J*=7.9, 1.1 Hz), 126.2–125.7 (m, 2C), 115.9 (d, *J*=21.3 Hz). Elemental Analysis for $C_{18}H_{12}FP$ (278.27): calcd (%) C 77.70, H 4.35; found C 77.82, H 4.35.

*4.2.2. 1-Methyl-5-phenyl-5H-dibenzophosphole (**3c**).* Colorless oil (40%). ^{31}P NMR ($CDCl_3$, 161 MHz): δ (ppm)=−10.5. ^1H NMR ($CDCl_3$, 300 MHz): δ (ppm)=8.14 (d, *J*=8.0 Hz, 1H), 7.69 (t, *J*=6.6 Hz, 1H), 7.53 (td, *J*=6.0, 2.9 Hz, 1H), 7.5–7.4 (m, 1H), 7.3–7.1 (m, 8H), 2.79 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): δ (ppm)=145.2 (d, *J*=2.6 Hz), 143.4, 143.3, 141.8 (d, *J*=2.1 Hz), 136.8 (d, *J*=20.2 Hz), 134.7, 132.9, 132.7, 132.1, 130.7 (d, *J*=22.6 Hz), 129.3, 128.7–128.5 (m, 4C), 127.1 (d, *J*=8.7 Hz), 126.8 (d, *J*=8.0 Hz), 125.5, 23.2. MS(EI): *m*/*z*(%)=274.1 (100) [M^+], 259.1 (73) [M^+−Me], 197.1 (22) [M^+−Ph], 183.1 (15) [M^+−Ph−Me].

*4.2.3. 1-Methoxy-5-phenyl-5H-dibenzophosphole (**3d**).* Yellow solid (49%). Mp 105–107 °C. ^{31}P NMR (161 MHz, $CDCl_3$): δ (ppm)=−7.7. ^1H NMR (300 MHz, $CDCl_3$): δ (ppm)=8.50 (d, *J*=7.9 Hz, 1H), 7.61 (d, *J*=6.3 Hz, 1H), 7.39 (td, *J*=7.4, 1.3 Hz, 1H), 7.3–7.1 (m, 8H), 7.0–6.9 (m, 1H), 3.97 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm)=157.6, 144.5 (d, *J*=125 Hz), 144.5 (d, *J*=124 Hz), 142.3, 136.9 (d, *J*=19 Hz), 133.2 (d, *J*=20 Hz), 132.0 (d, *J*=4 Hz, 2C), 130.3 (d, *J*=22 Hz), 129.7, 129.1, 129.0 (2C), 128.9 (d, *J*=9 Hz), 127.1 (d, *J*=8 Hz), 126.9, 122.9 (d, *J*=22 Hz), 111.3, 55.8. Elemental Analysis for $C_{19}H_{15}OP$ (290.09): calcd (%) C 78.61, H 5.21; found C 78.61, H 5.30.

*4.2.4. 1-Chloro-5-phenyl-5H-dibenzophosphole (**3e**).* Colorless solid (56%). Mp 110–111 °C. ^{31}P NMR ($CDCl_3$, 161 MHz): δ (ppm)=−8.9. ^1H NMR ($CDCl_3$, 300 MHz): δ (ppm)=8.83 (d, *J*=8.1 Hz, 1H), 7.64 (t, *J*=6.8 Hz, 1H), 7.51 (td, *J*=7.2, 1.0 Hz, 1H), 7.44 (td, *J*=7.4, 1.3 Hz, 1H), 7.38 (dd, *J*=7.9, 0.8 Hz, 1H), 7.4–7.2 (m, 1H), 7.3–7.1 (m, 6H). ^{13}C NMR (75 MHz, $CDCl_3$): δ (ppm)=146.1 (d, *J*=3.6 Hz), 143.0 (dd, *J*=10.7, 0.8 Hz, 2C), 139.5 (d, *J*=3.1 Hz), 135.8 (d, *J*=19.9 Hz), 133.1,

132.8, 131.2, 130.6, 130.4 (d, J=22.7 Hz), 129.6 (d, J=1.0 Hz), 128.9–128.6 (m, 4C), 127.9 (d, J=4.4 Hz), 127.8 (d, J=3.9 Hz), 126.3. MS(EI): m/z(%)=294.1 (68) [M^+], 259 (100) [M^+–Cl], 181.1 (38) [M^+–Cl–Ph]. HRMS for $C_{18}H_{12}ClNaOP$: calcd 333.0207; found 333.0184.

*4.2.5. 1-Bromo-5-phenyl-5H-dibenzophosphole (**3f**).* Colorless solid (37%). Mp 115–116 °C. ^{31}P NMR ($CDCl_3$, 161 MHz): δ (ppm)=−9.3. ^1H NMR ($CDCl_3$, 300 MHz): δ (ppm)=9.12 (d, J=8.2 Hz, 1H), 7.8–7.6 (m, 3H), 7.55 (td, J=7.8, 1.2 Hz, 1H), 7.41 (td, J=7.3, 1.7 Hz, 1H), 7.3–7.2 (m, 5H), 7.15 (td, J=7.6, 2.5 Hz, 1H). ^{13}C NMR (75 MHz, $CDCl_3$): δ (ppm)=146.7 (d, J=3.8 Hz), 143.3 (d, J=3.4 Hz, 2C), 140.7 (d, J=2.4 Hz), 135.9 (d, J=19.9 Hz), 134.9, 132.9 (d, J=20.4 Hz, 2C), 130.4 (d, J=22.7 Hz), 129.7, 129.6 (d, J=23.1 Hz), 128.8 (d, J=7.7 Hz, 2C), 128.3, 128.0 (m, 2C), 126.0, 118.7. MS(EI): m/z(%)=340.1 (38) [M^+], 259.2 (100) [M^+–Br], 181.1 (31) [M^+–Br–Ph]. HRMS for $C_{18}H_{12}BrNaP$: calcd 360.9752; found 360.9753.

*4.2.6. 1,5-Diphenyl-5H-dibenzophosphole (**3g**).* Colorless oil (63%). ^{31}P NMR (161 MHz, $CDCl_3$): δ (ppm)=−10.5. ^1H NMR (300 MHz, $CDCl_3$): δ (ppm)=7.7–7.6 (m, 2H), 7.5–7.3 (m, 5H), 7.3–7.1 (m, 11H), 7.00 (td, J=8.3, 1.4 Hz, 2H), 6.85 (d, J=8.0 Hz, 2H). ^{13}C NMR (75 MHz, $CDCl_3$): δ (ppm)=144.0 (d, J=2.7 Hz), 143.9 (d, J=1.6 Hz), 143.2, 142.0, 140.4 (d, J=2.7 Hz), 139.6, 136.6 (d, J=20.1 Hz), 132.9 (d, J=20.1 Hz, 2C), 131.4, 130.4 (d, J=22.4 Hz), 129.6 (d, J=22.9), 129.3 (d, J=5.0 Hz, 2C), 128.9–128.6 (m, 5C), 128.0, 127.6, 127.0 (d, J=8.0 Hz), 126.7 (d, J=8.6 Hz), 125.4. MS(EI): m/z(%)=336.2 (100) [M^+], 257.1 (89) [M^+–Ph], 226.1 (21) [M^+–Ph–P]. HRMS for $C_{24}H_{17}NaP$: calcd 359.0960; found 359.0969.

*4.2.7. 1-N,N-Dimethylamino-5-phenyl-5H-dibenzophosphole (**3h**).* Yellow oil (39%). ^{31}P NMR ($CDCl_3$, 161 MHz): δ (ppm)=−9.0. ^1H NMR (300 MHz, $CDCl_3$): δ (ppm)=8.62 (d, J=8.0 Hz, 1H), 7.62 (t, J=13.1 Hz, 1H), 7.42 (td, J=8.3, 1.2 Hz, 1H), 7.33 (td, J=7.1, 1.2 Hz, 1H), 7.3–7.0 (m, 8H), 2.82 (s, 3H), 2.76 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): δ (ppm)=152.0, 145.2 (d, J=1.2 Hz), 143.9 (d, J=2.9 Hz), 142, 7, 136.9 (d, J=19.9 Hz), 136.2 (d, J=3.1 Hz), 133.8 (d, J=19.5 Hz), 133.9, 133.7, 129.8 (d, J=22.1 Hz), 129.3, 128.7–128.4 (2C), 128.0 (d, J=9.0 Hz), 126.6 (d, J=8.0 Hz), 126.4, 124.9 (d, J=22.6 Hz), 119.1, 45.4, 44.0. MS(EI): m/z(%)=303.1 (100) [M^+], 262.1 (51) [M^+–NMe_2], 183.1 (40) [M^+–NMe_2–Ph].

*4.2.8. 1-Trifluoromethoxy-5-phenyl-5H-dibenzophosphole (**3i**).* Colorless solid (61%). Mp 50–51 °C. ^{31}P NMR (161 MHz, $CDCl_3$): δ (ppm)=−7.4. ^1H NMR (300 MHz, $CDCl_3$): δ (ppm)=8.30 (d, J=8.2 Hz, 1H), 7.65 (t, J=6.7 Hz, 1H), 7.6–7.5 (m, 1H), 7.45 (td, J=7.7, 1.3 Hz, 1H), 7.1–7.4 (m, 8H). ^{13}C NMR (75 MHz, $CDCl_3$): δ (ppm)=146.2 (d, J=3.9 Hz), 145.9 (d, J=1.0 Hz), 142.8 (d, J=1.9 Hz), 141.4 (d, J=1.8 Hz), 135.4 (d, J=19.3 Hz), 135.2 (d, J=3.6 Hz), 132.9 (d, J=20.5 Hz, 2C), 130.3 (d, J=22.5 Hz), 129.2 (d, J=0.9 Hz), 129.1, 128.9–128.5 (m, 3C), 128.2 (d, J=8.5 Hz), 128.0 (d, J=8.1 Hz), 126.0, 120.9 (q, J=257.0 Hz), 120.7 (2C). MS(EI): m/z(%)=344.1 (100) [M^+], 275.1 (38) [M^+–3 F], 257.1 (48) [M^+–OCF_3], 170.1 (58) [M^+–3 F–PPh]. HRMS for $C_{19}H_{12}NaOP$: calcd 367.0470; found 367.0510.

*4.2.9. 6-Phenyl-6H-benzo[2,3]phosphindolo[4,5-d][1,3]dioxole (**4a**).* Yellow oil (96%). ^{31}P NMR (161 MHz, $CDCl_3$): δ (ppm)=−5.5. ^1H NMR (300 MHz, $CDCl_3$): δ (ppm)=8.02 (dd, J=7.7, 0.6 Hz, 1H), 7.6–7.5 (m, 1H), 7.38 (td, J=7.5, 1.2 Hz, 1H), 7.3–7.0 (m, 7H), 6.77 (dd, J=7.8, 2.4 Hz, 1H), 6.07 (s, 2H). ^{13}C NMR (75 MHz, $CDCl_3$): δ (ppm)=148.8, 143.0–142.9 (m, 2C), 141.2 (d, J=1.4 Hz), 137.1 (d, J=20.5 Hz), 135.3 (d, J=2.7 Hz), 132.4 (d, J=20.2 Hz, 2C), 130.2 (d, J=22.0 Hz), 129.2, 128.8–128.6 (m, 3C), 127.4 (d, J=7.7 Hz), 126.4 (d, J=3.8 Hz), 124.7, 123.8 (d, J=24.3 Hz), 108.1 (d, J=8.8 Hz), 101.6. MS(EI): m/z(%)=304.1 (100) [M^+], 274.2 (47) [M^+–OCH_2], 227.1 (24) [M^+–Ph], 152 (11) [M^+–2 Ph]. HRMS for $C_{19}H_{13}NaO_2P$: calcd 327.0545; found 327.0574.

*4.2.10. 2,2-Difluoro-6-phenyl-6H-benzo[2,3]phosphindolo[4,5-d][1,3]dioxole (**4b**).* Yellow oil (30%). ^{31}P NMR ($CDCl_3$, 161 MHz): δ (ppm)=−4.53. ^1H NMR (300 MHz, $CDCl_3$): δ (ppm)=8.05 (d, J=7.7 Hz, 1H), 7.7–7.6 (m, 1H), 7.5 (td, J=7.5, 1.2 Hz, 1H), 7.4–7.3 (m, 2H), 7.3–7.1 (m, 5H), 7.00 (dd, J=8.0, 2.2 Hz, 1H). ^{13}C NMR (75 MHz, $CDCl_3$): δ (ppm)=144.3, 143.3 (d, J=4.8 Hz), 139.6, 138.5 (d, J=5.3 Hz), 135.8 (d, J=19.7 Hz), 132.5, 132.0 (t, J=256 Hz), 130.3 (d, J=21.9 Hz), 129.7, 129.2, 128.9–128.8 (m, 3C), 128.4–128.3 (m, 1C), 128.2 (d, J=25.0 Hz), 125.5 (d, J=24.1 Hz), 125.1, 123.9, 123.1, 108.5–108.3 (m, 1C). MS(EI): m/z(%)=340.1 (100) [M^+], 308.2 (15) [M^+–F–O], 273.2 (21) [M^+–OCF_2], 263.1 (34) [M^+–Ph], 234.2 (47) [M^+–PPh],169.1 (64) [M^+–PPh–OCF_2], 139.2 (80) [M^+–PPh–Ph–F].

*4.2.11. 2,2,3,3-Tetrafluoro-7-phenyl-3,7-dihydro-2H-benzo[2,3]phosphindolo[4,5-b][1,4]dioxine (**4c**).* Orange solid (45%). Mp 84–85 °C. ^{31}P NMR ($CDCl_3$, 161 MHz): δ (ppm)=−7.11. ^1H NMR (300 MHz, $CDCl_3$): δ (ppm)=8.34 (d, J=7.9 Hz), 7.36 (t, J=6.7 Hz), 7.46 (td, J=7.6, 1.2 Hz), 7.4–7.3 (m, 2H), 7.3–7.1 (m, 6H), 7.03 (dd, J=8.2, 2.3 Hz, 1H). ^{13}C NMR (75 MHz, $CDCl_3$): δ (ppm)=143.5 (d, J=2.9 Hz), 141.0 (d, J=4.4 Hz), 140.8 (d, J=1.1 Hz), 138.1, 135.1 (d, J=19.4 Hz), 134.5, 133.0, 132.8, 132.5 (d, J=4.3 Hz), 130.4 (d, J=22.3 Hz), 129.9, 129.3, 129.2, 129.0, 128.3 (d, J=8.1 Hz), 126.8 (d, J=23.4 Hz), 126.4, 116.6 (d, J=8.5 Hz), 112.5 (ttd, J=269.3, 81.0, 16.0 Hz, 2C). MS(EI): m/z(%)=390.1 (100) [M^+], 359.2 (29) [M^+–O–F], 313.1 (67) [M^+–Ph], 295.2 (14) [M^+–Ph–F], 202.2 (12) [M^+–PPh–CF_2–O–F], 169.1 (24) [M^+–PPh–Ph–2 F], 157.1 (44) [M^+–PPh–Ph–CF_2].

4.3. $^{31}P\{^1H\}$ NMR experiments for preparation of phosphole selenide compounds 6

To an NMR tube charged with 20 mg of phosphole and 20 mg of selenium was added 1 mL of $CDCl_3$. Samples were kept under argon during 24 h before being analyzed in $^{31}P\{^1H\}$ NMR experiments. ^{31}P NMR shifts and ^{31}P–^{77}Se coupling constants are reported in Table 2.

4.4. General procedure for the catalytic hydroformylation reactions

The catalyst precursor [$Rh(CO)_2acac$] (0.0236 mmol) and the ligand (0.0473 mmol) were dissolved in 30 mL of toluene under nitrogen. The substrate (23.6 mmol) and the internal standard (5.13 mmol of decane) were added to the solution. The reaction mixture was transferred into the autoclave 90 mL inox (TOP INDUSTRIE), which was flushed several times with H_2/CO gas, and the mixture was stirred at 200 rpm at room temperature. The autoclave was pressurized to an initial 10 bar pressure of syngas (CO/H_2=1:1), heated to the required temperature and then pressurized at 30 bar. The reaction mixture was stirred at 1000 rpm for the desired time and the pressure was adjusted to 30 bar permanently. After the catalytic reaction, the autoclave was then cooled and slowly depressurized. A sample was analyzed by GC (Perkin–Elmer Stabilwax®-AD equipped with a column (30 m length, 0.25 mm inner diameter and 0.25 μm film thickness), 14 psi He as carrier gas and FID detector).

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18. As already explained, dibenzophospholes of Table 1 were previously synthesized in Ref. 17. Since their synthesis in the present report follows a different procedure, the latter is described and accompanied with the full characterization data and corresponding NMR spectra.
19. The minimum barrier for atropoisomerism is defined to be of 23 kcal/mol. Atropoisomerism in the compounds of Table 1 would arise from the repulsion of both substituents ortho to the biarylic junction. However, 1) in dibenzophospholes, the two *ortho*-substituents are further in comparison with the corresponding biphenyls, and 2) none of the substituents here is sufficiently bulky to cause repulsion from the opposed hydrogen substituent and an out-of-plane deviation leading to atropoisomerism; see Lunazzi, M.; Mancinelli, A.; Mazzanti, S.; Lepri, R.; Ruzziconi, M.; Schlosser, M. *Org. Biomol. Chem.* **2012**, *10*, 1847–1855 and references cited therein.
20. The comparison of the net donating abilities (including both σ-donor ability and π-acceptor strength) by recording the IR frequency of CO in dicarbonyl complexes $[RhCl(L)(CO)_2]$ is usually not very significant in a phosphole ligand series; see: Ref. 7f.
21. The magnitude of the $^{31}P–^{77}Se$ coupling constant provides a measure of σ-basicity of the parent P-ligand through an inverse relationship between σ-basicity and the value of $^{1}J_{P–Se}$ (a) Allen, D. W.; Taylor, B. F. *J. Chem. Soc., Dalton Trans.* **1982**, *1*, 51–54; (b) Socol, S. M.; Verkade, J. G. *Inorg. Chem.* **1984**, *23*, 3487–3493; (c) Barnard, T. S.; Mason, M. R. *Organometallics* **2001**, *20*, 206–214.
22. Ligand **5** was prepared as its borane complex according to Ref. 6, followed by deprotection using DABCO in toluene.
23. Although dibenzophosphole-based ligands have been widely used in hydroformylation, **3a** has been studied for the Rh-mediated hydroformylation of styrene using a different catalytic system (see Ref. 5c). It has never been used as a ligand in the Rh-catalyzed hydroformylation of methylstyrene and octene.
24. No demetallation was observed after the catalytic reaction even when only 2 equiv of ligand per rhodium were used.
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