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Steric and electronic properties in bicyclic phosphines. Crystal and molecular structures of Se = Phoban-Q(Q = C_2, C_3Ph, Cy and Ph)

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Abstract

Reacting a series of the bicylic Phoban-Q (9-Q-9-phosphabicyclo[3.3.1]nonane and 9-Q-9-phosphabicyclo[4.2.1]nonane) derivatives (Q = alkyl, cyclo alkyl, aryl) with KSeCN results in the formation of the corresponding phosphine selenides. The first order phosphorus–selenium coupling constants, $^1J_{P-Se}$, ranges from 682 to 689 Hz for the [3.3.1] isomers and from 703 to 717 Hz for the [4.2.1] isomers indicating the former to be significantly more electron rich. The crystal structures of Se = Phoban[3.3.1]-Q (Q = CH_2CH_3, C_3H_6Ph, Cy, and Ph) and Se = Phoban[4.2.1]-Q (Q = Cy and Ph) are reported and reveal P=Se bond distances ranging from 2.1090(9) to 2.1245(7) Å. For Q = Cy and Ph the two isomers ([3.3.1] and [4.2.1]) co-crystallise in the same crystal enabling the determination of the molecular structures for both from the same data collection. The cone angles for all ligand derivatives were determined according to the Tolman model but by using the actual P–Se bond distances and were found to be virtually identical ranging from 165° to 175°. Changes in the Q substituent have a minor effect on the overall steric and electronic properties of the Phoban family of ligands and can be used to manipulate physical properties without changing the chemical properties significantly.

Keywords: Phoban; Phosphine selenides; Crystal structures; Electronic properties

1. Introduction

In 1969 Shell Oil Company patented [1] a special class of tertiary organophosphines as ligands for cobalt hydroformylation. These ligands could be described as bicyclic heterocyclic tertiary phosphines where the phosphorus atom is a member of a bridge linkage, but not a bridgehead atom. The smallest phosphorus containing ring should contain at least five atoms, see Scheme 1.

Where *y* and *z* represents positive integers whose sum is from 2 to 3 and each of which has a minimum value of 1 and R represents hydrogen and lower alkyl groups from 1 to 4 carbons. The third substituents, Q, may consist of only carbon and hydrogen, or contain a functional group such as carbonyl, carboxylic, nitro, amino, hydroxyl, cyano, sulfonyl and sulfoxyl groups. A special family of these ligands (Phoban) are derived from *cis*,*cis*-1,5-cyclooctadiene according to Scheme 2.

Q may be hydrogen or any of the substituents mentioned above. Two structural isomers are obtained from the reaction representing symmetrical and unsymmetrical addition to the double bonds resulting in the 9-phosphabicyclo[3.3.1]nonane and 9-phosphabicyclo[4.2.1]nonane isomers, respectively. These ligands rendered exceptional qualities to the catalyst system and have been considered the benchmark for modified cobalt hydroformylation ever since. It was claimed [1] that hydroformylation of 1-dodecene using a mixture of 9-eicosyl-9-phosphabicyclo[4.2.1]nonane and 9-eicosyl-9-phosphabicyclo[3.3.1]-nonane (Phoban-C_{20}) at 183 °C, 70 bar, H_2:CO of 2:1, 6 h, and P:Co = 1.5:1 resulted in 98.5% conversions of

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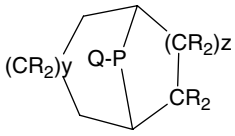
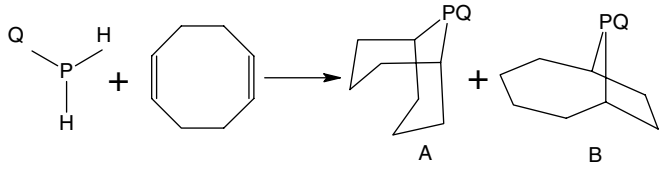


Scheme 1. Diagrammatical representation of the generic SHELL ligands.



Scheme 2. Formation of [3.3.1] and [4.2.1] Phoban derivatives by the radical addition of *cis*,*cis*-1,5-cyclooctadiene to a primary phosphine, QPH_2.

the olefin to yield 86.9% of the C13 alcohol with a linearity of 89%.

In addition to cobalt catalysed hydroformylation bidentate derivatives of this ligand family has since been shown to also display exceptional hydroformylation properties in platinum [2,3] and palladium [4–6] catalyst systems. Additional activity have also been demonstrated in carbonylation, [7] metathesis [8] and asymmetric catalysis [9]. The coordination chemistry, especially in palladium system, has been well documented [10].

It is well known that the steric and electronic properties of phosphine ligands have a major influence on the properties they induce on the metal centre. These properties are however difficult to separate and quantify since they are so closely related. Since acid base titrations in organic media is quite cumbersome [11,12] alternative experimental ways of quantifying the electronic properties of phosphine ligands have been developed to give easy spot-check indications of how a given phosphine compares with more well-know examples such as PPh_3 or PBu_3. Popular methodologies include making use of NMR or IR measurements of first order coupling constants [13–16] or CO stretching frequencies [17–19].

Several models [20] have also been developed to express the steric demand of a ligand with, although fairly simplistic, the Tolman cone angle [17] still the most widely used due to its ease of calculation from molecular models or crystallographic data.

As part of a continuous study [21–24] on the hydroformylation performance of different ligand classes in modified cobalt catalysis the Phoban phosphine family of ligands were also investigated systematically. In this paper, we report our results with regards to the synthesis and electronic properties of a range of these ligands as investigated through their corresponding $^1J_{P-Se}$ coupling constants. In addition the steric properties, as described by the Tolman model, were determined for selected derivatives from crystallographic studies of their corresponding selenides.

Edwards and co-workers assumed [10] that the electronic properties of the two Phoban isomers would be similar while there may be some steric differences due to ring strain within the molecules. Based on gas phase protonation calculations [25] of Phoban[3.3.1]-Ph they qualitatively concluded it to have a higher gas phase basicity than either PMe_2Ph or PPh_3. This is contrary to the results presented here where we unambiguously showed the steric differences to be of minor importance while the electronic properties of the two isomers are significantly different.

2. Experimental

2.1. Equipment and chemicals

All manipulations involving air sensitive compounds were conducted in Schlenk glassware under an argon atmosphere using degassed solvents. ^1H, ^{13}C and ^{31}P NMR spectra were recorded as $CDCl_3$ solutions on a Varian Unity spectrometer operating at 400.428, 100.698 and 162.109 MHz, respectively; the spectra were calibrated relative to the solvent peaks for ^1H and ^{13}C and relative to an external standard of 85% H_3PO_4 for ^{31}P. Elemental analysis of the Phoban selenides and additional ^1H and ^{13}C NMR data are available as supplementary material. The boiling points were determined using Simdist analysis and the ligands were routinely purified by Kugelrohr distillation.

Ethylene (Linde, 99.95%), 1-pentene (Sasol, 99.4%), allyldimethylamine (Fluka, 98%), allylbenzene (Aldrich, 98%), $CDCl_3$ (Aldrich, 99.8%), *cis*,*cis*-1,5-cyclooctadiene (Fluka, 98%), VAZO (Wako), H_2PCy (Cytec, 40% in toluene), Phoban-H (Rhodia, 60% m/m in toluene, mixture of isomers [3.3.1]:[4.2.1] 60:40), Phoban-C_{10} (Rhodia), Phoban-C_{12} (Rhodia), Phoban-C_{20} (Rhodia), Ph-Li (Merck, 20%, 2 M in cyclohexane:diethylether 7:3), BuLi (Aldrich, 2.5 M in hexanes), PCl_3 (Aldrich, 99%), fluorobenzene (Aldrich, 99%), iodobenzene (Fluka, >99%), NEt_3 (Aldrich 99.5%), $Pd(PPh_3)_4$ (Aldrich, 99%) and KSeCN (Aldrich, 97%) were used as received. All solvents were of the highest purity available and were dried and purified according to standard procedures [26] where applicable.

2.2. Preparation of Phoban-Q derivatives

Several distinct methodologies were used for the synthesis of the Phoban derivatives with a representative example for each given below. Derivatives with their abbreviations, ^{31}P NMR data, boiling points, method of preparation and the reaction yields for all phosphines are given in Table 1.

2.2.1. Method A: radical addition of an olefin to Phoban-H

Phoban-C_5: A toluene solution of Phoban-H (60 mL, 51.94 g 60% solution in toluene, 31.14 g Phoban-H; 219 mmol) and 1-pentene (37 mL, 23.15 g, 330 mmol) were placed in a 300 mL autoclave containing VAZO (4 g) and were thoroughly flushed with argon. The reactor was sealed and heated to 100 °C overnight. After 16 h conversion to Phoban-C_5 was complete as measured by ^{31}P NMR and the toluene and excess olefin were removed under vacuum.

Table 1
^{31}P NMR data for selected Phoban derivatives, ($^{1}J_{P-Se}$/Hz)

Q	Abbreviation	Source	Yield		Phoban-Q (ppm)		bp (°C)	Se = Phoban (ppm)		$^{1}J_{P-Se}$ (Hz)	
			g	%	[3.3.1]	[4.2.1]		[3.3.1]	[4.2.1]	[3.3.1]	[4.2.1]
H	Phoban-H	Rhodia			−48.35	−54.23	220	–	–	–	–
Cl	Phoban-Cl		See text		89.85	135.78	251	–	–	–	–
C_2H_5	Phoban-C_2	A	30.20	81	−31.49	5.44	240	37.63	61.65	688	709
C_5H_{11}	Phoban-C_5	A	36.73	79	−35.13	0.64	297	35.06	58.88	686	709
$C_{10}H_{23}$	Phoban-C_{10}	Rhodia			−35.32	0.59	374	34.65	58.66	688	710
$C_{12}H_{25}$	Phoban-C_{12}	Rhodia			−35.33	0.58	397	35.72	59.75	687	710
$C_{20}H_{41}$	Phoban-C_{20}	Rhodia			−35.58	0.54	475	35.72	59.76	687	710
C_3H_6Ph	Phoban-C_3Ph	A	42.19	74	−35.62	0.43	460	35.11	58.79	689	712
$C_3H_6NMe_2$	Phoban-C_3NMe_2	A	40.82	82	−34.98	1.04	319	35.52	59.20	687	709
C_6H_{11}	Phoban-Cy	B	See text		−24.82	13.13	322	42.90	69.12	682	703
C_6H_5	Phoban-Ph	B, C, D, E	See text		−23.23	7.90	321	27.78	51.94	689	717

In the case of Phoban-C_2 the reactor was pressurised with ethylene at room temperature to 50 bar and was subsequently heated overnight at 100 °C as described above. Isolated yields were in excess of 70% for all ligands prepared in this way.

2.2.2. Method B: radical addition of cis,cis-1,5-cyclooctadiene to H_2PCy

Phoban-Cy: The H_2PCy (30 mL, 26.15 g 40% solution in toluene, 10.45 g H_2PCy, 90 mmol) and *cis*,*cis*-1,5-cyclooctadiene (17 mL, 14.6 g, 135 mmol) was placed in a 300 mL autoclave containing VAZO (3 g) and was thoroughly flushed with argon. The reactor was sealed and heated to 100 °C for 36–48 h with the addition of fresh VAZO (2 g) after every 12 h. The reaction progress was followed using ^{31}P NMR. When no further conversion to products was observed the toluene and excess olefin were removed under vacuum and the residues purified as described above. An isolated yield of 63% (12.72 g) were obtained using this methodology.

2.3. Chlorination of Phoban-H with PCl_3

Phoban-Cl: PCl_3 (13 mL, 20.46 g, 149 mmol) was added drop-wise to a toluene solution of Phoban-H (50 mL, 43.5 g 60% solution, 26.1 g Phoban-H; 184 mmol) at room temperature. After the addition was complete the reaction mixture was stirred for 1 h. All volatile components were removed under vacuum and the remaining orange solids were repeatedly extracted with diethyl ether (3×30 mL). The solvent fractions were combined and filtered through a celite plug. The material obtained in this way was normally of sufficient purity for further use, yield 19.91 g, 61% as determined by ^{31}P NMR.

2.3.1. Method C: action of phenyllithium on Phoban-Cl

Phoban-Ph: Ph-Li (10 mL, 2 M, 20 mmol) was added drop-wise to an ether solution of Phoban-Cl (5.0 mL, 3 M, 15 mmol) at −78 °C over 30 min. The reaction mixture was allowed to reach room temperature over 90 min and was subsequently stirred overnight. ^{31}P NMR analysis of the reaction mixture indicated 71% (2.32 g) conversion to Phoban-Ph. The reaction mixture was quenched by the addition of aqueous NH_4Cl, the organic layer was separated and filtered through a short silica plug and subjected to Kugelrohr distillation for purification.

2.3.2. Method D: action of Phoban-Li on fluorobenzene

Phoban-Ph: Butyl lithium (3.9 mL, 2.5 M, 9.75 mmol) was added drop-wise to a solution of Phoban-H (1 mL, 5.63 M in hexane, 5.63 mmol) in diethyl ether (15 mL) at −78 °C. The mixture was stirred for 20 min while it was allowed to heat up to about −30 °C followed by the addition of fluorobenzene (0.7 mL, 7.44 mmol). The reaction mixture was allowed to warm up to 5 °C during which time the initial light yellow solution changed to a deep red. After stirring for another 1 h degassed aqueous ammonium chloride was added and the two phases were separated. The organic phase was dried with anhydrous sodium sulphate and filtered through a short silica plug to remove some phosphine oxides that formed during the reaction. The resultant mixture was shown to contain 63% (0.77 g) of the desired ligand and 31% of Phoban-H by ^{31}P NMR analysis.

2.3.3. Method E: palladium catalysed P–C coupling

Phoban-Ph: A reaction mixture containing Phoban-H (24 mL, 20.59 g 60% solution in toluene, 12.35 g Phoban-H, 86.9 mmol), iodobenzene (10 mL, 18.23 g, 89.3 mmol), NEt_3 (12 mL, 8.71 g, 86.1 mmol), $[Pd(PPh_3)_4]$ (250 mg, 0.022 mmol) and acetonitrile (15 mL) was prepared in an autoclave under an argon atmosphere and heated to 120 °C for 96 h. ^{31}P NMR analysis of the reaction mixture indicated 83% (15.74 g) of all the phosphorus containing components to correspond to the desired product. The reaction mixture was allowed to cool to room temperature and degassed toluene (30 mL) was added to precipitate the bulk of the $[Et_3NH]I$ which was subsequently removed by filtration. All volatiles were removed under vacuum and the final purification was done by Kugelrohr distillation.

2.4. Preparation of Se = Phoban-Q derivatives

All Se = Phoban-Q derivatives were prepared according to the method for Se = Phoban-C_2 described below. For all

the Phoban derivatives the yields were quantitative if oxidation were excluded, ^{31}P NMR data is summarised in Table 1.

[Se = Phoban-C$_2$]: A toluene solution (5 mL) of Phoban-C$_2$ (50 mg, 0.30 mmol) was treated with KSeCN (100 mg, 0.70 mmol) dissolved in methanol (5 mL) in an inert atmosphere and the resulting mixture was brought to reflux using a heat gun. The solution was stirred for 10 min and allowed to cool to room temperature. Thereafter the solvents were removed under vacuum and the solid residues extracted with chloroform. Filtration and evaporation of the chloroform gave the desired compound as a white solid in quantitative yield as determined by ^{31}P NMR.

2.5. Crystallography

Crystals suitable for X-ray diffraction were obtained from slow evaporation of the NMR samples. The data collection was done on either a Bruker X8 ApexII 4K Kappa CCD or a Bruker SMART 1K CCD diffractometer using ϕ-scans and Mo Kα (0.71073 Å) radiation. All reflections were merged and integrated using SAINT-Plus and XPREP [27] and were corrected for Lorentz, polarisation and absorption effects using multi-scans. After completion of the data collection the first 50 frames were repeated to check for decay of which none was observed. The structures were solved by the direct method and refined through full-matrix least squares cycles using the SHELXL97 [28] software package with $\sum(|F_o| - |F_c|)^2$ being minimised. All non-H atoms were refined with anisotropic displacement parameters while the H atoms were constrained to parent sites using a riding model. The co-crystallisation of both the [3.3.1] and [4.2.1] isomers in Se = Phoban-Ph and Se = Phoban-Cy were refined with the occupancy of the cyclooctyl component as a free variable. Bond and anisotropic restrains were used to keep the refinements of the disorders stable. The graphics were done with DIAMOND [29].

Cone angle calculations were done according to the Tolman model as described before [30] but by using the actual P–Se bond distances. In all cases a hydrogen atom on the

Table 2
Crystallographic data and refinement parameters

Q	C$_2$	C$_3$Ph	Cy	Ph
Empirical formula	$C_{10}H_{19}PSe$	$C_{17}H_{25}PSe$	$C_{14}H_{25}PSe$	$C_{14}H_{19}PSe$
Formula weight	249.18	339.30	303.27	297.22
Crystal system	Triclinic	Triclinic	Tetragonal	Orthorhombic
Space group	$P\bar{1}$	$P\bar{1}$	$I\bar{4}$	$Pca2_1$
a (Å)	6.9852(14)	6.9810(2)	19.8814(3)	10.9284(5)
b (Å)	7.8509(16)	10.5285(2)	19.8814(3)	14.3690(7)
c (Å)	10.750(2)	11.9066(3)	7.0463(3)	8.3785(4)
α (°)	90.31(3)	68.5080(10)	90	90
β (°)	93.59(3)	83.8120(10)	90	90
γ (°)	108.13(3)	84.8940(10)	90	90
V (Å^3)	559.0(2)	808.38(3)	2785.19(13)	1315.68(11)
Z	2	2	8	4
D_{calc} (g cm^{-3})	1.480	1.394	1.446	1.501
μ (mm^{-1})	3.452	2.408	2.785	2.947
T (K)	293(2)	150(2)	100(2)	100(2)
T_{max}/T_{min}	0.794/0.545	0.729/0.584	0.829/0.531	0.891/0.401
F(000)	256	352	1264	608
Crystal size (mm)	0.20 × 0.14 × 0.07	0.25 × 0.19 × 0.14	0.26 × 0.08 × 0.07	0.3 × 0.10 × 0.04
θ limit/°	1.90–28.29	1.84–28.37	1.45–28.40	1.42–28.31
Index ranges	$-8 \leqslant h \leqslant 9$, $-8 \leqslant k \leqslant 10$, $-14 \leqslant l \leqslant 13$	$-9 \leqslant h \leqslant 9$, $-13 \leqslant k \leqslant 14$, $-15 \leqslant l \leqslant 14$	$-26 \leqslant h \leqslant 20$, $-26 \leqslant k \leqslant 25$, $-9 \leqslant l \leqslant 9$	$-14 \leqslant h \leqslant 12$, $-19 \leqslant k \leqslant 19$,$-11 \leqslant l \leqslant 9$
Reflections collected/ Unique	3926/2706	9213/4035	9887/3421	9554/3187
R_{int}	0.021	0.018	0.028	0.032
Observed reflections [$I > 2\sigma I$]	1942	3616	3106	2747
Data/restraints/ parameters	2706/0/110	4035/0/172	3421/16/134	3187/17/134
Absolute structure parameter			0.011(10)	0.063(11)
Goodness-of-fit	1.004	1.083	1.047	1.025
R ($I > 2\sigma I$) R^a	0.0361	0.0460	0.0325	0.0287
wR^b	0.0756	0.1114	0.0682	0.0607
R (all data) R^a	0.0646	0.0516	0.0383	0.0377
wR^b	0.0856	0.1145	0.0700	0.0662
$\Delta\rho_{max}$; $\Delta\rho_{min}$ (e Å^{-3})	0.473; −0.292	3.560; −1.174	0.729; −0.347	0.539; −0.228

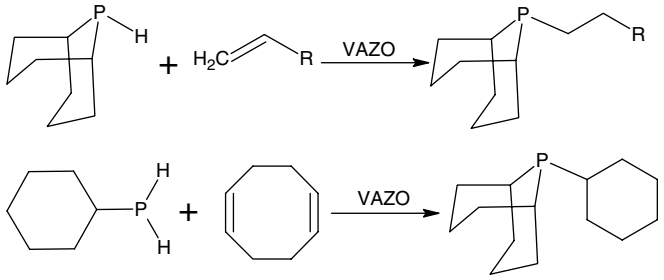
[a] $R = [(\sum \Delta F)/(\sum F_o)]$.
[b] $wR = \sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]^{1/2}$.

second carbon of the "Q" substituents were used for the respective half angle measurement. A summary of the general crystal data and refinement parameters is given in Table 2.

3. Results and discussion

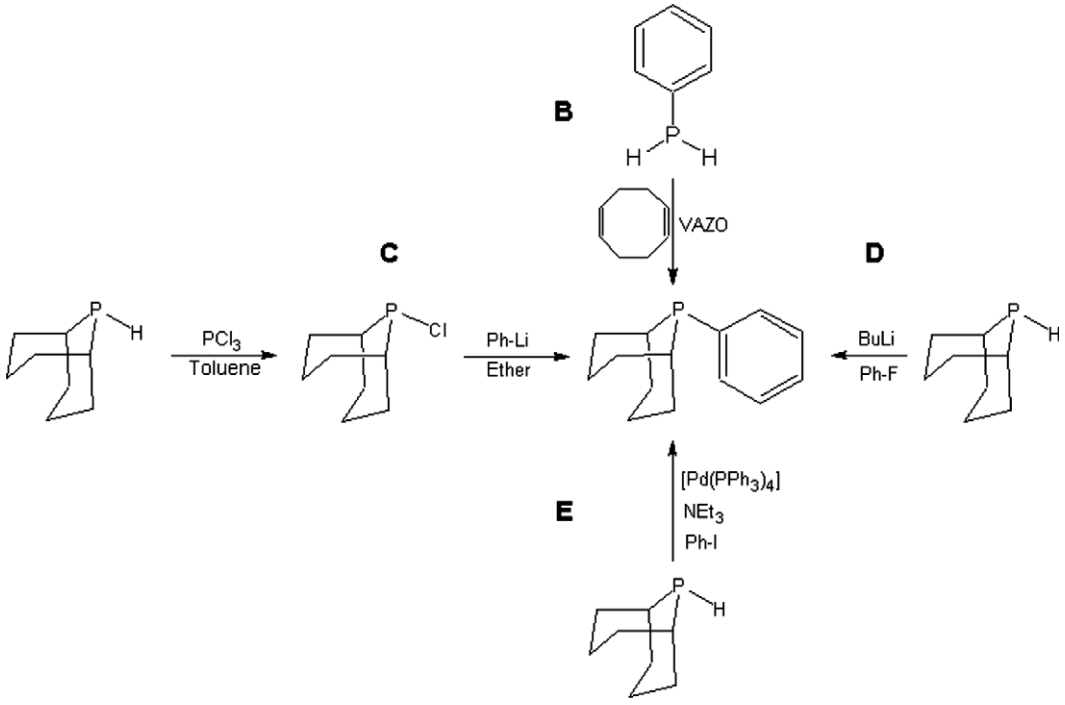
The syntheses of bicyclic tertiary phosphine ligands through the radical addition of a 1° – or 2° phosphine to an appropriate diene – or alkene have been well established [31], see Scheme 3. In the case of Phoban-Cy the reaction of cyclohexene with Phoban-H was very slow (method A) and resulted in significant formation of undesired side products such as P–P dimers. Radical addition of *cis*,*cis*-1,5-cyclooctadiene to H_2PCy (method B) however proceeded smoothly and produced Phoban-Cy in acceptable yields.

The synthesis of Phoban-Ph proved more challenging than was originally anticipated and several strategies were evaluated as reported in the experimental section. Method B was performed on small scale and gave satisfactory results, but the unavailability of $PhPH_2$ in South Africa implied the in-house preparation of gram quantities of the 1° phosphine which was rather abandoned due to safety considerations. Phoban-Cl was prepared in moderate yields by a modification of the procedure of Weferling [32] and used without further purification. Two organolithium approaches were evaluated with the P atom acting either as the electrophile (P–Cl, method C) or as the nucleophile (P–Li, method D), see Scheme 4. Both methods were moderately effective, but especially method C yielded some P–P dimeric species as a result of lithium/halogen scrambling. Additional unidentified side products were also observed and may be linked to deprotonation on one or both of the two 2 °C atoms of the cyclooctyl group attached directly to P. Even though nucleophilic aromatic substitution is normally an unfavourable process the use of fluorobenzene as electrophile in the preparation of aryl phosphines [33] has been demonstrated. Method D is superior to Method C since the additional preparation of Phoban-Cl can be circumvented.



Scheme 3. Synthetic methods A and B as illustrated for the [3.3.1] Phoban isomer.

The palladium catalysed P–C coupling reaction (Method E) was performed according to a modification of the procedure reported by Stelzer and coworkers [34], see Scheme 4. This methodology is usually employed when functional groups incompatible with Grignard or organolithium reagents are present in some of the reactants. This protocol has the added advantage that it is not particularly sensitive towards moisture and only inert conditions needed to be maintained to avoid oxidation of the phosphine. The iodobenzene, NEt_3 and acetonitrile were thus



Scheme 4. Summary of synthetic methods to prepare Phoban-Ph as illustrated for the [3.3.1] isomer. Radical addition of *cis*,*cis*-1,5-cyclooctadiene to $PhPH_2$, method B; the use of P as electrophile and nucleophile respectively methods C and D and the use of Pd as catalyst to facilitate the P–C coupling reaction, method E.

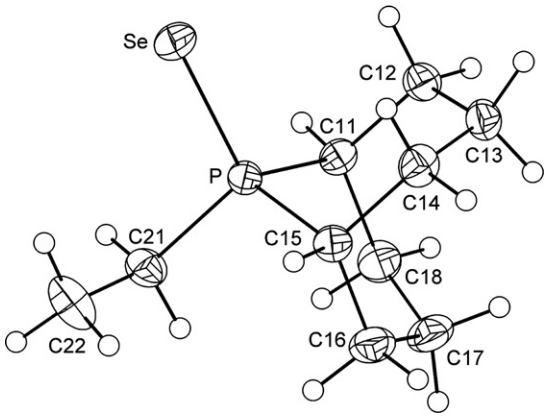


Fig. 1. Molecular diagram showing the numbering scheme and thermal displacement ellipsoids (30% probability level) for Se = Phoban[3.3.1]-C_2; hydrogen atoms are of arbitrary size.

used straight from the bottle without any further purification or drying steps performed on it. Even though this procedure took significantly more time than methods C and D it was not labour intensive and is superior in terms of product yield while no detectable side products were observed.

The direct reaction of KSeCN with tertiary phosphines to yield the corresponding phosphine selenides has been reported previously [35,16]; the reactions proceed smoothly and near quantitative yields were obtained in all cases.

All reaction products were unambiguously characterised by means of their very characteristic ^{31}P NMR spectra clearly exhibiting the coupling associated with the P–Se interaction (^{77}Se 7.58% spin 1/2), see Table 1. In addition X-ray crystallographic studies were performed on representative derivatives; see Figs. 1–4 for the molecular diagrams and numbering schemes and Table 3 for selected geometrical parameters. Additional analytical data, including ^{1}H- and ^{13}C NMR and elemental analysis, are available as supplementary material. In most cases the ^{1}H NMR data did not provide much additional information due to severe overlap in the CH and CH_2 region (1.4–2.4 ppm). In a few

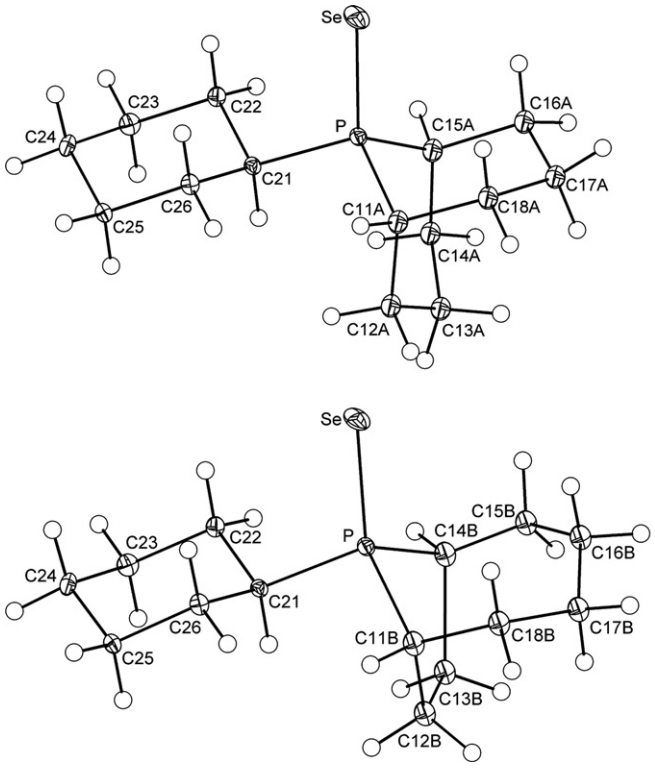


Fig. 3. Molecular diagrams showing the numbering schemes and thermal displacement ellipsoids (30% probability level) for Se = Phoban[3.3.1]-Cy (top, 68%) and for Se = Phoban[4.2.1]-Cy (bottom, 32%) co-crystallising on the same position in the unit cell; hydrogen atoms are of arbitrary size.

cases comparison between isolated signals (Ph in Q = Ph and C_3Ph and NMe_2 in Q = C_3NMe_2) and the protons in the above mentioned region proved useful. The ^{13}C NMR spectra were significantly more informative and showed clear distinctions between the two six-membered rings of the bicycle; i.e. adjacent to the Q-substituent or the lone-pair (or Se in the case of the P(V) selenides) respectively. In the [4.2.1] isomers the ^{13}C NMR evidence also suggested the Q substituent to be adjacent to the five-membered ring while the larger seven-membered ring is adjacent

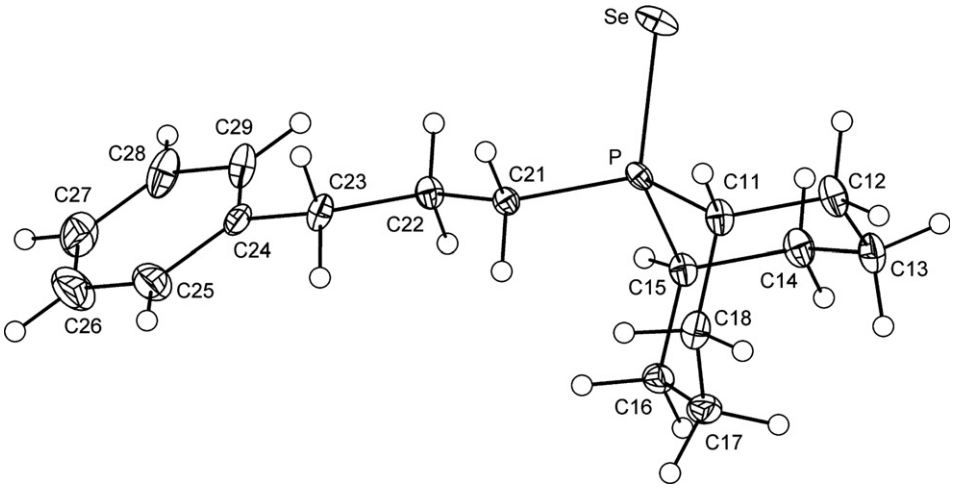


Fig. 2. Molecular diagram showing the numbering scheme and thermal displacement ellipsoids (30% probability level) for Se = Phoban[3.3.1]-C_3Ph; hydrogen atoms are of arbitrary size.

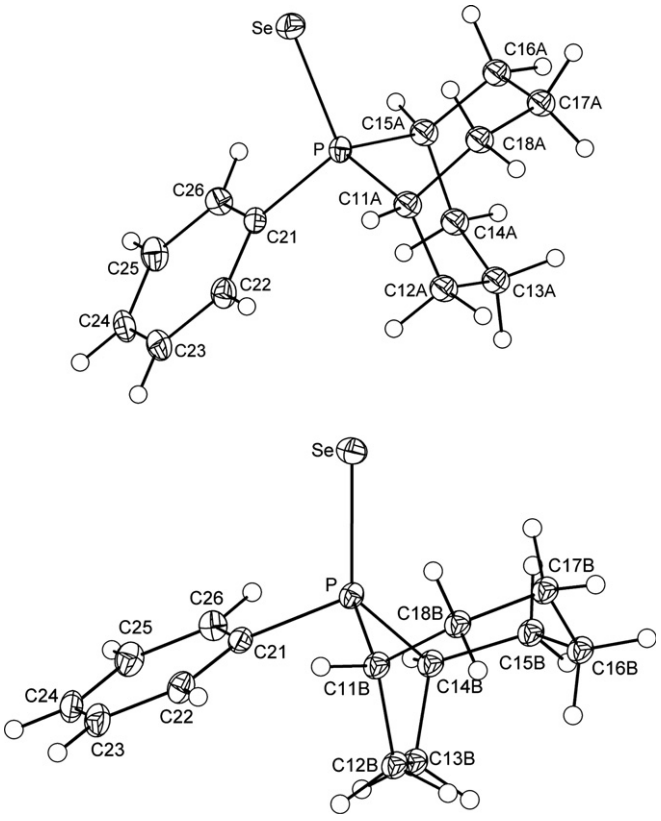


Fig. 4. Molecular diagrams showing the numbering schemes and thermal displacement ellipsoids (30% probability level) for Se = Phoban[3.3.1]-Ph (top, 60%) and for Se = Phoban[4.2.1]-Ph (bottom, 40%) co-crystallising on the same position in the unit cell; hydrogen atoms are of arbitrary size.

to either the lone pair or the Se atom. This observation was also confirmed by the structures of the Phoban[4.2.1]-Ph and Cy derivatives presented here. The $^1J_{PC}$ coupling constants in the parent P(III) molecules were in the 10–18 Hz range while in the P(V) selenides it was in the 35–45 Hz range clearly reflecting the lower electron density of the latter.

Se = Phoban[3.3.1]-C_2 and Se = Phoban[3.3.1]-C_3Ph both crystallise on general positions in the triclinic space group $P\bar{1}$. The calculation of the cone angle for the latter was based on the half angle to H22A even though larger angles were obtained to H28 and H29. This was done based on the closer vicinity of the former that should be a more realistic reflection of the steric impact the ligand would have on a coordinated metal.

Se = Phoban[3.3.1]-Cy and Se = Phoban[4.2.1]-Cy co-crystallised on a general position in the non-centric tetragonal space group $I\bar{4}$, the absolute structure parameter of 0.010(12) indicate that the correct isomers were refined. During the initial refinement of only the [3.3.1] isomer high

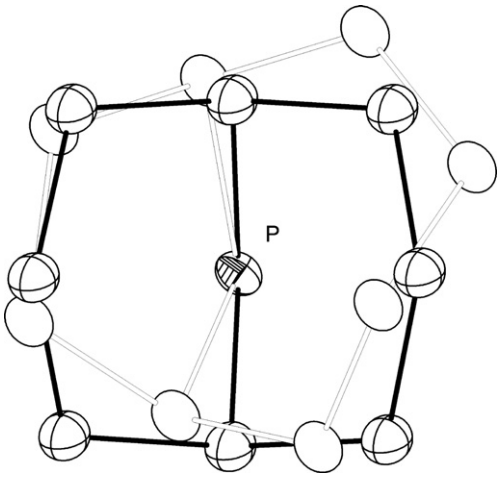


Fig. 5. Molecular diagram illustrating the disordered packing between Se = Phoban[3.3.1]-Ph (solid bonds, 60%) and Se = Phoban[4.2.1]-Ph (open bonds, 40%) on the same position in the unit cell. The Se and H atoms as well as the Ph ring have been omitted for clarity.

Table 3
Selected geometrical parameters for Se = Phoban[3.3.1]-Q (Q = C_2, C_3Ph, Cy and Ph) and for Se = Phoban[4.2.1]-Ph

Bond/Angle	C_2 (Å/°)	C_3Ph (Å/°)	[3.3.1]Cy (Å/°)	[4.2.1]Cy (Å/°)	[3.3.1]Ph (Å/°)	[4.2.1]Ph (Å/°)
P–Se	2.1171(9)	2.1245(7)	2.1160(9)	2.1160(9)	2.1090(9)	2.1090(9)
P–C(11)	1.824(3)	1.816(3)	1.817(7)	1.922(13)	1.809(8)	1.863(12)
P–C(14)				1.89(2)		1.853(8)
P–C(15)	1.812(3)	1.813(3)	1.810(10)		1.837(6)	
P–C(21)	1.817(3)	1.811(3)	1.832(3)	1.832(3)	1.816(3)	1.816(3)
Se–P–C(11)	115.22(9)	116.46(10)	112.78(18)	124.4(3)	116.6(2)	120.0(3)
Se–P–C(14)				120.6(4)		124.3(3)
Se–P–C(15)	114.98(10)	114.01(10)	114.3(2)		107.85(18)	
Se–P–C(21)	110.64(11)	110.39(9)	111.81(10)	111.93(10)	111.93(10)	111.93(10)
C(11)–P–C(14)				90.8(6)		93.4(4)
C(11)–P–C(15)	97.00(13)	97.71(14)	98.6(3)		98.4(3)	
C(11)–P–C(21)	108.30(14)	107.17(13)	109.0(2)	101.7(4)	111.6(2)	102.6(3)
C(14)–P–C(21)				103.7(5)		100.9(3)
C(15)–P–C(21)	109.85(14)	110.33(13)	109.6(2)		109.4(2)	
$(\theta/2)_1$	85.9	85.5	87.5	87.7	91.7	92.9
$(\theta/2)_2$	85.7	86.5	87.6	79.4	87.1	82.7
$(\theta/2)_Q$	86.4	85.4	88.1	88.1	71.7	71.7
θ_E	172	172	175	170	167	165

$(\theta/2)_n$ refers to the half angle to substituent n according to Tolman's definition.

thermal motion on the cyclooctyl backbone was encountered and during closer inspection it was found that it was actually both the [3.3.1] and the [4.2.1] isomers co-crystallising within the same structure also occupying the same position. The occupancy of the two isomers was refined to give a final value of 68% of the [3.3.1] isomer and 32% of the [4.2.1] isomer.

Se = Phoban[3.3.1]-Ph and Se = Phoban[4.2.1]-Ph co-crystallise on a general position in the non-centric orthorhombic space group $Pca2_1$, the absolute structure parameter of 0.063(11) indicate that the correct isomers were refined. In the original refinement the phenyl ring was well defined, but some high thermal motion was again encountered on the Phoban backbone. On closer inspection it became apparent that it was again both the [3.3.1] and the [4.2.1] isomers co-crystallising within the same structure also occupying the same position as encountered for the cyclohexyl derivative mentioned above (see Fig. 5). The occupancy of the two isomers was refined to yield 60% [3.3.1] and 40% of the [4.2.1] isomers, respectively.

In the first two cases crystals of the [3.3.1] isomers were obtain from the mixture of isomers present in the NMR solutions. This may be indicative of more crystalline properties associated with the symmetry of this isomer. No specific efforts have been made to intentionally target the isolation of either isomer even though we were fortunate enough to obtain crystals of both isomers in the same crystal for the latter two structures presented in this work.

The bicyclic cyclooctyl moiety displays a very similar geometry in all of the [3.3.1] isomers in such a way that the resulting two six-membered rings containing the P atom takes on the preferred chair conformation. All corresponding P–C bond lengths and Se–P–C and C–P–C angles are very similar for these structures, see Table 3. The geometry of the Se = Phoban[4.2.1]-Cy and Se = Phoban[4.2.1]-Ph isomers differ from the corresponding [3.3.1]-isomers with the most noticeable deviations in the P–C bond distances and the C–P–C angles. The strain in the five-membered ring of the [4.2.1] isomers result in C–P–C angles of only 90.8(6) and 93.4(4)°, respectively, with corresponding large Se–P–C angles of >120°. This deviation from an ideal tetrahedral geometry results in slightly longer than normal P–C bond distances as compared to the [3.3.1] isomers. In addition the deviation from the ideal geometry with resulting less effective orbital overlap and elongated P–C bonds should account for the [4.2.1] isomer being less electron rich than the [3.3.1] isomer.

The two instances of the Phoban isomers co-crystallising represent truly rare examples of random disorders and enabled us to obtain crystallographic data for both isomers from the same crystal structures. This phenomenon presents strong evidence that the steric demand of the two isomers is very similar as also evident from the cone angle calculations. As a result of the common geometry for the different derivatives the resulting cone angles were also very similar to that obtained from the other crystallographic studies. Selected geometrical and electronic properties obtained during this study are compared with representative data from the literature in Table 4.

It is generally accepted [41] that the coupling constant between two adjacent atoms is primarily governed by the Fermi-contact interactions between the respective s-orbitals. Electron withdrawing substituents results in an increase in the s-character of the phosphorous lone pair while electron donating substituents result in a decrease in s-character according to Bent's rule [42]. The two Phoban isomers differ significantly with regards to their electronic properties with ΔJ_{P-Se} values of 20–30 Hz for the derivatives reported here. The smaller values of 682–689 Hz corresponding to the [3.3.1] isomers indicate it to be significantly more electron rich than the [4.2.1] isomer that exhibits coupling constants in the 703–717 Hz range. For all derivatives the [3.3.1] isomer resonates upfield from the [4.2.1] isomer also confirming larger electronic shielding of the ^{31}P nucleus. The difference in chemical shifts of the isomers is in the range of 35 ppm for Phoban-Q and ~25 ppm for the Se = Phoban-Q derivatives, respectively, see Table 1.

It is expected that a decrease in the P=Se bond distance, resulting in more effective s-orbital overlap should correspond with an increase in the first order coupling constants. Although the P=Se bond distances are very similar for all molecules ($\Delta d = 0.019(1)$ Å) listed in Table 4, the first order coupling constants, however, differ considerably ($\Delta J_{P-Se} =$ 121 Hz), but not necessarily systematically with distance.

The difference in chemical properties of the [3.3.1] and [4.2.1] isomers as noted before was exploited to separate a mixture of 9-H-9-phosphabicyclo[3.3.1]nonane and 9-H-9-phosphabicyclo[4.2.1]nonane by a sequence of hydrophosphination/dehydrophosphination reactions [43]. Furthermore the difference in coordinating ability has been used to separate the isomers by selectively coordinating the [3.3.1] isomer by the addition of a metal to a solution containing both isomers [44,45]. This difference would also account for the increased reactivity in all cases where an increase in electron density has a beneficial effect. This is manifested in the preferred oxidation of the [3.3.1] isomer as well as the reaction with $SeCN^-$ where a two electron

Table 4
P=Se bond distances, $^1J_{P-Se}$ coupling constants and Tolman cone angles for selected phosphines

Phosphine	P–Se (Å)	$^1J_{P-Se}$ (Hz/$CDCl_3$)	Tolman (θ/°)	Reference
Phoban[3.3.1]-C_2	2.1171(9)	688	172	TW
Phoban[3.3.1]-C_3Ph	2.1245(7)	689	172	TW
Phoban[3.3.1]-Cy	2.1160(9)	682	175	TW
Phoban[4.2.1]-Cy	2.1160(9)	703	170	TW
Phoban[3.3.1]-Ph	2.1090(9)	689	167	TW
Phoban[4.2.1]-Ph	2.1090(9)	717	165	TW
PCy_3	2.108(1)	676	170	[36]
PMe_3	2.111(3)	684	118	[37]
P(2-Me-C_6H_4)$_3$	2.116(5)	708	194	[38]
PPh_3	2.106(1)	733	145	[39]
P(NMe_2)$_3$	2.120(1)	797	157	[40]

oxidation is required. During our investigation it was also qualitatively observed that the [3.3.1] isomer reacts preferentially with the $SeCN^-$ when <1 molar equivalent was added. Most notably the superior coordinating ability of the [3.3.1] isomer during cobalt hydroformylation catalyst was illustrated by high pressure NMR catalyst pre-forming studies [23] underlining the importance of this specific isomer in hydroformylation catalysis. Conversely is was noted that the Phoban[4.2.1]-Ph isomer is up to five times more active than the [3.3.1] isomer under identical conditions in some palladium catalysed carbonylation reactions [46].

The effect of the Q-substituent seems to be moderate as only minor differences could be induced by all groups evaluated. In this regard a maximum $^1J_{P-Se}$ of only 14 Hz could be induced between the [4.2.1] isomers for Q = Cy and Q = Ph; respectively the most electron donating and electron withdrawing substituents. The effect of the substituent seems to be slightly amplified in the [4.2.1] isomer as a difference of only 7 Hz was observed for the corresponding [3.3.1] isomers. In this regard the Q-substituent is available for manipulation of the physical properties (melting point, boiling point and solubility) of the Phoban ligands without affecting the chemical properties of the ligands drastically.

The findings in this report, for the first time, quantitatively established that the steric demands for the two Phoban isomers are very similar while the electronic properties are quite different. This is contrary to the intuitive notion that the ligands should be electronically similar while the [4.2.1] isomer should be more steric demanding than the [3.3.1] isomer [10].

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Appendix A. Supplementary material

CCDC 632825, 2632826, 632827 and 632828 contain the supplementary crystallographic data for Se = Phoban-[3.3.1]-C_2, Se = Phoban[3.3.1]-C_3Ph, Se = Phoban[3.3.1]/[4.2.1]-Cy and Se = Phoban[3.3.1]/[4.2.1]-Ph. These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ ccdc.cam.ac.uk. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jorganchem.2007.04.001.

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