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Oxide, Sulfide, Selenide, and Borane Derivatives of Indenylphosphines

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We report the preparation, isolation and characterization of oxide, sulfide, selenide, and borane derivatives of a series of indenylphosphines. Some members of the series had already been prepared, and we have completed the series. We have prepared (indenyl)_xPh_{3-x}PO (x = 1-3) for the oxide series, (indenyl)_xPh_{3-x}PS (x = 3) for the sulfides, (indenyl)_xPh_{3-x}PSe (x = 1, 2) for the selenides, and (indenyl)_xPh_{3-x}PBH₃ (x = 1-3) for the boranes. Linear relationships of the ³¹P NMR chemical shift with the number of indenyl groups were observed. The compounds were also characterized by ¹H and ¹³C NMR spectroscopy and mass spectrometry. The solidstate structure of diindenylphenylphosphine selenide was determined by X-ray crystallography and found to be isomorphous with diindenylphenylphosphine sulfide. The solid-state structure of triindenylphosphine sulfide was also determined by X-ray crystallography and the indenyl groups were confirmed to all be the inden-3-yl isomer. Additionally, pentacarbonyl(triindenylphosphine)molybdenum(0), 1,3-bis(diphenylphosphino)indene diborane, and *rac*-bis(1-(diphenylphosphino)indenyl)iron(II) diborane were prepared, isolated, and characterized.

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Introduction

Heteropolyfunctional ligands have attracted much interest in recent years due to their ability to form bi- and poly-metallic complexes.^[1] These complexes are of particular interest because of the possibility to introduce two or more metals with very different electronic and steric properties. This is usually achieved by a combination of early and late transition metals. One of the most common systems to be studied is the cyclopentadienyldiphenylphosphine ligand which is used extensively in the popular diphosphine chelate bis(diphenylphosphino)ferrocene (dppf).^[2] Generally, the cyclopentadienyl functional group is coordinated in an η^5 fashion to one metal while the phosphorus atom is coordinated to another metal. The number of papers reporting indenylphosphine compounds and their derivatives, in contrast, is very small.^[3–12] This is quite remarkable, given the possibility to generate planar chirality at the metal centre containing the coordinated indenyl ligand and given that indenyl complexes of the group 4 metals have proven especially attractive in Ziegler-Natta olefin polmerization.^[13-18] Oxide and sulfide derivates of phosphines are also proving to be of much interest in homogeneous catalysis.^[19-22] In this paper, we describe a series of polyfunctional indenylphosphine compounds and the formation of oxide, sulfide, selenide, borane, and pentacarbonylmolybdenum derivatives.

Results and Discussion

Syntheses

The series of indenylphosphines with one, two, or three indenyl groups have already been prepared (Scheme 1): Fallis et al. reported indenyldiphenylphosphine (1);^[5] Lensink and Gainsford reported diindenylphenylphosphine (2);^[7] and Heuer et al. reported triindenvlphosphine (3).^[4] We have also reported the isolation of 1,3-bis(diphenylphosphino)indene (4).^[6] A few of the oxide, sulfide, and selenide derivatives of these have been reported: Fallis et al. have prepared the sulfide (1b);^[5] Lensink and Gainsford, the sulfide (2b);^[7] the only reported derivative of (3) is the platinum complex $Pt(P(C_9H_7)_3)(PF_2C_9H_7)Cl_2$.^[4] Stradiotto et al. reported the oxide (4a) and sulfide (4b)^[3a] and we reported the selenide (4c).^[6] Compounds (1),^[5] (2b),^[7] (4a),^[3a] (4b),^[3a] and (4c)^[6] have also been crystallographically characterized. To fill in the gaps, therefore, we prepared: the oxides (1a), (2a), and (3a), the sulfide (3b), and the selenides (1c) and (2c). Additionally, the borane adducts (1d)-(4d), the pentacarbonylmolybdenum complex (3e), and the borane adduct of the ferrocene 1,1'-bis(diphenylphosphinoindenyl)iron(II) (5d), were prepared. These compounds were all prepared by standard methods, namely the oxides either by treatment of a toluene solution with hydrogen peroxide ((1a) and (3a)) or



Scheme 1.

by refluxing a toluene solution of the phosphine in air (2a), the sulfide (3b) by treatment of a diethyl ether solution of the phosphine with sulfur), the selenides (1c) and (2c) by heating a toluene solution to reflux with selenium), the borane adducts by treatment of the phosphine in dichloromethane with borane dimethylsulfide), and the pentacarbonylmolybdenum complex (3e) by heating a tetrahydrofuran solution of the phosphine with Mo(CO)₆ to reflux.

The compounds have all been characterized by ¹H, ¹³C, and ³¹P NMR spectroscopy. The borane adducts were also characterized by IR spectroscopy with observation of the BH₃ symmetric and asymmetric stretches at about 2350 and 2390 cm⁻¹, respectively. EI-MS of all the non-borane compounds have also been recorded. Under the conditions of EI-MS, the borane compounds all show mass spectra consistent with the initial loss of BH₃ to form the corresponding phosphine.

Both the allylic inden-1-yl and vinylic inden-3-yl isomers of (1) and its sulfide have been observed. For the selenide we isolated the vinylic isomer, but a small amount of the allylic isomer, about 10%, was seen in the ³¹P NMR spectrum of the product mixture. We observed only the vinylic isomer for the borane adduct whereas for the oxide we have only observed the allylic isomer in small amounts during decomposition of the ferrocenyldiphosphine (5). As with (2b), reported by Lensink and Gainsford,^[7] we found that the oxide (2a) also formed a mixture of the divinylic, allylic/vinylic, and diallylic isomers in refluxing toluene (we observed an 8:30:62 ratio of the isomers, respectively) starting from the divinylic isomer of the phosphine. The diallylic isomer exists as two *meso* isomers and one racemic pair, giving a 1:2:1 ratio in the ³¹P NMR spectrum at around 38 ppm, whereas the allylic/vinylic isomer exists as two diastereomers in a 1:1 ratio with a ³¹P chemical shift near 27 ppm. The divinylic isomer appears as a singlet at 17.1 ppm. We did not attempt to separate the isomers. The selenide and borane adducts were only observed to form the divinylic isomer. The selenide was heated to reflux in toluene, so presumably the most stable isomer was formed. We did not attempt to isomerize the borane adduct, however.

The NMR studies are consistent with formation of the trivinylic isomer for all of the triindenylphosphine compounds we prepared: ¹H NMR spectroscopy shows a peak around 3.5 ppm with an integral of two protons per indenyl for the CH₂ group (the corresponding ¹³C chemical shift lies at about 40 ppm) whereas allylic isomers show a peak at around 4.6 ppm with an integral of one proton per indenyl for the CHP group (the corresponding ¹³C chemical shift lies at around 50 ppm). Attempts to isomerize the oxide and sulfide were unsuccessful. The structure of the sulfide was also confirmed by X-ray crystallography, which showed that the isolated isomer has the sp² carbons attached to the phosphorus in all three indenyl rings. This differs from the Pt complex cis- $Pt(P(C_9H_7)_3)(PF_2C_9H_7)Cl_2$ in which two of the three indenyl rings are attached via sp³ carbon centres.^[4] It was thought that the formation of a bulky triindenylphosphine derivative might give a different isomer, thus the pentacarbonylmolybdenum adduct was prepared by refluxing hexacarbonylmolybdenum with triindenylphosphine. Only one isomer was obtained and this was found by NMR spectroscopy to be the trivinylic isomer

By preparing derivatives of 1,3-bis(diphenylphosphino)indene (4), we were able to provide examples of phosphorus in both the allylic and vinylic environments in order to make direct comparisons. As discussed below, there seems to be very little affect across the ring.

Although many derivatives of dppf are known, preparing derivatives of the indenyl analogue is more problematic owing to its increased sensitivity to nucleophilic reagents. We have recently provided evidence that even the solvent tetrahydrofuran is able to reversibly coordinate to the metal centre and displace the indenide.^[12] Unsurprisingly, therefore, we have been unable to prepare the oxide and sulfide analogues of (5) whereas the derivative that contains the electrophilic fragment BH₃ (5d) was readily prepared and isolated. The Mo(CO)₄ adduct, of both the *rac* and *meso* isomers, in which both the phosphorus atoms are coordinated to the Mo atom, has been reported previously.^[6]

³¹P NMR spectroscopy

Table 1 summarizes the ${}^{31}P{}^{1}H$ NMR spectroscopy data for all compounds characterized in this report and compares these values to some related compounds. For the vinylic

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Compound	Isomer	Phosphine	Oxide	Sulfide	Selenide (¹ J _{PSe} [Hz])	Borane	$Mo(CO)_x$ complex
PPh ₃		-4.8	29.8	42.6 ^[24]	34.1 (736) ^[30]	21 ^[31]	37.5 ^[32]
PPh2C9H7	1	$-4.3^{[5]}$	32.7 ^A	45.1 ^[5]	37.0 (735)	_	_
	3	-22.3	23.1	32.1	20.8 (721)	10.7	-
$PPh(C_9H_7)_2$	1,1	_	37.5, 37.6, 38.5	51.0, 51.2, 52.2 ^[7]	_	-	-
	1,3	_	27.3, 27.5	35.0, 35.3	_	_	-
	3,3	-40.3 ^B	17.1	20.6	5.9 (717)	1.2	_
P(C9H7)3	3,3,3	$-58.8^{[4]}$	10.0	9.6	_	-8.7	-8.7
$1,3-C_9H_6(PPh_2)_2$	P-1	$-1.1^{[6]}$	32.0 ^[3a]	46.9 ^[3a]	37.9 (750) ^[6]	25.7	_
, , , , , , , , , , , , , , , , , , , ,	P-3	-21.6	22.1	32.5	20.9 (730)	11.4	_
(PPh ₂ C ₉ H ₇) ₂ Fe		$-22.5^{[6]}$	-	-	_	16.5	33.1 ^[6]
(PPh ₂ C ₉ H ₆) ₂ Fe		-17.2 ^[33]	28.3 ^[34]	40.8 ^[35]	31.5 (737) ^[36]	16.5 ^[37]	28.5 ^[38]

Table 1. ³¹P{¹H} NMR spectroscopy data for indenylphosphine compounds in CDCl₃

^A Minor product observed in the decomposition of (5). ^B Our measurement.

isomers, there is an upfield shift, $\alpha_{\rm F}$, upon replacement of a phenyl group with an inden-3-yl group. The magnitude of this upfield shift is strongly dependent upon the nature of the phosphine adduct), thus, the phosphines give an upfield shift of 18.0 ppm for each substitution of a phenyl by an inden-3-yl, whereas the oxides give an upfield shift of 6.3 ppm per substitution. Figure 1 illustrates the trends observed for the chemical shifts of the phosphines and their oxide, sulfide, selenide, and borane derivatives. A simple equation for indenylphenylphosphine adducts can be derived in which the chemical shift δ is dependent on $\alpha_{\rm E}$, the chemical shift of triphenylphosphine as free species versus as an adduct $\Delta_{\rm E}$, and the number of indenyl groups, x: $\delta = \Delta_{\rm E} + \Sigma x \alpha_{\rm E} - 4.8$. Table 2 tabulates the $\alpha_{\rm E}$ and $\Delta_{\rm E}$ values for the indenyl phosphines we describe here as well as methyl-, ethyl-, and isopropylphenylphosphines and some of their adducts. One consequence of these different $\alpha_{\rm E}$ values is that whereas triphenylphosphine oxide (28.5 ppm) is upfield of the selenide (34.1 ppm) and the molybdenumpentacarbonyl adduct (37.5 ppm), the order is reversed for the triindenylphosphine adducts (10.0 ppm for the oxide versus -7.2 ppm (calculated) and -8.7 ppm for the selenide and molybdenumpentacarbonyl adducts, respectively).

The upfield shift from triindenylphosphine oxide to the sulfide (10.0 versus 9.6 ppm, respectively) goes against conventional wisdom, which says that 'in tetravalent and pentavalent phosphorus compounds the transition from oxygen to sulfur is accompanied in every case by a large downfield shift of around 30–80 ppm'.^[23] The diindenylphenylphosphine adducts show only a small downfield shift of 3.5 ppm. Selenide chemical shifts are generally very similar to the sulfides,^[24] so the 15 ppm upfield shift from the diindenylphosphine sulfide to the selenide would be considered large.

Substitution of a phenyl group by an inden-1-yl group results in a small downfield shift of less than 6 ppm for all of the compounds we have prepared. Comparison of inden-1and inden-3-yldiphenylphoshine and its adducts with 1,3bis(diphenylphosphino)indene and its adducts shows little difference (less than 4 ppm) across the indene ring upon substitution of a proton by a diphenylphosphino group. Thus, comparison of triphenylphosphine and its adducts



Fig. 1. ³¹P NMR chemical shifts of indenylphenylphoshines $(C_9H_7)_{x}$ -Ph_{3-x}P (x = 0-3), and their oxide, sulfide, selenide, and borane adducts.

Table 2. ³¹P NMR chemical shift parameters for substituted phenylphosphines $R_x Ph_{3-x}P(x = 0-3)$ and their adducts Based on the formula $\delta = 4\pi + \sum rom = 4.8$

Based on the formula $\delta = \Delta_{\rm E} + \Sigma x \alpha_{\rm E} - 4.8$							
Е	$\Delta_{\rm E}$	α _E (Ph)	$\alpha_{\rm E}$ (3-indenyl)	$\alpha_{\rm E}$ (1-indenyl)	$\alpha_{\rm E}$ (Me)	α _E (Et)	$\begin{pmatrix} \alpha_{\rm E} \\ ({\rm Pr}^i) \end{pmatrix}$
Lone pair	0.0	0	-18.0	2	-19.1	-5.1	8.1
0	34.6	0	-6.3	4	2.1	6.2	
S	49.4	0	-11.0	5	4.8	3.3	
Se	39.0	0	-14.1	4			
BH ₃	25.8	0	-9.9	5			
Mo(CO) ₅	42.5	0	-15.4	-			

with the chemical shift of the 1-diphenylphosphino group in 1,3-bis(diphenylphosphino)indene allows us to determine a consistent set of α_E values for the inden-1-yl group. As shown in Table 2, the α_E values for inden-1-yl (3 ± 2) do not vary much, in contrast to the α_E values for inden-3-yl (which range from -6.3 to -18.0), and are remarkably similar to phenyl (0, by definition).

Grim and McFarlane developed the equation $\delta = -62 + 100$ $\Sigma \sigma^{P}$ (based on $\sigma^{P}(Me) = 0$)^[25] for calculating the ³¹P chemical shifts of tertiary phosphines. Using this equation, we can calculate that σ^{P} (inden-3-yl) = 1, σ^{P} (inden-1-yl) = 19, σ^{P} $(C_5H_5Fe(C_5H_4PPh_2)) = 7$, and $\sigma^P(C_9H_6Fe(C_9H_6PPh_2)) = 2$. In comparison, $\sigma^{P}(Ph) = 19$ and $\sigma^{P}(pentyl) = 10$. Thus, the inden-3-yl resembles a methyl group and the inden-1-yl again resembles a phenyl group. This is opposite to what one might expect and suggests that the inden-3-yl group is a significantly better π -donor than phenyl. Schmidpeter and Brecht^[26] used the equation $\delta = 39.6 + 22.7\sigma_X$ to describe the ³¹P chemical shifts for phosphine oxides of the formula Ph₂P(O)X, where σ_X is the para-Hammett constant. We find that σ_X (inden-1-yl) = -0.304 and σ_X (inden-3-yl) = -0.727. These compare to -0.43 for phenyl, -0.52 for pentyl, -0.660 for NH₂, and -1.00 for O⁻. Again, the inden-1-yl most closely resembles a phenyl group and the inden-3-yl most closely resembles a π -donor group.

The ferrocenyldiphosphine (5) and its adducts show similar chemical shifts to the cyclopentadienyl analogues. The dppf derivatives are between 5 and 11 ppm downfield of the corresponding indenyldiphenylphosphine adduct.

${}^{13}C_{l}^{f1}H_{f}^{3}$ NMR Spectroscopy

Table 3 summarizes the ${}^{13}C{}^{1}H$ NMR spectroscopy for the indenyl rings of the indenyl compounds discussed in this report. The assignments of C1 and C2 are obvious from their chemical shifts. C4 is also easily assigned since it is often a doublet or is at least broadened by coupling to P. The pattern of resonances for C4 to C7 is well dispersed and invariant from one compound to another with each resonance varying by a range of less than 1.5 ppm. The assignments of C4 to C7 were confirmed by the observation of an NOE effect from H1 to H2 and H7 followed by a combination of ${}^{1}\text{H}{-}^{1}\text{H}$ COSY and ${}^{1}\text{H}{-}^{13}\text{C}$ HSQC spectroscopy of compound (2b), since this compound has well-separated ${}^{1}\text{H}$ resonances for H4–H7.The assignment of the quaternary carbons C3, C3a, C7a, and *ipso*-Ph is based on their chemical shifts and coupling constants and was confirmed by use of ${}^{1}\text{H}{-}^{13}\text{C}$ HMBC spectroscopy. The chemical shift of C7a varies by less than 1.5 ppm whereas C3a, being closer to the point of modification, has a much greater variation of 5 ppm (10 ppm if (3a) is included).

With the peculiar exception of triindenylphosphine oxide, a number of trends can be observed: The variation in chemical shift decreases as the number of bonds from the P atom increases), for C3 (one bond), the chemical shifts have a range of ± 7 ppm, for C2 (two bonds) ± 3.6 ppm, for C3a (two bonds) ± 2.5 ppm, for C1 (three bonds) ± 0.3 ppm, and for C7a (three bonds) ± 0.6 ppm. The magnitude of the coupling constants generally decrease C3 > C1 = C3a > C2 = C7a > C4. The phosphines have smaller coupling constants (except for C4) than the derivatives.

As expected, C4 has a small, at most 5 Hz, coupling constant to phosphorus compared with that of C1 and C7a since it is observed that in general ${}^{3}J_{PC-trans}$ is much larger and ${}^{3}J_{PC-cis}$.^[27] Two-bond coupling constants of phosphines tend to depend on the orientation of the phosphine lone pair (the coupling constant is larger for the atom it is closest to, so, generally, C3a > C2). Thus, it might be expected that, for the other derivatives, the coupling constant would also depend on the orientation of the phosphine substituent.

The chemical shifts and coupling constants of C3 and C3a of triindenylphosphine oxide are out of line with the above trends. The one bond coupling constant to C3 is only 10 Hz, versus over 100 Hz for the monoindenyl and diindenyl oxides, while the chemical shifts of C3 and C3a are significantly upfield of the other compounds: 128.8 ppm versus

Table 3. ${}^{13}C{}^{1}H$ NMR spectroscopy data for indenyl phosphine derivatives J_{PC} [Hz] data in parentheses

6	7 7a	1
5	3a 4	3 PBo

	C1	C2	C3	ipso-Ph	C3a	C4	C5	C6	C7	C7a
(C ₉ H ₇)PPh ₂ ^[5]	40.2(6)	142.0(6)	145.9(20)	136.0(9)	141.9(13)	121.5(5)	126.4	125.3	124.1	144.8(5)
$(C_9H_7)PPh_2O$	40.1(14)	148.8(10)	138.2(106)	131.7(106)	142.4(12)	122.6	126.6	125.6	123.8	143.8(10)
(C9H7)PPh2Se	39.8(13)	147.0(9)	136.8(78)	130.3(77)	141.7(13)	123.2	126.3	125.6	123.9	144.2(10)
(C9H7)PPh2BH3	40.2(11)	148.6(8)	134.5(57)	128.1(59)	142.7(11)	122.9	126.5	125.6	122.9	144.1(8)
(C9H7)2PPh	39.9(4)	141.7(4)	145.8(21)	133.8(5)	139.9(10)	121.3(5)	126.2	124.9	123.6	144.1(5)
(C9H7)2PPhO	39.9(14)	147.8(12)	137.7(109)	n. o.	142.3(12)	122.5	126.5	125.5	123.7	143.7(8)
$(C_9H_7)_2PPhS^{[7]}$	39.8(14)	146.7(10)	137.3(88)	131.0(88)	142.1(13)	123.2	126.5	125.7	123.9	144.2(10)
(C9H7)2PPhSe	39.8(14)	146.8(8)	135.6(80)	129.0(120)	141.9(14)	123.2	126.4	125.7	124.0	144.2(10)
(C9H7)2PPhBH3	40.3(11)	148.1(8)	133.5(59)	127.3(60)	142.9(12)	122.9	126.5	125.6	123.9	144.1(8)
$(C_9H_7)_3P^A$	40.2(4)	142.4(4)	146.1(22)		138.1(8)	121.6(5)	126.5	125.1	123.9	144.3(5)
$(C_9H_7)_3P=O$	40.1(14)	147.4(11)	128.8(10)		133.0(9)	122.7	126.6	125.6	123.8	143.8(10)
$(C_9H_7)_3P=S$	39.8(15)	147.0(10)	136.2(90)		142.0(12)	123.0	126.5	125.6	123.9	144.1(12)
(C9H7)3PBH3	40.2(11)	147.8(7)	132.3(59)		142.9(12)	122.8	126.5	125.5	123.8	144.0(8)
$(C_9H_7)_3PMo(CO)_5$	39.7(10)	145.4(11)	136.5(37)		143.1(11)	122.9	125.9	125.3	123.9	144.3(7)

^A Our assignment of the spectrum reported by Heuer et al.^[4]

(2c)		(3b)	
Se-P	2.1190(14)	P–S	1.946(2)
P-C(13)	1.787(5)	P-C(13)	1.781(6)
P-C(23)	1.791(5)	P-C(23)	1.787(5)
P–C(31)	1.808(5)	P-C(33)	1.773(6)
C(13)–P–Se	113.21(18)	C(13)–P–S	113.48(19)
C(23)–P–Se	112.99(18)	C(23)-P-S	110.3(2)
C(31)–P–Se	114.15(18)	C(33)–P–S	113.99(19)
C(13)–P–C(23)	105.8(2)	C(23) - P - C(13)	106.8(2)
C(13)–P–C(31)	104.5(2)	C(33) - P - C(13)	105.4(3)
C(23)–P–C(31)	105.4(2)	C(33)–P–C(23)	106.3(3)

Table 4. Selected bond lengths [Å] and angles $[\circ]$ for diindenylphenylphosphine selenide (2c) and triindenylphosphine sulfide (3b)

 Table 5. Selected dihedral angles [°] for diindenylphenylphosphine sulfide (2b),

 [7] diindenylphenylphosphine selenide (2c), and triindenylphosphine sulfide (3b)

(2b)	S-P-C1-C9	55.7(3)
	S-P-C11-C19	51.3(3)
	S-P-C20-C25 (Ph)	27.0(3)
(2c)	Se-P-C13-C13A	52.8(5)
	Se-P-C23-C23A	50.7(5)
	Se-P-C31-C36 (Ph)	37.2(5)
(3b)	S-P-C23-C23A	53.1(5)
	S-P-C33-C33A	49.5(5)
	S-P-C13-C13A	-168.2(4)

 139 ± 7 ppm for C3 and 133.0 ppm versus 140.6 ± 2.5 ppm for C3a. We cannot readily account for these observations.

Structures of Diindenylphenylphosphine Selenide (2c) and Triindenylphosphine Sulfide (3b)

Table 4 lists selected bond distances and angles for diindenylphenylphosphine selenide (2c) and triindenylphosphine sulfide (3b). Selected dihedral angles for the two compounds, as well as for (2b), are given in Table 5. For both compounds there are no anomalies in the structural parameters and there is good self-consistency in the indenyl ligands.

The solid-state structure of (2c), illustrated in Figure 2, is isomorphous to that of the sulfide (2b): It has the same space group, $P2_1/n$, and similar cell dimensions.^[7] As shown in Table 5, the orientations of the indenyl and phenyl rings are essentially the same: The benzo rings are oriented towards the selenium atom and the three rings adopt a propeller conformation. The Se–P–C angles are slightly smaller than for the sulfide: 113.2° and 113.0° versus 113.4° and 113.3° for the indenyl rings and 114.2° versus 114.5° for the phenyl ring. This is consistent with the decreased electronegativity of Se versus S, rather than a steric effect. The P–Se distances in (4c): 2.1251(14) and 2.1265(14) Å for the phosphorus on the sp² carbon atom and 2.1144(14) and 2.1138(15) Å for the phosphorus on the sp³ carbon atom.^[6]

The conformation adopted by (3b) in the solid state, illustrated in Figure 3, is also a propeller conformation but with two of the benzo rings oriented towards the S atom and the third oriented away from the S atom.



Fig. 2. Thermal ellipsoid plot (40%) of diindenylphosphine selenide (2c) showing the atomic labelling scheme.



Fig. 3. Thermal ellipsoid plot (40%) of triindenylphosphine sulfide (3b) showing the atomic labelling scheme.

Conclusion

We have described the completion of a series of indenylphenylphosphines and their oxide, sulfide, selenide, and borane adducts. Trends in their ³¹P and ¹³C NMR spectra have been observed and it was found that inden-1-yl groups appear to behave similarly to phenyl groups whereas the inden-3-yl groups are much more variable in their affects, presumably due to π -donor effects. The X-ray structures of triindenylphosphine sulfide and diindenylphenylphosphine selenide were much as expected with both adopting propeller conformations.

Experimental

All manipulations and reactions were carried out under an inert atmosphere (Ar or N₂) by use of standard Schlenk line techniques. Reagent grade solvents were dried and distilled prior to use: diethyl ether and tetrahydrofuran from Na/benzophenone; dichloromethane and petroleum ether (50–70°C fraction) from CaH₂. Indenyldiphenylphosphine,^[5]1,3-bis(diphenylphosphino)indene,^[6] and bis(1-(diphenylphosphino)- η^5 -indenyl)iron(II)^[6] were prepared by published procedures. All other reagents were purchased from Aldrich or Sigma. ¹H, ¹³C{¹H}, and ³¹P{¹H} NMR spectroscopy data were collected on either a Varian XL- or UNITY-300 spectrometer operating at 300, 75, and 121 MHz respectively. NOE, ¹H–¹H COSY, ¹H–¹³C HSQC, and ¹H–¹³C HMBC spectra were collected on a Varian INOVA-500 spectrometer operating at 500 and 125 M for ¹H and ¹³C, respectively. Spectra were measured at ambient temperature with residue solvent peaks as internal standard for ¹H and ¹³C{¹H} NMR spectroscopy. ³¹P{¹H} NMR spectroscopy chemical shifts were reported relative to external 85% H₃PO₄, positive shifts representing deshielding. EI mass spectra were collected on a Kratos MS80RFA mass spectrometer. Infrared spectra were obtained on a Shimadzu FTIR-8201PC spectrophotometer. Elemental analysis was done by Campbell Microanalytical Services, Otago University, Dunedin. Yields have not been optimized.

Preparation of Indenyldiphenylphosphine Oxide (1a)

To a solution of indenyldiphenylphosphine (2.53 g, 8.4 mmol) in toluene (50 mL) was added an excess of aqueous hydrogen peroxide (2 mL, 50% w/w). The reaction mixture was stirred at ambient temperature for 12 h. After filtering, the solvent was removed in vacuo to leave a yellow oily residue. Recrystallization (diethyl ether) afforded *indenyldiphenylphosphine oxide* (1a) (0.93 g, 35%) as a yellow powder. (Found: M^{+•} 316.10186. C₂₁H₁₇OP requires M^{+•} 316.10170). $\delta_{\rm H}$ (CDCl₃) 7.8–6.8 (15 H, m, H2, H4–H7, and Ph), 3.57 (2 H, s, H3). $\delta_{\rm C[H]}$ (CDCl₃) 148.8 (d, ²*J*_{PC} 10, C2), 143.8 (d, ³*J*_{PC} 10, C7a), 142.4 (d, ²*J*_{PC} 12, C3a), 138.2 (d, ¹*J*_{PC} 106, C3), 132.0 (d, ⁴*J*_{PC} 3, *para*-Ph), 131.7 (d, ¹*J*_{PC} 106, *ipso*-Ph), 131.6 (d, ²*J*_{PC} 10, *ortho*-Ph), 128.5 (d, ³*J*_{PC} 12, *meta*-Ph), 126.6 (s, C5), 125.6 (s, C6), 123.8 (s, C7), 122.6 (s, C4), 40.1 (d, ³*J*_{PC} 14, C1). $\delta_{\rm P[H]}$ (CDCl₃) 23.85. *m*/*z* (EI) 316 (47%, M⁺), 201 (100, [M–C9H₇]⁺), 115 (26, C9H₇⁺), 77 (30, C₆H₅⁺).

Preparation of Indenyldiphenylphosphine Selenide (1c)

To a solution of indenyldiphenylphosphine (0.40 g, 1.33 mmol) in tetrahydrofuran (30 mL) was added selenium powder (0.16 g, 2.0 mmol). The reaction mixture was stirred at ambient temperature for 16 h. After filtering through Celite, the solvent was removed in vacuo to afford indenyldiphenylphosphine selenide (1c) (0.47 g, 93%) as a white powder. (Found: M^{+•} 380.02262. C₂₁H₁₇PSe requires M^{+•} 380.02331). $\delta_{\rm H}$ (CDCl₃) 7.9–6.6 (15 H, m, H2, H4–H7, Ph), 3.58 (2 H, s, H3). $\delta_{\rm C[H]}$ (CDCl₃) 147.0 (d, ²*J*_{PC} 9, C2), 144.2 (d, ³*J*_{PC} 10, C7a), 141.7 (d, ²*J*_{PC} 13, C3a), 136.8 (d, ¹*J*_{PC} 78, C3), 132.4 (d, ²*J*_{PC} 11, *ortho*-Ph), 131.7 (d, ⁴*J*_{PC} 3, *para*-Ph), 130.3 (d, ¹*J*_{PC} 77, *ipso*-Ph), 128.6 (d, ³*J*_{PC} 12, *meta*-Ph), 126.3 (s, C5), 125.6 (s, C6), 123.9 (s, C7), 123.2 (s, C4), 39.8 (d, ³*J*_{PC} 13, C1). $\delta_{\rm P[H]}$ (CDCl₃) 20.79 (m, *J*_{PSe} 721). *m/z* (EI) 380 (20%, M⁺), 300 (77, [M–Se]⁺), 265 (53, Ph₂PSe⁺), 185 (100, Ph₂P⁺), 115 (24, C₉H⁺₇), 77 (24, Ph⁺).

Preparation of Indenyldiphenylphosphine Borane (1d)

Indenyldiphenylphosphine (1.00 g, 3.3 mmol) was dissolved in dichloromethane (50 mL). Borane dimethylsulfide (2 mL, 2 mol L^{-1} , 4.0 mmol) was added and the reaction mixture stirred overnight. The solvent was removed in vacuo and a recrystallization carried out with dichloromethane and petroleum ether. A second recrystallization was carried out with hot ethanol to give indenyldiphenylphosphine borane (1d) (0.757 g, 72%) as a light-yellow powder. (Found: C 78.68, H 6.41%. $C_{21}H_{20}BP$ requires C 80.28, H 6.42%). ν/cm^{-1} (KBr) 3057 s, 2390 vs, 2345 ms, 1458 s, 1437 vs, 1059 vs, 739 vs, 694 vs, 608 s, 488 s. δ_H (CDCl₃) 7.70 (5 H, m, H4, ortho-Ph), 7.46 (5 H, m, H7, meta-Ph), 7.19 (4 H, m, H5, H6, para-Ph), 6.80 (1 H, dt, ³J_{PH} 8.7, ³J_{HH} 2, H2), 3.57 (2 H, d, J 2, H1), 1.3 (3 H, m, BH₃). δ_{C{H}} (CDCl₃) 148.6 (d, ²J_{PC} 8, C2), 144.1 (d, ${}^{3}J_{PC}$ 8, C7a), 142.7 (d, ${}^{2}J_{PC}$ 11, C3a), 134.5 (d, ${}^{1}J_{PC}$ 57, C3), 133.0 (d, ${}^{2}J_{PC}$ 10, *ortho*-Ph), 131.4 (d, ${}^{4}J_{PC}$ 3, *para*-Ph), 128.8 (d, ³ J_{PC} 10, meta-Ph), 128.1 (d, ¹ J_{PC} 59, ipso-Ph), 126.5 (s, C5), 125.6 $(s, C6), 123.9 (s, C7), 122.9 (s, C4), 40.2 (d, {}^{3}J_{PC} 11, C1). \delta_{P\{H\}} (CDCl_{3})$ 10.77 (br).

Preparation of Diindenylphenylphosphine (2)

Lensink and Gainsford^[7] obtained an oil and reported their NMR spectra in C_6D_6 . We report here a synthesis that produces a powder and we report the NMR spectra in CDCl₃ for consistency with the other compounds reported here.

To a solution of indene (2.2 g, 2.0 mmol) in diethyl ether (25 mL) at -78°C was added a solution of BuⁿLi (12.5 mL, 1.6 M, 2.0 mmol). After stirring the reaction mixture at ambient temperature for 1 h, the solution was again cooled to -78° C. PhPCl₂ (1.8 g, 1.0 mmol) was then added and the solution then stirred at ambient temperature for 1 h before filtration through an alumina column (10×1.5 cm). The solvent was removed in vacuo and the residue washed with methanol to give diindenylphenylphosphine (2) (2.5 g, 74%) as a cream powder. (Found: C 83.03, H 5.53%. C₂₄H₁₉P requires C 85.19, H 5.66%). δ_H (CDCl₃) 7.5-7.1 (13 H, m, H4-H7, Ph-H), 6.27 (2 H, s, H2), 3.38 (4 H, s, H1). $\delta_{C\{H\}}$ (CDCl₃) 145.76 (d, ¹J_{PC} 21, C3), 144.14 (d, ³J_{PC} 5, C7a), 141.65 $^{2}J_{PC}$ 4, C2), 139.91 (d, $^{2}J_{PC}$ 10, C3a), 134.05 (d, $^{2}J_{PC}$ 20, ortho-(d. Ph), 133.78 (d, ¹J_{PC} 5, *ipso*-Ph), 129.07 (s, *para*-Ph), 128.47 (d, ³J_{PC} 8, meta-Ph), 126.22 (s, C5), 124.87 (s, C6), 123.62 (s, C7), 121.33 (d, ${}^{3}J_{PC}$ 5, C4), 39.87 (d, ${}^{3}J_{PC}$ 4, C1). $\delta_{P\{H\}}$ (CDCl₃)-40.33.

Preparation of Diindenylphenylphosphine Oxide (2a)

Diindenylphenylphosphine (0.4 g, 1.2 mmol) was dissolved in freshly distilled toluene (25 mL) and heated in air to reflux for 4 h. Removal of solvent in vacuo gave an isomeric mixture of diindenylphenylphosphine oxide (2a) as a yellow oil, which could not be crystallized. Microanalysis was not attempted due to the oily nature of the mixture. (Found: $M^{+\bullet}$ 354.11709. $C_{24}H_{19}OP$ requires $M^{+\bullet}$ 354.11735). ν/cm^{-1} (Nujol) 2225 w, 1590 m, 1549 w, 1450 s, 1377 s, 1260 s, 1233 w, 1178 w, 1150 m, 1100 m, 1020 m, 957 w, 907 m, 799 s, 762 s, 721 s, 694 s, ¹¹⁵ ¹¹⁵ ¹¹⁶ ¹¹⁷ ¹¹⁶ ¹¹⁷ Ph), 131.2 (d, ² J_{PC} 10, ortho-Ph), 128.4 (d, ³ J_{PC} 12, meta-Ph), 126.5 (s, C5), 125.5 (s, C6), 123.7 (s, C7), 122.5 (s, C4), 39.9 (d, ³*J*_{PC} 14, C1). No ipso-Ph carbon atoms were observed. Peaks corresponding to C1 of the allylic/vinylic isomers were also observed: 52.4 (d, ${}^{1}J_{PC}$ 64), 53.0 (d, ${}^{1}J_{PC}$ 64). $\delta_{P\{H\}}$ (CDCl₃) 38.50 (2%, s), 37.65 (4%, s), 37.50 (2%, s), 27.52 (15%, s), 27.28 (15%, s), 17.08 (62%, s). m/z (EI) 354 (82%, M⁺), 239 (90, [M–C₉H₇]⁺), 192 (42, PhC₉H₇⁺), 115 (100, C₉H₇⁺).

Preparation of Diindenylphenylphosphine Selenide (2c)

Diindenylphosphine (0.4 g, 1.2 mmol) was dissolved in freshly distilled toluene (25 mL). Powdered selenium (89 mg, 1.1 mmol) was added and the mixture heated to reflux for 1.5 h. The solvent was removed in vacuo from the clear yellow solution. Recrystallization (toluene/hexane) afforded diindenylphenylphosphine selenide (2c) (0.20 g, 46%) as light-brown crystals. (Found: C 69.70, H 4.74%. $C_{24}H_{19}PSe$ requires C 69.07, H 4.59%). ν/cm^{-1} (Nujol) 1278 m, 1261 m, 1234 m, 1195 w, 1180 w, 1165 w, 1096 s, 1018 m, 995 w, 955 s, 920 w, 805 w (P = Se), 775 m, 760 s, 748 s, 735 s, 716 s, 691 s, 635 s, 602 s. $\delta_{\rm H}~({\rm CDCl_3})$ 7.96 (2 H, dd, J 8, 14, ortho-Ph), 7.73 (2 H, m, H4), 7.46 (5 H, m, H7, para-Ph, meta-Ph), 7.20 (4 H, m, H5, H6), 6.86 (2 H, d, ${}^{3}J_{\text{PH}}$ 11, H2), 3.56 (4 H, s, H1). $\delta_{C\{H\}}$ (CDCl₃) 146.82 (d, ${}^{2}J_{\text{PC}}$ 8, C2), 144.19 (d, ${}^{3}J_{\text{PC}}$ 10, C7a), 141.87 (d, ${}^{2}J_{\text{PC}}$ 14, C3a), 135.56 (d, ${}^{1}J_{\text{PC}}$ 80, C3), 132.40 (d, ²*J*_{PC} 11, *ortho*-Ph), 131.94 (d, ⁴*J*_{PC} 3, *para*-Ph), 128.68 (d, ³ J_{PC} 13, meta-Ph), 129.01 (d, ¹ J_{PC} 120, ipso-Ph), 126.44 (s, C5), 125.71 (s, C6), 123.98 (s, C7), 123.20 (s, C4), 39.78 (d, ³J_{PC} 14, C1). $\delta_{P\{H\}}$ (CDCl₃) 5.94 (m, J_{PSe} 717). m/z (EI) 418 (46%, M⁺), 338 $(37, [M-Se]^+), 303 (55, [M-C_9H_7]^+), 223 (69, PhPC_9H_7^+), 192 (42, 100)$ $PhC_{9}H_{7}^{+}$), 191 (42, $PhC_{9}H_{6}^{+}$), 145 (33, $C_{9}H_{6}P^{+}$), 115 (100, $C_{9}H_{7}^{+}$).

Preparation of Diindenylphenylphosphine Borane (2d)

Dindenylphenylphosphine (0.547 g, 1.62 mmol) was dissolved in dichloromethane (40 mL). Borane dimethylsulfide (0.81 mL, 2.0 mol L⁻¹, 1.62 mmol) was added and the reaction mixture stirred overnight. The solution was filtered through an alumina column (10 × 1.5 cm) and the solvent evaporated under reduced pressure to afford *diindenylphenylphosphine borane* (2d) (0.240 g, 42%) as a light-yellow powder. $\delta_{\rm H}$ (CDCl₃) 7.8 (2 H, m, H4), 7.5 (6 H, m, H7, *meta*-Ph, *ortho*-Ph), 7.2 (5 H, m, H5, H6, *para*-Ph), 6.96 (2 H, dt, ³J_{PH} 9.3, ³J_{HH} 2.0, H2), 3.57 (4 H, s, H1), 1.3 (3 H, m, BH₃). $\delta_{\rm C[H]}$ (CDCl₃) 148.05 (d, ²J_{PC} 8, C2), 144.05 (d, ³J_{PC} 8, C7a), 142.89 (d, ²J_{PC} 12, C3a), 133.45 (d, ¹J_{PC} 59,

C3), 133.05 (d, ${}^{2}J_{PC}$ 10, *ortho*-Ph), 131.48 (d, ${}^{4}J_{PC}$ 2, *para*-Ph), 128.84 (d, ${}^{3}J_{PC}$ 10, *meta*-Ph), 127.29 (d, ${}^{1}J_{PC}$ 60, *ipso*-Ph), 126.54 (s, C5), 125.59 (s, C6), 123.92 (s, C7), 122.87 (s, C4), 40.25 (d, ${}^{3}J_{PC}$ 11, C1). $\delta_{P[H]}$ (CDCl₃) 1.21 (br).

Preparation of Triindenylphosphine (3)

Heuer et al. prepared triindenylphosphine from lithium indenide and triphenylphosphite under reflux in diethyl ether and obtained a 37% yield.^[4] We report here a higher-yielding synthesis.

To a solution of indene (3.3 g, 3.0 mmol) in diethyl ether (100 mL) at -78° C was added a solution of BuⁿLi (18.8 mL, 1.6 M, 3.0 mmol). After warming to ambient temperature, the solution was stirred for 1 h and cooled again to -78° C. PCl₃ (1.37 g, 1.0 mmol) was then added and the solution was then stirred for 2 h at ambient temperature before filtering through an alumina column (10 × 1.5 cm). The solvent was removed in vacuo and the residue washed with methanol to give *triindenylphosphine* (3) (2.2 g, 60%) as a cream powder. ¹H, ¹³C, and ³¹P NMR were consistent with that reported by Heuer et al.^[4]

Preparation of Triindenylphosphine Oxide (3a)

Triindenylphosphine (0.249 g, 0.66 mmol) was dissolved in toluene (25 mL) and an excess of aqueous hydrogen peroxide (1 mL, 50% w/w) added. This was stirred overnight before the reaction mixture was filtered and the solvent evaporated under vacuum. Recrystallization (dichloromethane/petroleum ether) afforded *triindenylphosphine oxide* (3a) (0.198 g, 80%) as a light-brown solid. (Found: M^{+•} 392.13439. C₂₇H₂₁OP requires M^{+•} 392.13300). ν/cm^{-1} (KBr) 2961 s, 1713 s, 1458 s, 1381 ms, 1261 vs, 1236 s, 1022 vs, br, 959 s, 806 vs, 717 s, 646 s, 605 w, 498 s. $\delta_{\rm H}$ (CDCl₃) 7.74 (3 H, dd, ⁴J_{PH} 3.5, 5.5, H4), 7.50 (3 H, m, H7), 7.24 (6 H, m, H5, H6), 7.15 (3 H, d, ³J_{PH} 10, H2), 3.59 (6 H, s, H1). $\delta_{\rm C[H]}$ (CDCl₃) 147.4 (d, ²J_{PC} 11, C2), 143.8 (d, ³J_{PC} 10, C7a), 133.0 (d, ²J_{PC} 9, C3a), 128.8 (d, ¹J_{PC} 10, C3), 126.6 (s, C5), 125.6 (s, C6), 123.8 (s, C7), 122.7 (s, C4), 40.1 (d, ³J_{PC} 14, C1). $\delta_{\rm P[H]}$ (CDCl₃) 10.03. *m*/*z* (EI) 392 (13%, M⁺), 277 (31, [M–C9H₇]⁺), 201 (20, C₁₂H₁₀OP⁺), 115 (100, C9H₇⁺).

Preparation of Triindenylphosphine Sulfide (3b)

An excess of elemental sulfur (0.100 g, 1.37 mmol) was suspended in a freshly prepared solution of triindenylphosphine (0.258 g, 0.69 mmol) in diethyl ether (25 mL) and stirred overnight at ambient temperature. The reaction mixture was filtered through a column containing silica and the solvent evaporated under vacuum. Recrystallization was carried out first using dichloromethane and petroleum ether. A second recrystallization (hot ethanol) afforded triindenylphosphine sulfide (3b) (0.178 g, 64%) as a yellow powder. (Found: M^{+•} 408.10979. C₂₇H₂₁PS requires M^{+•} 408.11016). v/cm⁻¹ (KBr) 3317 s, br, 2963 s, 1458 s, 1381 s, 1263 s, 1236 m, 1096 vs, 1020 vs, 800 vs, 760 vs, 679 s, 640 ms, 613 m. δ_H (CDCl₃) 7.81 (3 H, m, H4), 7.50 (3 H, m, H7), 7.24 (6 H, m, H5, H6), 7.17 (3 H, d, ³ J_{PH} 11, H2), 3.58 (6 H, s, H1). δ_{C{H}} (CDCl₃) 147.0 (d, ²*J*_{PC} 10, C2), 144.1 (d, ³*J*_{PC} 10, C7a), 142.0 (d, ²*J*_{PC} 12, C3a), 136.2 (d, ¹J_{PC} 90, C3), 126.5 (s, C5), 125.6 (s, C6), 123.9 (s, C7), 123.0 (s, C4), 39.8 (d, ${}^{3}J_{PC}$ 15, C1). $\delta_{P\{H\}}$ (CDCl₃) 9.60 (s). m/z (EI) 408 (10%, M^+), 259 (14, $[M-C_9H_9S]^+$), 230 (21, $C_{18}H_{14}^+$), 146 (35, $C_9H_6S^+$), $115(100, C_9H_7^+).$

Preparation of Triindenylphosphine Borane (3d)

Triindenylphosphine (0.285 g, 0.76 mmol) was dissolved in dichloromethane (40 mL). Borane dimethylsulfide (0.45 mL, 2 mol L⁻¹, 0.91 mmol) was added and the reaction mixture stirred overnight. The solvent was evaporated under reduced pressure and the product recrystallized (dichloromethane/petroleum ether). A further recrystallization (hot ethanol) afforded *triindenylphosphine borane* (3d) (0.210 g, 71%) as a light-yellow powder. ν/cm^{-1} (KBr) 2399 s, 2357 ms, 1711 ms, 1458 s, 1375 ms, 1065 s, 1020 ms, 914 mw, 764 s, 716 s, 499 vs. δ_{H} (CDCl₃) 7.64 (3 H, m, H4), 7.49 (3 H, m, H7), 7.22 (6 H, m, H5, H6), 7.13 (3 H, dm, ³ J_{PH} 9, H2), 3.58 (6 H, s, H1), 1.1 (3 H, m, BH₃). $\delta_{\text{C}(\text{H})}$ (CDCl₃) 147.8 (d, ² J_{PC} 7, C2), 144.0 (d, ³ J_{PC} 8, C7a), 142.9 (d, ${}^{2}J_{PC}$ 12, C3a), 132.3 (d, ${}^{1}J_{PC}$ 59, C3), 126.5 (s, C5), 125.5 (s, C6), 123.8 (s, C7), 122.8 (s, C4), 40.2 (d, ${}^{3}J_{PC}$ 11, C1). $\delta_{P[H]}$ (CDCl₃) -8.70 (br).

Preparation of Pentacarbonyl(triindenylphosphine)-Molybdenum(0) (3e)

Triindenylphosphine (0.251 g, 0.67 mmol) was dissolved in tetrahydrofuran (25 mL) and hexacarbonylmolybdenum (0.176 g, 0.67 mmol) added. This was stirred overnight before being heated to reflux for 1.5 h. The solvent was removed under vacuum and the solid redissolved in diethylether. This was filtered through a column containing silica to give pentacarbonyl(triindenylphosphine)molybdenum(0) (3e) (0.189 g, 42%) as a yellow powder upon removal of solvent in vacuo. (Found: C 61.80, H 3.82%. C₃₂H₂₁MoO₅P requires C 62.76, H, 3.46%). v/cm⁻¹ (KBr) 2071 s, 1987 s, 1933 vs, br, 1898 ms, sh, 1713 w, 1458 mw, 1263 m, 760 m, 719 mw, 583 mw, 419 w. $\delta_{\rm H}$ (CDCl₃) 7.57 (6 H, m, H4, H7), 7.26 (9 H, m, H2, H5, H6), 3.69 (6 H, s, H1). δ_{C{H}} (CDCl₃) 209.9 (d, ²J_{PC} (9 II, II, II2, II2, II2, II2), 3.07 (011, 9, II1), 6C(II1 (CDC)) (11, C2), 142, 22, trans-CO), 205.9 (d, ${}^{2}J_{PC}$ 9, cis-CO), 145.4 (d, ${}^{2}J_{PC}$ 11, C2), 144.3 (d, ${}^{3}J_{PC}$ 7, C7a), 143.1 (d, ${}^{2}J_{PC}$ 11, C3a), 136.5 (d, ${}^{1}J_{PC}$ 37, C3), 125.9 (s, C5), 125.3 (s, C6), 123.9 (s, C7), 122.9 (s, C4), 39.7 (d, ³ J_{PC} 10, C1). $\delta_{P\{H\}}$ (CDCl₃) -8.72. m/z (EI) 614 (4%, M⁺), 586 (10, [M-CO]⁺), 558 (82, [M-2 CO]⁺), 530 (8, [M-3 CO]⁺), 502 (5, [M-4 CO]⁺), 474 (73, $[P(C_9H_6)_3Mo]^+), 472 (100, [P(C_9H_6)_3Mo-2H]^+).$

Preparation of 1,3-Bis(diphenylphosphino)indene Diborane (4d)

1,3-Bis(diphenylphosphino)indene (0.595 g, 1.23 mmol) was dissolved in dichloromethane (50 mL). Borane dimethylsulfide (1.23 mL, 2.0 M, 2.46 mmol) was added and the solution was then stirred overnight at ambient temperature. The solution was filtered through an alumina column (10×1.5 cm) and the solvent removed in vacuo to give 1,3bis(diphenylphosphino)indene diborane (4d) (0.212 g, 34%) as a white powder. 8H (CDCl3) 7.6-7.0 (23 H, m), 6.88 (1 H, m), 6.57 (1 H, m, H2), 4.68 (1 H, br d, ${}^{2}J_{PH}$ 18, H1), 1.3 (6 H, m, BH₃). δ_{C} (H) (CDCl₃) 145.20 (dd, ² J_{PC} 7, 2, C2), 133.48 (d, ² J_{PC} 9, ortho-Ph), 133.07 (d, ² J_{PC} 10, ortho-Ph), 132.87 (d, ²J_{PC} 10, ortho-Ph), 132.34 (d, ²J_{PC} 9, ortho-Ph), 132.22 (d, ⁴J_{PC} 3, *para*-Ph), 131.62 (d, ⁴J_{PC} 3, *para*-Ph), 131.58 (d, ⁴J_{PC} 3, para-Ph), 131.42 (d, ⁴J_{PC} 3, para-Ph), 128.90 (d, ³J_{PC} 10, meta-Ph), 128.83 (d, ³J_{PC} 10, meta-Ph), 128.83 (d, ³J_{PC} 10, meta-Ph), 128.72 (d, ${}^{3}J_{PC}$ 10, *meta*-Ph), 127.81 (s, C5), 125.98 (s, C6), 124.44 (s, C7), 123.60 (s, C4), 49.61 (dd, ${}^{3}J_{PC}$ 11, ${}^{1}J_{PC}$ 26, C1). No peaks could be unambiguously assigned to quaternary carbon atoms. $\delta_{P\{H\}}$ (CDCl₃) 25.67 (br), 11.41 (br).

Preparation of rac-Bis(1-(diphenylphosphino)indenyl)iron(11) Diborane (5d)

To a solution of *rac*-bis(1-(diphenylphosphino)indenyl)iron(II) (0.51 g, 0.811 mmol) in tetrahydrofuran (30 mL) was added a solution of borane dimethylsulfide complex (1.1 mL, 2 M, 2.2 mmol). The reaction mixture was stirred at ambient temperature for 12 h. The mixture was filtered through Celite and the solvent removed in vacuo to leave a brown residue. Chromatography of the residue on silica gel afforded rac-*bis(1-(diphenylphosphino)indenyl)iron(11) diborane* (5d) (0.46 g, 83%) as a brown powder. (Found: C 72.06, H 5.62%. C₄₂H₃₈B₂FeP₂ requires C 73.95, H 5.62%). $\delta_{\rm H}$ (CDCl₃) 7.6–6.4 (28 H, m, H4–H7 and Ph), 5.81 (2 H, d, ³ J_{HH} 2.4, H3), 3.42 (2 H, t, ³ J_{HH} 2.4, H2), 1.65 (6 H, m, BH₃). $\delta_{\rm C[H]}$ (CDCl₃) 135.4 (d, ² J_{PC} 21, *o*-Ph), 132.4 (d, ² J_{PC} 20, *o*-Ph), 131.2 (d, ⁴ J_{PC} 2, *p*-Ph), 131.0 (d, ¹ J_{PC} 58, *ipso*-Ph), 130.8 (d, ⁴ J_{PC} 3, *p*-Ph), 129.9 (d, ¹ J_{PC} 60, *ipso*-Ph), 128.5 (d, ³ J_{PC} 6, *m*-Ph), 128.4 (d, ³ J_{PC} 7, C7a), 89.3 (d, ² J_{PC} 13, C3a), 73.5 (d, ² J_{PC} 4, C2), 68.3 (d, ³ J_{PC} 5, C3), 62.0 (d, ¹ J_{PC} 64, C1). $\delta_{\rm P[H]}$ (CDCl₃) 16.53 (br).

Crystal Structure, Data Collections, Solutions, and Refinements

For each compound, a crystal was attached to a thin glass fibre and mounted on a Siemens P4 SMART diffractometer with a Siemens CCD area detector. Empirical absorption corrections were determined with SADABS and applied to the data.^[28] Data processing was undertaken with SAINT^[28] and the structures were solved by direct methods and

Diindenylphenylphosphine Selenide (2c). C₂₄H₁₉PSe, M 417.32, monoclinic, space group P2₁/n, a 14.4260(7), b 7.1810(3), c 19.3353(9) Å, β 101.025(1)°, V 1966.04(16) Å³, T 160(2) K, D_{calc} 1.410 g cm⁻³, Z 4, crystal size 0.50 × 0.36 × 0.10 mm, λ (Mo_{Kα}) 0.71073 Å, μ (Mo_{Kα}) 1.995 mm⁻¹, F(000) 848, T(SADABS)_{min,max} 0.435, 0.825, 2 θ _{max} 48°, *hkl* range -16 ≤ *h* ≤ 16, -8 ≤ *k* ≤ 7, -22 ≤ *l* ≤ 21, *N* 13 348, *N*_{ind} 3072 (*R*_{int} 0.040), no. of parameters 235, *R* (*I* > 2 σ (*I*)) 0.063, *R*_w 0.167, ρ _{max,min} 1.16, -0.77 e Å⁻³.

Triindenylphosphine Sulfide (*3b*). C₂₇H₂₁PS, *M* 408.47, triclinic, space group *P*Ī, *a* 8.9640(18), *b* 10.745(2), *c* 12.560(3) Å, *α* 99.41(3), *β* 98.26(3), *γ* 113.90(3)°, *V* 1061.2(4) Å³, *T* 293(2) K, *D*_{calc} 1.278 g cm⁻³, *Z* 2, crystal size 0.35 × 0.26 × 0.15 mm, *λ*(Mo_{Kα}) 0.71073 Å, μ (Mo_{Kα}) 0.239 mm⁻¹, *F*(000) 428, *T*(SADABS)_{min,max} 0.921, 0.965, 2*θ*_{max} 53.6°, *hkl* range $-9 \le h \le 9$, $-13 \le k \le 13$, $-15 \le l \le 15$, *N* 5417, *N*_{ind} 2806 (*R*_{int} 0.099), no. of parameters 262, *R* (*I* > 2*σ*(*I*)) 0.059, *R*_w 0.115, *ρ*_{max,min} 0.28, $-0.26 ε Å^{-3}$.

Accessory Materials

Crystallographic data for this paper has been deposited with the Cambridge Crystallographic Data Centre (nos. 199 507 for (2c) and CCDC 199 506 for (3b)).

References

- (a) D. W. Stephan, Coord. Chem. Rev. 1989, 95, 41. (b)
 P. Braunstein, M. Knorr, C. Stern, Coord. Chem. Rev. 1998, 178/179/180, 903. (c) N. Wheatley, P. Kalck, Chem. Rev. 1999, 99, 3379.
- [2] K.-S. Gan, T. S. A. Hor, in *Ferrocenes: Homogeneous Catalysis,* Organic Synthesis, Materials Science (Eds. A. Togni, T. Hayashi) 1995, p. 3 (VCH: Weinheim).
- [3] (a) M. Stradiotto, C. M. Kozak, M. J. McGlinchey, J. Organomet. Chem. 1998, 564, 101. (b) M. Stradiotto, M. J. McGlinchey, Coord. Chem. Rev. 2001, 219/220/221, 311.
- [4] L. Heuer, U. K. Bode, P. G. Jones, R. Schmutzler, Z. Naturforsch. 1989, 44b, 1082.
- [5] K. A. Fallis, G. K. Anderson, N. P. Rath, *Organometallics* 1992, 11, 885.
- [6] J. J. Adams, D. E. Berry, J. Browning, D. Burth, O. J. Curnow, J. Organomet. Chem. 1999, 580, 245.
- [7] C. Lensink, G. J. Gainsford, Aust. J. Chem. 1998, 51, 667.
- [8] R. Aumann, B. Jasper, R. Froehlich, Organometallics 1995, 14, 231.
- [9] H. G. Alt, M. Jung, J. Organomet. Chem. 1998, 568, 127.
- [10] C. J. Schaverien, R. Ernst, W. Terlouw, P. Schut, O. Sudmeijer, P. H. M. Budzelaar, J. Mol. Catal. A: Chem. 1998, 128, 245.

- [11] K. H. Doetz, I. Pruskil, U. Schubert, K. Ackermann, Chem. Ber. 1983, 116, 2337.
- [12] O. J. Curnow, G. M. Fern, Organometallics 2002, 21, 2827.
- [13] I. E. Nifant'ev, P. V. Ivchenko, Organometallics 1997, 16, 713.
- [14] A. Vogel, T. Priermeier, W. A. Herrmann, J. Organomet. Chem. 1997, 527, 297.
- [15] J. L. Huhmann, J. Y. Corey, N. P. Rath, *Organometallics* 1996, 15, 4063.
- [16] S. C. Sutton, M. H. Nantz, S. R. Parkin, Organometallics 1993, 12, 2248.
- [17] Y. Chen, M. D. Rausch, J. C. W. Chien, Organometallics 1993, 12, 4607.
- [18] R. L. Halterman, *Chem. Rev.* **1992**, *92*, 965, and references therein.
- [19] M. Concepcion, P. G. Jones, A. Laguna, C. Sarroca, J. Chem. Soc. Dalton Trans. 1995, 3563, and references therein.
- [20] R. Broussier, S. Ninoreille, C. Legrand, B. Gautheron, J. Organomet. Chem. 1997, 532, 55.
- [21] S. Ninoreille, R. Broussier, R. Amardeil, M. M. Kubicki, B. Gautheron, Bull. Soc. Chim. Fr. 1995, 132, 128.
- [22] V. I. Bakhmutov, M. Visseaux, D. Baudry, A. Dormond, P. Richard, *Inorg. Chem.* 1996, 35, 7316.
- [23] S. Berger, S. Braun, H.-O. Kalinowski, in *NMR Spectroscopy* of the Non-metallic Elements **1996**, p. 806 (John Wiley: Chichester).
- [24] S. Berger, S. Braun, H.-O. Kalinowski, NMR Spectroscopy of the Non-metallic Elements 1996 (John Wiley: Chichester).
- [25] S. O. Grim, W. McFarlane, Nature 1965, 208, 995.
- [26] A. Schmidpeter, H. Brecht, Z. Naturforsch. 1968, 23B, 1529.
- [27] J. G. Verkade, L. D. Quin, *Phosphorus-31 NMR Spectroscopy* in Stereochemical Analysis 1987 (VCH: Weinheim).
- [28] SAINT and SADABS 1994 (Siemens Analytical: Madison, WI).
 [29] G. M. Sheldrick, SHELXTL ver 5.1 1998 (Bruker AXS: Madison WI)
- [30] W. McFarlane, D. S. Rycroft, J. Chem. Soc., Dalton Trans. 1973, 2162.
- [31] W. P. Power, J. Am. Chem. Soc. 1995, 117, 1800.
- [32] S. O. Grim, D. A. Wheatland, W. McFarlane, J. Am. Chem. Soc. 1967, 89, 5573.
- [33] A. L. Bandini, G. Banditelli, M. A. Cinellu, G. Sanna, G. Minghetti, F. Demartin, M. Manassero, *Inorg. Chem.* 1989, 28, 404.
- [34] T. S. A. Hor, H. S. O. Chan, K.-L. Tan, L.-T. Phang, Y. K. Yan, L.-K. Liu, Y.-S. Wen, *Polyhedron* 1991, 10, 2437.
- [35] Z. Fang, T. S. A. Hor, Y. Wen, L. Liu, T. C. W. Mak, *Polyhedron* 1993, 14, 2403.
- [36] D. Cauzzi, C. Graiff, M. Lanfranchi, G. Predieri, A. Tiripicchio, J. Organomet. Chem. 1997, 536/537, 497.
- [37] K. J. Donaghy, P. J. Carroll, L. G. Sneddon, *Inorg. Chem.* 1997, 36, 547.
- [38] T. S. A. Hor, L. T. Phang, J. Organomet. Chem. 1989, 373, 319.