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A C_2-symmetric analogue of dppf: synthesis and structures of the indenyl-diphosphine complex 1,3-$(Ph_2PSe)_2(C_9H_6)$ and the racemic and *meso* isomers of the heterobimetallic complex $Mo(CO)_4(1\text{-}PPh_2\text{-}\eta^5\text{-}C_9H_6)_2Fe$

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Abstract

The preparation, isolation and characterisation of 1,3-bis(diphenylphosphino)indene (**1**) from indene and chlorodiphenylphosphine is described. The reaction of **1** with selenium gives the diselenide adduct 1,3-bis(diphenylselenophosphino)indene (**2**) which was characterised crystallographically. Deprotonation of **1** and treatment with ferrous chloride gives the unstable tetraphosphine complex bis(1,3-bis(diphenylphosphino)indenyl)iron(II) (**3**). Complex **3** decomposes to the diphosphine complex bis(1-diphenylphosphinoindenyl)iron(II) (**4**) via replacement of one diphenylphosphine substituent per indenyl ligand by a hydrogen atom. Complex **4** was also prepared by treatment of two equivalents of 1-diphenylphosphinoindenide with ferrous chloride. The heterobimetallic complex tetracarbonyl(bis(1-diphenylphosphinoindenyl)iron(II))molybdenum(0) (**5**) was also prepared and crystal structures of both the *meso* (**5a**) and C_2-symmetric racemic (**5b**) isomers are reported. © 1999 Elsevier Science S.A. All rights reserved.

Keywords: Indenyl-phosphine complexes; Heterobimetallic; Chiral ligands

1. Introduction

The use of multifunctional ligands is increasing rapidly because of their utility in the preparation of polymetallic complexes in which the metal centres may exhibit co-operative effects: the polymetallic complex may behave differently from the sum of the individual moieties. Phosphines and cyclopentadienyls are two of the most commonly used classes of ligands because they are easy to tune and can be functionalised readily. Most investigations involving tethered cyclopentadienyl-phosphine ligands have the functionalities directly bound, as in diphenylphosphinocyclopentadienyl [1,2]. There are also many investigations with two-atom bridges [3] as well as a number with one- or three-atom bridges [4,5]. We have reported recently the coordination chemistry of the ligand bis(2-cyclopentadienylethyl)phenylphosphine with iron and zirconium [6]. Investigations of indenyl complexes are not as extensive as their cyclopentadienyl counterparts, even though they have many of the same properties and are often more catalytically active due to the ease with which they can undergo ring-slippage reactions. These ring-slippage reactions can, however, make the indenyl complexes more difficult to isolate and characterise. Little coordination chemistry has been investigated with phosphino-substituted indene and indenyl ligands. Most complexes are of the indene coordinated through the phosphorus atom [7–9] and most π-coordinated systems are with group 4 metals [10]. McGlinchey has reported recently the manganese π-

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complex $\{1,3\text{-}(Ph_2P)_2\text{-}\eta^5\text{-}C_9H_5\}Mn(CO)_3$ [11]. Diphosphine-indenyl ligands are rare and include McGlinchey's complex above and the *P*,*P*′-coordinated complex $\{(1,2\text{-}(Ph_2P)_2)(3\text{-}OEt)C_9H_5\}Cr(CO)_4$ [8].

The complex 1,1′-bis(diphenylphosphino)ferrocene (dppf) is the most studied complex that contains a ligand with both phosphine and cyclopentadienyl functionalities [2]. This is because it is also a chelating diphosphine ligand that provides the ability to rigidly control two coordination sites and take advantage of the extra stability imparted through the chelate effect. Derivatives containing chiral functional groups are being used in asymmetric synthesis [12], however, C_2-symmetric systems are very rare [12,13].

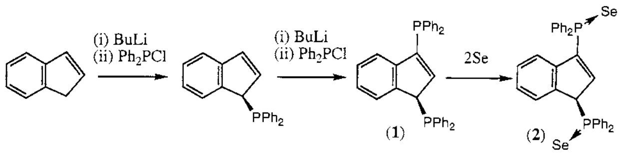
In this paper we report the preparation, isolation and characterisation of 1,3-bis(diphenylphosphino)indene (**1**), a selenium adduct of **1**, an indenyl analogue of dppf, of which one isomer has C_2 symmetry, and a heterobimetallic complex utilising this dppf analogue. Compound **1** has been reported by McGlinchey and co-workers; however, it was not isolated or characterised [11].

2. Results and discussion

2.1. Diphosphino-indenes

1,3-Bis(diphenylphosphino)indene (**1**) is prepared readily in a two-step procedure from indene (Scheme 1) by, firstly, the sequential addition of one equivalent of *n*-BuLi and chlorodiphenylphosphine to give diphenylphosphinoindene, and, secondly, the addition of another sequential equivalent of *n*-BuLi and chlorodiphenylphosphine. Filtration through alumina, removal of solvent, and washing with ethanol, in which it is sparingly soluble, provides **1** in high yield (87%).

Compound **1** has been characterised by ^{1}H-, ^{13}C-, ^{31}P-NMR spectroscopy, microanalysis and EI mass spectrometry. Two doublets in the ^{31}P-NMR spectrum at − 1.1 ppm and − 21.6 ppm are consistent with Ph_2P groups on sp^3 and sp^2 carbon atoms, respectively, and are similar to those found for 1-diphenylphosphinoindene (− 4.3 ppm) and 3-diphenylphosphinoindene (− 22.3 ppm) [9]. The four-bond P–P coupling constant is 4 Hz. The ^{13}C-NMR spectra of **1** and the other compounds presented herein are discussed in a later section.



Scheme 1.

The diselenium adduct of **1**, 1,3-bis(diphenylselenophosphino)indene (**2**) is prepared readily by heating a toluene solution of **1** with selenium (Scheme 1). The downfield shifts, compared to **1**, of the resonances in the ^{31}P-NMR spectrum (37.9 ppm and 20.9 ppm) and the observation of one-bond P–Se coupling constants (750 and 730 Hz, respectively) confirm coordination of the phosphorus atoms to selenium. The four-bond P–P coupling constant has increased slightly to 6 Hz. The corresponding chemical shifts reported for the oxide and sulfide analogues are 32.0/22.1 ppm and 46.9/32.5 ppm, respectively [11]. McGlinchey and co-workers assigned the downfield shifts to the phosphorus atom on C-1 and the upfield shifts to the phosphorus atom on C-3 on the basis that $\delta\ ^{31}P(sp^3) > \delta\ ^{31}P(sp^2)$. Although this trend applies to phosphines, and their oxides and sulfides, the trend is reversed for selenides; thus, $\delta(Ph_3PSe)\ 34.1 > \delta(Ph_2MePSe)\ 22.3 > \delta(Me_3PSe)\ 8.0$ [14]. Therefore, we assign the downfield resonance to the phosphorus atom on C-3 and the upfield resonance to the phosphorus atom on C-1. This assignment is also consistent with the $^1J_{PSe}$ trend in which $^1J_{PSe}(Ph_3PSe)\ 735.5 > {}^1J_{PSe}(Ph_2MePSe)\ 725 > {}^1J_{PSe}(Me_3PSe)\ 684$ [14].

The molecular structure of **2** was further confirmed by an X-ray crystallographic analysis. Bond distances are given in Table 1, selected bond angles in Table 2, crystal data and structure refinement parameters in Table 3, and the atomic coordinates and equivalent isotropic displacement parameters are given in Table 4. The asymmetric unit contains two crystallographically independent molecules of **2** along with one molecule of dichloromethane solvate. Fig. 1 shows a thermal ellipsoid plot of one of the two molecules with the adopted numbering scheme. The conformer of the other molecule is very similar; no torsion angle differs by more than 10° between the two molecules. The torsion angles that describe the Se atom orientation are: Se(1)–P(1)–C(1)–C(2) = 58.4(4); Se(2)–P(2)–C(3)–C(2) = 118.7(4); Se(1′)–P(1′)–C(1′)–C(2′) > 48.4(4); Se(2′)–P(2′)–C(3′)–C(2′) = 115.2(4). A comparison with those found for the oxide and sulfide analogues, which have very similar conformations to each other, shows that **2** has adopted a different conformation: although the selenide on C3 has a similar orientation to that of the oxidised and sulfided analogues (O2–P2–C3–C2 = 102.3° and S2–P2–C3–C2 = 110.6°), the selenide on C1 is oriented to the other side of the indenyl ring and away from the C1 hydrogen atom (O1–P1–C1–C2 = − 57.0° and S1–P1–C1–C2 = − 59.9°) [11].

2.2. Complexes of iron

We desired to prepare a complex containing two diphosphino-indenyl ligands on the one metal centre to give a tetraphosphine ligand. The indene **1** was deprotonated and added to a solution containing one half-

Table 1
Selected bond distances (Å)

Bond	**2**	**2′**	**5a**	**5a′**	**5b**
Mo–P			2.5577(14)	2.5691(15)	2.5658(7)
Fe–C(1)			2.056(5)	2.038(5)	2.058(2)
Fe–C(2)			2.041(5)	2.014(6)	2.071(2)
Fe–C(3)			2.014(6)	2.048(5)	2.0718(19)
Fe–C(4)			2.092(5)	2.101(5)	2.1038(19)
Fe–C(9)			2.095(6)	2.100(5)	2.085(2)
C(1)–C(2)	1.514(6)	1.527(6)	1.417(8)	1.433(8)	1.426(3)
C(2)–C(3)	1.354(6)	1.366(6)	1.435(8)	1.439(7)	1.444(3)
C(3)–C(4)	1.483(6)	1.475(6)	1.457(8)	1.456(8)	1.460(3)
C(4)–C(5)	1.386(6)	1.401(7)	1.421(8)	1.428(8)	1.435(3)
C(5)–C(6)	1.387(7)	1.382(7)	1.360(9)	1.369(8)	1.373(3)
C(6)–C(7)	1.391(7)	1.388(7)	1.416(9)	1.401(8)	1.431(4)
C(7)–C(8)	1.405(7)	1.389(7)	1.347(8)	1.360(8)	1.355(4)
C(8)–C(9)	1.382(6)	1.394(7)	1.427(8)	1.420(8)	1.442(3)
C(1)–C(9)	1.523(7)	1.512(7)	1.430(8)	1.432(8)	1.437(3)
C(4)–C(9)	1.416(6)	1.414(6)	1.438(8)	1.450(7)	1.452(3)
P–C(3)	1.803(4)	1.803(5)	1.826(6)	1.818(6)	1.8264(19)
P(1)–C(1)	1.859(4)	1.862(4)			
P(1)–Se(1)	2.1144(14)	2.1138(15)			
P(2)–Se(2)	2.1251(14)	2.1265(14)			

equivalent of ferrous chloride (Scheme 2); the resultant solution, before work-up, shows a single peak in the ^{31}P-NMR spectrum at -19.9 ppm which is assigned to the desired product, bis(1,3-bis(diphenylphosphino)indenyl)iron(II) (**3**). The ^{31}P-NMR spectrum of the residue obtained by removing the solvent in vacuo, however, shows a complex spectrum. Chromatography on silica produced only bis(1-(diphenylphosphino)indenyl)iron(II) (**4**), in 20% yield, in which one diphenylphosphino group on each indenyl has been replaced by a hydrogen atom. The ^{31}P-NMR spectrum of **4** shows a single peak at -22.5 ppm. Steric congestion coupled with facile ring-slippage decomposition routes are believed to be responsible for the instability of complex **3**.

Table 2
Selected bond angles (Å)

2			
C(1)–P(1)–Se(1)	113.69(15)	C(1′)–P(1′)–Se(1′)	112.68(15)
C(3)–P(2)–Se(2)	112.74(14)	C(3′)–P(2′)–Se(2′)	112.10(15)
C(2)–C(1)–P(1)	110.9(3)	C(2′)–C(1′)–P(1′)	109.6(3)
C(9)–C(1)–P(1)	111.5(3)	C(9′)–C(1′)–P(1′)	112.6(3)
C(2)–C(1)–C(9)	102.9(4)	C(2′)–C(1′)–C(9′)	103.2(4)
C(4)–C(3)–P(2)	123.9(3)	C(4′)–C(3′)–P(2′)	125.3(3)
C(2)–C(3)–P(2)	126.3(4)	C(2′)–C(3′)–P(2′)	124.8(4)
C(2)–C(3)–C(4)	109.5(4)	C(2′)–C(3′)–C(4′)	109.5(4)
5a			
Fe–C(3)–P	126.7(3)	P′–C(3′)–Fe	133.3(3)
C(3)–P–Mo	124.3(2)	Mo–P′–C(3′)	117.6(2)
P–Mo–P′	98.71(5)	C(3)–Fe–C(3′)	112.5(2)
P–C(3)–C(2)	129.8(4)	P′–C(3′)–C(2′)	119.4(4)
C(2)–C(3)–C(4)	106.5(5)	C(2′)–C(3′)–C(4′)	106.5(5)
C(4)–C(3)–P	123.5(4)	C(4′)–C(3′)–P′	133.1(4)
5b			
Fe–C(3)–P	128.97(10)	P–C(3)–C(2)	129.54(15)
C(3)–P–Mo	122.18(6)	C(2)–C(3)–C(4)	106.47(16)
P–Mo–P′	99.44(3)	C(4)–C(3)–P	123.74(14)
C(3)–Fe–C(3′)	113.64(10)		

The diphosphine **4** was prepared in higher yield (40%) by treatment of ferrous chloride with two equivalents of $[Ph_2PC_9H_6]^-$ (Scheme 2). Complex **4** can exist in two isomeric forms; a meso form, **4a**, and a racemic form, **4b**. Surprisingly, these isomers are chemically and spectroscopically almost identical. The ^{1}H-, ^{13}C-, and ^{31}P-NMR spectra suggest only one isomer however, we have been able to isolate, vide infra, single crystals of a heterobimetallic complex of **4** containing the *meso* isomer as well as single crystals containing the racemic isomer. Whereas the *meso* isomer exhibits C_s symmetry, the racemic isomer exhibits C_2 symmetry, thus, in each complex, the indenyl rings are equivalent and they would be expected to show the same patterns in their NMR spectra. To date, we have been unable to determine the racemic:*meso* ratio using chiral shift reagents.

2.3. Heterobimetallic iron-molybdenum complexes

To investigate the coordination chemistry of diphosphine **4**, the tetracarbonylmolybdenum complex tetracarbonyl(bis(1-diphenylphosphinoindenyl)iron(II))-molybdenum(0) (**5**) was prepared in 40% yield by treatment of $Mo(CO)_4(piperidine)_2$ with one equivalent of **4**. As with **4**, the heterobimetallic complex **5** has racemic and *meso* isomers. Curiously, crystals of **5** prepared

Table 3
Crystal data and structure refinement parameters for **2**, **5a** and **5b**

Compound	**2**	**5a**	**5b**
Empirical formula	$C_{33.5}H_{27}ClP_2Se_2$	$C_{47}H_{34}Cl_2FeMoO_4P_2$	$C_{46}H_{32}FeMoO_4P_2$
Formula weight	684.86	947.37	862.45
Temperature (K)	158(2)	150(2)	158(2)
Wavelength (Å)	0.71073	0.71073	0.71073
Crystal system	Orthorhombic	Monoclinic	Monoclinic
Space group	$Pca2_1$	$P2_1/c$	$C2/c$
a (Å)	20.316(8)	18.1287(11)	18.103(5)
b (Å)	12.054(5)	12.4033(7)	11.230(3)
c (Å)	25.007(10)	19.0262(10)	19.901(6)
α (°)	90	90	90
β (°)	90	108.3750(10)	99.468(9)
γ (°)	90	90	90
Volume (Å^3)	6124(4)	4060.0(4)	3990.7(19)
Z	8	4	4
Calculated density (Mg/m^3)	1.486	1.550	1.435
Absorption coefficient (mm^{-1})	2.628	0.922	0.801
F(000)	2744	1920	1752
Crystal size (mm)	$0.4 \times 0.35 \times 0.15$	$0.5 \times 0.3 \times 0.2$	$0.7 \times 0.5 \times 0.3$
θ range for data collection (°)	2.75 to 26.53	3.17 to 23.28	2.82 to 26.29
Limiting indices	$-25 \leq h \leq 14$	$-19 \leq h \leq 19$	$-22 \leq h \leq 20$
	$-14 \leq k \leq 12$	$-13 \leq k \leq 12$	$-13 \leq k \leq 13$
	$-27 \leq l \leq 30$	$-7 \leq l \leq 21$	$-24 \leq l \leq 24$
Reflections collected/unique	22827/11336 [$R_{int} > 0.0398$]	9239/5404 [$R_{int} > 0.0306$]	22105/3920 [$R_{int} > 0.0210$]
Completeness to θ_{max}	94.6%	92.4%	96.7%
Absorption correction	SADABS	SADABS	SADABS
Data/restraints/parameters	11336/1/694	5404/0/509	3920/0/245
Goodness-of-fit on F^2	0.950	1.092	1.076
Final R indices [$I > 2\sigma(I)$]			
R_1	0.0371	0.0558	0.0237
wR_2	0.0675	0.1504	0.0574
R indices (all data)			
R_1	0.0641	0.0652	0.0291
wR_2	0.0742	0.1605	0.0612
Largest diff. peak (e Å^{-3})	0.664	2.595	0.431
Largest diff. hole (e Å^{-3})	−0.414	−1.147	−0.372

from **4** via diphenylphosphinoindenide were revealed, by X-ray crystallography, to be the meso isomer **5a**, whereas crystals of **5** obtained when **4** was prepared via the tetraphosphine **3** were revealed, also by X-ray crystallography, to be the racemic isomer **5b**. Spectra obtained using individual crystals of **5a** and **5b** shows them to be almost indistinguishable spectroscopically. The isolation of a single crystal of one particular isomer of complex **5** does not preclude the presence of both isomers in the mixture and hence it is impossible to ascertain, from the data, whether both isomers are present in **4**. Therefore, we are also unable to determine whether the preparative route is relevant. Like **4**, both isomers of **5** have symmetrically identical indenyl ligands and a single resonance in the ^{31}P-NMR spectrum at 33.1 ppm is observed that is similar to that of the dppf analogue $Mo(CO)_4$(dppf) (33.9 ppm) [15].

The infrared spectrum of $Mo(CO)_4$(dppf) shows a medium intensity band at 2020 cm^{-1}, a strong band at 1921 cm^{-1}, and a very strong band at 1901 cm^{-1} [15]. Both **5a** and **5b** show the same high-frequency medium-intensity band at 2021 cm^{-1}, essentially unchanged from that found for $Mo(CO)_4$(dppf). The other bands, however, are at lower energy and have different relative intensities from those found for $Mo(CO)_4$(dppf). For the C_2-symmetric isomer **5b**, the band at 1913 cm^{-1} is now the strongest band and the lowest energy band at 1878 cm^{-1} has approximately half the intensity of the 1913 cm^{-1} band. The infra-red spectrum of the meso isomer **5a** is almost identical to **5b** but has a slight splitting of the strongest band (to 1916 and 1909 cm^{-1}).

The X-ray structural analysis of **5a** shows one independent molecule in the asymmetric unit. Bond distances are given in Table 1, selected bond angles in Table 2, crystal data and structure refinement parameters in Table 3, and the atomic coordinates and equivalent isotropic displacement parameters are given in Table 5. Fig. 2 shows a thermal ellipsoid plot with the adopted numbering scheme. Each indenyl-phosphine ligand is coordinated to an iron atom in an η^5 coordination mode via the indenyl five-membered ring, and

Table 4
Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($Å^2 \times 10^3$) for **2**[a]

	x	y	z	U_{eq}
Se(1)	5702(1)	−3871(1)	4762(1)	38(1)
Se(2)	2286(1)	−3398(1)	5487(1)	34(1)
P(1)	5661(1)	−2532(1)	5306(1)	28(1)
P(2)	3224(1)	−4175(1)	5475(1)	26(1)
C(1)	4810(2)	−2046(3)	5449(2)	28(1)
C(2)	4394(2)	−2977(3)	5674(2)	26(1)
C(3)	3884(2)	−3212(3)	5344(2)	25(1)
C(4)	3905(2)	−2461(4)	4875(2)	26(1)
C(5)	3496(2)	−2380(4)	4432(2)	32(1)
C(6)	3615(3)	−1554(5)	4058(2)	43(1)
C(7)	4132(3)	−813(5)	4132(2)	47(2)
C(8)	4558(3)	−895(4)	4573(2)	38(1)
C(9)	4447(2)	−1734(4)	4938(2)	27(1)
C(11)	6015(2)	−2849(4)	5959(2)	28(1)
C(12)	5920(2)	−2184(4)	6411(2)	34(1)
C(13)	6242(3)	−2396(5)	6885(2)	47(2)
C(14)	6668(3)	−3300(5)	6923(2)	47(2)
C(15)	6759(2)	−3979(4)	6485(2)	41(1)
C(16)	6431(2)	−3775(4)	6007(2)	34(1)
C(21)	6082(2)	−1295(4)	5071(2)	29(1)
C(22)	6149(2)	−351(4)	5403(2)	36(1)
C(23)	6459(2)	595(4)	5207(2)	42(1)
C(24)	6711(3)	618(4)	4691(3)	45(1)
C(25)	6639(3)	−282(5)	4362(2)	45(1)
C(26)	6330(2)	−1242(4)	4548(2)	35(1)
C(31)	3423(2)	−4843(4)	6104(2)	26(1)
C(32)	3661(2)	−5937(4)	6132(2)	32(1)
C(33)	3779(3)	−6430(4)	6623(2)	38(1)
C(34)	3667(2)	−5835(4)	7090(2)	38(1)
C(35)	3447(2)	−4755(4)	7068(2)	37(1)
C(36)	3324(2)	−4262(4)	6575(2)	32(1)
C(41)	3296(2)	−5219(4)	4956(2)	29(1)
C(42)	3901(2)	−5450(4)	4716(2)	39(1)
C(43)	3947(3)	−6287(4)	4337(2)	45(2)
C(44)	3396(3)	−6908(4)	4203(2)	46(2)
C(45)	2792(3)	−6672(4)	4433(2)	42(1)
C(46)	2737(2)	−5825(4)	4806(2)	34(1)
Se(1′)	5832(1)	−9233(1)	7532(1)	36(1)
Se(2′)	9235(1)	−8536(1)	6996(1)	34(1)
P(1′)	5868(1)	−7704(1)	7119(1)	28(1)
P(2′)	8304(1)	−9339(1)	7012(1)	27(1)
C(1′)	6724(2)	−7195(3)	7018(2)	26(1)
C(2′)	7149(2)	−8129(4)	6793(2)	26(1)
C(3′)	7641(2)	−8382(3)	7144(2)	26(1)
C(4′)	7594(2)	−7652(4)	7616(2)	29(1)
C(5′)	7978(3)	−7583(4)	8080(2)	41(1)
C(6′)	7847(3)	−6757(5)	8449(2)	45(2)
C(7′)	7340(3)	−6008(4)	8359(2)	43(1)
C(8′)	6941(2)	−6069(4)	7909(2)	35(1)
C(9′)	7063(2)	−6910(4)	7539(2)	29(1)
C(11′)	5510(2)	−7766(4)	6450(2)	28(1)
C(12′)	5636(2)	−6969(4)	6053(2)	34(1)
C(13′)	5319(3)	−7023(4)	5563(2)	45(1)
C(14′)	4860(2)	−7870(5)	5465(2)	45(1)
C(15′)	4734(2)	−8652(4)	5847(2)	38(1)
C(16′)	5051(2)	−8609(4)	6340(2)	33(1)
C(21′)	5472(2)	−6559(4)	7479(2)	32(1)
C(22′)	5357(2)	−5539(4)	7230(2)	41(1)
C(23′)	5108(3)	−4650(4)	7521(3)	53(2)
C(24′)	4971(3)	−4787(5)	8064(3)	61(2)
C(25′)	5074(3)	−5787(5)	8307(3)	58(2)
C(26′)	5333(3)	−6678(4)	8012(2)	42(1)
C(31′)	8107(2)	−10014(4)	6380(2)	25(1)
C(32′)	7866(2)	−11097(4)	6351(2)	36(1)
C(33′)	7756(3)	−11589(4)	5858(2)	39(1)
C(34′)	7885(2)	−11011(4)	5394(2)	35(1)
C(35′)	8108(2)	−9928(4)	5414(2)	34(1)
C(36′)	8235(2)	−9438(4)	5905(2)	30(1)
C(41′)	8232(2)	−10406(4)	7523(2)	28(1)
C(42′)	7606(3)	−10730(4)	7704(2)	41(1)
C(43′)	7545(3)	−11616(4)	8054(2)	48(2)
C(44′)	8110(3)	−12183(4)	8223(2)	48(2)
C(45′)	8724(3)	−11859(4)	8054(2)	40(1)
C(46′)	8789(2)	−10964(4)	7703(2)	34(1)
C(10)	4772(3)	8678(5)	8406(3)	63(2)
Cl(1)	4496(1)	8009(2)	8982(1)	94(1)
Cl(2)	5556(1)	8191(1)	8212(1)	59(1)

the phosphorus atom is coordinated to a molybdenum atom. The indenyl rings are twisted by 35.6° (C3–CNT–CNT′–C3′; CNT = centroid of the five-membered ring) with respect to each other to give a synclinal (or gauche) conformation. The molybdenum atom has the two phosphorus atoms bound in a *cis* fashion to give an octahedral geometry with the other four coordination sites occupied by carbonyl ligands. In order to accommodate the large molybdenum atom, either a half-chair (**6a** and **6b**) or twist-boat (**6c**) conformation must be adopted (Fig. 3). Half-chair conformations are rare in chelated dppf complexes and it can be seen that for **6a** there is an unfavourable phenyl-phenyl interaction. The other half-chair conformation, **6b**, has two unfavourable phenyl-benzo interactions as well as a phenyl-phenyl interaction. The twist-boat conformation, **6c**, is the preferred conformation; there are no phenyl-phenyl interactions and there is only one phenyl–benzo interaction. It should be noted that this conformation removes the C_s symmetry of the molecule that is found in the NMR spectra. The phenyl-benzo interaction has a dramatic effect on the diphenylphosphine group: the phenyl ring is forced perpendicular to the benzo ring which brings H15″ within the van der Waals radii of C5, H5, and C16* (2.68, 2.30 and 2.76 Å, respectively). Consequently, P′ deviates 0.230 Å from its C_5 ring, away from the iron atom, compared to 0.005 Å for P (towards the iron atom) and 0.017/0.026 Å for $Mo(CO)_4$(dppf) [16]. The average deviation for chelated dppf complexes is 0.05 Å towards the Fe atom and the largest deviation reported in the review by Gan and Hor [2] is 0.157 Å, away from the iron atom, for the eclipsed synperiplanar complex $NiBr_2$(dppf) [16]. The CNT′–C3′–P′ angle of 169.2° is smaller than the CNT–C3–P angle of 176.1°. The P–Mo–P′ bite angle of 98.71° is slightly larger than the dppf analogue (95.3(1)°) and the Mo–P distances (Mo–P = 2.5577(14) Å and Mo–P′ = 2.5691(15) Å) are similar to each other as well as the dppf analogue (2.560(16) Å). Other conformational measures are typical of chelated dppf complexes (the corresponding values for $Mo(CO)_4(dppf)$ are given in parentheses [16]): the torsional twist (C3–CNT–CNT′–C3′) = 35.6° (41.9°), CNT–Fe–CNT′ = 176.5° (179.0°), θ (the angle between the C_5 planes) = 5.9° (2.2°), P...P = 3.881 Å (3.783 Å).

The X-ray structural analysis of **5b** revealed one independent half-molecule with the other half being related by a C_2 axis through the Fe and Mo atoms. Bond distances are given in Table 1, selected bond angles in Table 2, crystal data and structure refinement parameters in Table 3, and the atomic coordinates and equivalent isotropic displacement parameters are given in Table 6. Fig. 4 shows a thermal ellipsoid plot with the adopted numbering scheme. As with **5a**, either a half-chair (**7a**) or twist-boat conformation (**7b** and **7c**) must be adopted to accommodate the molybdenum atom. The half-chair conformation has one benzo-phenyl interaction as well as a phenyl-phenyl interaction. Of the two twist-boat conformations, **7b** has two phenyl-benzo interactions whereas **7c** has neither phenyl-benzo nor phenyl-phenyl interactions. Consequently, the adopted conformation **7c** is the least sterically-strained conformation. Notably, this conformation also retains the C_2 symmetry that is observed in the NMR spectra. Unlike **5a**, the P atom does not deviate significantly from its C_5 ring (0.048 Å away from the iron atom) and the CNT–C3–P angle of 175.8° is normal. The P–Mo–P′ bite angle of 99.44(3)° is slightly larger than in **5a** (98.71°) and the dppf analogue (95.3(1)°) and the torsional twist (C3–CNT–CNT′–C3′ = 25.8°) is significantly less than in both **5a** (35.6°) and $Mo(CO)_4(dppf)$ (41.9°). The other conformational measures are typical of chelated dppf complexes: Mo–P = 2.5658(7) Å; CNT–Fe–CNT′ = 174.8°; θ = 5.7°; and P...P = 3.914 Å.

2.4. ^{13}C-NMR spectroscopy

Table 7 summarises the ^{13}C chemical shifts and P–C coupling constants for the carbon atoms in the five-membered ring of the indene and indenyl compounds. The labelling scheme is shown in Fig. 5: we have labelled **4** and **5** with the phosphorus-bound carbon atoms as C-3 for ease of comparison.

Houlton and co-workers found that functionalisation of Cp with PPh_2 causes a downfield shift for all ring-carbon resonances and that, as with phenyl-phosphines, $^2J_{PC}$ is greater than $^1J_{PC}$ and $^3J_{PC}$ for $FeCp(C_5H_4PPh_2)$, δ(Cp) 69.0, $\delta(C_P)$ 76.6 ($^1J_{PC} = 0$ Hz), $\delta(C_\alpha)$ 72.8 ($^2J_{PC} = 14.7$ Hz), and $\delta(C_\beta)$ 70.6 ($^3J_{PC} = 3.4$ Hz); and for dppf, $\delta(C_P)$ 77.6 ($^1J_{PC} = 4$ Hz), $\delta(C_\alpha)$ 74.6 ($^2J_{PC} = 15$ Hz), and $\delta(C_\beta)$ 73.1 ($^3J_{PC} = 3.5$ Hz) [17]. For $(\eta^5\text{-}C_9H_7)_2Fe$, the unique carbon atom, C-2, is 8.0 ppm downfield of C-1/C-3 (70.3 ppm versus 62.3 ppm, respectively) and the quaternary carbon atoms, C-4/C-9, are a further 17.3 ppm downfield at 87.6 ppm [18]. Based on the above trends, the ^{13}C spectrum of **4** is assigned as follows: the resonance at δ 91.0, with a large P–C coupling constant (25 Hz), is assigned to C-4 and the resonance at δ 89.7 (with a smaller $^3J_{PC}$ of 4 Hz) to the other quaternary carbon, C-9. Atom C-3, which appears further upfield at δ 68.1 with $^1J_{PC} = 9$ Hz, is distinguishable by its lower intensity compared to the C-1 and C-2 resonances. C-2 appears 5.9 ppm downfield of C-1, δ 72.0 versus δ 66.1, respectively. C-2 has a much smaller $^2J_{PC}$ (4 Hz) than C-4 (25 Hz) which indicates that the phosphorus lone pair is oriented towards C-4 [19] thereby minimising steric interactions between H-5 and the phenyl ring. $^3J_{PC}$ for C-1 is the same as that of C-9.

The phenyl rings on each phosphorus atom are inequivalent, so two sets of phenyl resonances are observed. As is typical of phenyl-phosphine compounds, $^2J_{PC}$ (22 and 18 Hz) is greater than $^1J_{PC}$ (10 and 7 Hz) and $^3J_{PC}$ (8 and 5 Hz). Of the benzo carbon atoms, only C-5 shows PC coupling: $^3J_{PC} = 9$ Hz.

Coordination of **4** to a $Mo(CO)_4$ fragment reduces significantly the P-C coupling constants and causes downfield shifts for C-3 (8.3 ppm to δ 76.4) and C-2 (7.9 ppm to δ 79.9), whereas C-4 and C-9 exhibit small upfield shifts (1.3 ppm and 2.6 ppm, respectively). C-1 is relatively unchanged.

The assignments of the C-1 and C-2 resonances of **1**, are readily made based on their chemical shifts, intensities, and coupling constants: C-1 is significantly upfield at δ 49.5 and appears as a doublet of doublets, the larger coupling constant of 23 Hz is $^1J_{PC}$ and the smaller coupling constant of 4 Hz is $^3J_{PC}$. These coupling constants are both smaller than the corresponding values for $1\text{-}Ph_2P(C_9H_7)$ (34 Hz) and $3\text{-}Ph_2P(C_9H_7)$ (6 Hz) [9]. C-2 at δ 142.4 has greater intensity than the slightly upfield resonance of C-3 at δ 141.6. The larger of the two-bond coupling constants for C-2 (7 Hz) is assigned to coupling with the P atom on C-1 and the smaller (3 Hz) with the P atom on C-3: C-4 shows a large $^2J_{PC}$ (18 Hz) indicating that the lone pair of the P atom on C-3 is oriented towards C-4, this would then give the observed small $^2J_{PC}$ for C-2. $^3J_{PC}$ for C-4 is very small at 2 Hz, but this is similar to that of $1\text{-}Ph_2P(C_9H_7)$ at 1.5 Hz. The one-bond coupling constant of 14 Hz for C-3 is typical of an sp^2 carbon atom; $^3J_{PC}$ is somewhat smaller at 5 Hz. C-9 has a moderate $^2J_{PC}$ of 8 Hz (cf. 9 Hz for $1\text{-}Ph_2P(C_9H_7)$) and a typical $^3J_{PC}$ of 4 Hz (cf. 5 Hz for $3\text{-}Ph_2P(C_9H_7)$). The chemical shifts of C-4 and C-9 are both downfield of the other indene resonances at δ 145.3 and δ 144.9, respectively. Our assignment for $3\text{-}Ph_2P(C_9H_7)$ differs from that of

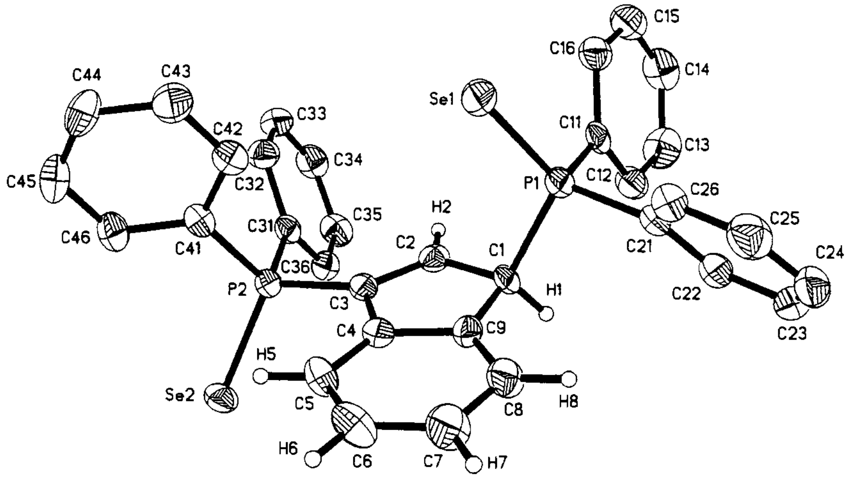
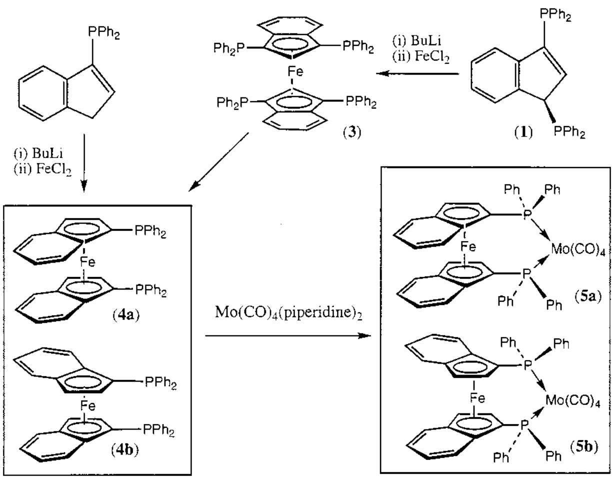


Fig. 1. Thermal ellipsoid plot of one molecule of **2**.

Anderson and co-workers who assigned the downfield resonance at δ 145.9, with the large coupling constant of 20 Hz, to C-3 and the upfield resonance at δ 141.9, with a moderate coupling constant of 13 Hz, to C-4.

Since **1** has a stereocentre at C-1, the four phenyl rings are inequivalent and four sets of resonances are observed. The *meta*, *para* and *ortho* carbons have similar chemical shifts and coupling constants: δ 128.0–128.4 ($^3J_{PC} = 6–9$ Hz, *m*-Ph), 128.6–129.2 (*p*-Ph), 133.3–133.9 ($^2J_{PC} = 19–21$ Hz, *o*-Ph). The *ipso* carbons have similar chemical shifts but exhibit two sizes of $^1J_{PC}$: The smaller coupling constants are attributed to the phenyl rings on the phosphorus atom attached to the sp^3 carbon atom C-1 (δ 135.3 ($^1J_{PC} = 8$ Hz), 135.3 ($^1J_{PC} = 8$ Hz)); and the larger coupling constants are attributed to the phenyl rings on the phosphorus atom attached to the sp^2 carbon atom C-3 (δ 135.8 ($^1J_{PC} = 18$ Hz), 136.2 ($^1J_{PC} = 19$ Hz)). Given our ability to distinguish the four inequivalent phenyl rings in **1**, it seems peculiar that the *rac* and *meso* isomers of **4** and **5** are so similar.



Scheme 2.

Coordination of the phosphorus atoms of **1** to selenium to give compound **2** causes downfield shifts for both C-1 (δ 49.5 to δ 55.3) and C-2 (δ 142.4 to δ 143.5) as well as an increase in the coupling constants (see Table 7).

3. Conclusions

We have isolated and characterised the diphosphinoindene compound 1,3-$(Ph_2P)_2C_9H_6$ (**1**). The ferrocene complex of the corresponding indenide is unstable to formation of the bis(phosphinoindenyl)iron complex **4**. This complex exists in two isomeric forms: a racemic form with C_2 symmetry and a meso form with C_s symmetry. The racemic isomer, in particular, has significant potential in the area of asymmetric synthesis and catalysis as a C_2 analogue of dppf. We have reported initial investigations into its coordination chemistry: Coordination of **4** to a $Mo(CO)_4$ fragment gives a heterobimetallic Fe–Mo complex with racemic and meso isomers. Whereas the racemic isomer exhibits only C_2 symmetry, the meso isomer exhibits C_1 symmetry in the solid state and solution infra-red spectrum but C_s symmetry in the NMR solution spectra. Efforts to understand the formation of **4** from the tetraphosphine **3**, to determine the racemic:meso ratio of **4** and to separate these isomers are continuing.

4. Experimental

4.1. General considerations

All manipulations and reactions were carried out

Table 5
Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters (Å$^2 \times 10^3$) for **5a**[a]

Atom	x	y	z	U_{eq}
Mo	3167(1)	8415(1)	3920(1)	26(1)
Fe	1912(1)	6967(1)	1650(1)	26(1)
P	2760(1)	9222(1)	2616(1)	25(1)
Pí	2576(1)	6527(1)	3593(1)	25(1)
C(1)	1568(3)	7749(4)	646(3)	30(1)
C(1′)	2509(4)	5628(4)	1523(3)	33(1)
C(2)	2252(3)	8221(4)	1129(3)	29(1)
C(2′)	2845(3)	6107(4)	2238(3)	30(1)
C(3)	2110(3)	8562(4)	1796(3)	28(1)
C(3′)	2279(3)	6125(4)	2625(3)	26(1)
C(4)	1288(3)	8374(4)	1684(3)	26(1)
C(4′)	1582(3)	5610(4)	2140(3)	27(1)
C(5)	803(3)	8581(4)	2128(3)	28(1)
C(5′)	829(3)	5399(4)	2198(3)	30(1)
C(6′)	271(3)	4943(4)	1613(3)	30(1)
C(6)	55(4)	8227(5)	1889(3)	35(1)
C(7)	−247(4)	7668(5)	1209(3)	37(1)
C(7′)	420(4)	4675(5)	955(3)	35(1)
C(8′)	1129(4)	4842(4)	872(3)	33(1)
C(8)	178(3)	7490(5)	754(3)	35(1)
C(9′)	1734(3)	5305(4)	1462(3)	29(1)
C(9)	966(3)	7850(4)	980(3)	29(1)
C(10′)	3218(3)	5375(5)	3984(3)	27(1)
C(10″)	1726(3)	6217(4)	3888(3)	26(1)
C(10)	3634(3)	9503(4)	2353(3)	29(1)
C(10*)	2302(3)	10562(4)	2488(3)	28(1)
C(11′)	3698(4)	5398(5)	4713(4)	49(2)
C(11*)	2000(3)	10986(5)	1776(4)	36(1)
C(11)	3970(4)	10526(5)	2463(3)	39(2)
C(11″)	1668(4)	5294(5)	4291(3)	37(1)
C(12*)	1673(4)	12001(5)	1658(4)	41(2)
C(12′)	4179(5)	4518(6)	5024(4)	63(2)
C(12″)	997(4)	5089(5)	4459(4)	42(2)
C(12)	4668(4)	10720(5)	2323(4)	45(2)
C(13″)	371(4)	5774(6)	4232(4)	46(2)
C(13)	5022(4)	9900(6)	2059(4)	45(2)
C(13′)	4151(4)	3594(5)	4599(4)	49(2)
C(13*)	1633(4)	12620(5)	2253(3)	40(2)
C(14′)	3670(4)	3550(5)	3901(4)	39(2)
C(14)	4707(4)	8887(5)	1955(3)	37(1)
C(14*)	1909(4)	12205(5)	2952(4)	39(2)
C(14″)	417(4)	6693(6)	3840(4)	43(2)
C(15″)	1100(3)	6925(5)	3683(3)	33(1)
C(15)	4021(3)	8690(5)	2109(3)	33(1)
C(15*)	2250(4)	11177(5)	3080(3)	35(1)
C(15′)	3203(3)	4430(5)	3595(3)	35(1)
C(16)	3569(4)	8074(5)	4999(4)	35(1)
C(16*)	2221(4)	9018(5)	4142(3)	34(1)
C(16″)	3739(4)	9808(5)	4213(4)	41(2)
C(16′)	4144(4)	7764(5)	3777(3)	33(1)
C(17)	3289(7)	12570(12)	836(6)	113(4)
O(16)	3809(3)	7987(4)	5630(3)	50(1)
O(16*)	1717(3)	9372(4)	4312(3)	46(1)
O(16′)	4706(3)	7384(4)	3738(3)	51(1)
O(16″)	4089(3)	10582(4)	4415(3)	65(2)
Cl(1)	2458(2)	12858(3)	122(1)	110(1)
Cl(2)	3498(2)	13310(2)	1607(2)	113(1)

[a] U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensor.

under an inert atmosphere by use of standard Schlenk line techniques. Reagent grade solvents were dried and distilled prior to use: diethyl ether, toluene and tetrahydrofuran from Na/benzophenone; dichloromethane, heptane and pentane from CaH_2; ethanol from magnesium. Indene was distilled prior to use and cyclohexane and ethylacetate were saturated with dinitrogen prior to use. $Mo(CO)_4(piperidine)_2$ was prepared as described in the literature [20]. All other reagents were used as supplied by Aldrich Chemical Company. ^1H-, $^{13}C\{^1H\}$- and $^{31}P\{^1H\}$-NMR data were collected on a Varian XL-300 spectrometer operating at 300, 75 and 121 MHz, respectively, except for the ^1H-NMR spectrum of **2** which was collected on a Varian Unity 300 using an inverse-detection probe. Unless otherwise stated, spectra were measured at ambient temperature with residue solvent peaks as internal standard for ^1H- and $^{13}C\{^1H\}$-NMR. $^{31}P\{^1H\}$-NMR chemical shifts are reported relative to external 85% H_3PO_4, positive shifts representing deshielding. EI and FAB mass spectra were collected on a Kratos MS80RFA mass spectrometer. IR spectra were obtained on a Shimadzu FTIR-8201PC spectrophotometer. Elemental analyses were done by Campbell Microanalysis Services, Otago University, Dunedin.

4.2. Preparation, isolation and characterisation of 1,3-bis(diphenylphosphino)indene (**1**)

To a solution of indene (1.16 g, 1 mmol) in diethylether was added *n*-BuLi (6.25 ml, 1.6 M, 1 mmol) at −80°C. After stirring the reaction mixture for 30 min at ambient temperature and followed by cooling to −80°C, $ClPPh_2$ (2.2 g, 1 mmol) was added. After 1 h stirring at ambient temperature, the solution was again cooled to −80°C and *n*-BuLi (6.25 ml, 1.6 M, 1 mmol) was added. The solution was then stirred for 30 min before the addition of a second equivalent of $ClPPh_2$ (2.2 g, 1 mmol) at −80°C. After 1 h of stirring at ambient temperature, the reaction mixture was filtered through alumina, the solvent evaporated and the residue washed with ethanol to give 4.2 g (87% yield) of **1** as a white powder. ^1H-NMR ($CDCl_3$): δ 4.46 (s, 1H, H-1), 6.04 (s, 1H, H-2), 6.9–7.4 (m, 24H, H-5–H-8 and Ph). $^{31}P\{^1H\}$-NMR ($CDCl_3$): δ −21.6 (d, $^4J_{PP} = 4$ Hz, PC-3), −1.1 (d, $^4J_{PP} = 4$ Hz, PC-1). $^{13}C\{^1H\}$-NMR ($CDCl_3$): δ 49.5 (dd, $^3J_{PC} = 4$ Hz, $^1J_{PC} = 23$ Hz, C-1), 121.7 (d, $^3J_{PC} = 5$ Hz, C-5), 123.8 (d, $^3J_{PC} = 5$ Hz, C-8), 124.9 (s, C-6), 126.5 (s, C-7), 128.0 (d, $^3J_{PC} = 6$ Hz, *m*-Ph), 128.36 (d, $^3J_{PC} = 7$ Hz, *m*-Ph), 128.37 (d, $^3J_{PC} = 9$ Hz, *m*-Ph), 128.4 (d, $^3J_{PC} = 7$ Hz, *m*-Ph), 128.6 (s, *p*-Ph), 128.7 (s, *p*-Ph), 128.9 (s, *p*-Ph), 129.2 (s, *p*-Ph), 133.3 (d, $^2J_{PC} = 19$ Hz, *o*-Ph), 133.7 (d, $^2J_{PC} = 20$ Hz, *o*-Ph), 133.7 (d, $^2J_{PC} = 20$ Hz, *o*-Ph), 133.9 (d, $^2J_{PC} = 21$ Hz, *o*-Ph), 135.3 (d, $^1J_{PC} = 8$ Hz, *ipso*-Ph),

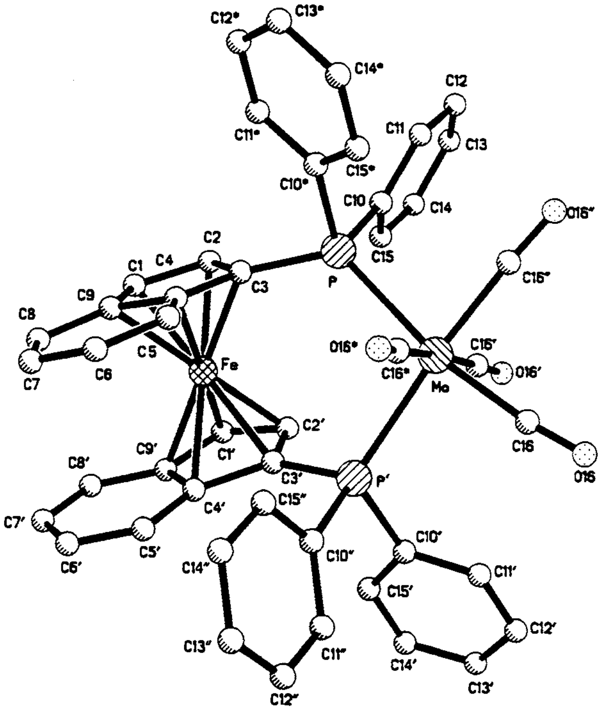


Fig. 2. Thermal ellipsoid plot of **5a**.

135.8 (d, $^1J_{PC}=18$ Hz, *ipso*-Ph), 136.2 (d, $^1J_{PC}=19$ Hz, *ipso*-Ph), 141.6 (dd, $^2J_{PC}=5$ Hz, $^3J_{PC}=14$ Hz, C-3), 142.4 (dd, $^2J_{PC}=3$ Hz, $^2J_{PC}=7$ Hz, C-2), 144.9 (dd, $^2J_{PC}=4$ Hz, $^3J_{PC}=8$ Hz, C-9), 145.3 (dd, $^1J_{PC}=18$ Hz, $^3J_{PC}=2$ Hz, C-4). Mass spectra (EI, *m*/*z* (%)): 484 (29, M^+), 299 (100, M^+-PPh_2), 185 (24, PPh_2^+), 108 (20, PPh^+). Anal. Calc. for $C_{33}H_{26}P_2$: C, 81.8; H, 5.41. Found: C, 80.4; H, 5.58. The carbon analysis may be low due to oxide formation.

Table 6

Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($Å^2 \times 10^3$) for **5b**[a]

Atom	x	y	z	U_{eq}
Mo	5000	8512(1)	2500	25(1)
Fe	5000	12594(1)	2500	28(1)
P	6091(1)	9989(1)	2567(1)	24(1)
C(1)	5934(1)	13661(2)	2569(1)	41(1)
C(2)	6063(1)	12567(2)	2244(1)	33(1)
C(3)	5970(1)	11584(2)	2691(1)	27(1)
C(4)	5823(1)	12108(2)	3328(1)	29(1)
C(5)	5750(1)	11605(2)	3977(1)	35(1)
C(6)	5621(1)	12349(2)	4492(1)	46(1)
C(7)	5546(1)	13607(2)	4391(1)	53(1)
C(8)	5630(1)	14126(2)	3794(1)	50(1)
C(9)	5793(1)	13392(2)	3242(1)	38(1)
C(10)	6487(1)	9900(2)	1771(1)	27(1)
C(11)	6102(1)	10416(2)	1171(1)	33(1)
C(12)	6357(1)	10288(2)	553(1)	41(1)
C(13)	6985(1)	9603(2)	515(1)	48(1)
C(14)	7356(1)	9043(3)	1098(1)	57(1)
C(15)	7118(1)	9210(2)	1727(1)	45(1)
C(16)	6926(1)	9719(2)	3230(1)	33(1)
C(17)	7013(1)	8664(2)	3608(1)	41(1)
C(18)	7662(1)	8470(3)	4094(1)	53(1)
C(19)	8213(1)	9322(3)	4204(1)	58(1)
C(20)	8132(1)	10379(3)	3840(1)	57(1)
C(21)	7491(1)	10576(2)	3350(1)	45(1)
C(22)	5132(1)	8403(2)	3541(1)	37(1)
C(23)	4230(1)	7250(2)	2496(1)	41(1)
O(1)	5211(1)	8233(2)	4120(1)	61(1)
O(2)	3796(1)	6498(1)	2512(1)	67(1)

[a] U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensor.

4.3. Preparation of 1,3-bis(diphenylselenophosphino)indene (2)

Compound **1** (0.89 g, 1.8 mmol) and selenium (0.291 g, 3.7 mmol) were stirred in toluene (25 ml) for 12 h

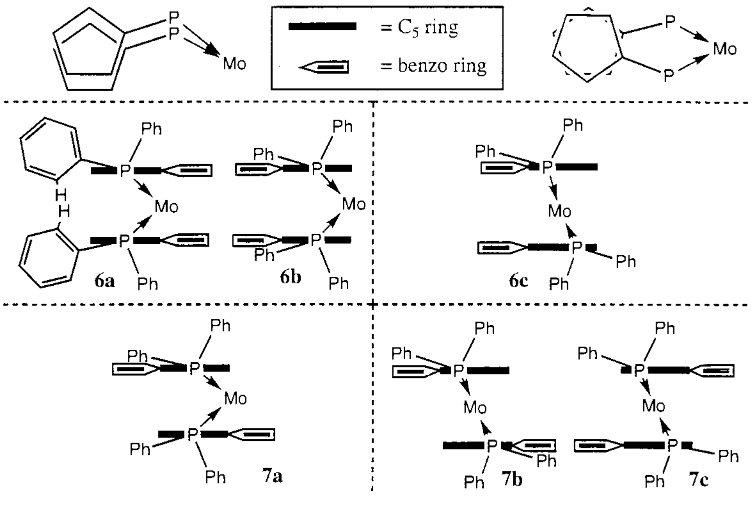


Fig. 3. The possible half-chair and twist-boat conformations of **5a** and **5b**.

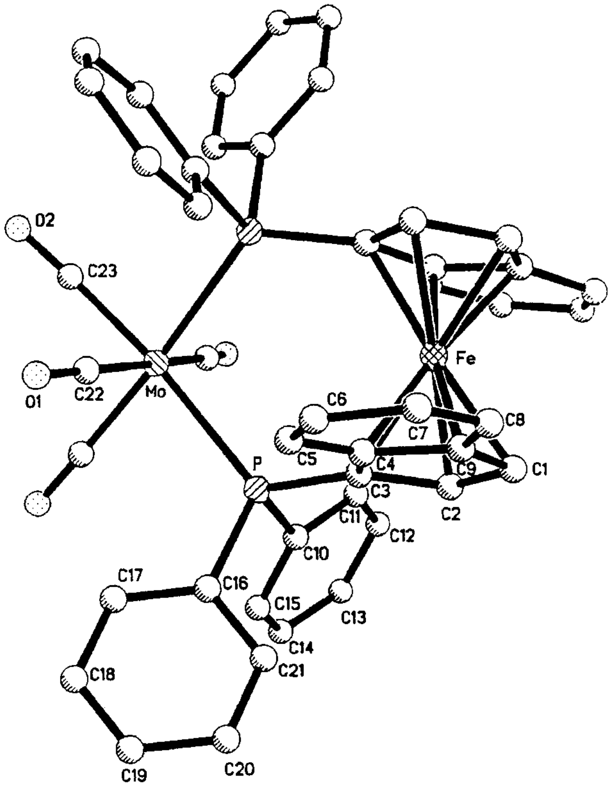


Fig. 4. Thermal ellipsoid plot of **5b**.

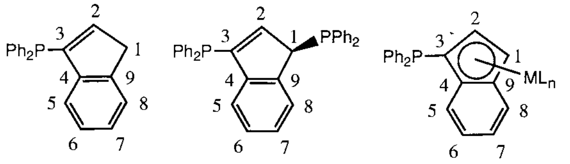


Fig. 5. The adopted atom labelling scheme for the phosphino-indene and -indenyl compounds.

at ambient temperature and then heated to reflux for 2 h. ^{31}P-NMR spectroscopy indicated 100% conversion. Colourless crystallographic-quality crystals (0.527 g, 45% yield), containing one half-equivalent of CH_2Cl_2 solvate, were obtained by recrystallisation from CH_2Cl_2/pentane. ^{1}H-NMR ($CDCl_3$): δ 5.13 (ddd, $^1J_{PH} = 22$ Hz, $^3J_{HH} = 2$ Hz, $^4J_{PH} = 2$ Hz, 1H, H-1), 6.40 (ddd, $^3J_{PH} = 10$ Hz, $^3J_{PH} = 4$ Hz, $^3J_{HH} = 2$ Hz, 1H, H-2), 6.87 (d, $^3J_{HH} = 7$ Hz, 1H, H-5), 7.03 (dd, $^3J_{HH} = 8$ Hz, 1H, H-7), 7.14 (dd, $^3J_{HH} = 8$ Hz, 1H, H-6), 7.32 (m, 1H, H-8), 7.8–7.3 (m, 20H, Ph). $^{31}P\{^1H\}$-NMR ($CDCl_3$): δ 37.9 (m, $^4J_{PP}$ 6 Hz, $^1J_{SeP}$ 750 Hz, PC-1), 20.9 (m, $^4J_{PP} = 6$ Hz, $^1J_{SeP} = 730$ Hz, PC-3). $^{13}C\{^1H\}$-NMR ($CDCl_3$): δ 55.3 (dd, $^3J_{PC} = 12$ Hz, $^1J_{PC} = 38$ Hz, C-1), 123.8 (C-8), 124.5 (C-5), 126.2 (s, C-7), 128.0 (s, C-6), 128–129 (Ph), 131–133 (Ph), 143.5 (dd, $^2J_{PC} = 11$ Hz, $^2J_{PC} = 4$ Hz, C-2). Mass spectra (EI, m/z (%)): 644 (5, M^+), 564 (5, M^+-Se), 484 (1, M^+-2Se), 380 (20, $SePPh_2C_9H_7^+$), 299 (50, $PPh_2C_9H_6^+$), 185 (100, PPh_2^+), 108 (80, PPh^+). Anal. Calc. for $C_{33}H_{26}P_2Se_2 \cdot 0.5CH_2Cl_2$: C, 58.75; H, 3.97. Found: C, 58.91; H, 3.98.

*4.4. Preparation of bis(1-diphenylphosphinoindenyl)iron(II) (**4**) from **1** via bis(1,3-bis(diphenylphosphino)indenyl)iron(II) (**3**)*

To a solution of **1** (9.6 g, 2 mmol) in tetrahydrofuran (100 ml) at −80°C was added a solution of n-BuLi (12.5 ml, 1.6 M, 2 mmol). After allowing to warm to ambient temperature over one hour, $FeCl_2$ (1.26 g, 1 mmol) was added and the reaction mixture stirred for a further 2 h. ^{31}P-NMR spectroscopy of the solution showed a single peak at δ −19.9 which is attributed to **3**. The solvent was then removed in vacuo. The residue shows a complex ^{31}P-NMR spectrum. Chromatography on silica gel with a 5:1 mixture of cyclohexane and ethylacetate gave dark

Table 7
^{13}C-NMR chemical shifts (ppm) for the indenyl five-membered-ring carbon atoms[a]

Compound	C-1	C-2	C-3	C-4	C-9
1-$Ph_2P(C_9H_7)$[b]	48.6 (34)	132.1 (5)	135.0 (4)	144.6 (1.5)	144.0 (9)
3-$Ph_2P(C_9H_7)$[b,c]	40.2 (6)	142.0 (5.5)	145.9 (20)	141.9 (13)	144.8 (5)
3-$Ph_2P(C_9H_7)$[d]	40.2 (6)	142.0 (5.5)	141.9 (13)	145.9 (20)	144.8 (5)
1,3-$(Ph_2P)_2C_9H_6$ (**1**)	49.5 (23,4)	142.4 (7,3)	141.6 (14,5)	145.3 (18,2)	144.9 (8,4)
1,3-$(Ph_2PO)_2C_9H_6$[e]	55.0	144.6	–	–	–
1,3-$(Ph_2PS)_2C_9H_6$[e]	56.3	143.5	–	–	–
1,3-$(Ph_2PSe)_2C_9H_6$ (**2**)	55.3 (38,12)	143.5 (11,4)	–	–	–
4	66.1 (4)	72.0 (4)	68.1 (9)	91.0 (25)	89.7 (4)
5	66.8	79.9 (5)	76.4	89.7	87.1
$(C_9H_7)_2Fe$[f]	62.3	70.3	62.3	87.6	87.6

[a] PC coupling constants (Hz) are given in parentheses.

[b] Fallis et al. [9].

[c] In CH_2Cl_2, all others are in $CDCl_3$.

[d] Our assignment.

[e] Stradiotto et al. [11].

[f] Benn et al. [18].

green **4** which was recrystallised from toluene to give 2.2 g (20% yield) of product. ^{1}H-NMR (CDCl$_3$): δ 3.07 (s, 2H, H-1), 4.92 (s, 2H, H-2), 6.4–7.4 (m, 28H, H-5–H-8 and Ph). ^{13}C{^{1}H}-NMR (CDCl$_3$): δ 66.1 (d, $^{2}J_{PC} = 4$ Hz, C-1), 68.1 (d, $^{1}J_{PC} = 9$ Hz, C-3), 72.0 (d, $^{3}J_{PC} = 4$ Hz, C-2), 89.7 (d, $^{2}J_{PC} = 4$ Hz, C-9), 91.0 (d, $^{3}J_{PC} = 25$ Hz, C-4), 122.5 (s, C-7), 122.9 (s, C-6), 123.6 (s, C-8), 124.1 (d, $^{3}J_{PC} = 9$ Hz, C-5), 127.6 (s, *p*-Ph), 128.0 (d, $^{3}J_{PC} = 5$ Hz, *m*-Ph), 128.3 (d, $^{3}J_{PC} = 8$ Hz, *m*-Ph), 129.3 (s, *p*-Ph), 131.7 (d, $^{2}J_{PC} = 18$ Hz, *o*-Ph), 135.2 (d, $^{2}J_{PC} = 22$ Hz, *o*-Ph), 136.7 (d, $^{1}J_{PC} = 7$ Hz, *ipso*-Ph), 139.8 (d, $^{1}J_{PC} = 10$ Hz, *ipso*-Ph). ^{31}P{^{1}H}-NMR (CDCl$_3$): δ −22.5 (s). Anal. Calc. for $C_{42}H_{22}FeP_2$: C, 77.2; H, 5.59. Found: C, 75.2; H, 5.21. C and H low due to oxide formation. Mass spectra: (EI, *m*/*z* (%)): 654 (42, M$^+$), 300 (81, HIP$^+$), 185 (100, P–Ph$_2^+$). High resolution: M$^+$ Calc., 654.13283; Found, 654.13318.

4.5. Preparation of **4** from 3-(diphenylphosphino)indene

To a solution of 3-(diphenylphosphino)indene (6.0 g, 2 mmol) in tetrahydrofuran (100 ml) at −80°C was added a solution of *n*-BuLi (12.5 ml, 1.6 M, 2 mmol). After 1 h, FeCl$_2$ (1.26 g, 1 mmol) was added and the reaction mixture stirred for 2 h at ambient temperature. The solvent was removed in vacuo and the residue chromatographed on silica gel with a 10:1 mixture of cyclohexane/ethylacetate. The dark green **4** was recrystallised from toluene to give 2.6 g (40% yield) of product.

4.6. Preparation of meso- and rac-tetracarbonyl(bis(1-diphenylphosphinoindenyl)iron(II))molybdenum(0) (**5a** and **5b**)

To a solution of **4** (0.89 g, 0.1 mmol), prepared from 3-(diphenylphosphino)indene, in tetrahydrofuran (50 ml) was added Mo(CO)$_4$(piperidine)$_2$ (0.38 g, 0.1 mmol). The solution was then heated to reflux for 2 h, the solvent removed in vacuo, and the dark green residue chromatographed with 1:1 cyclohexane/ethylacetate. Recrystallisation from CH$_2$Cl$_2$/heptane gave 0.052 g (40% yield) of the *meso* isomer **5a** as dark green/red crystals. Starting with **4** prepared from the diphosphine **1**, crystals of the racemic isomer **5b**, with identical spectral properties, were isolated. ^{1}H-NMR (CDCl$_3$): δ 3.68 (s, 2H, H-1), 4.31 (s, 2H, H-2), 6.4–7.4 (m, 28H, H5–H8 and Ph). ^{13}C{^{1}H}-NMR (CDCl$_3$): δ 66.8 (s, C-1), 76.4 (s, C-3), 79.9 (t, $^{3}J_{PC} = 5$ Hz, C-2), 87.1 (s, C-9), 89.7 (s, C-4), 124.9 (s, C-7), 125.1 (s, C-6), 127.8 (t, $^{3}J_{PC} = 5$ Hz, *m*-Ph), 128.3 (t, $^{3}J_{PC} = 5$ Hz, *m*-Ph), 129.1 (s, C-5 or C-8), 129.1 (s, C-5 or C-8), 129.4 (s, *p*-Ph), 129.9 (s, *p*-Ph), 132.4 (t, $^{2}J_{PC} = 7$ Hz, *o*-Ph), 134.4 (d, $^{2}J_{PC} = 7$ Hz, *o*-Ph), 135.0 (m, *ipso*-Ph), 139.0 (m, *ipso*-Ph). ^{31}P{^{1}H}-NMR (CDCl$_3$): δ 33.1. Anal. Calc. for $C_{46}H_{32}FeMoO_4P_2$: C, 61.44; H, 4.01. Found: C, 62.07; H, 3.66. Mass spectra: (FAB, *m*/*z* (%)): 864 (3, M$^+$) 836 (3, M$^+$–CO), 808 (5, M$^+$–2CO), 780 (2, M$^+$–3CO), 752 (15, M$^+$–4CO), 396 (25, [MoPPh$_2$C$_9$H$_5$]$^+$), 307 (55), 154 (90), 136 (100). Infra-red (CHCl$_3$): **5a**; 2021 (m), 1916 (sh, br), 1909 (s, br), 1878 (m, br) cm^{-1}. **5b**; 2021 (m), 1913 (s, br), 1878 (m, br) cm^{-1}.

4.7. Crystal structure determinations

X-ray crystallographic data for **2**, **5a** and **5b** were collected from single-crystal samples, which were mounted on a glass fibre. Data was collected at ca. 150 K using a Siemens P4 diffractometer equipped with a Siemens SMART 1K charge-coupled device (CCD) area detector (using the program SMART [21]) and graphite monochromated Mo–K$_\alpha$ radiation ($\lambda > 0.71073$ Å). The crystal to detector distance was 6.0 cm and the data collection was carried out in 512 × 512 pixel mode utilising 2 × 2 pixel binning. The initial unit cell parameters were determined by least-squares fit of the angular settings of strong reflections in 100 frames over three different parts of reciprocal space (300 frames in total). One complete hemisphere of data was collected to better than 0.8 Å resolution. Processing was carried out by use of the program SAINT [22] which applied Lorentz and polarisation corrections to three-dimensionally integrated diffraction spots. The program SADABS [23] was utilised for the scaling of diffraction data, the application of a decay correction, and empirical absorption correction based on redundant reflections. The structures for **2** and **5a** were solved by the direct methods procedure, the **5b** structure was solved by the Patterson method procedure in the SHELXTL program library [24]. The structures were refined by least-squares methods on F^2 with anisotropic thermal parameters for all non-hydrogen atoms. Hydrogen atoms were added as riding contributors at calculated positions, with isotropic thermal parameters based on the attached carbon atom. Crystal data and structure refinement parameters are given in Table 3.

5. Supplementary material

Tables of crystal data, structure refinement details, atomic coordinates, bond lengths and angles, anisotropic displacement parameters, and hydrogen coordinates are available from the authors or from the Cambridge Crystallographic Data Centre, Lensfield Road, Cambridge, CB2 1EW, United Kingdom.

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