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A synthetic and X-ray crystallographic study of the indenyl-phosphine complexes 1,3-$(Ph_2P{=}X)_2(C_9H_6)$, (X = O, S) and $(\eta^5\text{-}C_9H_5(Ph_2P{=}S)_2)[Mn(CO)_3]$: versatile ligands for the preparation of heteropolymetallic complexes

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Abstract

The syntheses and X-ray crystal structures of the oxidized indenyl-diphosphines, 1,3-$(Ph_2P{=}X)_2C_9H_6$, where X is O, S, are reported. The sulfur complex is readily deprotonated to form the corresponding 1,3-disubstituted indenide anion, which yields a crystallographically-characterized η^5-$Mn(CO)_3$ complex upon treatment with bromopentacarbonylmanganese. The relevance of these molecules to mixed-metal catalytic systems is discussed. © 1998 Elsevier Science S.A. All rights reserved.

Keywords: Indenyl-phosphine complexes; Versatile ligands; Crystal structures

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1. Introduction

The preparation of heteropolyfunctional ligands has attracted considerable interest recently, as a result of their utility in the formation of homo- and bimetallic complexes [1,2]. Such bi- and trimetallic systems in which the metal centers possess markedly different electron counts are thought to be attractive synthetic targets, in that the metal centers have the potential to interact in a simultaneous and cooperative fashion in the activation of organic substrates [3]. The successful preparation of suitable polymetallic complexes necessitates that the metal centers be rigidly linked, such that the structural integrity of the catalyst is maintained throughout the catalytic process.

Polyfunctional ligands which incorporate both cyclopentadienyl and phosphine moieties, such as the diphenylphosphinocyclopentadienyl (dppc) ligand, have proven extremely effective in the construction of constrained polymetallic systems in which transition metals are held in close proximity [4,5]. In the case of heterobimetallic systems, the dppc ligand typically coordinates to an ‘early’ transition metal in an η^5-fashion via the cyclopentadienyl fragment and to a ‘late’ transition metal through the phosphine moiety. The versatility of the dppc ligand and its derivatives is exemplified by the numerous reports on the synthesis and catalytic properties of complexes derived from the commercially available 1,1′-bis(diphenylphosphino)ferrocene (dppf) [6] fragment, as well as many other homopolymetallic [4] and heteropolymetallic [5] systems. Moreover, the chemistry of such dppc-based systems has been further expanded via oxidation, which transforms the phosphorus center into an oxygen or sulfur donor ([1], [2]a, [5]c, [7]), while the incorporation of two phosphine units onto a single cyclopentadiene ring has allowed for the formation of chelates [1].

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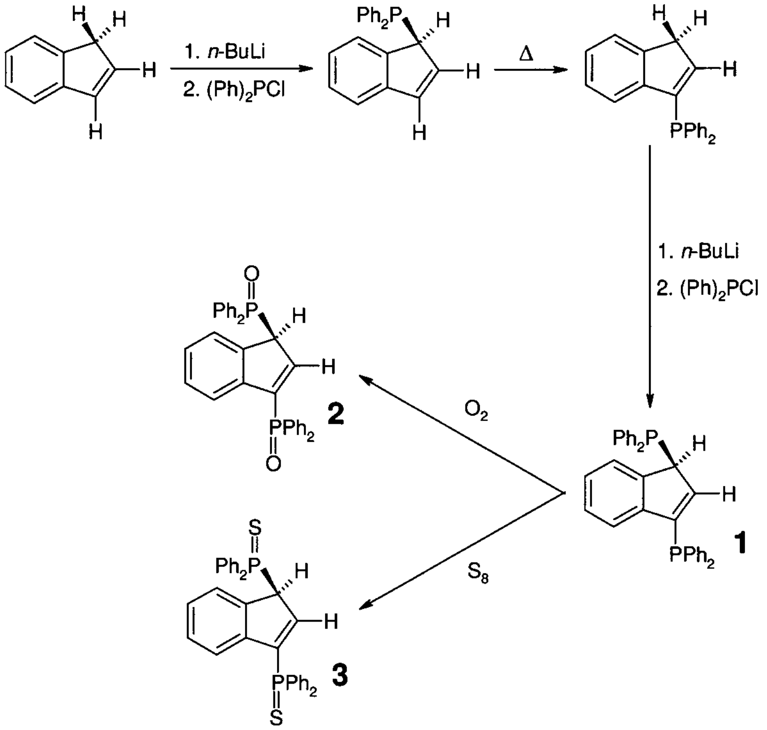


Scheme 1. The preparation of compounds **1**, **2** and **3**.

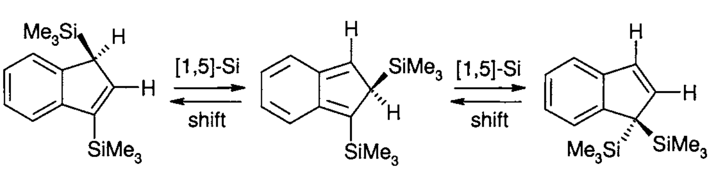
Although cyclopentadienyl-based ligands have received much attention, there exists a paucity of reports on the chemistry of systems which incorporate the corresponding indenyl framework [8,9]. Given the heightened catalytic activity exhibited by indenyl-based *ansa*-bridged metallocenes in the stereospecific polymerization of alkenes [10], and our continued interest in the synthesis and study of main-group and transition metal indenyl complexes [11], we chose to probe the utility of the 1,3-bis(diphenylphosphino)indene (bdppi) ligand, **1**, with respect to the preparation of constrained polymetallic systems. Herein we report the synthesis and characterization of bdppi, its oxidation products, and some preliminary results concerning the preparation of transition metal derivatives of these ligands.

2. Results and discussion

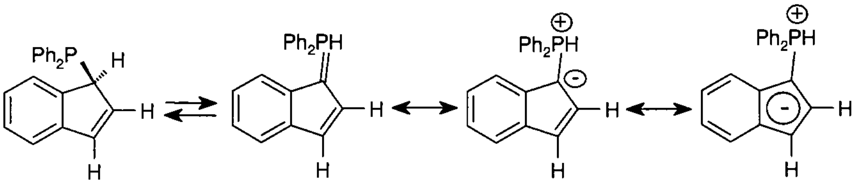
The diphosphine, **1**, is readily preparable by treatment of 1-(diphenylphosphino)-indene [8] with one molar equivalent of *n*-BuLi, followed by quenching with chlorodiphenylphosphine. Such air-sensitive solutions of **1** can either be used directly in the preparation of organometallic complexes [12], or converted cleanly to the corresponding dioxide, **2**, or disulfide, **3**, as depicted in Scheme 1.

Interestingly, the preparation of **1**, **2** or **3** gives rise exclusively to the 1,3-disubstituted product, whereas the addition of a second trimethylsilyl substituent to trimethylsilylindene produces approximately equimolar amounts of the 1,1 and 1,3 isomers of bis(trimethylsilyl)indene, which interconvert via silatropic shifts (Scheme 2) [13]. In addition to the increased steric demand of the diphenylphosphino fragment relative to the trimethylsilyl unit at the C-1 position of the substituted indene, such an observation can be rationalized in terms of the propensity of 1-(diphenylphosphino)indene to rearrange to the thermodynamically-favored 3-(diphenylphosphino) isomer, even at ambient temperature [8]. While such a rearrangement involves the overall transfer of a proton from C-1 to C-3, it is unlikely to proceed at low temperatures via sequential [1,5]-sigmatropic shifts, given the large activation energy associated with these processes. However, it is possible to envisage an acid- or base-catalyzed proton transfer mechanism, mediated by zwitterionic or Wittig-type intermediates (Scheme 3) [14], which would be available to the phosphine but not the silane [15]. It has also been demonstrated by Broussier and co-workers that an *sp*^{3}-substituted product is formed upon quenching of the 1, 2, 3-trimethylcyclopentadienyl anion with chlorodiphenyphosphine at − 10°C, whereas *sp*^{2}-bound phosphines are formed when the analogous reaction is carried out under ambient conditions [1].

The molecular structures of **2** and **3** were initially elucidated based upon NMR spectroscopic data, including those obtained by use of ^{31}P{^{1}H} selective decoupling and two-dimensional NMR experiments. The observed deshielding of δ^{31}P on going from the



Scheme 2. The interconversion of 1,1- and 1,3-bis(trimethylsilyl)indene, via silatropic shifts.



Scheme 3. Possible Wittig-type intermediates in the isomerization of 1-(diphenylphosphino)indene to 3-(diphenylphosphino)indene.

dioxide, **2** (32.0 and 22.1 ppm), to the disulfide, **3** (46.9 and 32.5 ppm), is the same as that observed for the corresponding oxidized triphenylphosphine systems [16], while the observation that $\delta^{31}P(sp^3) > \delta^{31}P(sp^2)$ is a trend which is evident in related systems [1,8]. Both high and low resolution mass spectrometric data obtained for **2** and **3** are in agreement with these NMR spectroscopic data.

The solid-state structures of **2** and **3** were unambiguously determined by use of single-crystal X-ray diffraction techniques, and are presented in Figs. 1 and 2; important crystallographic parameters and selected geometrical data are summarized in Tables 1–5, respectively. The crystal structures of **2** and **3** fully corroborate the aforementioned spectroscopic data, and possess features which are generally quite similar to those previously reported for related complexes ([6]c, [8]). Although gratified by the geometric confirmation provided by these structural determinations, the sterically-demanding nature of the diphenylphosphino fragments in both **2** and **3** prompted us to question the accessibility of the C_5 ring. Towards this end, an attempt was made to complex a transition metal onto the indenyl five-membered ring.

Treatment of **3** with one molar equivalent of n-BuLi, followed by quenching with $Mn(CO)_5Br$ yields the organometallic complex, **4**, which has been unequivocally characterized by use of NMR spectroscopy and X-ray crystallography (Scheme 4). From the structure presented in Fig. 3 it can be observed that, in the solid state, **4** deviates only modestly from ideal C_s symmetry. In addition, close inspection of the bond lengths in **4** reveals that the bonding of the metal center has 'slipped' [17] slightly from η^5 to η^3, while the uncomplexed C_6 ring of the indenyl unit clearly contains a diene moiety, which could be utilized in complexation of an additional metal center [18].

3. Summary

The numerous coordination modes available to the indenyl ligand make it a logical candidate in the attempt to expand the organometallic chemistry of cyclopentadienyl-based systems. We have demonstrated that polyfunctional organometallic precursors such as **2** and **3** are synthetically-available species, and that the

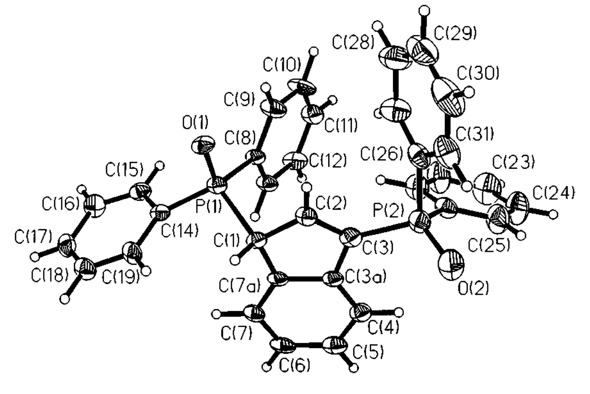


Fig. 1. The X-ray crystal structure of **2**, showing the atom numbering scheme, with thermal ellipsoids at the 30% probability level (solvate eliminated for clarity).

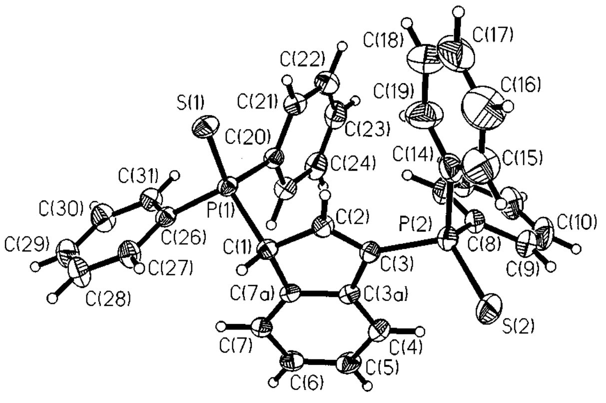


Fig. 2. The X-ray crystal structure of **3**, showing the atom numbering scheme, with thermal ellipsoids at the 30% probability level (solvate eliminated for clarity).

Table 1
Crystal data and structure refinement parameters for **2**·CH_3CH_2OH, **3**·H_2O, and **4**

	2·CH_3CH_2OH	**3**·H_2O	**4**
Empirical formula	$C_{35}H_{32}O_3P_2$	$C_{33}H_{28}O_1P_2S_2$	$C_{36}H_{25}O_3P_2S_2Mn_1$
Molecular weight	562.55	566.61	686.56
Colour	Colourless	Colourless	Yellow
Morphology	Plate	Prism	Plate
Temperature (K)	302(2)	302(2)	302(2)
Crystal system	Monoclinic	Triclinic	Monoclinic
Space group	$C2/c$	$P\bar{1}$	$P2_1/c$
a (Å)	35.2038(2)	9.082(4)	12.4768(2)
b (Å)	9.4035(2)	10.073(4)	18.4965(2)
c (Å)	17.2041(2)	16.864(5)	14.3648(3)
α (°)	90	89.07(2)	90
β (°)	107.342(1)	82.96(2)	100.75(1)
γ (°)	90	80.91(1)	90
Volume (Å^3)	5436.3(2)	1512(1)	3256.9(1)
Z	8	2	4
$D_{calc.}$ (g cm^{-3})	1.375	1.245	1.408
μ (mm^{-1})	0.197	0.306	0.667
Scan mode	ω-scans	ω-scans	ω-scans
F(000)	2368	592	1408
θ-Range for collection (°)	1.21 to 22.50	2.05 to 22.50	1.82 to 22.50
Index ranges	$-45 \leq h \leq 45$	$-11 \leq h \leq 11$	$-15 \leq h \leq 15$
	$-11 \leq k \leq 9$	$-12 \leq k \leq 12$	$-22 \leq k \leq 22$
	$-22 \leq l \leq 22$	$-21 \leq l \leq 21$	$-17 \leq l \leq 17$
No. reflections collected	15113	10971	18565
No. independent reflections	3556	3865	4250
Data/restraints/parameters	3556/0/362	3864/0/352	4244/0/398
Goodness-of-fit on F	0.866	0.921	1.019
Final R indices ($I > 2\sigma(I)$)[a]			
R_1	0.0985	0.0568	0.0377
wR_2	0.2290	0.1795	0.0787
R indices (all data)[a]			
R_1	0.1391	0.0669	0.0577
wR_2	0.2615	0.1902	0.0867
Effective trans. Max.	0.979	0.950	0.959
Effective trans. Min.	0.713	0.725	0.677
Largest difference peak (e Å^{-3})	0.864	0.937	0.232
Largest difference hole (e Å^{-3})	−0.636	−0.200	−0.214

[a] $R_1 = \Sigma(||F_o - F_c||)/\Sigma|F_o|$; $wR_2 = [\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]]^{0.5}$.

introduction of a transition metal to the indenyl five-membered ring is facile. Moreover, the disubstituted nature of **2** and **3** make them ideal chelating precursors of heteropolymetallic complexes, which could contain two or more different metal fragments held together, not only via a bridging ligand, but also as a result of direct metal–metal bonding. The utilization of the novel ligands described herein in the quest for catalytically-synergistic polymetallic compounds will be the subject of future reports.

4. Experimental

4.1. General procedure

All reactions were carried out under an atmosphere of dry nitrogen in oven-dried glassware using solvents which were previously dried according to standard procedures. Indene (Aldrich) was distilled prior to use, diphenylchlorophosphine (Aldrich) was used without purification and $Mn(CO)_5Br$ was prepared using published methods [19]. Microanalytical data are from Guelph Chemical Laboratories, Guelph, Ontario, Canada. Mass spectra (DEI) were obtained on a VG Analytical ZAB-SE spectrometer with an accelerating potential of 8 kV and a resolving power of 10000. All NMR spectra were acquired on a Bruker Avance DRX-500 spectrometer, equipped with an 11.74 T superconducting magnet. These experiments consisted of 1D ^1H, ^{13}C and ^{31}P NMR spectra as well as 2-D $^1H-^1H$ COSY, $^1H-^{13}C$ shift-correlated and long range $^1H-^{13}C$ shift-correlated spectra. All NMR spectra were recorded on spinning samples (except during the acquisition of 2D spectra), locked to a solvent signal. Proton and carbon signals were referenced to a residual ^1H

signal of the solvent or to a ^{13}C solvent signal, while phosphorus signals were referenced to external H_3PO_4.

4.2. Crystal structure determinations

X-ray crystallographic data for **2**·CH_3CH_2OH, **3**·H_2O and **4** were collected from single crystal samples, which were mounted on a glass fiber. Data were collected using a P4 Siemens diffractometer, equipped with a Siemens SMART 1K charge coupled device (CCD) area detector (using the program SMART [20]a) and a rotating anode using graphite-monochromated Mo–K_α radiation ($\lambda = 0.71073$ Å). The crystal-to-detector distance was 3.991 cm, and the data collection was carried out in 512 × 512 pixel mode, utilizing 2 × 2 pixel binning. The initial unit cell parameters were determined by a least-squares fit of the angular settings of the strong reflections, collected by a 4.5° scan in 15 frames over three different parts of reciprocal space (45 frames total). One complete hemisphere of data was collected, to better than 0.8 Å resolution. Upon completion of the data collection, the first 50 frames were recollected in order to improve the decay corrections analyses. Processing was carried out by use of the program SAINT ([20]b), which applied Lorentz and polarization corrections to three-dimensionally integrated diffraction spots. The program SADABS ([20]c) was utilized for the scaling of diffraction data, the application of a decay correction, and an empirical absorption correction based on redundant reflections. The structure was solved by using the Patterson method procedure in the Siemens SHELXTL program library ([20]d), and refined by full-matrix least-squares methods on F^2 with anisotropic thermal parameters for all non-hydrogen atoms. Hydrogen atoms were added as fixed contributors at calculated positions, with isotropic thermal parameters based on the carbon atom to which they are bonded.

Table 2
Selected bond lengths (Å) and angles (°) for **2**·CH_3CH_2OH, **3**·H_2O and **4**

1,3-($Ph_2P{=}O)_2(C_9H_6)\cdot CH_3CH_2OH$			
P(1)–O(1)	1.447(4)	O(1)–P(1)–C(14)	112.1(3)
P(2)–O(2)	1.445(5)	O(1)–P(1)–C(8)	111.6(3)
P(1)–C(1)	1.801(6)	O(1)–P(1)–C(1)	110.4(3)
P(2)–C(3)	1.730(7)	O(2)–P(2)–C(3)	114.0(3)
C(1)–C(2)	1.446(8)	O(2)–P(2)–C(20)	113.1(3)
C(2)–C(3)	1.309(8)	O(2)–P(2)–C(26)	111.7(4)
1,3-($Ph_2P{=}S)_2(C_9H_6)\cdot H_2O$			
P(1)–S(1)	1.955(1)	C(26)–P(1)–S(1)	111.8(1)
P(2)–S(2)	1.954(2)	C(20)–P(1)–S(1	113.1(1)
P(1)–C(1)	1.855(4)	C(1)–P(1)–S(1)	110.0(1)
P(2)–C(3)	1.796(4)	C(3)–P(2)–S(2)	112.3(1)
C(1)–C(2)	1.498(5)	C(14)–P(2)–S(2)	113.7(2)
C(2)–C(3)	1.332(5)	C(8)–P(2)–S(2)	113.6(2)
(η^5-$C_9H_5(Ph_2P{=}S)_2[Mn(CO)_3]$			
Mn(1)–C(1)	2.140(3)	O(32)–C(32)–Mn(1)	177.9(3)
Mn(1)–C(2)	2.117(3)	O(33)–C(33)–Mn(1)	177.2(3)
Mn(1)–C(3)	2.155(3)	O(34)–C(34)–Mn(1)	177.7(3)
Mn(1)–C(3A)	2.233(3)	C(33)–Mn(1)–C(2)	89.0(1)
Mn(1)–C(7A)	2.237(3)	C(32)–Mn(1)–C(2)	135.5(1)
P(1)–S(1)	1.960(1)	C(34)–Mn(1)–C(2)	132.3(1)
P(2)–S(2)	1.958(1)	C(33)–Mn(1)–C(1)	108.1(1)
P(1)–C(1)	1.819(3)	C(32)–Mn(1)–C(1)	160.1(1)
P(2)–C(3)	1.813(3)	C(34)–Mn(1)–C(1)	95.7(1)
C(4)–C(5)	1.367(4)	C(33)–Mn(1)–C(3)	107.3(1)
C(4)–C(5)	1.367(4)	C(32)–Mn(1)-C(3)	100.2(1)
C(5)–C(6)	1.412(5)	C(34)–Mn(1)–C(3)	155.5(1)
C(6)–C(7)	1.367(5)		

Table 3
Atomic coordinates (× 10^4) and equivalent isotropic displacement parameters ($A^2 \times 10^3$) for **2**·CH_3CH_2OH

	x	*y*	*z*	U_{eq}^{a}
P(1)	7347(1)	6749(2)	6146(1)	37(1)
P(2)	5959(1)	5066(2)	4490(1)	49(1)
O(1)	7315(1)	8215(4)	5880(2)	44(1)
O(2)	5807(2)	4384(7)	3705(3)	76(2)
C(1)	7131(2)	5586(6)	5297(3)	35(1)
C(2)	6724(2)	6036(7)	4942(3)	39(2)
C(3)	6472(2)	4991(7)	4892(4)	43(2)
C(3A)	6700(2)	3715(6)	5182(3)	37(2)
C(4)	6585(2)	2351(7)	5214(4)	49(2)
C(5)	6863(2)	1351(7)	5515(4)	51(2)
C(6)	7251(2)	1699(7)	5793(4)	47(2)
C(7)	7367(2)	3060(7)	5751(3)	40(2)
C(7A)	7094(2)	4095(6)	5447(3)	34(2)
C(8)	7087(2)	6447(6)	6862(3)	36(1)
C(9)	6860(2)	7493(7)	6990(4)	53(2)
C(10)	6646(2)	7317(8)	7525(5)	65(2)
C(11)	6654(2)	6084(8)	7907(4)	53(2)
C(12)	6886(2)	5012(7)	7790(4)	52(2)
C(13)	7101(2)	5186(7)	7260(4)	44(2)
C(14)	7842(2)	6225(6)	6579(4)	37(1)
C(15)	8022(2)	6349(7)	7375(4)	45(2)
C(16)	8414(2)	6200(8)	7688(4)	56(2)
C(17)	8637(2)	5837(7)	7190(4)	50(2)
C(18)	8458(2)	5699(7)	6398(4)	51(2)
C(19)	8067(2)	5895(7)	6083(4)	47(2)
C(20)	5772(2)	4311(7)	5247(4)	49(2)
C(21)	5961(2)	4433(8)	6041(5)	63(2)
C(22)	5797(2)	3888(10)	6591(5)	80(3)
C(23)	5455(3)	3181(11)	6340(7)	95(3)
C(24)	5264(3)	3086(10)	5545(7)	91(3)
C(25)	5424(2)	3623(10)	4998(5)	76(2)
C(26)	5838(2)	6895(8)	4441(5)	55(2)
C(27)	5928(3)	7753(9)	5089(5)	69(2)
C(28)	5831(3)	9146(10)	5019(7)	88(3)
C(29)	5630(3)	9661(12)	4301(9)	90(3)
C(30)	5535(3)	8841(14)	3654(8)	96(3)
C(31)	5633(2)	7428(10)	3709(5)	72(2)
O(3)	5666(4)	1955(11)	2866(7)	185(5)
C(98)	5489(7)	2455(23)	2078(10)	215(11)
C(99)	5360(5)	1401(25)	1626(11)	193(7)

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

4.3. Preparations

4.3.1. In situ preparation of 1,3-($Ph_2P)_2(C_9H_6$), (**1**)

To a solution of indene (0.93 g, 8.0 mmol) in freshly distilled diethyl ether (100 ml) at −78°C was added *n*-butyllithium (5.0 ml of a 1.6 M hexane solution, 8.0 mmol) over a 1 h period, followed by stirring for an additional 2 h at −78°C. Diphenylchlorophosphine (1.77 g, 8.0 mmol) was then added and the mixture heated under reflux for 3 h. After cooling the mixture to −78°C, *n*-butyllithium (5.0 ml of a 1.6 M hexane solution, 8.0 mmol) was again added over a 1 h period, followed by the addition of diphenylchlorophosphine (1.77 g, 8.0 mmol). After refluxing the mixture for 18 h, stirring was stopped and the solution cooled in order to allow for the precipitated LiCl to settle. The resulting diethylether solution, containing 1,3-(diphenylphosphino)indene was removed from the precipitated LiCl via cannula then used immediately in the preparation of **2** and **3**.

Table 4
Atomic coordinates (×10^4) and equivalent isotropic displacement parameters ($A^2 \times 10^3$) for **3**·H_2O

	x	y	z	U_{eq}^{a}
P(1)	2325(1)	6264(1)	4628(1)	36(1)
P(2)	4689(1)	7332(1)	1726(1)	51(1)
S(1)	2717(1)	4299(1)	4613(1)	50(1)
S(2)	6597(1)	7889(2)	1305(1)	78(1)
C(1)	4003(4)	6941(3)	4153(2)	37(1)
C(2)	4335(4)	6440(4)	3308(2)	42(1)
C(3)	4335(4)	7460(4)	2795(2)	41(1)
C(3A)	4032(4)	8737(3)	3241(2)	38(1)
C(4)	3952(5)	10065(4)	2980(2)	50(1)
C(5)	3648(5)	11080(4)	3553(3)	55(1)
C(6)	3438(5)	10778(4)	4358(2)	49(1)
C(7A)	3834(4)	8445(3)	4047(2)	36(1)
C(7)	3538(4)	9462(3)	4615(2)	42(1)
C(8)	3063(5)	8382(4)	1398(2)	54(1)
C(9)	3257(6)	9235(5)	753(3)	71(1)
C(10)	2031(7)	10094(6)	527(3)	87(2)
C(11)	635(7)	10093(6)	927(3)	84(2)
C(12)	442(6)	9256(6)	1554(3)	78(2)
C(13)	1632(5)	8421(5)	1800(3)	64(1)
C(14)	4576(6)	5599(5)	1496(3)	64(1)
C(15)	5759(8)	4816(6)	1076(4)	103(2)
C(16)	5708(12)	3498(8)	903(5)	139(3)
C(17)	4494(12)	2916(7)	1147(5)	121(3)
C(18)	3325(11)	3657(7)	1570(5)	119(2)
C(19)	3335(8)	5000(6)	1747(4)	99(2)
C(20)	774(4)	6957(4)	4089(2)	40(1)
C(21)	137(5)	6096(4)	3653(2)	55(1)
C(22)	−1067(6)	6584(6)	3244(3)	71(1)
C(23)	−1650(5)	7932(6)	3286(3)	70(1)
C(24)	−1017(5)	8803(5)	3711(3)	61(1)
C(25)	185(4)	8324(4)	4116(2)	50(1)
C(26)	1953(4)	6921(3)	5635(2)	38(1)
C(27)	3139(5)	6784(4)	6094(2)	54(1)
C(28)	2882(5)	7117(5)	6891(3)	67(1)
C(29)	1453(6)	7617(5)	7238(3)	67(1)
C(30)	270(5)	7749(5)	6788(3)	66(1)
C(31)	516(4)	7404(4)	5989(2)	50(1)
O(1)	9836(8)	3773(7)	252(7)	233(5)

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

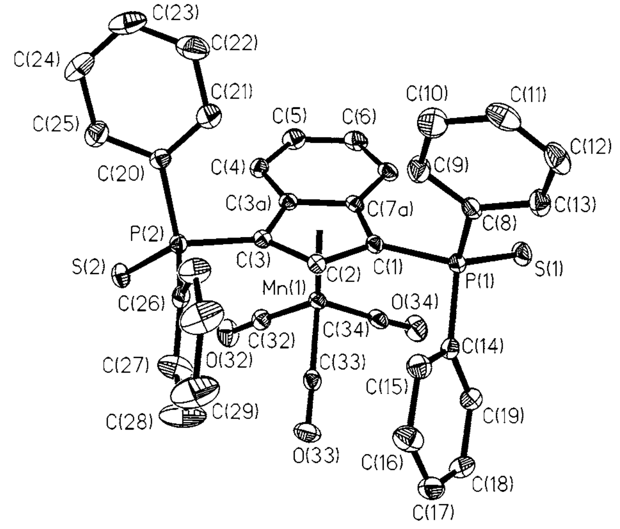
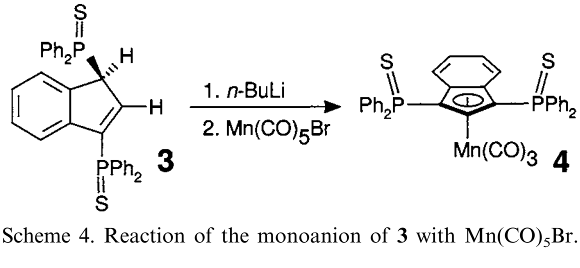


Fig. 3. The X-ray crystal structure of **4**, showing the atom numbering scheme, with thermal ellipsoids at the 30% probability level.

4.3.2. 1,3-($Ph_2P{=}O)_2(C_9H_6$), (**2**)

The dioxygen compound, 1,3-($Ph_2PO)_2(C_9H_6$), **2**, was prepared by bubbling air through a freshly prepared solution of **1** in diethyl ether for 48 h. After removal of the solvent, the desired product was isolated as a white solid by recrystallization from a 50:50 mixture of CH_2Cl_2 and 95% ethanol (2.58 g, 5.0 mmol, 63%). Single crystals suitable for X-ray diffraction studies (0.28 × 0.26 × 0.06 mm) were grown from 95% ethanol and were found to contain one molecule of ethanol per asymmetric unit. ^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.62–7.13 (m, 24H, benzo and phenyl), 6.95 (d of d of d, $^3J_{PH} = 9.1$ Hz, $^3J_{PH} = 2.4$ Hz and $^3J_{HH} = 2.0$ Hz, 1H, H-2), 4.94 (d of d of d, $^2J_{PH} = 26.8$ Hz, $^3J_{HH} = 2.0$ Hz and $^4J_{PH} = 1.8$ Hz, 1H, H-1). ^{13}C NMR ($CDCl_3$, 125 MHz): δ 144.6 (m, C-2), 143.2–139.8 (C-3, C-3a and C-7a), 134.0 (d, $J_{PC} = 20.4$ Hz, Ph), 133.7 (d, $J_{PC} = 20.3$ Hz, Ph), 132.5 (d, $J_{PC} = 10.6$ Hz, Ph), 132.1 (d, $J_{PC} = 13.5$ Hz, Ph), 131.7 (d, $J_{PC} = 8.4$ Hz, Ph), 131.4 (m, Ph), 128.6 (Ph), 128.4 (Ph), 127.9 (C-5), 126.2 (C-6), 125.0 (C-4), 123.4 (C-7), 55.0 (m, C-1). ^{31}P{^{1}H} NMR ($CDCl_3$, 202 MHz): δ 32.0 (PC-1), 22.1 (PC-3). Mass spectra: (DEI, m/z (%)): 516 (32) ($[M]^+$), 500 (51)



Scheme 4. Reaction of the monoanion of **3** with $Mn(CO)_5Br$.

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

	x	y	z	U_{eq}^{a}
Mn(1)	1708(1)	2295(1)	7539(1)	25(1)
P(1)	−882(1)	1531(1)	7613(1)	28(1)
P(2)	3478(1)	782(1)	7297(1)	25(1)
S(1)	−1944(1)	2283(1)	7120(1)	41(1)
S(2)	4787(1)	1373(1)	7333(1)	36(1)
C(1)	381(3)	1555(2)	7154(2)	25(1)
C(2)	1346(3)	1180(2)	7601(2)	24(1)
C(3)	2187(3)	1261(2)	7058(2)	23(1)
C(3A)	1720(3)	1670(2)	6211(2)	25(1)
C(4)	2164(3)	1894(2)	5411(2)	32(1)
C(5)	1516(3)	2266(2)	4697(2)	39(1)
C(6)	423(3)	2431(2)	4745(2)	39(1)
C(7A)	608(3)	1843(2)	6263(2)	25(1)
C(7)	−42(3)	2247(2)	5501(2)	32(1)
C(8)	−1389(3)	611(2)	7359(2)	29(1)
C(9)	−782(3)	64(2)	7043(2)	46(1)
C(10)	−1212(3)	−628(2)	6875(3)	56(1)
C(11)	−2245(4)	−783(2)	7030(3)	53(1)
C(12)	−2858(3)	−247(2)	7341(2)	50(1)
C(13)	−2443(3)	449(2)	7498(2)	38(1)
C(14)	−420(3)	1576(2)	8897(2)	31(1)
C(15)	54(3)	982(2)	9424(2)	38(1)
C(16)	484(3)	1054(2)	10391(2)	47(1)
C(17)	410(3)	1716(2)	10831(2)	49(1)
C(18)	−72(3)	2300(2)	10323(2)	51(1)
C(19)	−491(3)	2234(2)	9358(2)	41(1)
C(20)	3289(3)	94(2)	6369(2)	29(1)
C(21)	2269(3)	−207(2)	6014(2)	48(1)
C(22)	2164(4)	−747(2)	5329(3)	61(1)
C(23)	3057(4)	−988(2)	4990(2)	57(1)
C(24)	4070(4)	−694(2)	5334(3)	56(1)
C(25)	4182(3)	−151(2)	6021(2)	43(1)
C(26)	3412(3)	325(2)	8408(2)	30(1)
C(27)	3822(4)	677(2)	9265(2)	56(1)
C(28)	3708(5)	366(3)	10116(3)	82(2)
C(29)	3213(5)	−294(3)	10134(3)	84(2)
C(30)	2795(4)	−643(2)	9310(3)	68(1)
C(31)	2889(3)	−333(2)	8447(2)	46(1)
O(32)	3683(2)	3171(1)	7446(2)	50(1)
C(32)	2917(3)	2824(2)	7467(2)	32(1)
O(33)	2342(2)	2279(1)	9628(2)	46(1)
C(33)	2086(3)	2303(2)	8813(2)	31(1)
C(34)	863(3)	3102(2)	7497(2)	35(1)
O(34)	305(2)	3605(1)	7444(2)	55(1)

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

($[M-O]^+$), 316 (11) ($[(C_9H_6)POPh_2]^+$), 299 (32) ($[(C_9H_6)PPh_2]^+$), 201 (100) ($[POPh_2]^+$) 77 (52) ($[C_6H_5]^+$); (high resolution, DEI): calculated for mass $^{12}C_{33}H_{26}P_2O_2$, 516.1408 amu; observed, 516.1412 amu.

4.3.3. *1,3-($Ph_2P{=}S)_2(C_9H_6)$, (**3**)*

The disulfide compound, 1,3-$(Ph_2PS)_2(C_9H_6)$ **3**, was prepared by suspending an excess of elemental sulfur in a freshly prepared solution of 1,3-(diphenylphosphino)indene in diethyl ether for 48 h, under nitrogen. After removal of the residual solid by filtration and evaporation of the solvent, the desired product was isolated as a yellow powder, m.p. 188–190°C (3.81 g, 7.0 mmol, 87%). Single crystals suitable for X-ray diffraction studies (0.30 × 0.22 × 0.15 mm) were grown from 95% ethanol, and were found to contain one molecule of water per asymmetric unit. ^1H NMR ($CDCl_3$, 500 MHz): δ 7.83–6.86 (m, 24H, benzo and phenyl), 6.42 (d of d of d, $^3J_{PH} = 10.1$ Hz, $^3J_{PH} = 3.9$ Hz and $^3J_{HH} = 2.3$ Hz, 1H, H-2), 4.93 (d of d of d, $^2J_{PH} = 21.9$ Hz, $^3J_{HH} = 2.3$ Hz and $^4J_{PH} = 2.1$ Hz, 1H, H-1). ^{13}C NMR ($CDCl_3$, 125 MHz): δ 143.5 (m, C-2), 143.1–138.2 (C-3, C-3a and C-7a), 132.4–128.4 (phenyl carbons), 127.9 (C-5), 126.1 (C-6), 124.7 (C-4), 123.8 (C-7), 56.3 (m, C-1). $^{31}P\{^1H\}$ NMR ($CDCl_3$, 202 MHz): δ 46.9 (PC-1), 32.5 (PC-3). Mass spectra: (DEI, m/z (%)): 548 (30) ($[M]^+$), 516 (3) ($[M-S]^+$), 331 (13) ($[(C_9H_6)PSPh_2]^+$), 217 (100) ($[PSPh_2]^+$); (high resolution, DEI): calculated for mass $^{12}C_{33}H_{26}P_2S_2$, 548.0951 amu; observed, 548.0952 amu. Anal.:Calc. for $C_{33}H_{26}P_2S_2$: C 72.25; H 4.78. Found: C 72.31; H 4.71.

4.3.4. *(η^5-$C_9H_5(Ph_2P = S)_2)[Mn(CO)_3]$, (**4**)*

To a solution of **3** (0.69 g, 1.2 mmol) in freshly distilled tetrahydrofuran (75 ml) at −78°C was added *n*-butyllithium (0.8 ml of a 1.6 M hexane solution, 1.3 mmol) over a 1 h period, followed by stirring for an additional 3 h at −78°C. Freshly prepared $Mn(CO)_5Br$ (0.34 g, 1.3 mmol) was then added and the mixture heated under reflux for 12 h. Removal of the solvent yielded a dark red oil, which was subjected to flash chromatography on silica gel. Elution with hexane\$CH_2Cl_2$ (70:30) yielded **4** as a yellow solid, m.p. 170–172°C (0.30 g, 0.44 mmol, 37%). Single crystals suitable for X-ray diffraction studies (0.24 × 0.18 × 0.08 mm) were grown from CH_2Cl_2. ^1H NMR ($CDCl_3$, 500 MHz): δ 8.44 (m, 2H, H-4/7 or H-5/6), 7.44–7.14 (m, 20H, phenyl), 7.02 (m, 2H, H-5/6 or H-4/7), 4.07 (m, 1H, H-2). ^{13}C NMR ($CDCl_3$, 125 MHz): δ 220.6 ($C{\equiv}O$), 131.8–128.6 (phenyl carbons), 128.2 (C-5/6 or C4/7), 125.8 (C-4/7 or C5/6), 108.5 (m, C-1/3), 101.3 (t, $J_{PC} = 9.7$ Hz, C-2). $^{31}P\{^1H\}$ NMR ($CDCl_3$, 202 MHz): δ 37.7. Mass spectra: (DEI, m/z (%)): 686 (2) ($[M]^+$), 602 (32) ($[M-3(CO)]^+$), 217 (100) ($[PSPh_2]^+$). Anal. Calc. for $C_{36}H_{25}P_2S_2O_3Mn_1$: C 62.98; H 3.67. Found: C 62.90; H 3.70.

5. Supplementary material

X-ray crystallographic data, including complete bond lengths and angles, anisotropic displacement parameters and hydrogen atom coordinates for $\mathbf{2} \cdot CH_3CH_2OH$, $\mathbf{3} \cdot H_2O$, and **4** (19 pages) are available upon request.

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