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A zwitterionic phosphanyl-substituted phosphonio-benzo[*c*]phospholide as bridging ligand towards dinuclear transition metal carbonyls

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Dedicated to Professor François Mathey on the occasion of his 60th birthday

Abstract

The zwitterionic 1-triphenylphosphonio-3-diphenylphosphanyl-benzo[*c*]phospholide (**3**) reacts with $M_2(CO)_{10}$ (M = Mn, Re) to form the dinuclear complexes $[\{M(CO)_4\}_2(\mu\text{-}\mathbf{3})]$ (**7**, **8**) in which the metal–metal bond is retained and both metals are bound via the two phosphorus lone-pairs. In contrast, reaction of **3** with $Cp_2Mo_2(CO)_4$ (Mo≡Mo) proceeds with complete cleavage of the metal–metal bond to yield as final product a complex $[\{MoCp(CO)_2\}_2(\mu\text{-}\mathbf{3})]$ (**10**) in which both phosphorus lone-pairs of **3** co-ordinate to one metal atom, and the second metal atom is attached in a $\eta^2(\pi)$-co-ordination mode to the benzophospholide π-electron system. All complexes **7**, **8**, and **10** were characterised by analytic and spectroscopic data and X-ray diffraction studies. The formation of **10** is preceded by that of an intermediate which could likewise be isolated and whose constitution was assigned on the basis of spectroscopic studies as an isomer of **10** which still contains a metal–metal single bond. The behaviour of **3** marks an interesting contrast to that of 2-phosphanyl-phosphinines which react under similar conditions exclusively under co-ordination via the phosphorus lone-pairs, and fail to induce any breakage of metal–metal bonds. The origin for the observed deviations is discussed in terms of the different π-acceptor properties of the two types of ligands. © 2002 Elsevier Science B.V. All rights reserved.

Keywords: Phosphorus heterocycles; Benzophospholides; Metal carbonyls; Metal–metal bonds; Hybrid ligands

1. Introduction

Aromatic phosphorus heterocycles like phosphinines and phospholides are extremely versatile ligands [1–3]. Both types of compounds may bind transition metals via the cyclic π-electron system and the phosphorus lone-pair, but, owing to the different electronic situation, their disposition for a certain co-ordination mode differs. Phospholides prefer to form π-complexes which are isoelectronic and isolobal to metal cyclopentadienyls [1,2], and as there, the metal–ligand interaction appears to be dominated by L → M charge transfer contributions [2]. For phosphinines, the formation of π- and σ(P)-complexes is frequently competitive, with the latter — in which the ligand behaves as a pronounced π-acceptor — being often energetically favoured [3]. Recently, phosphinine and phospholide derivatives which are capable to act as multidentate ligands have gained particular attention. Beside 2,2′-bis-phosphinines [4] and 2,2′-bis-phospholides [5], the emphasis is on mixed ligands with additional phosphane [6] or nitrogen based [7] donor sites whose electronic properties differ notably from that of the phosphinine or phospholide moiety. 'Hybrid' ligands of this type are sought after because the available electronic differentiation of the binding sites allows significant improvements of selectivity and activity in homogeneous catalysis. Lately, first examples for the successful application of P,N-chelating phosphinines as hydroformylation catalysts were reported [7].

We have recently found that reduction of the bis-triphenylphosphonio-benzo[*c*]phospholide (2-phosphaindenide) (**1**) gives access to neutral phosphonio-

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benzophospholides (**2**, **3**) and anionic phosphanyl-benzophospholides (**4**, Scheme 1) [8]. First studies of the co-ordination chemistry of the neutral and cationic derivatives revealed that the phosphonio-groups decrease the π-nucleophilicity and enhance the π-acidity of the benzophospholide moiety. The zwitterion **2** thus showed a balanced co-ordination behaviour, being capable to bind a chromium carbonyl fragment both via the phosphorus lone pair in [Cr(η^1(P)-**2**)(CO)$_5$] or the π-electron system in [Cr(η^5-**2**)(CO)$_3$] [8b]. A still increased π-acceptor quality for a bis-phosphonio-benzophospholide was illustrated by the synthesis of complexes **5**, **6** whose spectroscopic data suggested that the two co-ordinate phosphorus atom in the ligand is electronically similar to a phosphite [9].

In the present work, we report on a first co-ordination chemical study of the phosphanyl-substituted zwitterion **3**. In contrast to the bidentate ligand in **5**, **6**, the P–C–P backbone between the donor sites is less flexible and imposes similar geometrical constraints as in bis-diphenylphosphino-methane (dppm) or 2-phosphanyl-phosphinines [6]. Similar as for these systems, a wide range of dinuclear complexes, either with or without metal–metal bonds, may thus likewise accessible for **3**. Focussing on two possible routes to the target complexes, viz. (a) ligand displacement at a suitable precursor with a metal–metal single bond, or (b) formal addition of **3** to a metal–metal multiple bond, we now present some results concerning the reactions of **3** with [M$_2$(CO)$_{10}$] (M = Mn, Re) and Cp$_2$Mo$_2$(CO)$_4$, respectively.

2. Results

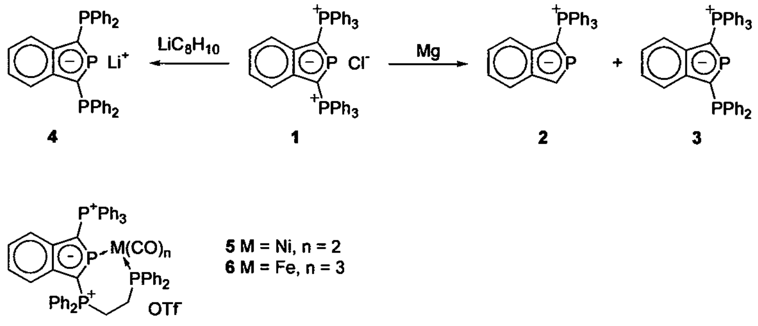
2.1. Reactions with manganese and rhenium carbonyls

Reactions of zwitterion **3** with [Mn$_2$(CO)$_{10}$] in boiling toluene or with [Re$_2$(CO)$_{10}$] in boiling xylene proceeded cleanly with quantitative formation of the dinuclear complexes **7**, **8** which precipitated as orange or yellow crystalline solids after cooling the reaction mixtures to ambient temperature. Both products were isolated in good yield and their constitution established by elemental analysis and spectroscopic (NMR, IR, FAB-MS) studies. Even under forcing conditions (prolonged refluxing in xylene), **3** failed to produce detectable amounts of a Mn$_2$(CO)$_5$ complex analogous to [(dppm)$_2$Mn$_2$(CO)$_5$] which was obtained from dppm under similar conditions [10].

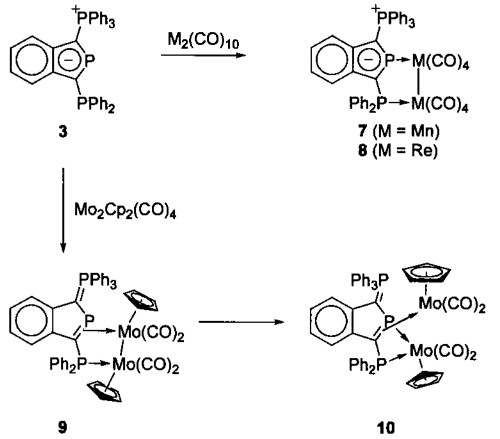
The κ^2(*P*, *P′*)-co-ordination of the ligand **3** in the complexes **7** and **8** was deduced from the characteristic co-ordination shifts ($\Delta\delta^{\mathrm{coord}} = \delta(\mathrm{complex}) - \delta(\mathrm{ligand})$) of the ^{31}P-NMR signals of the phosphorus atoms in the Ph$_2$P group ($\Delta\delta^{\mathrm{coord}} = +35.5$ (**7**), -22.5 (**8**)) and in the ring ($\Delta\delta^{\mathrm{coord}} = +6.1$(**7**), -65.1 (**8**)). The upfield shift of δ^{31}P induced by the formal replacement of the Mn by Re atoms is in accord with a general trend of co-ordination shifts in complexes of phosphorus ligands [11]. The presence of two chemically inequivalent M(CO)$_4$ moieties was inferred from the number of signals in the ^{13}C{^{1}H}-NMR spectra. The IR spectra (in CH$_2$Cl$_2$ solution) displayed five (**7**) or six (**8**) bands between 2070 and 1900 cm^{-1} attributable to *ν*(CO) vibrational modes of terminal carbonyl ligands. The absence of *ν*(CO) bands at lower wavenumbers ruled out the presence of bridging carbonyls. Considering that a single *cis*-configurated M(CO)$_4$-unit has four IR-active *ν*(CO) vibrations, we interpret the occurrence of excess bands as a result of vibrational coupling between two M(CO)$_4$-moieties which are still connected by a metal–metal bond. The proposed molecular structures of **7**, **8** were confirmed by the results of single crystal X-ray diffraction studies (see below).

2.2. Reaction with Cp$_2$Mo$_2$(CO)$_4$ (Mo≡Mo)

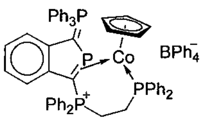
Expecting that **3** should in analogy to 2-phosphanyl-phosphinines or dppm undergo addition to metal–metal multiple bonds, we investigated its interaction with an equimolar amount of Cp$_2$Mo$_2$(CO)$_4$. The reaction proceeded smoothly at ambient temperature, however, a ^{31}P-NMR spectroscopic assay indicated that it followed actually a two-step mechanism and was thus more



Scheme 1.



Scheme 2.



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Scheme 3.

complicated than anticipated. The spectroscopic data revealed that the first reaction step was complete within a couple of hours, whereas conversion of the detected intermediate into the final product required several days. The final product was isolated by precipitation with hexane after completion of the reaction. Isolation of the intermediate was likewise feasible since selective precipitation of this product was observed when the reaction was carried out in a THF–toluene mixture. The composition of both compounds was determined by analytic and spectroscopic studies.

The (+)-Xe-FAB mass spectrum of the final product displayed a molecular ion peak whose relative mass ($m/e = 1014$) and isotope pattern is in accord with the formation of an 1:1 addition product [(**3**)$Cp_2Mo_2(CO)_4$]. This composition was confirmed by the ^{1}H-, ^{13}C-, and ^{31}P-NMR spectra which showed a set of signals attributable to co-ordinated **3** together with further resonances pointing at the presence of two chemically inequivalent cyclopentadienyl and four inequivalent carbonyl moieties. The presence of two metal atoms with different co-ordination spheres was further substantiated by the observation of two equally intense signals in the ^{95}Mo-NMR spectrum ($\delta^{95}Mo = -1007, -1309$). The IR spectrum displayed three strong bands ($\bar{\nu} = 1952, 1873, 1792$ cm^{-1}) attributable to ν(CO) vibrations of terminal carbonyls, thus disclosing as in **7**, **8** the absence of bridging CO moieties. Comparison of the ^{31}P chemical shifts with those of **3** revealed for the phosphorus atom in the Ph_2P-moiety a downfield shift ($\Delta\delta^{coord} = +58.0$) whose size is typical for co-ordinated phosphanyl groups [11]. The ring phosphorus atom displayed, in contrast, a large negative co-ordination shift ($\Delta\delta^{coord} = -340.6$) whose magnitude strongly suggests π-co-ordination of the benzophospholide moiety. This hypothesis was further supported by large negative co-ordination shifts of the carbon atoms in 1- and 3-position of the annulated ring system ($\Delta\delta^{coord} = -32.9$ (C-1), -88.1 (C-8)).

Even if the available spectroscopic data can be consistently interpreted by assuming that the ligand **3** binds two $CpMo(CO)_2$-fragments via the Ph_2P-group and a P=C-double bond of the benzophospholide moiety, a complete structural assignment proved unfeasible since no decision regarding the presence or absence of a metal–metal bond could be made. This remaining assignment problem was finally solved by an X-ray diffraction study which revealed the presence of a complex **10** (Scheme 2) with two separate $CpMo(CO)_2$-units.

The ^{1}H-, ^{31}P-, and ^{95}Mo- ($\delta^{95}Mo = -1001, -1514$) NMR spectra of the reaction intermediate displayed the same number of signals as those of **10**, and the (+)-Xe-FAB mass spectrum showed an identical molecular ion peak, suggesting that both complexes are isomers. The co-ordination shift of the phosphorus atom in the Ph_2P moiety ($\Delta\delta^{coord} = +53.2$) is similar as in **10** whereas the ring phosphorus atom exhibits a negative co-ordination shift ($\Delta\delta^{coord} = -137.5$) which is smaller than in **10**, but comparable to that of other π-complexes of phosphonio-benzophospholides [8b,12]. The IR spectrum displayed three bands in the ν(CO) region ($\bar{\nu} = 1969, 1911, 1867$ cm^{-1}) which appear in contrast to those of **10** at higher frequencies as compared to $Cp_2Mo_2(CO)_4$ ($\bar{\nu} = 1954, 1892, 1833$ cm^{-1}). Combining the available information, and assuming that by analogy to the reaction of 2-phosphanyl-phosphinines with $Cp_2Mo_2(CO)_4$ [6e] the initial reaction step should involve most likely co-ordinative addition of **3** to the metal–metal triple bond, we assign the molecular structure of the intermediate as **9** (Scheme 2). The η^2(P=C)-co-ordination of the benzophospholide unit has precedence in that of a bis-phosphonio-benzophospholide ligand in the Co-complex **11** [12] (Scheme 3). An attempt to confirm this assignment by an X-ray diffraction study failed since **9** rearranged into **10** during the crystallisation process.

2.3. Crystal structure studies

The Mn and Re complexes **7**, **8** crystallise as solvates with one molecule of solvent (**7**: toluene, **8**: CH_2Cl_2) per formula unit. An ORTEP-style drawing of the molecular structure of **8** is depicted in Fig. 1 together with selected bond distances and angles. The molecular structure of **7** deviates not significantly from that of **8**, and a separate illustration has therefore been omitted. Important bond

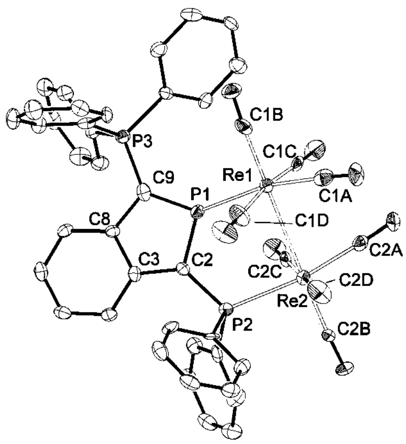


Fig. 1. Molecular structure of **8** in the crystal, ORTEP view thermal ellipsoids are at the 50% probability level, H atoms omitted for clarity. Selected bond distances (Å) (corresponding values for **7** are given in brackets: Re(1)–Re(2) 3.0365(4) [Mn(1)–Mn(2) 2.917(2)], Re(1)–P(1) 2.423(2) [Mn(1)–P(1) 2.287(3)], Re(1)–C(1A) 1.961(10) [Mn(1)–C(1A) 1.785(12)], Re(1)–C(1B) 1.929(9) [Mn(1)–C(1B) 1.808(12)], Re(1)–C(1C) 1.994(9) [Mn(1)–C(1C) 1.790(13)], Re(1)–C(1D) 1.987(9) [Mn(1)–C(1D) 1.772(11)], Re(2)–P(2) 2.4569(19) [Mn(2)–P(2) 2.331(3)], Re(2)–C(2A) 1.966(8) [Mn(2)–C(2A) 1.723(11)], Re(2)–C(2B) 1.930(8) [Mn(2)–C(2B) 1.788(12)], Re(2)–C(2C) 1.971(9) [Mn(2)–C(2C) 1.773(12)], Re(2)–C(2D) 1.981(9) [Mn(2)–C(2D) 1.783(11)], P(1)–C(2) 1.729(7) [P(1)–C(2) 1.715(9)], P(1)–C(9) 1.729(7) [P(1)–C(9) 1.743(8)], C(2)–C(3) 1.445(9) [C(2)–C(3) 1.430(11)], C(3)–C(8) 1.422(9) [C(3)–C(8) 1.450(11)], C(8)–C(9) 1.469(9) [C(8)–C(9) 1.482(11)] C(2)–P(2) 1.770(7) [C(2)–P(2) 1.781(9)], C(9)–P(3) 1.748(8) [C(9)–P(3) 1.727(9)].

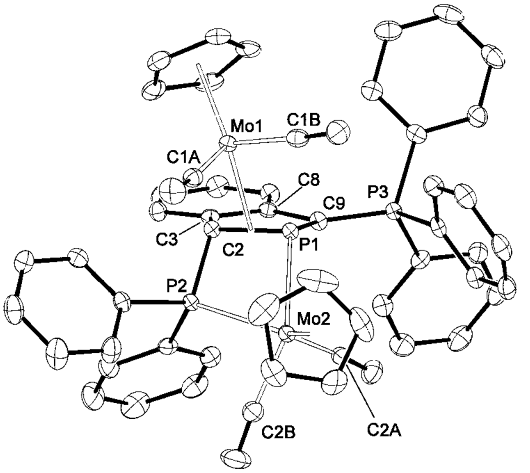


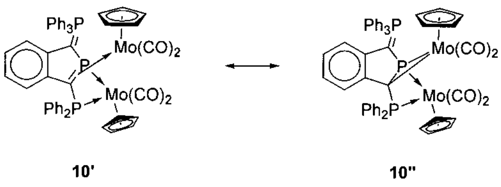
Fig. 2. Molecular structure of **10** in the crystal, ORTEP view thermal ellipsoids are at the 50% probability level, H atoms omitted for clarity. Selected bond distances (Å) (Z(PC) and Z(cp1,2) denote the centroids of the P1–C2 bond and the Cp rings on the Mo1 and Mo2 atoms, respectively): Mo(1)–C(1A) 1.930(2), Mo(1)–C(1B) 1.953(2), Mo(1)–Z(PC) 2.222(1), Mo(1)–Z(cp1) 2.034(1), Mo(2)–P(1) 2.5746(5), Mo(2)–P(2) 2.4804(5), Mo(2)–C(2A) 1.950(2), Mo(2)–C(2B) 1.969(2), Mo(2)–Z(cp2) 2.011(1), P(1)–C(9) 1.7944(18), P(1)–C(2) 1.8113(18), C(2)–C(3) 1.488(2), C(3)–C(8) 1.426(3), C(8)–C(9) 1.459(3), C(2)–P(2) 1.8059(18), C(9)–P(3) 1.7119(18).

distances and angles are given in brackets together with the corresponding data of **8** in Fig. 1.

The geometry of the benzophospholide ligand in **7** and **8** is normal and deserves no special comments. The Mn1[Re1]–P1 bond (2.287(3) [2.323(2)] Å) involving the ring phosphorus atom is shorter than the Mn2[Re2]–P2(phosphanyl) bond (2.331(3) [2.457(2)] Å). This deviation is attributable to the different formal hybridisation of the phosphorus atoms and allows no direct comparison of bond orders. The sum of valence angles at the ring phosphorus atom P1 (355° in both **7** and **8**) indicates a deviation from planar co-ordination geometry which is larger than in other complexes containing σ(P)-co-ordinated phosphonio-benzophospholides ($\Sigma\angle > 358°$ [8b,13]) but still by far smaller as in the σ-phospholyl complex $[CpW(CO)_3(\eta^1\text{-}PC_4Me_2)]$ ($\Sigma\angle$ 320° [14]). The metal co-ordination geometries can be described as interpenetrating distorted octahedrons in which the two phosphorus atoms of **3** occupy equatorial (with respect to the M–M axis) sites. The equatorial ligands at adjacent metal atoms adopt a staggered conformation similar as in $M_2(CO)_{10}$, [15] but the dihedral angles between corresponding equatorial CO ligands on adjacent metal atoms (38–41° (**7**), 38–42° (**8**)) are significantly larger than the P1–M–M–P2 angles (29.5° (**7**), 30.3° (**8**)). As a consequence, the Mn1[Re1] atom which carries the benzophospholide unit displays a more pronounced deviation from regular octahedral co-ordination geometry than the Mn2[Re2] atom. We attribute both this distortion and the notable pyramidalisation at the P1 atom to steric interference between the bulky Ph_3P-substituent in **3** with the adjacent axial CO ligand rather than electronic effects. Comparison of M–C distances to carbonyl ligands reveals no significant differences between the bonding situation at both metal atoms. This is in accordance with the fact that a σ(P)-co-ordinated zwitterionic phosphonio-benzophospholide should be electronically similar to a phosphane type ligand [8b]. The metal–metal bonds (Mn1–Mn2 2.917(2) (**7**), Re1–Re2 3.037(1) Å (**8**)) compare well to those of the corresponding decacarbonyls [15] (M–M: 2.904 ($Mn_2(CO)_{10}$), 3.042 Å ($Re_2(CO)_{10}$)).

The dimolybdenum complex **10** crystallises as solvate with one molecule of THF per formula unit. An ORTEP-style representation of the molecular structure is shown in Fig. 2 together with selected bond distances and angles.

The absence of a metal–metal bond is clearly evidenced by observation of an Mo1–Mo2 distance of 4.409(2) Å. The co-ordination environment at the metal atoms can be described as three (Mo1) or four legged (Mo2) piano-stool geometry, respectively. The distances between the metal atoms and the centroid of the cyclopentadienyl rings (Cp–Mo1 2.03, Cp–Mo2 2.01 Å) and the carbon atoms of CO ligands (1.93–1.97 Å) are similar for both metal atoms and display no peculiari-



Scheme 4.

ties [16]. The P2–Mo2 distance (2.480(1) Å) is close to the value of 2.46 ± 0.09 Å in complexes [Cp-$Mo(CO)_2(PR_3)X$] [16]. The P1–Mo2 bond (2.575(1) Å) is nearly 10 pm longer and lies near the upper limit of known bond distances in molybdenum complexes containing μ_2-bridging phosphides (Mo–P(μ-PR_2) 2.306–2.689, mean 2.456 Å [16]). The distance between Mo2 and the centre of the P1–C1 bond (2.222(2) Å) is close to the corresponding distance in [{$\mu_2(\eta^1{:}\eta^2)$-Ph-PCMe}$Cp_2Mo_2(CO)_2$] (2.240 Å [17]). The geometry of the phosphonio-benzophospholide fragment in **10** differs significantly from those of the $\kappa^2(P,P')$-co-ordinated ligands in **7**, **8** and that of free **3**, but resembles closely that of the $\eta^2(\pi)$-co-ordinated bis-phosphonio-benzophospholide unit in the Co-complex **11**. The most remarkable structural features comprise the pyramidalisation at the C2 carbon atom (sum of intra–ligand bond angles 326°) which is even more pronounced than for the corresponding atom in **11** ($\Sigma\angle$ 337° [12]), and the lengthening (relative to **3** [8c]) of the exocyclic P2–C2 (1.806(2) Å) and the endocyclic P1–C2 (1.812(2) Å), P1–C9 (1.794(2) Å), and C2–C3 (1.488(2) Å) bonds in the phospholide ring.

The discussed structural features suggest that the bonding situation in **10** may be explained by assuming that the phosphanyl-benzophospholide **3** binds via the $\eta^2(\pi)$-co-ordinated P1–C2 double bond to the Mo1 atom and via the lone-pairs at the P1 and P2 atoms to the Mo2 atom. As in the complex **11** [12], the lengthening of the co-ordinated double bond and the pronounced pyramidalisation at the C2 atom point in the frame of the Dewar–Chatt–Duncanson model to a high degree of $d(M) \rightarrow \pi^*(L)$ charge-transfer and thus considerable metallacycle character. Taking this into account, the electronic situation in **10** may be described in terms of a resonance between two canonical structures **10′** and **10″** (Scheme 4). Presuming that both metal atoms obey the 18e-rule, the metal atoms in **10′** are then assigned formal oxidation states of -1 (Mo1) and $+1$ (Mo2), whereas in **10″** both metal atoms are assigned a formal oxidation state of $+1$, and a formal reduction of the ligand has taken place.

3. Discussion

The presented results merit some comments. The observed reactivity of the zwitterion **3** towards $Mn_2(CO)_{10}$ and $Re_2(CO)_{10}$ matches that of 2-phosphanyl-substituted phosphinines which was investigated by Mathey and co-workers [6e]. As there, the phosphorus compound acts as bidentate bridging ligand via the lone-pairs of two phosphorus atoms, and the reaction stops after substitution of one carbonyl ligand at each metal atom. Even if the reason for the failure to observe poly-substituted complexes of similar constitution as $(dppm)_2Mn_2(CO)_5$ is not yet totally clear, it may be argued that the different formal hybridisation of the ring phosphorus atoms (sp^2) as compared to a phosphane centre (sp^3) renders phosphinine- and phosphonio-benzophospholide based ligands weaker nucleophiles than dppm. The carbonyl stretching frequencies of **7** ($\bar{\nu} = 2054$, 1992, 1969, 1946, 1911 cm^{-1}) appear all at lower wavenumbers as those of [$Mn_2(CO)_8${3,4-dimethyl-2-(3′,4′-dimethyl-1′-phospholyl)-phosphinine}] (**12**) ($\bar{\nu} = 2059$, 1997, 1974, 1951, 1925 cm^{-1}) [6e], suggesting the zwitterion **3** to be a less efficient π-acceptor than the phospholyl-phosphinine ligand in **12**.

The formation of the molybdenum complex **9** via co-ordinative addition of **3** to the metal–metal triple bond in $Cp_2Mo_2(CO)_4$ still mirrors in a formal sense the behaviour of 2-phosphanyl-phosphinines [6e], but differs insofar as the heterocyclic ligand fragment is bound via the π-electron system and not the phosphorus lone-pair. The shift from σ(P)- (in **7**, **8**) to π-co-ordination of the benzophospholide unit coincides with an increased π-basicity of the $CpMo(CO)_2$– as compared to an isolobal $Mn[Re](CO)_4$-fragment and parallels the observation of π(P=C)-co-ordination of a bis-phosphonio-substituted benzophospholide to an electron rich Cobalt atom in **11** [12]. The $\eta^2(\pi)$-co-ordination of the fused ring system implies a partial π-bond localisation which is presumably facilitated by the comparatively low aromatic stabilisation energies in phosphonio-benzophospholides [8c,18] and the possibility to compensate for the loss of resonance energy by increased ylidic character of the exocyclic C–P(phosphonio) bond [12].

The rearrangement **9** → **10** with concomitant cleavage of the metal–metal bond is unprecedented in the chemistry of phosphanyl-phosphinines. Considering the contribution from canonical structure **10″** in the bonding description, the rupture of the metal–metal bond is accompanied by a net $d(M) \rightarrow \pi^*(L)$ charge-transfer, or in other words, a (partial) reduction of the phosphonio-benzophospholide moiety. This point being taken into account, the different reactivities of **3** and phosphanyl-phosphinines towards complexes with electron rich metal atoms can be explained by assuming that the former is more prone to undergo reduction processes. Even if this argument seems surprising in the light of the higher π-acceptor character of phosphanyl-phosphinines in $Mn_2(CO)_8$ complexes (vide supra), the apparent contradiction can be resolved: whereas the relative π-acceptor powers of ligands bound to metal atoms of low π-back-donating power (e.g. in **7**, **12**) are in the first place determined by the relative LUMO energies, the situation may change with increasing extent of M → L charge-transfer under the influence of different charge-capacities. In this context, the observed metal–metal bond cleavage in **10** suggests that the 10π-electron system of a phosphonio-benzophospholide is easier polarisable, and may accommodate a larger amount of excess electronic charge, than the 6π-electron system of a phosphinine.

4. Experimental

4.1. General remarks

All manipulations were carried out under dry argon. Solvents were dried by standard procedures. Compound **3** [8b] was prepared as described. NMR spectra: Bruker AMX300 (^{1}H: 300.1 MHz, ^{31}P: 121.5 MHz, ^{13}C: 75.4 MHz, ^{95}Mo: 19.5 MHz). Chemical shifts were referenced to ext. Me_4Si (^{1}H, ^{13}C), 85% H_3PO_4 (Ξ = 40.480747 MHz), aq. MO_4^{2-} (Ξ = 6.516926 MHz); positive signs of chemical shifts denote shifts to lower frequencies, and coupling constants are given as absolute values. Prefixes *i*-, *o*-, *m*-, *p*- denote atoms of phenyl substituents, and atoms in the benzophospholide ring are denoted as 4-C, 5-H, etc. assignment of resonances were derived in ambiguous cases from analysis of 2D ^{1}H,^{13}C-HMQC and HMBC NMR spectra. MS: Kratos Concept 1H, Xe-FAB, *m*-NBA matrix. FT-IR spectra: Nicolet Magna 550, in CH_2Cl_2 solution. Elemental analyses: Heraeus CHNO-Rapid. Melting points were determined in sealed capillaries.

4.1.1. Preparation of octacarbonyl-{μ-(3-diphenylphosphino-1-triphenylphosphonio-benzo[c]phospholide)-1κP,2κP′}dimanganese (Mn–Mn) (**7**)

A mixture of 200 mg (0.33 mmol) of **3** and 150 mg (0.38 mmol) of $Mn_2(CO)_{10}$ was dissolved in 9 ml of toluene in a 25 ml Schlenk tube and refluxed for 6 h. The resulting red solution was then cooled to ambient temperature and stored in a refrigerator at 2 °C. An orange crystalline precipitate formed which was collected by filtration, washed with little cold toluene, and dried in high vacuum. Yield: 280 mg (0.31 mmol, 94%), m.p. 252 °C (dec.). ^{1}H-NMR (THF-d_8): 6.40–6.60 [4 H, 4-H to 7-H], 7.06–8.12 [25 H, C_6H_5]. ^{31}P{^{1}H}-NMR (THF-d_8): 228.6 [dd, $^{2}J_{\mathrm{P,P}}$ = 170.2, 57.2 Hz, P-2], 13.9 [dd, $^{2}J_{\mathrm{P,P}}$ = 170.2 Hz, $^{4}J_{\mathrm{P,P}}$ = 8.3 Hz, –$P^{+}Ph_3$], 35.5 [dd, $^{2}J_{\mathrm{P,P}}$ = 57.2 Hz, $^{4}J_{\mathrm{P,P}}$ = 8.3 Hz, PPh_2]. ^{13}C{^{1}H}-NMR (THF-d_8): 98.5 [ddd, $^{1}J_{\mathrm{P,C}}$ = 15.3 Hz, 103.1 Hz, $^{3}J_{\mathrm{P,C}}$ = 6.4 Hz, C-1], 118.9 [dd, $^{3}J_{\mathrm{P,C}}$ = 4.3, 4.3 Hz, C-7], 119.6 [s, C-5/6], 119.9 [d, $^{4}J_{\mathrm{P,C}}$ = 2.5 Hz, C-5/6], 120.4 [dd, $^{3}J_{\mathrm{P,C}}$ = 1.8 Hz, 12.1 Hz, C-4], 124.4 [dd, $^{1}J_{\mathrm{P,C}}$ = 90.0 Hz, $^{3}J_{\mathrm{P,C}}$ = 1.5 Hz, *i*-C(PPh_3)], 128.3 [d, $^{3}J_{\mathrm{P,C}}$ = 9.7 Hz, *m*-C(PPh_2)], 129.6 [d, $^{4}J_{\mathrm{P,C}}$ = 1.9 Hz, *p*-C(PPh_2)], 130.0 [d, $^{3}J_{\mathrm{P,C}}$ = 12.6 Hz, *m*-C(PPh_3)], 132.2 [d, $^{2}J_{\mathrm{P,C}}$ = 9.9 Hz, *o*-C(PPh_2)], 134.0 [d, $^{4}J_{\mathrm{P,C}}$ = 2.7 Hz, *p*-C(PPh_3)], 134.8 [d, $^{2}J_{\mathrm{P,C}}$ = 10.3 Hz, *o*-C(PPh_3)], 135.6 [d, $^{1}J_{\mathrm{P,C}}$ = 42.6 Hz, *i*-C(PPh_2)], 141.4 [ddd, $^{1}J_{\mathrm{P,C}}$ = 4.3 Hz, 14.7 Hz, $^{3}J_{\mathrm{P,C}}$ = 4.3 Hz, C-3], 147.4 [dd, $^{2}J_{\mathrm{P,C}}$ = 8.2 Hz, 16.3 Hz, C-7a], 147.9 [ddd, $^{2}J_{\mathrm{P,C}}$ = 34.5 Hz, 46.8 Hz, $^{3}J_{\mathrm{P,C}}$ = 10.4 Hz, C-3a], 220.2 [br, CO], 221.2 [br, CO], 223.4 [br, CO], 224.9 [br, 2CO], 225.9 [br, CO], 227.9 [br, 2CO]. FAB-MS: *m*/*z* (%) = 913 (10) [M^{+}], 800 (20) [$M^{+} - Mn(CO)_4$], 745 (20) [$M^{+} - Mn(CO)_4$], 717 (100) [$M^{+} - Mn(CO)_5$]. IR (CH_2Cl_2, CaF_2): *v*(CO) = 2054, 1992, 1969, 1946, 1911 cm^{-1}. Anal. Calc. for $C_{46}H_{29}Mn_2O_8P_3$ (912.5): C, 60.55; H, 3.20. Found: C, 60.0; H, 3.2%.

4.1.2. Preparation of octacarbonyl-{μ-(3-diphenylphosphino-1-triphenylphosphonio-benzo[c]phospholide)-1κP,2κP′}dirhenium (Re–Re) (**8**)

A mixture of 200 mg (0.33 mmol) of **3** and 220 mg (0.34 mmol) of $Re_2(CO)_{10}$ was dissolved in 10 ml of *p*-xylene in a 25 ml Schlenk tube and refluxed for 18 h. The resulting brownish–yellow solution was then cooled to ambient temperature and stored in a refrigerator at 2 °C. A yellow crystalline precipitate formed which was collected by filtration, washed with little cold pentane, and dried in high vacuum. Yield: 380 mg (0.32 mmol, 97%), m.p. 281 °C (dec.). ^{1}H-NMR (THF-d_8): 6.44–6.68 [4 H, 4-H to 7-H], 7.3–8.1 [25 H, C_6H_5]. ^{31}P{^{1}H}-NMR (THF-d_8): 157.4 [dd, $^{2}J_{\mathrm{P,P}}$ = 166.6, 57.9 Hz, P-2], 13.9 [dd, $^{2}J_{\mathrm{P,P}}$ = 166.6 Hz, $^{4}J_{\mathrm{P,P}}$ = 7.6 Hz, –$P^{+}Ph_3$], – 22.5 [dd, $^{2}J_{\mathrm{P,P}}$ = 57.9 Hz, $^{4}J_{\mathrm{P,P}}$ = 7.6 Hz, PPh_2]. ^{13}C{^{1}H}-NMR (THF-d_8): 93.4 [ddd, $^{1}J_{\mathrm{P,C}}$ = 13.2 Hz, 104.0 Hz, $^{3}J_{\mathrm{P,C}}$ = 3.2 Hz, C-1], 119.2 [dd, $^{3}J_{\mathrm{P,C}}$ = 4.4 Hz, 5.2 Hz, C-4], 119.7 [s, C-5/6], 120.4 [d, $^{4}J_{\mathrm{P,C}}$ = 2.9 Hz, C-5/6], 120.9 [d, $^{3}J_{\mathrm{P,C}}$ = 2.4 Hz, C-7], 124.2 [dd, $^{1}J_{\mathrm{P,C}}$ = 90.2 Hz, $^{3}J_{\mathrm{P,C}}$ = 1.9 Hz, *i*-C(PPh_3)], 128.4 [d, $^{3}J_{\mathrm{P,C}}$ = 10.1 Hz, *m*-C(PPh_2)], 129.8 [d, $^{4}J_{\mathrm{P,C}}$ = 2.1 Hz, *p*-C(PPh_2)], 130.0 [d, $^{3}J_{\mathrm{P,C}}$ = 12.6 Hz, *m*-C(PPh_3)], 132.2 [d, $^{2}J_{\mathrm{P,C}}$ = 10.7 Hz, *o*-C(PPh_2)], 134.1 [d, $^{4}J_{\mathrm{P,C}}$ = 2.9 Hz, *p*-C(PPh_3)], 134.9 [d, $^{2}J_{\mathrm{P,C}}$ = 10.3 Hz, *o*-C(PPh_3)], 136.6 [dd, $^{1}J_{\mathrm{P,C}}$ = 47.2 Hz, $^{3}J_{\mathrm{P,C}}$ = 8.7 Hz, *i*-C(PPh_2)], 143.5 [ddd, $^{2}J_{\mathrm{P,C}}$ = 7.3 Hz, 2.1 Hz, $^{3}J_{\mathrm{P,C}}$ = 14.7 Hz, C-3a], 146.7 [dd, $^{2}J_{\mathrm{P,C}}$ = 8.7 Hz, 17.2 Hz, C-7a], 148.9 [ddd, $^{1}J_{\mathrm{P,C}}$ = 56.0 Hz, 54.7 Hz, $^{3}J_{\mathrm{P,C}}$ = 10.1 Hz, C-3], 189.3 [d, $^{2}J_{\mathrm{P,C}}$ = 6.7 Hz, CO], 190.4 [d, $^{2}J_{\mathrm{P,C}}$ = 7.4 Hz, CO], 195.6 [dd, $^{2}J_{\mathrm{P,C}}$ = 45.6 Hz, $^{3}J_{\mathrm{P,C}}$ = 5.3 Hz, CO], 197.2 [dd, $^{2}J_{\mathrm{P,C}}$ = 58.8 Hz, $^{3}J_{\mathrm{P,C}}$ = 1.7 Hz, CO], 198.2 [dd, $^{2}J_{\mathrm{P,C}}$ = 13.0 Hz, $^{3}J_{\mathrm{P,C}}$ = 2.3 Hz, 2 CO], 202.9 [dd, $^{2}J_{\mathrm{P,C}}$ = 9.6 Hz, $^{3}J_{\mathrm{P,C}}$ = 4.5 Hz, 2 CO]. FAB-MS: *m*/*z* (%) = 1176 (100) [M^{+}]; 1064 (50) [$M^{+} - 4CO$]. IR (CH_2Cl_2, NaCl): *v*(CO) = 2069, 2017, 1983, 1975, 1951, 1907 cm^{-1}. Anal. Calc. for $C_{46}H_{292}O_8P_3Re$ (1175.1): C, 50.62; H, 3.07. Found: C, 50.06; H, 3.08%.

4.1.3. Preparation of complex **9**

A mixture of 200 mg (0.33 mmol) of **3** and 150 mg (0.33 mmol) of $Cp_2Mo_2(CO)_4$ was dissolved in 2 ml of THF and 10 ml of toluene in a 25 ml Schlenk tube and stirred for 56 h at ambient temperature. The resulting red crystalline precipitate was collected by filtration, washed with hexane, and dried in high vacuum. Yield: 210 mg (0.21 mmol, 64%), m.p. 199 °C (dec.). ^{1}H-NMR (THF-d_8): 4.56 [s, 5H, Cp], 4.65 [s, 5H, Cp], 6.3–6.7 [4 H, 4-H to 7-H], 7.0–8.1 [25 H, C_6H_5]. $^{31}P\{^1H\}$-NMR (THF-d_8, −20 °C): 89.7 [dd, $^2J_{P,P} = 189.5$ Hz, 97.9 Hz, P-2], 32.5 [dd, $^2J_{P,P} = 189.5$ Hz, $^4J_{P,P} = 3.5$ Hz, $-PPh_2$], −16.0 [dd, $^2J_{P,P} = 97.9$ Hz, $^4J_{P,P} = 3.5$ Hz, $-P^+Ph_3$]. ^{95}Mo-NMR (THF): −1001, −1514. FAB-MS: m/z (%) = 1014 (100) [M^+]. IR (CH_2Cl_2, NaCl): $\nu(CO) = 1969, 1911, 1867\ cm^{-1}$.

4.1.4. Preparation of [μ-(3-diphenylphosphino-1-triphenylphosphonio-benzo[c]phospholide)-1κ^{2}P,P′,2κ-(η^2-P=C)-bis-(η^5-cyclopentadienyl–dicarbonyl–molybdenum)] (**10**)

A mixture of 200 mg (0.33 mmol) of **3** and 150 mg (0.33 mmol) of $Cp_2Mo_2(CO)_4$ was dissolved in 10 ml of THF in a 25 ml Schlenk tube and stirred for 4 days at ambient temperature. The resulting mixture was filtered and the filtrate evaporated in vacuum. The residue was dissolved in 3 ml of THF and the solution layered with 20 ml of hexane. A dark brown precipitate formed slowly which was collected by filtration, and dried in high vacuum. Complex **10** was likewise formed in quantitative yield (by ^{31}P-NMR spectroscopy) when a THF solution of **9** was stirred for 24 h at ambient temperature. Yield: 250 mg (0.25 mmol, 76%), m.p. 208 °C

Table 1
Crystallographic data, structure solution and refinement parameters of **7**, **8**, and **10**

	7	**8**	**10**
Empirical formula	$C_{46}H_{29}Mn_2O_8P_3\cdot 1/2$toluene	$C_{46}H_{292}O_8P_3Re\cdot CH_2Cl_2$	$C_{52}H_{39}Mo_2O_4P_3\cdot$THF
Formula weight	958.55	1259.93	1084.73
Temperature (K)	123(2)	123(2)	123(2)
Wavelength (Å)	0.71073	0.71073	0.71073
Crystal system	Monoclinic	Monoclinic	Triclinic
Space group	$P2_1/c$ (No.14)	$P2_1/c$ (No.14)	$P\bar{1}$ (No.2)
Unit cell dimensions			
a (Å)	12.815(1)	13.0944(7)	11.2592(2)
b (Å)	24.678(3)	24.6514(13)	11.4543(2)
c (Å)	14.989(2)	15.0265(7)	19.5723(3)
α (°)			84.923(1)
β (°)	112.59(1)	113.678(3)	83.897(1)
γ (°)			68.871(1)
V (Å^3)	4376.6(9)	4442.2(4)	2337.70(7)
Z	4	4	2
$\rho_{calc.}$ (g cm^{-3})	1.455	1.884	1.541
μ (mm^{-1})	0.74	0.74	0.69
F(000)	1956	2424	1104
Dimensions (mm)	$0.40\times 0.10\times 0.02$	$0.20\times 0.10\times 0.03$	$0.35\times 0.20\times 0.10$
Diffractometer	Nonius Kappa CCD	Nonius Kappa CCD	Nonius Kappa CCD
Radiation	Mo–K$_\alpha$	Mo–K$_\alpha$	Mo–K$_\alpha$
2θ max. (°)	45.0	50.0	50.0
	$-13\leq h\leq 11$	$-15\leq h\leq 13$	$-13\leq h\leq 13$
	$-23\leq k\leq 26$	$-20\leq k\leq 29$	$-13\leq k\leq 12$
	$-12\leq l\leq 16$	$-17\leq l\leq 17$	$-23\leq l\leq 23$
Measured data	20 481	25 432	30 137
Unique data	5705	7773	8212
R_{int}	0.201	0.099	0.041
Absorption correction	None	Empirical from multiple reflections	Empirical from multiple reflections
Refinement method	F^2	F^2	F^2
Parameters/restraints	549/7	559/0	595/6
Final R indices [$I>2\sigma(I)$]	0.072	0.038	0.024
R indices (all data)	0.166	0.072	0.063
Max./min. difference peak (e Å^{-3})	0.43 and −0.53	1.95 and −1.12	−0.58 and −0.55

(dec.). ^{1}H-NMR (THF-d_8): 4.74 [s, 5H, Cp], 5.25 [d, $^3J_{P,H} = 0.7$ Hz, 5H, Cp], 6.01 [m, 1H, 4/7-H], 6.18 [m, 1H, 5/6-H], 6.26 [m, 1H, 5/6-H], 6.58 [m, 1H, 4/7-H], 6.70–8.26 [25 H, C_6H_5]. ^{13}C{^{1}H}-NMR (THF-d_8): 55.5 [ddd, $^1J_{P,C} = 24.7$ Hz, 24.7 Hz, $^3J_{P,C} = 5.1$ Hz, C-3], 60.3 [dd, $^1J_{P,C} = 22.0$ Hz, 110.9 Hz, C-1], 91.6 [s, Cp], 92.7 [dd, $^2J_{P,C} = 5.3$ Hz, 0.7 Hz, Cp], 117.0 [s, C-4/7], 118.6 [dd, $J_{P,C} = 4.1$ Hz, 4.1 Hz, C-4/7], 122.4 [s, C-5/6], 125.5 [s, C-5/6], 147.7 [ddd, $J_{P,C} = 9.7$ Hz, 7.1 Hz, 12.0 Hz, C-3a], 148.5 [dd, $^2J_{P,C} = 2.7$ Hz, 17.7 Hz, C-7a], 233.9 [dd, $^2J_{P,C} = 10.8$ Hz, 2.6 Hz, CO], 241.5 [d, $^2J_{P,C} = 20.6$ Hz, CO], 250.1 [dd, $^2J_{P,C} = 33.8$ Hz, 2.5 Hz, CO], 256.3 [d, $^2J_{P,C} = 32.8$ Hz, CO]; signals attributable to C_6H_5 groups could not be unambiguously assigned due to severe dynamic broadening, presumably owing to hindered rotation of the Ph_3P-moiety. ^{31}P{^{1}H}-NMR (THF-d_8): -118.1 [dd, $^2J_{P,P} = 67.1$ Hz, 53.1 Hz, P-2], 37.3 [dd, $^2J_{P,P} = 67.1$ Hz, $^4J_{P,P} = 2.5$ Hz, $-PPh_2$], 11.7 [dd, $^2J_{P,P} = 53.1$ Hz, $^4J_{P,P} = 2.5$ Hz, $-P^+Ph_3$]. ^{95}Mo-NMR (THF): -1007, -1309. FAB-MS: m/z (%) = 1014 (100) [M$^+$]. IR (CH_2Cl_2, NaCl): ν(CO) = 1952, 1873, 1792 cm^{-1}. Anal. Calc. for $C_{52}H_{39}Mo_2O_4P_3$ (1012.7)·hexane: C, 63.40; H, 4.86. Found: C, 63.70; H, 4.95%.

*4.1.5. Crystal structure determinations of complexes **7**, **8**, and **10***

Single crystals of **7** × 0.5 toluene, **8** × CH_2Cl_2, and **10** × THF were grown from toluene–CH_2Cl_2 (**7**, **8**) or toluene–THF (**10**) solutions. The diffraction data were collected on a Nonius Kappa CCD diffractometer at − 150 °C using Mo–K$_\alpha$ radiation. The structures were solved by direct methods (SHELXS-97 19a). The non-hydrogen atoms were refined anisotropically, H atoms were refined using a riding model (full-matrix least-squares refinement on F^2 (SHELXL-97 [19b]). The solvent molecule in the crystal structure of **7** is disordered. Details of data collection and refinement are given in Table 1.

5. Supplementary material

Crystallographic data (excluding structure factors) for the structures reported in this work have been deposited with the Cambridge Crystallographic Data Centre as publication no. CCDC 164401 (**7**), CCDC 164402 (**8**), and CCDC 164403 (**10**), respectively. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

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