Ambident σ- and π-donor ability of a neutral 10π-aromatic phosphoniobenzophospholide†

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1-Triphenylphosphoniobenzo[*c*]phospholide 2 which is accessible *via* NaBH$_4$ reduction of 1,3-bis(triphenylphosphonio)benzophospholide 1 displays an ambident coordination ability similar to a phosphinine; this is shown by its reactions with (cyclooctene)Cr(CO)$_5$ and (naphthalene)Cr(CO)$_3$ which gave (σ(*P*)-2)Cr(CO)$_5$ and (η^5-2)Cr(CO)$_3$, the first π-complex of a 10π-aromatic phosphorus heterocycle with a d-block metal.

Phosphinines **I** and phospholides **II** are aromatic phosphorus heterocycles whose use as ligands in transition metal complexes receives substantial current interest,[1] in particular in connection with possible applications in catalysis.[2] As compared to their organic analogues, *viz.* arenes and cyclopentadienides, **I**, **II** are more versatile ligands which may bind to metals not only *via* the π-electron system (η^5/η^6-coordination) but also *via* the phosphorus lone-pair (σ(*P*)-coordination), or a combination of both.[1] For phosphinines, formation of σ(*P*)-complexes in which the ligand displays σ-donor/π-acceptor-properties similar as a phosphane or phosphite is generally more favourable with metals in low oxidation states, although complexes with η^6-coordinated phosphinines are also accessible for various metal centres.[1] Phospholides prefer, in contrast, π-coordination and the vast majority of complexes feature η^5-bound ligands; pure σ(*P*)-phospholide complexes are known,[3] but remain rare.

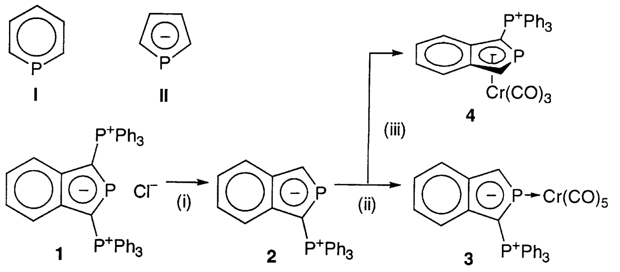
We have recently established that cationic 1,3-bis-triphenylphosphonio-benzophospholide **1** binds to various transition metals in a σ(*P*)- or μ$_2$(*P*)-coordination mode.[4,5] The donor ability of the π-electron system in **1** was found to be inferior to that of the phosphorus lone-pair, and on the whole the structural features of the complexes resembled more closely those of topologically related phosphinine complexes rather than genuine phospholide complexes.[4] These findings suggested that the reduction of π-nucleophilicity and enhancement of π-electrophilicity induced by the phosphonio groups is of pivotal importance for the complexation regioselectivity and lead us to conclude that mono-phosphonio-substituted benzophospholides might display a balanced ligand behaviour with prospects for both σ(*P*)- and π-coordination, similar to the case of phosphinines. Here, we report on the synthesis and coordination studies of the phosphonio-benzophospholide **2** which lead to the isolation and structural characterisation of the first π-complex of a 10π-aromatic phosphaarene with a d-block transition metal.[6]

During our studies of reductive fragmentation reactions of the cation **1**[7] we discovered that **1**[Cl] reacts selectively with excess NaBH$_4$ *via* cleavage of PPh$_3$ to form neutral species **2** (Scheme 1). The latter was isolated in satisfactory yield after recrystallisation from THF–isopropyl alcohol and its constitution established by analytical and spectroscopic data.† Interestingly, the first UV–VIS absorption band of **2** [$\lambda_{\max}$ (CH$_2$Cl$_2$) = 352 nm] which is attributable to a π–π* transition of the benzophospholide chromophore occurs at nearly the same wavelength as for **1** [$\lambda_{\max}$ (CH$_2$Cl$_2$) = 354 nm[5]], thus indicating similar frontier orbital gaps in both molecules. As the effect of the positive charge in **1** should shift all orbitals to more negative energies,[8] neutral **2** is thus expected to behave as a better π-donor but less effective π-acceptor than **1**.

To survey the coordination behaviour of **2**, we explored reactions with equimolar amounts of [(cyclooctene)Cr(CO)$_5$] and [(naphthalene)Cr(CO)$_3$], respectively. Both reactions proceeded according to an ^{31}P NMR spectroscopic assay with quantitative formation of a single phosphorus containing species. The products were isolated after precipitation with hexane and recrystallisation from toluene, and their nature as the complexes **3**, **4** was established by microanalytical and spectroscopic data and single crystal X-ray diffraction studies.[9]

Complex **3** displays a moderate negative coordination shift for the endocyclic phosphorus atom [$\delta^{\text{coord}} = \delta(\text{ligand}) - \delta(\text{complex}) = -29$] while coordination shifts for the benzophospholide carbon atoms are insignificant ($\delta^{\text{coord}} < \pm 3$) and the proton at C3 is slightly deshielded ($\delta^{\text{coord}} = 0.3$). All these features are characteristic for complexes featuring σ(*P*)-coordinated low valent phosphorus species.[1] The carbonyl region of the IR spectrum of **3** displays the expected pattern of a M(CO)$_5$ moiety with the band at highest energy ($\nu = 2064$ cm^{-1}) appearing at slightly lower wavenumbers than in [(Ph$_3$P)Cr(CO)$_5$] ($\tilde{\nu} = 2070$ cm^{-1}) or the phosphinine complex [σ-(2,4,6-triphenylphosphinine)Cr(CO)$_5$] **5** ($\tilde{\nu} = 2071$ cm^{-1} [10]). Although comparison of this vibrational frequency in LM(CO)$_5$ complexes has been used to relate the π-acceptor qualities of L,[2] a more common and quantitative approach is provided by evaluation of Tolman's electronic parameter χ which can be obtained from vibrational spectra of LNi(CO)$_3$ complexes.[11] We have therefore recorded IR spectral data of the Ni(CO)$_3$ complex of **2** (prepared *in situ* from equimolar amounts of **2** and Ni(CO)$_4$) and determined a value of $\chi = 13$ indicating that the π-acceptor ability of **2** should match that of PPh$_3$ ($\chi = 13$[11]) but is lower than that of P(OMe)$_3$ ($\chi = 23$[11]) or 2,4,6-triphenylphosphinine ($\chi = 23$[2]).

The ^{1}H, ^{13}C and ^{31}P NMR spectra of complex **4** reveal large negative coordination shifts for the endocyclic phosphorus ($\delta^{\text{coord}} = -158$), the hydrogen at C3 ($\delta^{\text{coord}} = -2.6$) and the carbon atoms in the five membered ring ($\delta^{\text{coord}} = -17$ to -24) whereas the remaining nuclei in the benzophospholide unit exhibit similar chemical shifts as in free **2**. Altogether, these



Scheme 1 *Reagents and conditions*: i, excess NaBH$_4$, THF, 24 h, r.t.; ii, 1 equiv. [(cyclooctene)Cr(CO)$_5$], THF, 6 h, r.t.; iii, 1 equiv. [(naphthalene)Cr(CO)$_3$], THF, 6 h, r.t.

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† Electronic supplementary information (ESI) available: analytical and spectroscopic data for **2-4**. See http://www.rsc.org/suppdata/cc/b0/b005130f/

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data indicate π-coordination of **2** *via* the five-membered ring which has likewise been observed for indenyl complexes such as [(η^5-indenyl)Cr(CO)$_3$]$^-$ **6**.[12] The carbonyl stretching vibrations in the IR spectrum of **4** ($\tilde{\nu}$ = 1925, 1835, 1826 cm^{-1}) appear at higher wavenumbers than in both **6** ($\tilde{\nu}$ = 1895, 1791 cm^{-1} [12] and [η^5-(C$_5$H$_4$PPh$_3$)Cr(CO)$_3$] **7** ($\tilde{\nu}$ = 1900, 1805, 1785 cm^{-1} [13]), indicating that the amount of π-electron density transferred to the metal is lower for **2** than for the carbocyclic ligands $C_9H_7^-$ and $C_5H_4PPh_3$, respectively.

The results of the X-ray structure analysis of complex **3** [Fig. 1(a)] confirms the presence of a σ(*P*)-coordinated benzophospholide ligand with a planar annulated ring system. Unlike as in known complexes of σ(*P*)-coordinated phospholides,[3] the metal-bound phosphorus atom lacks any evidence for pyramidalisation (sum of bond angles 360°). The exocyclic P–C bond [P2–C2 1.744(1) Å] is similar as in complexes of **1** (1.75 ± 1 Å[4]) whereas of the endocyclic P–C distances the one to the protonated carbon atom is shortened [P1–C9 1.691(2) Å] and the other lengthened [P1–C2 1.767(2) Å]. The P1–Cr1 bond [2.376(5) Å] matches that in the phosphinine complex **5** [2.372(15) Å[4]]. The Cr–C distances in **3** [Cr–C$_{trans}$ 1.862(4) Å, Cr–C$_{cis}$ 1.895–1.912, av. 1.902 Å] are generally longer than those in **5** [Cr–C$_{trans}$ 1.822(12) Å, Cr–C$_{cis}$ 1.825–1.865, av. 1.843 Å[10]]. Although interpretation of these data in terms of electronic effects is difficult in view of sterically induced distortions in both structures, the more pronounced shortening of the *trans*-relative to the *cis*-Cr–C bonds in **3** agrees with a lower π-acceptor ability of **2** as compared to 2,4,6-Ph$_3$H$_2$C$_5$P which was predicted on grounds of the spectroscopic data.

The molecular structure of **4** [Fig. 1(b)] displays a three-legged piano-stool geometry with the coordinated five membered ring featuring a flat twist conformation. The Cr–C distances range between 2.229(2) and 2.341(3) Å with the closest distances observed for the carbons atoms C2, C9 adjacent to P1 which are presumably the centres of highest π-electron density,[8] and the Cr–P distance amounts to 2.407(4) Å. The distances between the metal and the carbonyl C-atoms [1.806(3)–1.837(3) Å] and the centroid of the phospholide ring [1.874(3) Å], respectively, compare well with the corresponding values of [η^5-(C$_5$H$_4$PPh$_3$)Cr(CO)$_3$] **7** (Cr–CO 1.77–1.83, Cr–Cent. 1.862 Å[13]) and [(η^6-2,4,6-triphenylphosphinine)Cr(CO)$_3$] (Cr–CO 1.80–1.82, Cr–Cent. 1.686 Å[14]). The exocyclic P2–C2 bond in **4** [1.755(3) Å] is similar than in **3** but the endocyclic P–C [1.744(2), 1.805(2) Å] and adjacent C–C bonds [1.426(3), 1.460(3) Å] are lengthened as expected for a π-complex. The extent of this lengthening is somewhat more pronounced for the P–C than for the C–C bonds which agrees with the finding that the largest coefficients in the frontier orbitals of benzo[*c*]phospholides are found at the phosphorus and the two adjacent carbon atoms.[8]

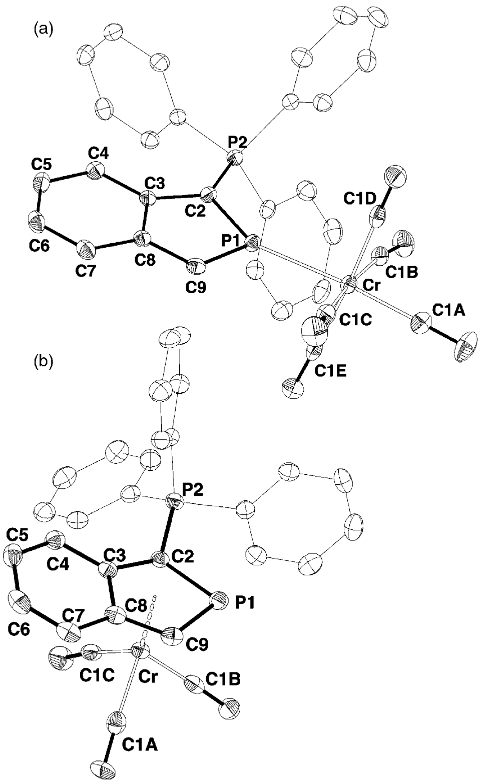

Fig. 1 Molecular structures of **3** (a) and **4** (b). Thermal ellipsoids are drawn at 50% probability level, and H atoms have been omitted for clarity. Selected bond lengths (Å); for **3**, Cr–P1 2.3760(5), P1–C9 1.6910(17), C9–C8 1.414(2), C–C7 1.422(2), C7–C6 1.370(3), C6–C5 1.398(3), C5–C4 1.379(2), C4–C3 1.417(2), C3–C8 1.430(2), C3–C2 1.456(2), C2–P1 1.7670(18), C2–P2 1.7438(17), Cr1–C1D 1.9030(19), Cr–C1B 1.912(2), Cr–C1E 1.8953(19), Cr–C1A 1.862(2). For **4**: P1–C9 1.744(4), C9–C8 1.426(0), C8–C7 1.429(3), C7–C6 1.354(0), C6–C5 1.418(1), C5–C4 1.367(3), C4–C3 1.419(0), C3–C8 1.436(1), C3–C2 1.460(2), C2–P1 1.805(0), C2–P2 1.755(3), Cr–C1A 1.826(2), Cr–C1B 1.806(1), Cr–C1C 1.837(1).

Preliminary studies indicate that analogous complexes as **3**, **4** are likewise accessible with molybdenum and tungsten. In conclusion, our reported findings strongly suggest that the electron withdrawing effect of the PPh$_3$ group induces a balanced coordination behaviour which enables the benzophospholide **2** to act both as a phosphine-like σ-donor/π-acceptor ligand in σ(*P*)-complexes and a phosphaarene like ligand in π-complexes. A similar switching between different coordination modes was previously known for phosphinines,[1] but scarcely for phospholide type species. Further exploration of this feature as well as the possible exploitation of the chiral nature of **4** are currently under investigation and may possibly add new facets to the coordination chemistry of phospholide ligands.

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