

Ligand Electronics | Very Important Paper |

VIP A Self-Assembling Ligand Switch That Involves Hydroxide Addition to an sp^2 Hybridised Phosphorus Atom – A System Allowing OH^- Mediated Uptake of $[\text{MCl}_2]$ ($\text{M} = \text{Pd}, \text{Pt}$) CentresYves Cabon,^[a] Louis Ricard,^[a] Gilles Frison,^{*[a]} and Duncan Carmichael^{*[a]}

In appreciation of the work of Prof. Koop Lammertsma and Prof. Edgar Niecke, on their 70th and 80th birthdays, respectively.

Abstract: The coordination chemistry of the 1,1'-diphosphacobaltocenium salt $[\text{Co}(\eta^5\text{-2-TBS-3,4-Me}_2\text{-PC}_4\text{H})_2]^+ \text{BF}_4^-$ (*rac-1*) and its derivatives with respect to $[\text{MCl}_2]$ ($\text{M} = \text{Pd}, \text{Pt}$) centres is presented. *Rac-1*, showing two sp^2 hybridised phosphorus atoms and a positive charge, is stable towards strong electrophiles (PhCH_2Br , MeI), but undergoes attack by hydroxide at phosphorus with subsequent rearrangement to form the neutral conjugate base $[\text{Co}\{\eta^5\text{-(2-TBS-3,4-Me}_2\text{-PC}_4\text{H)}\}\{\eta^4\text{-(1-O,1-H-2-TBS-3,4-Me}_2\text{-PC}_4\text{H)}\}]$ (*rac-2*). *Rac-1* undergoes reaction with $[\text{MCl}_2(\text{PhCN})_2]$ ($\text{M}=\text{Pd}, \text{Pt}$) in damp chloroform to form the $\text{P}_{sp^2}\text{-P}_{sp^3}$ chelating *sec*-phosphinite complexes $[\text{MCl}_2\{\text{Co}\{\eta^5\text{-(2-TBS-}$

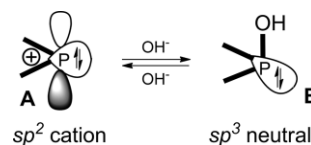
$3,4\text{-Me}_2\text{-PC}_4\text{H)}\}\{\eta^4\text{-(1-OH-2-TBS-3,4-Me}_2\text{-PC}_4\text{H)}\}]$ **4** ($\text{M} = \text{Pd}, \text{Pt}$), which are also accessible directly, but under more forcing conditions, from *rac-2*. Computational analysis (M06/def2-TZVP) indicates that the conjugate base, in the form of its *sec*-phosphinite tautomer *rac-3*, shows significantly stronger bonding to the metal centre than does the parent 1,1'-diphosphacobaltocenium salt *rac-1*. The uptake and subsequent release of a $[\text{PtCl}_2]$ centre as a function of the *pH* of the reaction medium hints at the potential for employing the *rac-1/rac-2* ligand acid-base couple as a *pH*-driven coordination switch.

Introduction

Molecules that respond to external stimuli^[1] can allow fine control over both coordination chemistry^[2] and catalysis,^[3,4] thus providing the potential to create sophisticated structures such as molecular muscles,^[5] switched rotors,^[6] pumps,^[7] compressors^[8] etc.^[8,9] Redox,^[10] photochemical^[11] and *pH*^[12] toggles are regularly employed; of these, *pH*-based switches can potentially be very attractive if the hydroxide ion is incorporated directly into the system, thus conferring significant electronic changes upon the conjugate product as it triggers the switch.

Phosphanes have traditionally been designed as “spectator” ligands but, largely subsequent to elegant supramolecular work in the Breit and Reek/van Leeuwen groups,^[13] a well-developed nonclassical chemistry has also emerged.^[14] *pH*-responsive phosphanes nonetheless remain quite a rare class,^[15] and one in which switching effects are not always strong.^[16] A quite seductive approach to *pH* switching at phosphorus might involve an OH^- driven hybridisation state change^[17] from a cationic $sp^2\text{-(}\sigma^2\lambda^3\text{)}$ to neutral $sp^3\text{-(}\sigma^3\lambda^3\text{)}$ state (respectively **A** and **B**, Scheme 1); higher electron density is available at the hydroxide-bound phosphorus in form **B**, and this electron density is also localised better in space because it occupies an orbital of higher *p*-character. Both of these effects imply improved bind-

ing. The obvious difficulty in making such a method operational lies in the highly favoured nature of most OH^- additions to simple cationic or sp^2 hybridised^[18] phosphorus centres, so that the creation of a reversible manifold presupposes a *sec*-phosphane oxide showing a highly stabilised conjugate acid **A**.^[19]



Scheme 1. An outline hydroxide-driven switch of phosphorus from the cationic $sp^2\text{-(}\sigma^2\lambda^3\text{)}$ **A** to neutral $sp^3\text{-(}\sigma^3\lambda^3\text{)}$ **B** state.

In having a charge that is largely localised at cobalt, the recently reported 1,1'-diphosphacobaltocenium salt class **1**^[20] meets this criterion quite nicely, and provides two ‘desirables’ for generating a pronounced “OFF” state in the switch. The first is a poor aptitude towards coordination in the sp^2 state, whose cationic nature will diminish its ability to donate electrons significantly.^[21] The second is the parallel orientation of the *s*-electron rich lone pairs in the cation, which is a relatively poor configuration for coordination to a single metal centre.^[22] The potential of this kind of structural element is supplemented by its sandwich-type form. This potentially provides modularity, so that the overall architecture can be varied to allow matching of morphology to function if the system is to be exploited for delivery, or in catalysis.^[23] Given that the putative OH^- -included conjugate base *rac-3* was expected to coordinate adequately,

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a first examination of the ligating behaviour of a model 1,1'-diphosphacobaltocenium-based system was undertaken. It is presented briefly here.

Results and Discussion

Experimental Studies

Initial studies concerned the reactivity of the 1,1'-diphosphacobaltocenium salt *rac-1*^[20] (as its fluoroborate salt) towards organic electrophiles. These confirmed that its phosphorus lone pairs show very low reactivity, with no reaction occurring towards ten equivalents of iodomethane or benzyl bromide in refluxing CDCl₃ over several hours. The nucleophilicity of 1,1'-diphosphacobaltocenium salts is therefore low relative to classical phosphanes, but also with respect to 1,1'-diphosphaferrocenes.^[19f] Predictably, the 1,1'-diphosphacobaltocenium salt is more sensitive towards nucleophiles; treatment of **1** with NEt₃/H₂O or sodium bicarbonate solution immediately and quantitatively gives the air-stable Co^I/σ⁴λ⁵-P conjugate **2**, which can be purified conveniently by chromatography on silica in acetone (Scheme 2). The crystal structure of *rac-2* (Figure 1) confirms that any initial adduct (*rac-3*) of the hydroxide with the diphosphacobaltocenium salt is unstable under the reaction conditions and, as might be expected,^[24] evolves through a formal internal Co^{III}/σ²λ³-P → Co^I/σ⁴λ⁵-P redox reaction to give what is an essentially classical secondary phosphane oxide. As expected,^[25] the mean P–C bond lengths found by X-ray crystallographic analysis [1.795(4) to CSi and 1.772(4) Å to CH] in the unit cell remain short, the mean Co–P_(v) distance of 2.6804(7) Å is close to literature values in related complexes (2.698–2.744 Å)^[25] and is clearly non-bonding, whilst the Co–P_(sp2) distance of 2.2867(8) Å is classical for η⁵-phospholyl ligands at monomeric cobalt(I).^[26] The P(1)–Ct–Ct–P(2) twist of 57.1° provides a near-eclipsed structure wherein the phosphorus atoms are oriented into broadly the same region of space. The corresponding *meso-2* was also prepared and investigated crystallo-

graphically (Figure 2). Most of its data [Co–P_(sp2): 2.298(2); Co–P_(v): 2.675(2)] resemble those of *rac-2* except for a significantly increased P(1)–Ct–Ct–P(2) angle of 215.7° that minimises interactions between the silyl substituents. Because of the likelihood of strong interactions between the silyl groups in a chelating configuration, this *meso*-configuration was not investigated further and our work was conducted upon *rac-2*.

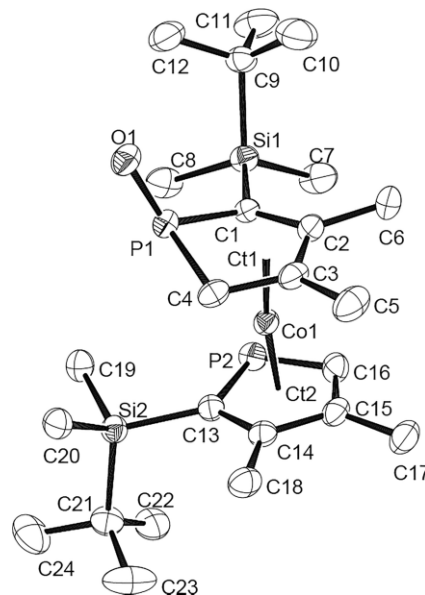
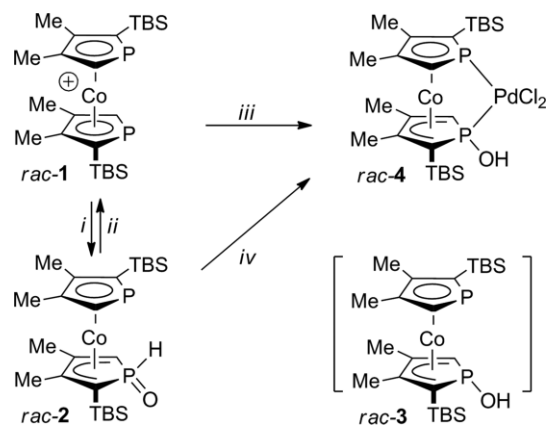


Figure 1. Crystal structure showing one of the two discrete molecules in the unit cell of *rac-2* (50 % probability ellipsoids). Selected distances (Å): P1–C1 1.796(4), C1–C2 1.453(6), C2–C3 1.434(7), C3–C4 1.432(6), C4–P1 1.767(4), P1–O1 1.483(3), P1–H1p 1.29(5), P2–C13 1.785(4), C13–C14 1.442(6), C14–C15 1.437(6), C15–C16 1.390(6), C16–P2 1.762(5), Co–P1 2.681(1), Co–C1 2.096(4), Co–C2 1.990(4), Co–C3 1.987(4), Co–C4 2.035(4), Co–P2 2.287(1), Co–C13 2.112(4), Co–C14 2.048(4), Co–C15 2.106(4), Co–C16 2.091(4). The discussion in the text uses mean values obtained from both of the discrete molecules in the unit cell.



Scheme 2. Interconversions of phosphacobaltocenium salt *rac-1* and cobalt(I) phospholyl complex *rac-2*, and their coordination chemistry with respect to [MCl₂L₂] (L₂ = 1,5-cod, 2PhCN). Reagents and conditions: *i*) Na₂CO₃, H₂O, THF, 20 °C, 5 min, *ii*) HBF₄·Et₂O (1.1 equiv.), Et₂O, 20 °C, 45 min, *iii*) [PdCl₂(1,5-cod)], water-saturated CH₂Cl₂, 20 °C, 1 min, *iv*) [PdCl₂(PhCN)₂] (1 equiv.), CHCl₃, 50 °C, 30 min.

An initial objective of our studies was to establish a degree of pH-dependent reversible reactivity within the proligand couple *rac-1* and *rac-2*. The addition of strong acids (CF₃CO₂H or HBF₄) to solutions of *rac-2* in CH₂Cl₂ was monitored by ³¹P NMR experiments. At room temperature, addition of these acids rapidly provoked the regeneration of the charge-dissociated 1,1'-diphosphacobaltocenium cation *rac-1* (Scheme 2). According to in situ ³¹P NMR studies, this occurred with no evidence for desilylation and complete conservation of diastereomeric integrity. Reversible OH[−] addition to *rac-1* is therefore readily achievable.

Coordination studies of both *rac-1* and *rac-2* towards a simple [PdCl₂] centre were undertaken. Treatment of *rac-1* with [PdCl₂(1,5-cod)] in freshly distilled, phosphorus pentoxide-dried CH₂Cl₂ gave no discernible reaction over 24 hours at ambient temperature; however, in water-saturated CH₂Cl₂, the robust, air-stable phosphinite complex *rac-4* was obtained instantly. No other species were detectable in solution by ³¹P NMR spectroscopy, and some indication of the nature of the hydroxide ion binding was provided by clear and distinct ³¹P resonances (δ = 8.3, −177.8 ppm, ²J_{PP} = 196 Hz) that confirm non-fluxionality on the NMR timescale.^[27]

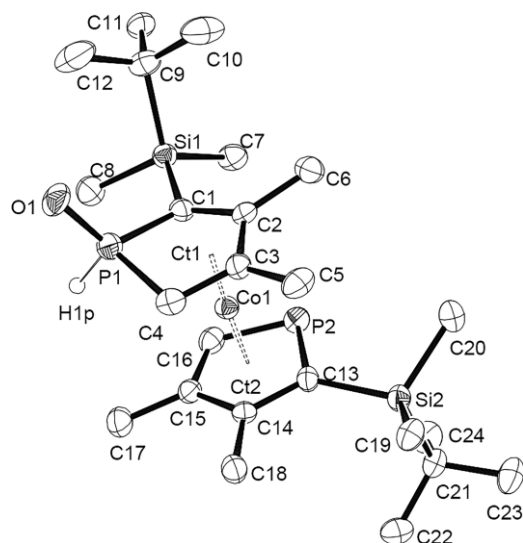


Figure 2. Crystal structure of *meso-2* (50 % probability ellipsoids). Selected distances (Å): Co(1)–C(3) 1.991(5), Co(1)–C(2) 2.001(5), Co(1)–C(4) 2.040(5), Co(1)–C(14) 2.071(5), Co(1)–C(16) 2.075(6), Co(1)–C(1) 2.081(5), Co(1)–C(15) 2.083(5), Co(1)–C(13) 2.152(5), Co(1)–P(2) 2.298(2), Co(1)–P(1) 2.675(2), P(1)–O(1) 1.487(4), P(1)–C(4) 1.765(6), P(1)–C(1) 1.793(5), P(1)–H(1P) 1.42(6), P(2)–C(16) 1.768(6), P(2)–C(13) 1.799(6), Si(1)–C(8) 1.867(6), Si(1)–C(7) 1.869(6), Si(1)–C(1) 1.883(6), Si(1)–C(9) 1.914(6), Si(2)–C(19) 1.863(6), Si(2)–C(13) 1.882(5), Si(2)–C(20) 1.891(6), Si(2)–C(21) 1.910(6).

Given that *sec*-phosphane oxides usually serve as excellent ligand precursors,^[28] a parallel investigation into the reactivity of the secondary phosphane oxide *rac-2* towards palladium complexes was also made. Reaction of *rac-2* with [PdCl₂(PhCN)₂] in chloroform quantitatively provided complex *rac-4* (Figure 3), but it proved entirely unreactive towards [PdCl₂(1,5-cod)] under the same conditions. *Rac-2* therefore has the potential to provide complex *rac-4* directly, but under conditions that are harsher than when *rac-1* is used as the proligand. This suggests that the formation of **4** from *rac-1* can be better attributed to self-assembly of the ligand within the palladium coordination sphere^[29] than through the transient intervention of phosphinite *rac-3*.

An X-ray diffraction study of *rac-4* confirms a classical square planar environment at palladium and near-perfectly eclipsed rings in the ligand. The presence of the hydroxyl functionality, whose hydrogen atom was localised directly from the electron density map, was fully confirmed but a degree of structural disorder compromises interpretation of the space in the direct vicinity of the P-bound oxygen. The Pd–P_{sp²} distance of 2.3298(8) Å is unequivocally long when compared with phosphalkenes^[30] [2.1744(4)^[30e] to 2.2194(1) Å^[31]] or 1,4-diphosphabutadienes^[32,31,33,34,35] [2.236(1)^[35] to 2.2667(2) Å^[32]] that lie *trans* to chloride in Pd^{II} complexes, and also far longer than the value of 2.2304(6) Å for the *sp*² phosphaferrrocene donor found *trans* to chloride in [Pd{Fe(PC₄Pr₄)₂]₂·2[PdCl₂].^[36] The *trans*-influence of the P_{sp²} donor, as reflected in the Pd–Cl1 distance of 2.3405(8) Å, is characteristically weak [compare 2.3193(2)^[30a] to 2.3545(4) Å^[30e] for Pd–Cl *trans* to phosphalkenes]. The P_{sp³} donor shows a classical Pd–P distance of 2.2570(7) Å, and a far greater *trans*-influence [Pd–Cl2 2.3833(7) Å] than the P_{sp²}.

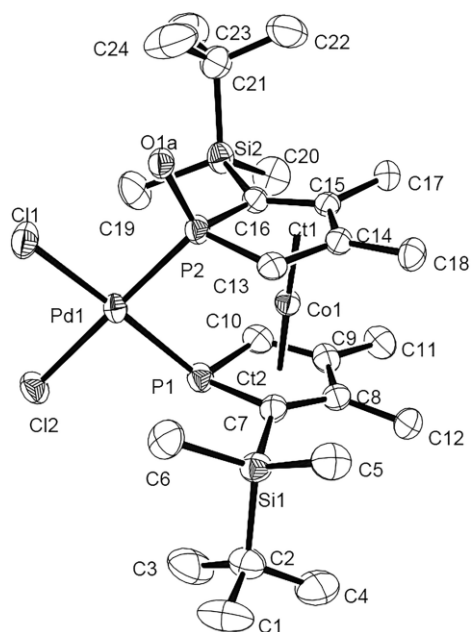
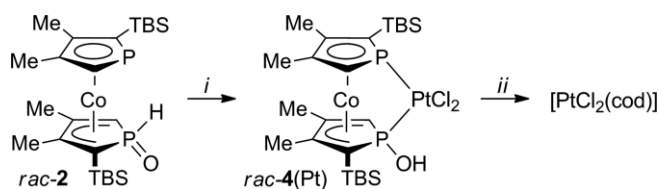


Figure 3. X-ray crystal structure of *rac-4* (50 % probability ellipsoids, CHCl₃ and C₇H₈ of solvation omitted for clarity). The H atom of the phosphorus OH function was found and refined. Selected bond lengths (Å) and angles (°): P1–C7 1.814(3), C7–C8 1.435(4), C8–C9 1.437(4), C9–C10 1.416(4), C10–P1 1.773(3), P2–C13 1.770(3), C13–C14 1.424(4), C14–C15 1.435(4), C15–C16 1.438(8), C16–P2 1.793(1), P1–Co 2.3172(8), C7–Co 2.066(3), C8–Co 2.093(3), C9–Co 2.096(3), C10–Co 2.032(3), P2–Co 2.4261(8), C13–Co 2.043(3), C14–Co 2.031(3), C15–Co 2.035(3), C16–Co 2.079(3), P2–O1a 1.621(2), P1–Pd 2.3298(8), P2–Pd 2.2570(7), Pd–Cl1 2.3405(8), Pd–Cl2 2.3833(7), P1–C7–C8 110.1(2). Some disorder appears between P1 and P2, so that 10 % of O1 appears in the vicinity of P(2). The corresponding P(1)–O(1b) distance is 0.74(1) Å.

The presence of the relatively labile chloride ligands within the coordination spheres of a complex such as **4** means that demonstrating a clear-cut pH-dependent ligation switch is likely to be difficult; their presence allows the possibility that an initially metal-bound halide could move to a phosphorus atom if protonation were able to release the OH[−] functionality from the *sp*³ phosphorus. Such a halide shift would then allow a relatively coordinating *sp*³ (chlorophosphane) donor to be retained, and this would hamper the generation of any long-lived phosphacobaltocenium ligand that could reasonably be expected to dissociate. Consistently, our initial results in this area have been ambiguous. However, after some experimentation (and with difficulty, Scheme 3) a system was found where it was possible to release a platinum centre by gross CF₃CO₂H (50 equiv.) acidification of **4**_{Pt} in methanol in the presence of excess 1,5-cod. Under these conditions, the highly insoluble [PtCl₂(1,5-cod)] product

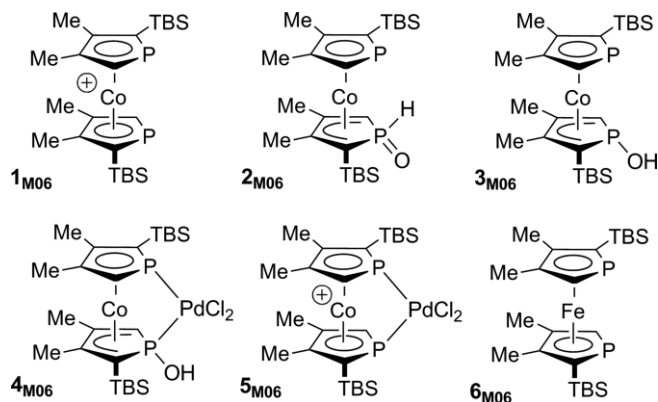


Scheme 3. Capture and release of a platinum(II) centre by *rac-2*. Reagents and conditions: *i*) [PtCl₂(PhCN)₂] damp CHCl₃, 50 °C, 30 min, *ii*) CF₃CO₂H (50 equiv.) MeOH, 20 °C.

precipitates from solution and can be recovered by filtration in 96 % yield on a 6 mmol scale. No precipitation was observed in control systems that were not treated with acid. Studies are ongoing to determine the fate of the coligand.

Computational Studies

The complexity of our experimental systems led us to undertake computational studies to delineate the properties of the 1,1'-diphosphacobaltocenium salt *rac-1* and to investigate how it differs from the ligand *rac-3* that is found in complex *rac-4*. Calculations made upon **1–4** include their full substituent groups, and were made at the M06/def2-TZVP level with solvation described where required by the IEFPCM method. The computed structures are labelled **1_{M06}–6_{M06}** for convenience (Scheme 4), and full data are presented as Supporting Information. Some interring torsion angles are reproduced imperfectly,^[37] but the computed structures represent the observed geometries of *rac-1*, *rac-2* and *rac-4* quite acceptably.



Scheme 4. DFT computed structures. All calculations were carried out at the M06/def2-TZVP level.

Given the nature of the hydroxide addition reaction, a first study examined the charge differences upon passing from the well-known phosphaferrrocene class, exemplified by **6_{M06}**^[36b] to the isoelectronic 1,1'-diphosphacobaltocenium cation **1_{M06}**.^[38] The increased positive charge in the 1,1'-diphosphacobaltocenium salt affects the atoms of its periphery anisotropically and is felt significantly more at phosphorus (which shows +0.77; compare +0.68 in the iron analogue **6_{M06}**) than at the peripheral ring carbon atoms (mean of positions α - to phosphorus: -0.69 ; β -: -0.01 respectively in **1_{M06}** -0.71 ; β -: -0.02 for **6_{M06}**; see Figure 4). The site of charge-controlled attack by "hard" incoming nucleophiles is therefore anticipated to be at phosphorus, as is generally case for phosphametalloenes,^[19f] with this preference probably being accentuated in the 1,1'-diphosphacobaltocenium cation class.

Calculations performed upon the tautomeric pair *rac-2* and *rac-3* also gave acceptable geometries. The computed gas phase energies place *rac-3_{M06}* higher than *rac-2_{M06}* by 33 kJmol⁻¹, which is consistent with our inability to observe *rac-3* experimentally. The association of the hydroxide anion with **1** to generate *rac-3_{M06}* has a significant effect upon the orbital energies. The HOMO-1 (-6.32 eV) clearly defines the *Psp*³ lone

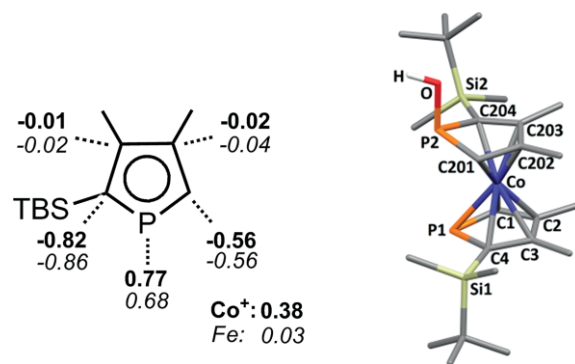


Figure 4. Left: Comparison of charges on the metals and phospholyl ligands in models for the 1,1'-phosphaferrrocene **6_{M06}** (italic) and 1,1'-phosphacobaltocenium cation **1_{M06}** (bold). Right: The computed structure for the unobserved free phosphinite ligand *rac-3_{M06}*. Selected computed lengths for *rac-3_{M06}*: Co-P1, 2.287; Co-P2, 2.674; P-O, 1.680; O-H, 0.961Å.

pair; the *Psp*² nonbonding electron density is much less clearly identifiable, and it contributes significantly to a number of MO's, notably HOMO-2 (-6.72), HOMO-12 (having the largest *Psp*² quotient and lying at -8.40 eV) and HOMO-13 (-8.53 eV). The degree of splitting out of the *Psp*³ and *Psp*² orbitals can be obtained from the localised orbitals provided by an NBO analysis, and this gives a *Psp*³ to *Psp*² energy gap of 2.57eV in *rac-3_{M06}*. It should be noted that two higher-lying Co-P bonding orbitals (HOMO: -5.89 and HOMO-6, -7.45 eV) also show significant electron density in the regions close to the *Psp*² lone pair. In addition to its electronic influence, the presence of the hydroxy- functionality has the secondary effect of orienting the

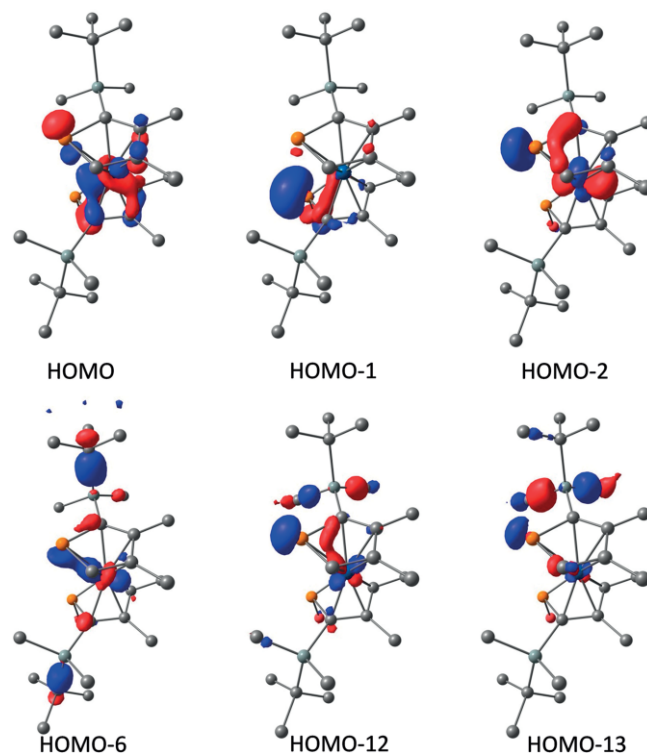


Figure 5. M06/def2-TZVP the top left in the images HOMO-1: -6.32 ; HOMO-2: -6.72 ; HOMO-6: -7.45 ; HOMO-12 -8.40 ; HOMO-13 -8.53 eV.

sp^3 -hybridised phosphorus lone pair electron density more strongly into the region of space between the phospholyl-derived rings than does the sp^2 lone pair (compare HOMO-1 with HOMO-12, Figure 5). The overall conclusion is therefore that binding of the sp^2 - sp^3 hybrid donor in *rac*-3 to transition metal complexes should be significantly better than *rac*-1 on electronic grounds alone, but that coordination is also likely to be assisted by a spatial arrangement that is better adapted to chelation.

The hypothetical complexation of *rac*-1 to $PdCl_2$ was simulated in 5_{M06} . Comparison of 1_{M06} with the experimentally unobserved 5_{M06} shows that the coordination to palladium brings about a marginal shortening of the Co-P bonds of the 1,1'-phosphacobaltocenium salt (by 0.02Å) but leaves the ligand substantially unchanged.^[39] The computed NBO charge increase at each phosphorus upon binding to the palladium centre is +0.10 (from +0.77 in 1_{M06} to +0.87 in 5_{M06}) which is comparable with the increase calculated for phosphaferrrocene ligands upon binding to $(GaCl_2^+; +0.099)$,^[40] and is similar to the effect of passing from the phosphaferrrocene in 6_{M06} to the phosphacobaltocenium salt 1_{M06} (*vide supra*). The coordination process was further modelled through freezing the geometries of the 1,1'-diphosphacobaltocenium salt and the $PdCl_2$ fragment found in the complex and determining their individual single-point fragment energies. Comparison of these values with those of the relaxed 1,1'-diphosphacobaltocenium salt 1_{M06} and $[PdCl_2]$ allowed data pertaining to the nature of the gas phase coordination process to be deduced. The overall coordination energy of 5_{M06} from the relaxed precursors 1_{M06} and $[PdCl_2]$ is computed to be -176 kJ mol^{-1} , which is composed of a favourable term of -203 kJ mol^{-1} arising from metal ligand interactions between the two fragments in the geometries found in the product, and deformation energies $+12 \text{ kJ mol}^{-1}$ for the $PdCl_2$ fragment and 14 kJ mol^{-1} for the 1,1'-diphosphacobaltocenium salt. For comparison, the computed metal-ligand interaction is 168 kJ mol^{-1} in a water force field (Figure 6). These values are quite small and are consistent with the non-observation of the complex under the experimental conditions.^[41]

The experimentally observed coordination complex, *rac*-4, was modelled analogously. The calculation suggests that the site disorder of the OH- group gives a slightly overestimated

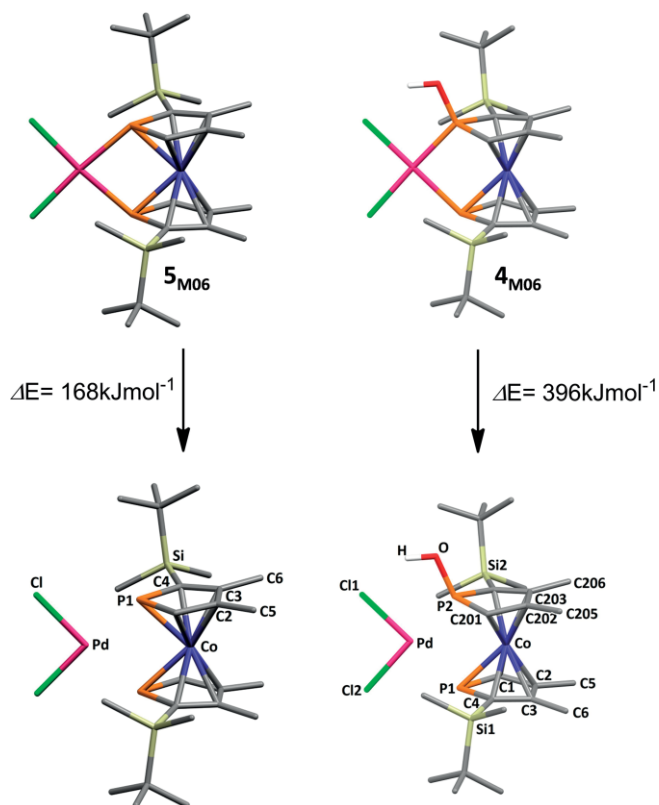
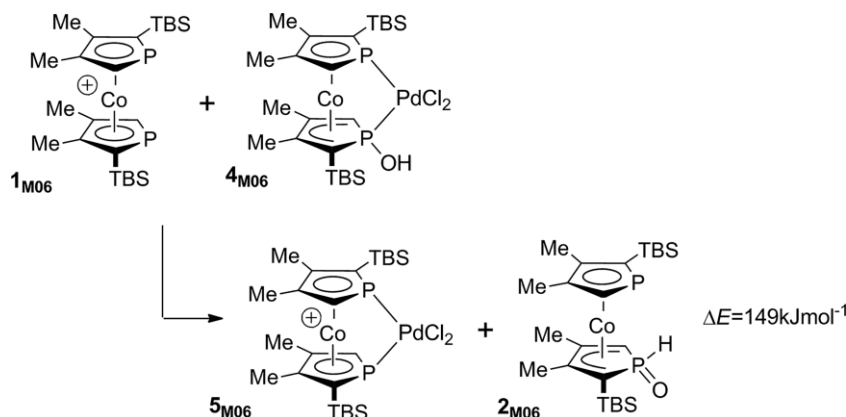


Figure 6. A comparison of the computed complexes 5_{M06} (not observed experimentally, left) and 4_{M06} (right) computed at M06/def2-TZVP along with their metal-ligand interaction energies as described in the text (with dissociated fragments at infinite separation). Selected computed structural data for coordination complexes 4_{M06} Co-P1, 2.266; Pd-P1, 2.347; Pd-Cl, 2.292 Å; P1-Pd-P1', 84.0; Cl1-Pd-Cl1', 93.2° and 5_{M06} : Co-P1, 2.311; Co-P2, 2.485; Pd-P1, 2.384; Pd-P2, 2.281; Pd-Cl1, 2.345; Pd-Cl2, 2.361 Å; P1-Pd-P1' 92.6 Cl1-Pd-Cl1' 94.3°.

experimental P-O distance [exp: 1.621(2), calc: 1.5983Å] and lengthened Pd-P_{sp3} separation [exp: 2.3172(8); calc: 2.2808Å], whilst the long computed Pd-P_{sp2} distance [exp 2.3298(8); calcd. 2.3835 Å; see Supporting Information for full data] suggests that M-L interactions in the vicinity of the Psp² atom may be underestimated.^[42] An analogous decomposition of the



Scheme 5. DFT evaluation of the relative gas phase coordination affinities of 1,1'-diphosphacobaltocenium salt-derived ligands towards $PdCl_2$ fragments.

complex by freezing the geometry of its component ligand and PdCl₂ fragments provides an estimated overall metal ligand gas phase bonding energy of -358 kJ mol⁻¹; this is comprised of the metal-ligand interaction energy -451 (-396 kJ mol⁻¹ in water), a ligand reorganisation energy from **3** of 63 kJ mol⁻¹ and a PdCl₂ reorganisation of +30 kJ mol⁻¹.^[43] A further summation of the individual energies for the components in the displacement reaction given in Scheme 5 shows that the gas phase displacement of the coordinated 1,1'-diphosphacobaltocenium complex by its conjugate base from the palladium centre is highly exothermic.^[44]

The computational chemistry results are therefore in accord with the experimental data, in confirming the very large influence of the P-bound hydroxyl functionality and the preferential coordination of pligand *rac-3* over *rac-1*.

Conclusions

The chemistry and coordination behaviour of neutral phosphametalloenes is quite well developed^[45] but cationic late transition metal phosphametalloenes are much less well-known.^[20c,46,47] The study here shows clearly that the heightened electrophilicity of the phosphorus atom in the 1,1'-diphosphacobaltocenium salt *rac-1* provokes substantially different coordination behaviour from that found in the corresponding 1,1'-diphosphaferrocene.^[36b] Computational data indicate that the *sp*² centres of the phosphacobaltocenium salt **5**_{M06} bind poorly to a [PdCl₂] centre, and that overall binding is improved significantly in complex **4**_{M06} which contains the phosphinite tautomer of the corresponding conjugate base. The stabilisation of the *sp*²-hybridised phosphorus centre within the cationic environment of *rac-1*_{M06} has therefore allowed a system to be developed in which overall ligand self-assembly occurs. If—as seems possible—this self-assembly process is driven to a significant degree by the energy gained upon transforming a transient and weak Pd–P*sp*² link into the more classical Pd–P*sp*³ bond that is found in the product, it becomes reasonable to speculate that a combination of soft transition metals and poorly coordinating cations such as *rac-1* might be capable of activating rather more challenging bonds than the OH link of the water molecule that is cleaved here. This area will be examined further.

CCDC 1869683 (for *rac-2*), 1869684 (for *meso-2*), and 1869685 (for *rac-4*) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre.

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Keywords: Phosphametalloene · Self-assembly · Switchable ligands · Palladium · pH control

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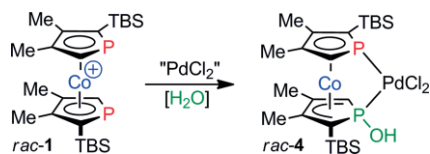
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Ligand Electronics

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**A Self-Assembling Ligand Switch
That Involves Hydroxide Addition to
an sp^2 Hybridised Phosphorus Atom
– A System Allowing OH^- Mediated
Uptake of $[MCl_2]$ ($M = Pd, Pt$) Cen-
tres**



A reversible Lewis acid conjugate base system involving *rac-1* has been established. Coordination of *rac-1* to $[PdCl_2]$ centres in the presence of moisture provokes the assembly of *rac-4*. Experimental and DFT studies pertaining to ligand binding are described.

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