Synthesis and Properties of [CoCp*(2,5-PC$_4$*t*Bu$_2$H$_2$)]: The First Monophosphacobaltocene

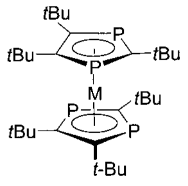
Claire Burney,[b] Duncan Carmichael,*[a] Kareen Forissier,[a] Jennifer C. Green,*[b] François Mathey,*[a] and Louis Ricard[a]

Abstract: The reduction of the phosphacobaltocenium salt [CoCp*(2,5-PC$_4$*t*Bu$_2$H$_2$)]$^+$[BPh$_4$]$^-$ (**3**; Cp* = pentamethylcyclopentadienyl) by magnesium in tetrahydrofuran (THF) furnishes the stable air-sensitive phosphacobaltocene [CoCp*(2,5-PC$_4$*t*Bu$_2$H$_2$)] (**4**) in yields of up to 80%. The crystal structure of **4** shows long Co–C$_\alpha$ and short C$_\alpha$–C$_\beta$ bonds in the phospholyl ligand, consistent with a semi-occupied molecular orbital (SOMO) having a″ symmetry. A combined Amsterdam density functional (ADF)/photoelectron spectroscopic study, which confirms this assignment, gives ionisation energies (IE) of 5.02 eV from the SOMO and 8.89 eV from the phosphorus "lone pair". A comparison of cyclovoltammograms for **3** and the corresponding cyclopentadienyl complex [CoCp*(1,3-C$_5$*t*Bu$_2$H$_3$)]$^+$ [BPh$_4$]$^-$ (**5**) shows that replacing a CH group by an sp^2 phosphorus atom results in an anodic first reduction potential shift of 0.29 V.

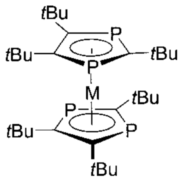
Keywords: cobalt · electronic structure · phosphametallocenes · photoelectron spectroscopy · redox chemistry

Introduction

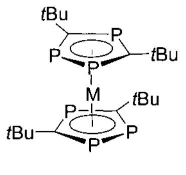
The modification of cyclopentadienyl rings to confer specific physical, electronic, and steric properties upon metal centres is becoming one of the most sophisticated areas in organometallic chemistry.[1] The recognition that phosphorus, which combines moderate electronegativity with relatively strong and weakly polarized λ^3-P=C bonds,[2] is well-adapted to replacing a CR group in cyclopentadienyl ligands has produced an extensive chemistry of simple diamagnetic sandwich complexes that contain η^5-phospholyls, which have recently found uses as catalysts for hydroformylation,[3, 4] ring-opening,[5] cross-coupling[6, 7] and olefin polymerization[8–12] reactions as well as enantioselective isomerisations,[13, 14] allylic alkylations,[15–17] copper-catalysed alkylzinc additions to enones[18] and hydrogenations.[19] Paramagnetic phosphametallocene sandwiches are much less well understood, but they may have potential as unusual ligands and have also been suggested as building blocks for materials chemistry.[20] Almost all of the data pertaining to neutral paramagnetic species have been obtained from complexes that incorporate highly substituted di- and triphospholyl ligands (below).[21–26]



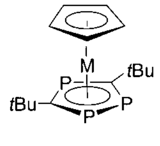
M = Sc



M = V



M = Cr, Mn



M = Co (metastable)

We had a number of reasons for wishing to prepare paramagnetic monophosphametallocenes. Firstly, the rapidly developing organic chemistry of phospholes provides a pool of monophospholyl ligands that may be used to stabilize and/or elaborate any chosen metal centre.[27–29] Simple volatile phosphametallocenes incorporating mono- rather than di- or triphospholyl ligands are also ideal systems for studying the perturbations that result from the presence of the phosphorus atom in the ring. Finally, neutral, paramagnetic transition-metal monophosphametallocene sandwiches are very rare.

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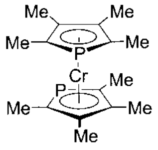
The only well-characterized[30] example published to date is a (crystallographically proven) diphosphachromocene **1**,[20] so that no simple transition-metal monophosphametallocene sandwich complex with more than 18 valence electrons (VE) exists. Given that electron-excessive paramagnetic phosphametallocenes might be expected to have a significant degree of electron spin delocalised over the phospholyl ligand, we wished to prepare and study the first monophosphacobaltocene.



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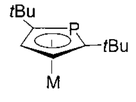

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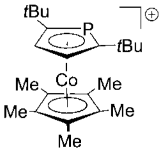

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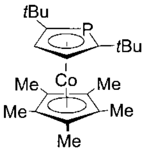

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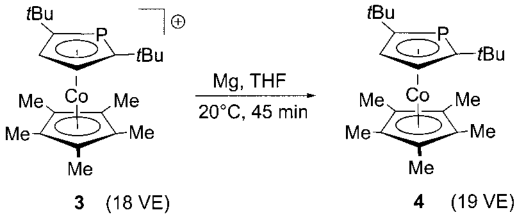
Results

Synthesis: The hindered 2,5-di-*tert*-butylphospholyl ligand **2** was employed in this work. Bulky groups have often been useful for isolating unusual phosphorus-containing species,[31–34] and our previous studies have shown that the *tert*-butyl groups in **2** serve both to diminish the potential for coordination through the phosphorus lone pair[35, 36] and to lower the tendency of the phospholide anion to undergo redox chemistry at transition-metal[37] and main-group[38] centres. In this study, we used the 2,5-di-*tert*-butylphospholyl ligand, because it provides access to the only known phosphacobaltocenium salt **3**.[39] However, the hindrance about phosphorus may also confer some stability upon the phosphacobaltocene product.

The desired monophosphacobaltocene **4** may be prepared conveniently from **3** by reduction [Eq. (1)]. Initial experiments with excess alkali metal resulted in decomposition and,



(1)

to date, the most straightforward synthesis of **4** involves stirring **3** with metallic magnesium in THF. After removal of the solvent under reduced pressure, extraction into pentane, filtration and sublimation (70 °C, 1×10^{-2} mmHg), **4** is obtained as pure, purple crystals in yields approaching 80%. Further experiments conducted by ^{1}H and ^{31}P NMR spectroscopy indicate that **4** is also found in a mixture of compounds obtained from the reaction of [Co(acac)Cp*][40] with Li(2,5-$PC_4t Bu_2H_2$)·2THF[37] in THF, but this approach provides material that is difficult to purify and the isolated yield is low. Whilst solutions of **4** are quite sensitive, the crystalline phosphacobaltocene may be handled without difficulty for short periods (1–2 min) in air.

X-ray diffraction: Crystals of phosphacobaltocene **4** suitable for an X-ray diffraction study were obtained by reduced-pressure (1×10^{-2} mmHg) sublimation at 70 °C and measured at 150 K. A straightforward refinement revealed a classical sandwich structure, whose eclipsed ligands straddle a crystallographic mirror plane that lies perpendicular to the phospholyl ligand and bisects the P and Co atoms (Figure 1). Sites of residual electron density totaling one electron were found lying between the vertical axis and the C_β atoms on the side of the five-membered rings remote from the cobalt atom.

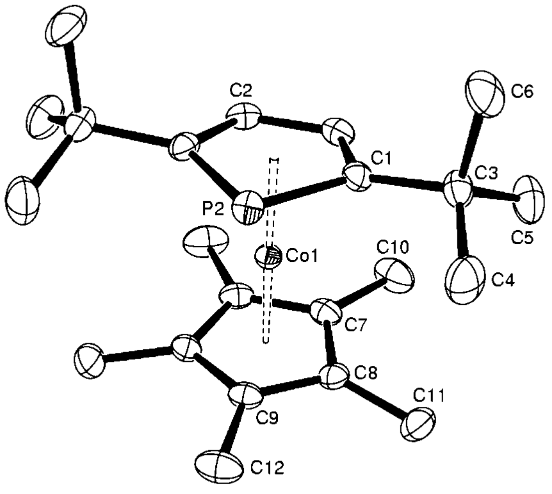


Figure 1. Molecular structure of [CoCp*(2,5-$PC_4tBu_2H_2$)] (**4**). Bond lengths [Å] Co1–P2, 2.3238(6); Co1–C1, 2.220(1); Co1–C2, 2.110(1); Co1–C7, 2.101(1); Co1–C8, 2.159(1); Co1–C9, 2.106(2); P2–C1, 1.782(1); C1–C2′, 1.409(2); C2–C2′, 1.436(3); C7–C7′, 1.446(3); C7–C8, 1.414(2); C8–C9, 1.434(2).

Abstract in French: *La réduction du sel de phosphacobaltocenium [CoCp*(2,5-$PC_4tBu_2H_2$)]$^+$[BPh_4]$^-$ (**3**; Cp* = pentaméthylcyclopentadiényle) par le magnésium dans le tétrahydrofuranne (THF) fournit avec un rendement de 80% le phosphacobaltocène [CoCp*(2,5-$PC_4tBu_2H_2$)] (**4**), stable mais sensible à l'air. La structure de **4** aux rayons-X met en évidence des liaisons Co–C_α et C_α–C_β courtes, en accord avec une orbitale moléculaire semi-occupée (SOMO) de symétrie a″. Les études théoriques (Amsterdam density functional, ADF) et la spectroscopie photoélectronique étayent cette attribution et donnent des énergies d'ionisation (IE) de 5.02 eV pour la SOMO et 8.89 eV pour la "paire libre" du phosphore. La comparaison par voltammétrie cyclique du complexe **3** et de son analogue en série cyclopentadiényle [CoCp*(1,3-$C_5tBu_2H_3$)]$^+$[BPh_4]$^-$ (**5**) montre que le remplacement du groupement CH par un atome du phosphore sp^2 dans le complexe **5** entraine un déplacement anodique du potentiel de 0.29 V.*

Figure 2 shows that significant structural modifications occur upon the reduction of the phosphacobaltocenium salt **3**[39] to phosphacobaltocene **4**. The most striking changes that involve the phospholyl ligand are a disproportionate increase in the mean Co–C$_\alpha$ bond length (+3.4%) when compared to Co–P and Co–C$_\beta$ (+0.8% and +2.5%, respectively), an elongated (+1.3%) C$_\beta$–C$_{\beta'}$ separation and a slightly shortened (−0.3%) mean C$_\alpha$–C$_\beta$ distance, although this last datum is not statistically significant at the 3σ level. The P–C lengths are not significantly affected (−0.2%). These perturbations result in a folding of the phospholyl ligand towards the metal about the C$_\alpha$–C$_\alpha$′ axis by 5.7° in **4**. Analogous changes of similar magnitude are also found within the Cp* portion of the molecule. Distortions of this type reflect the preferred orientation of the unpaired electron with respect to the nondegenerate ligand π-orbitals and are well known in more classical carbocyclic cobaltocene structures in which the fivefold rotational symmetry of the complex is broken by the presence of substituents.[41, 42] For **4**, they very clearly indicate that the metal centre has a more antibonding interaction with the phospholyl π_{as} orbital than with π_s[41] (Figure 3), thus implying a SOMO with a″ symmetry. This accords fully with the results obtained from the ADF calculations presented below.

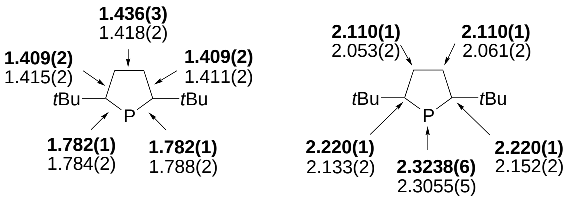


Figure 2. A comparison of bond lengths [Å] for the phospholyl ligand in [CoCp*(2,5-PC$_4$*t*Bu$_2$H$_2$)] (**4**) (bold) and [CoCp*(2,5-PC$_4$*t*Bu$_2$H$_2$)]$^+$[BPh$_4$]$^-$ (**3**). Left: intracyclic separations, right: distances to cobalt.

Figure 3. Phospholyl π-orbitals.

Electrochemistry: Cyclic voltammetry in THF shows that **3** undergoes two (−0.74 V, reversible[39] and −1.85 V, irreversible, SCE) electrochemical reductions and that no oxidation occurs before the onset of solvent breakdown. These are the only quantitative data available to date for Group 9 monophosphametallocenes and may be compared with oxidation data for selected substituted cobaltocene derivatives, which are given in Table 1. In an effort to gain a more precise estimate of the electronic perturbation occurring upon incorporation of a phosphorus atom into cobaltocenes, we prepared and measured 1,3-di-(*tert*-butyl)cyclopentadienyl-(pentamethylcyclopentadienyl)-cobalt tetraphenylborate (**5**), which was found to have a reversible half-wave potential of −1.03 V under conditions identical to those used for the reduction of **3**. In the related (although semi-irreversible) 18 to 19 VE reduction of phosphaferrocenes, the replacement of a cyclopentadienyl CH group by phosphorus is associated with an anodic potential shift of about 0.39 V;[43–46] it is clear that the incorporation of the sp^2 phosphorus atom confers greater stabilization upon a ferrocenide anion than the corresponding cobaltocene (0.29 V). The anodic potential of **4** relative to [CoCp$_2^*$] is reflected in its increased first ionization potential (see below).

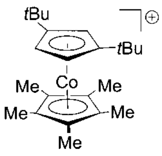


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Table 1. First oxidation potentials for selected cobaltocenes (in V vs SCE).

Complex	$E_{(ox)}$	Solvent	Reference
[Co(NC$_4$*t*Bu$_2$H$_2$)$_2$]	−0.44	MeCN	[a]
[Co(C$_5$HPh$_4$)$_2$]	−0.69	THF	[b]
[CoCp*(2,5-PC$_4$*t*Bu$_2$H$_2$)]	−0.74	THF	this work
[Co(C$_5$H$_4$PPh$_2$)$_2$]	−0.80	MeCN	[c]
[CoCp$_2$]	−0.89	DMF	[d]
[CoCp$_2$]	−0.94	MeCN	[e]
[CoCp*(1,3-C$_5$*t*Bu$_2$H$_3$)]	−1.03	THF	this work
[Co{1,3-C$_5$H$_3$(CMe$_2$CH$_2$CH=CH$_2$)$_2$}$_2$]	−1.10	CH$_2$Cl	[f]
[CoCp*Cp]	−1.17	DMF	[d]
[CoCp$_2^*$]	−1.47	MeCN	[g]

[a] N. Kuhn, M. Köckerling, S. Stubenrauch, D. Bläser, R. Boese, *Chem. Commun.* **1991**, 1368; [b] M. P. Castellani, S. G. Geib, A. L. Rheingold, W. C. Trogler, *Organometallics*, **1987**, 6, 1703; [c] D. L. Dubois, C. W. Eigenbrot, Jr., A. Miedaner, J. C. Smart, *Organometallics*, **1986**, 5, 1410; [d] B. Gloaguen, D. Astruc, *J. Am. Chem. Soc.* **1990**, 112, 4607; [e] J. D. L. Holloway, W. E. Geiger, Jr., *J. Am. Chem. Soc.* **1979**, 101, 2038; [f] D. Vos, A. Salmon, H.-G. Stammler, B. Neumann, P. Jutzi, *Organometallics*, **2000**, 19, 3874; [g] J. L. Robbins, N. Edelstein, B. Spencer, J. C. Smart, *J. Am. Chem. Soc.* **1982**, 104, 1882.

NMR measurements: NMR is relatively easy to observe for classical cobaltocenes,[47] and solution-phase ^{1}H spectra of **4** ([D$_6$]benzene, 298 K) give moderately sharp lines. Integration shows that the phospholyl CH protons lie to high field and the Cp* and *t*Bu protons to low field of their positions in the diamagnetic standard **3**. All resonances move away from TMS as the sample temperature is lowered ([D$_8$]THF), with the largest effects being felt at the Cp* methyl groups (Figure 4).

At room temperature, the Cp* resonance ($\delta = 41.8$ ppm) is found close to the value for [CoCp$_2^*$] ($\delta = 40$ ppm),[48] and the *t*Bu protons ($\delta = 7.3$ ppm) resonate in the region anticipated for *tert*-butyl groups in carbocyclic cobaltocenes.[49, 50] However, the phospholyl C*H* protons ($\delta = -15.9$ ppm) are only

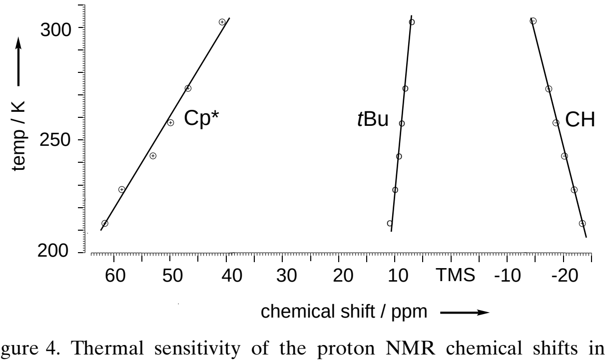


Figure 4. Thermal sensitivity of the proton NMR chemical shifts in **4** ([D$_8$]THF).

slightly shifted when compared to [CoCp$_2$] (−51 ppm).[51] ^{1}H NMR chemical shifts in simple cobaltocenes are generally dominated by a positive scalar coupling between metal e$_g$ orbitals and the cyclopentadienyl carbon atom; this is relayed to the protons through spin polarization induced within the CH bonds,[47, 52] and the modestly shifted phospholyl C*H* resonance in **4** fits with small π_{as} SOMO localization coefficients at the C_β atom. However, the upfield shift would not be expected for polarization induced by the negligible and negative electron-spin density found at C_β (−0.004 e) by ADF; therefore, this mechanism seems unlikely to dominate in **4**.

The SOMO node at phosphorus in **4** is reflected in a broad ^{31}P NMR resonance ($\delta = -122$ ppm, $\nu_{1/2} = 670$ Hz) lying 98 ppm to high field of the diamagnetic precursor **3**. The upfield shift implies a small negative spin density at the phosphorus atom[47] and is in qualitative agreement with the −0.045 e value found in the ADF calculations.

Evans' method determinations[53, 54] give a magnetic susceptibility (χ_m) for **4** of 1.69 μ_B ([D$_6$]benzene, 298 K), which is close to the spin only value for a single unpaired electron. Variable temperature determinations ([D$_8$]THF) indicate that **4** respects the Curie law between 200 and 300 K.

Photoelectron spectroscopy: The He I and He II photoelectron (PE) spectra of [CoCp*(2,5-PC$_4t$Bu$_2$H$_2$)] are shown in Figure 5 and ionization energies are given in Table 2. The low-energy region of the spectrum, bands A–D, shows a striking resemblance to those of [CoCp$_2$] and [CoCp$^*_2$],[55] with IEs lying between those of the two cobaltocene compounds and being closer to those of the permethylated cobaltocene. The first band, A, in the He I spectrum, coincides with the line due to He being ionised by He II radiation, but its clear presence in the He II spectrum identifies it unambiguously. Bands A–D can thus be assigned by analogy with previous work (Table 2).

Band E has no analogue in the PE spectra of [CoCp$_2$] and [CoCp$^*_2$]. It shows a relative decrease in intensity in the He II spectrum. This suggests that it arises from a σ orbital of the phospholyl ring that is largely localised on the P atom.

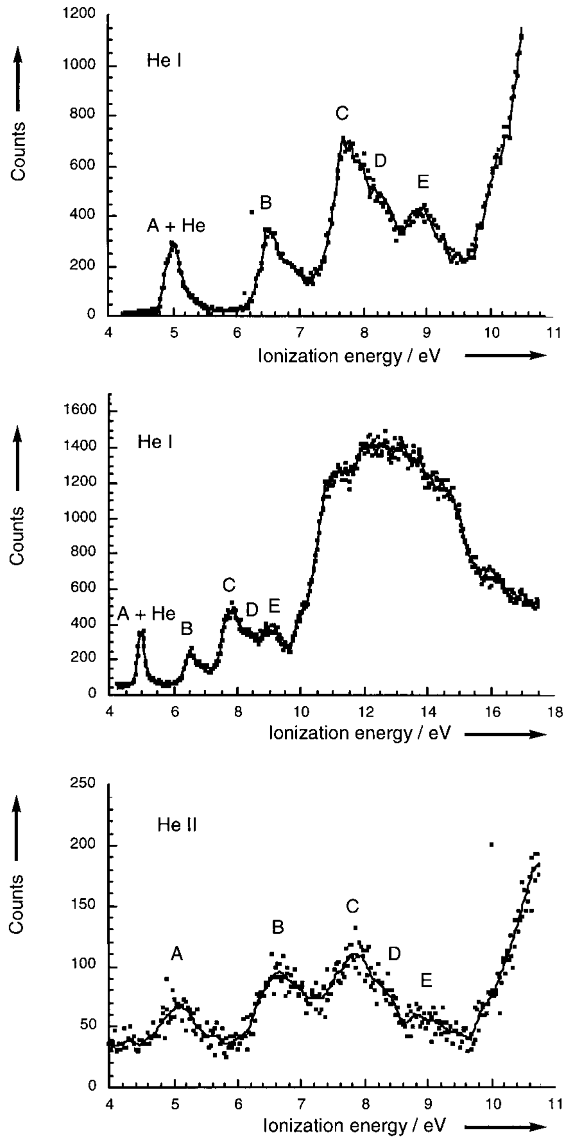


Figure 5. He I and He II PE spectra of [CoCp*(2,5-PC$_4t$Bu$_2$H$_2$)] (**4**).

Density functional calculations: Selected bond lengths from the geometry optimisation of [CoCp*(2,5-PC$_4t$Bu$_2$H$_2$)] with C_s symmetry are shown in Figure 6. Good agreement is found with the X-ray values. Calculated IEs give reasonable agreement with experimental values (Table 2), especially in the lower energy bands. Thus, both structurally and electronically, the calculation can be assumed to give a realistic picture of the electronic structure of [CoCp*(2,5-PC$_4t$Bu$_2$H$_2$)].

The SOMO, 32a″, is an orbital of a″ symmetry with a node at the P atom, consistent with the interpretation of the

Table 2. Calculated and experimental IE for [CoCp*(2,5-PC$_4t$Bu$_2$H$_2$)] (**4**), comparison with IE of [CoCp$_2$] and [CoCp$^*_2$], and assignment of the metallocene spectra.

Orbital	MCp$_2$ analogue	IE calcd α spin	IE calcd β spin	IE exptl. **4**	IE exptl. CoCp$_2$	IE exptl. CoCp$^*_2$	MCp$_2$ assignment
32a″	e$_{1g}$*	5.00		5.02 (A)	5.55	4.71	^{1}A$_{1g}$
31a″	e$_{2g}$	6.84	6.49	6.51 (B)	7.15	6.39	^{3}E$_{1g}$, ^{3}E$_{2g,}$^{3}E$_{1g}$, ^{1}E$_{1g}$,^{1}E$_{2g}$,^{1}E$_{1g}$
41a′	e$_{2g}$	6.80	6.53				
40a′	a$_{1g}$	7.13	6.84				
30a″	e$_{1u}$	7.45	7.33	7.77 (C)	8.72	7.55	^{1}E$_{1u}$, ^{3}E$_{1u}$, ^{3}E$_{1g}$
39a′	e$_{1g}$	7.36	7.39				
38a′	e$_{1u}$	8.17	8.06				
29a″	e$_{1g}$	8.37	7.85	8.24 (D)	9.92	8.30	^{1}E$_{1g}$
37a′	P σ	8.62	8.54	8.89 (E)			

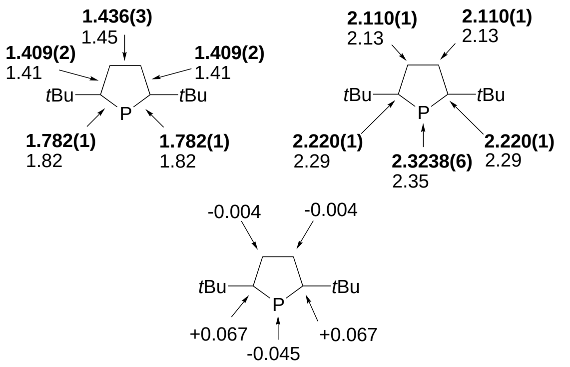


Figure 6. Experimental (bold) and calculated (eclipsed configuration) data for the phospholyl ligand in [CoCp*(2,5-$PC_4tBu_2H_2$)] (**4**). Left: intracyclic separations [Å], right: distances to cobalt [Å]. Bottom: calculated signs and magnitudes of phospholyl ligand spin density [e].

crystallographic and NMR data. Its nodal character, Figure 7, shows it to be similar to an e_{1g}* orbital of cobaltocene. The SOMO–LUMO gap is 0.5 eV.

The isosurfaces of two orbitals with significant P character, 37a′ and 38a′, are shown in Figure 7. The more stable one is principally localised on the PC_4 ring, but shows a bonding interaction with the Co atom. Thus the assignment of band E in the PE spectrum is confirmed. The stability of this phosphorus-based orbital suggests that coordination through phosphorus will not be highly favoured. The less stable 38a′ orbital has pπ character on the phosphorus atom. The spin density at P is calculated as -0.045, thus accounting for the small high field shift found in the ^{31}P NMR spectrum.

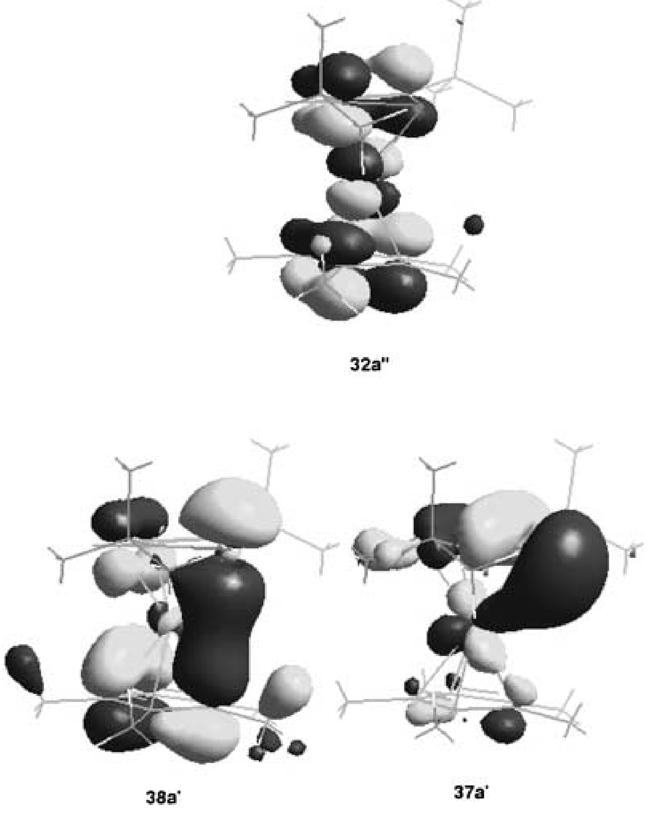
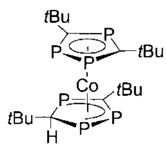


Figure 7. Isosurfaces for the 32a″, 38a′ and 37a′ orbitals of [CoCp*(2,5-$PC_4tBu_2H_2$)] (**4**).

Discussion

From the uncomplicated access to monophosphacobaltocene **4**, it seems clear that the 2,5-di-*tert*-butylphospholyl ligand confers a greater stability upon the 19 VE metallocene configuration than its polyphospholyl analogues. In detailed studies of the reaction of Co^{II} compounds with solutions containing [$LiP_3C_2tBu_2$], Nixon and colleagues have obtained a triphospholyl(triphosphacyclopentadiene)cobalt(I) complex **6**[56] and a dimetallic cubane derivative **7**,[57] but no unequivocal evidence for a phosphacobaltocene. Instead, they suggest that **6** is formed from the transient hexaphosphacobaltocene **8** through radical abstraction from the solvent and support their hypothesis by demonstrating increased yields of triphosphadiene **6** when doping their reaction mixture with an H source such as cyclopentadiene.[56] Zenneck and co-workers note that **9**, prepared through the coordination and oxidative addition of the corresponding triphenylstannyltriphosphole to [$CpCo(C_2H_4)_2$], may be formulated as a triphosphacobaltocene derivative[58] and have also obtained some EPR evidence for the decomposition of **9** into the reactive triphosphacobaltocene **10** upon reaction with florisil in pentane.[26] However, **10** proved too sensitive to allow full characterization.[59] Finally, although the reaction of the phosphaalkyne *tert*-BuC≡P with metal atoms generally provides a rich source of electron-deficient phosphametallocenes,[21, 22, 60, 61] its reaction with cobalt atoms gave complexes **11**, **12** and **13**[62] rather than phosphacobaltocenes. With these data, it seems reasonable to assign a lower stability to polyphosphacobaltocenes than the monophosphacobaltocene derivative **4**.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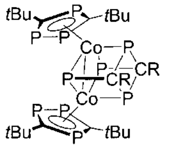
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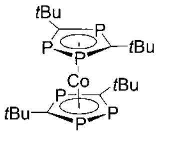
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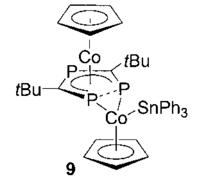
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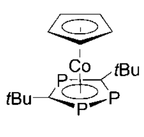
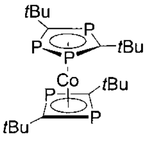
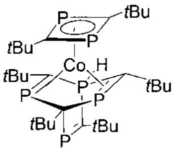

10

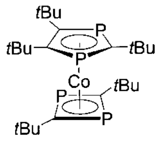
Most studies concerning simple sandwich phosphametallocenes have involved metals of the iron group and a comparison of **4** with phosphaferrocenide anions is interesting. The seminal early Fenske–Hall theoretical treatment of phosphaferrocenes[63] gave a monophosphaferrocene LUMO with a′ symmetry and a total ligand contribution of about 32 %; this may be compared with the a″ SOMO showing 33 % ligand character that is found for the phosphacobaltocene by ADF. Cyclic voltammetry data for phosphaferrocenes[43–46, 64] suggest, broadly, that the reversibility of the phosphaferrocene reduction wave falls as the number of phosphorus atoms rises, and Winter and Geiger have recently provided evidence that the pentaphosphaferrocenide radical anion [Cp^*FeP_5]$^-$



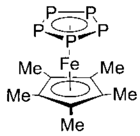
11



12



13



14

(**14**) undergoes rapid dimerisation through two ring phosphorus atoms.[65] Given the comparatively poor π-acceptor properties of the monophospholyl ligand with respect to its polyphospholyl analogues,[60] the stability of these 19 VE monophosphametallocene derivatives with respect to the corresponding polyphosphametallocenes seems likely to reflect a lesser ligand participation in the SOMO. For **4**, the presence of steric protection about the phosphorus atom and the C_α positions, where the highest phospholyl SOMO density is found, may provide additional stabilisation.

The simple access to **4** and the wide variety of readily available phospholide anions[29] implies that phosphacobaltocenes and -cobaltocenium salts bearing substitution patterns that are much more elaborate than 2,5-di-*tert*-butyl may be accessible. It seems certain that the lone pairs in complexes such as **3** and **4** will behave very differently from those in classical phosphines and from each other. Given the rapidly growing coordination chemistry of phosphametallocenes, the possibility that sp^2-phosphorus may have a useful role to play in catalysis[66–69] and the current interest in electroactive ligands,[70, 71] more detailed studies aimed at understanding and controlling the properties of **3** and **4** are in progress.

Experimental Section

All operations were performed either by using cannula techniques on Schlenk lines under an atmosphere of dry nitrogen or in a Braun Labmaster 130 drybox under purified argon. $[CoCp^*(2,5\text{-}PC_4tBu_2H_2)]^+[BPh_4]^-$[39] and $C_5H_4tBu_2$[72] were prepared as described previously, and magnesium powder (50 mesh) was purchased from Sigma–Aldrich. THF and [D$_6$]benzene were distilled from sodium benzophenone ketyl and pentane from sodium benzophenone ketyltetraglyme under an atmosphere of dry nitrogen and stored over activated 4 Å molecular sieves prior to use. Electrochemical measurements are referenced to SCE and were made on a Digital DEA-1 apparatus at platinum electrodes under dry argon in THF with a 0.3 M Bu_4NBF_4 electrolyte. NMR measurements were made on a Bruker AM200 spectrometer and are referenced to internal C_6D_5H or C_4D_7HO and external H_3PO_4. Mass spectra were obtained under 70 eV electron impact by using direct inlet methods on a Hewlett–Packard 5989B spectrometer. He I and He II photoelectron spectra were recorded by using a PES Laboratories 0078 spectrometer interfaced to an Atari microprocessor. They were calibrated with He, Xe and N_2.

Theoretical methods: Calculations were performed using density functional methods of the Amsterdam Density Functional Package (version 2000.02[73, 74]). Type IV basis sets were used with triple ζ accuracy sets of Slater type orbitals, with a single polarisation function added to the main group atoms. The cores of the atoms were frozen up to 2p for Co, 1s for C and 2p for P. The generalised gradient approximation (GGA nonlocal) method was used, by means of Vosko, Wilk and Nusair's local exchange correlation[75] with nonlocal exchange corrections by Becke[76] and nonlocal correlation corrections by Perdew.[77] Ionisation energies were calculated by direct calculations on the molecular ions in their ground and appropriate excited states, and subtraction of the energy of the neutral molecule.

Synthesis of 4: Magnesium powder (1.00 g, 41.1 mmol) suspended in dry, freeze-pump-thaw-cycled THF (30 mL) was activated by stirring with 1,2-dibromoethane (ca. 0.30 g, 1.6 mmol) for 15 mins at room temperature. Powdered **3** (1.00 g, 1.41 mmol) was then added against a nitrogen countercurrent and stirring was continued for 30 mins until the mixture was deep red. The solution was pumped to dryness, extracted with dry, degassed pentane (2 × 30 mL) and filtered through dried Celite. After further evaporation to dryness, air and moisture-sensitive deep purple single crystals of the product were obtained by sublimation (70 °C, 1×10^{-2} mmHg) (0.450 g, 83 %). MS (70 eV): m/z (%): 389 (100) [M^+], 359 (55), 330 (19), 317 (36) [$M^+ - C_5H_{12}$]; ^1H NMR (200 MHz, [D$_6$]benzene): $\delta = 41.9$ (s, $\nu_{1/2} = 145$ Hz; Cp*), 7.3 (s, $\nu_{1/2} = 30$ Hz; *t*Bu), -15.9 ppm (s, $\nu_{1/2} = 180$ Hz; CH); ^{31}P NMR (80 MHz, ([D$_6$]benzene): $\delta = -126$ pm (s, $\nu_{1/2} = 730$ Hz); χ_m[53, 54] $= 1.69\ \mu_B$ ([D$_6$]benzene, 298 K).

Synthesis of 5: A solution of *n*-butyllithium in hexane (1.6 M, 3.4 mL, 5.44 mmol) was added dropwise to a solution of 1,3-di-*tert*-butylcyclopentadiene (1.00 g, 5.65 mmol) in THF (30 mL) at 4 °C. After stirring at room temperature for 2 h, the reaction was cooled to −30 °C, treated with solid $PbCl_2$ (850 mg, 3.06 mmol) and stirred for 30 minutes. The yellow solution was treated with solid $[\{Cp^*CoI_2\}_2]$ (2.00 g, 2.23 mmol), stirred at room temperature for 30 minutes and evaporated to dryness to give a brown-yellow solid. Metathesis with $NaBPh_4$ (1.92 g, 5.61 mmol) in MeOH gave the crude metallocenium salt, which was extracted into $CHCl_3$ and recrystallised by addition of pentane. Pale rectangular air-stable crystals of $[CoCp^*1,3\text{-}(C_5tBu_2H_3)]^+[BPh_4]^-$ were harvested, washed with pentane and dried in vacuo (yield: 2.55 g, 75 %). ^1H NMR (200 MHz, [D]chloroform): $\delta = 7.39$ (br m, 8 H; *o*-C_6H_5), 7.01 (t, $^3J(H,H) = 7.0$ Hz, 8 H; *m*-C_6H_5), 6.87 (t, $^3J(H,H) = 7.2$ Hz, 4 H; *p*-C_6H_5), 4.49 (t, $^4J(H,H) = 1.65$ Hz, 1 H; C=CH), 4.38 (d, $^4J(H,H) = 1.65$ Hz, 2 H; C=CH), 1.75 (s, 15 H; CH_3), 1.19 ppm (s, 18 H; $C(CH_3)_3$); ^{13}C NMR (50 MHz, [D]chloroform): $\delta = 164.8$ (q, $^1J(B,C) = 49.4$ Hz, BC), 136.9 (s, Ph), 126.1 (s, Ph), 122.3 (s, Ph), 119.4 (s, C*t*Bu), 97.3 (s, CMe), 80.2 (s, C−H), 75.2 (s, C−H), 32.5 (s, CMe_3), 31.0 (s, $(CH_3)_3$), 12.1 ppm (s, CH_3); MS (70 eV): m/z (%): 371 (70) [$M^+ + H - HBPh_4$]; elemental analysis calcd (%) for $C_{47}H_{56}BCo$ (690.7): C 81.73, H 8.17; found: C 80.81, H 8.14.

Crystal data for 4: $C_{22}H_{35}CoP$, $M_r = 389.40$, orthorhombic, space group *Pnma*, $a = 11.3090(4)$, $b = 17.7930(4)$, $c = 10.5960(6)$ Å, $V = 2132.14(15)$ Å^3, $Z = 4$, $\rho_{calcd} = 1.213\ g\,cm^{-3}$, $F(000) = 836$. Monochromated $Mo_{K\alpha}$ radiation $\lambda = 0.71070$, $\mu = 0.881\ cm^{-1}$, $T = 150$ K. Of 3203 independent reflections with h: −15 to 12, k: −25 to 16, l: 11 to 14° taken from a purple crystal of about 0.22 × 0.22 × 0.20 mm and collected on a Kappa CCD diffractometer, 2859 with intensity $> 2\sigma(I)$ were refined on F^2 using direct methods in SHELXS. $wR_2 = 0.0991$, $R_1 = 0.0342$, GOF = 1.036.

CCDC 146295 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12 Union Rd, Cambridge CB2 1EZ, UK; Fax: (+44) 1233 336033 or email: deposit@ccdc.cam.ac.uk).

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