Synthesis of a Cobalt−Phospholyl Half-Sandwich Complex and Its Transformation into a Phosphacobaltocene

Yves Cabon, Duncan Carmichael,* Kareen Forissier, François Mathey, Louis Ricard, and Nicolas Seeboth

Laboratoire “Hétéroéléments et Coordination”, Ecole Polytechnique, CNRS,
91128 Palaiseau Cedex, France

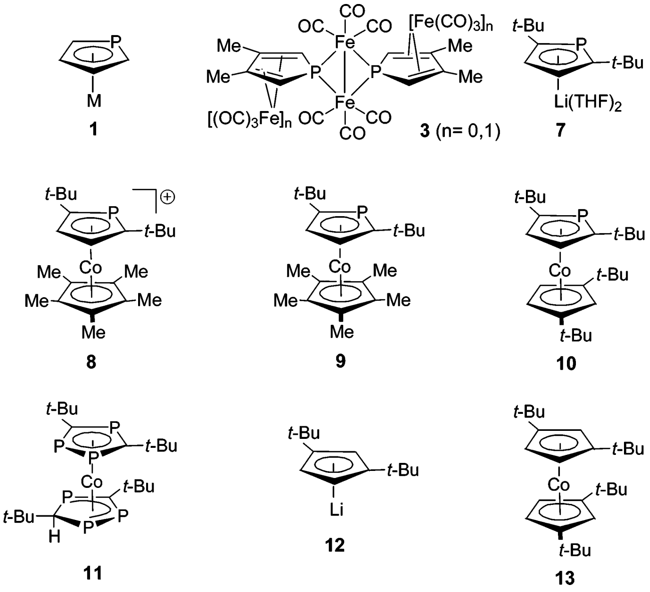
Received December 1, 2006

Low-temperature reaction of [Li(PC_4H_2t-Bu_2)·2thf] (thf = tetrahydrofuran) (**7**) with [Co(acac)$_2$] (Hacac = acetylacetone) gives the reactive half-sandwich complex [Co(η^5-PC_4H_2t-Bu_2)(acac)] (**6**). The crystal structure of **6** shows an unusual ene/2-phosphaallyl distortion, which indicates an a′ symmetric SOMO of the type found in the related alicyclic complex [M(η^5-Cp*)(acac)] (**5**). Reaction of **6** with the bulky lithium cyclopentadienide Li(1,3-C_5t-Bu_2H_3) (**12**) results in the displacement of acetylacetonate and formation of the corresponding air-sensitive purple monophosphacobaltocene [Co(η^5-2,5-PC_4t-Bu_2H_2)(η^5-1,3-C_5t-Bu_2H_3)] (**10**), which shows fluxional behavior in solution.

Introduction

Easily accessible, stable precursors exemplified by [CpFe(CO)$_2$Br] and [Cp*MX$_2$] (M= Co,[1] Ru,[2] Rh,[3] Ir,[3] X = halogen) have provided sound foundations for late transition metal cyclopentadienyl chemistry over many years. However, the preparation of the related phospholyl (**1**) analogues of such compounds might reasonably be expected to be difficult;[4] high oxidation state complexes such as [M(η^5-phospholyl)X$_n$] are unknown for all but the very “hardest” metals,[4−6] and it is not usually possible to prepare half-sandwich phospholyl complexes by classical routes. For example, thermolysis of biphosphole precursors with iron carbonyls gives diphosphaferrocenes[7] and dimers such as **3**[4,8] instead of the desired analogues of [FeCp(CO)$_2$]$_2$.[9] Phospholyl-containing half-sandwich compounds that can serve as reaction partners for simple metathesis reactions with anionic reagents such as LiR are therefore rare[10] and, to the best of our knowledge, the only such compound providing a potentially useful route to more elaborate structures through reactions with anions is **4**, (eq 1) a complex that is accessible only through a relatively long and wasteful pathway involving the preparation and subsequent loss of an acylphospholyl ligand (eq 1).[11] As a consequence, it has never been employed synthetically. This dearth of useful precursors has been detrimental to the development of phospholyl chemistry and, in the light of interest in late transition metal phosphametallocenes as ligands for catalysis,[12−26] it would clearly be beneficial to have

Chart 1



---

* Corresponding author. Fax: intl + 33 1 69333990. Tel: intl + 33 1 69334571. E-mail: Duncan.Carmichael@polytechnique.

(1) Frith, S. A.; Spencer, J. L. *Inorg. Synth.* **1990**, *28*, 273−280.

(2) Koelle, U.; Kossakowski, J. *Inorg. Synth. 29*, 225−226.

(3) White, C.; Yates, A.; Maitlis, P. M. *Inorg. Synth. 29*, 228−230.

(4) Mathey, F. *Coord. Chem. Rev.* **1994**, *137*, 1−52.

(5) Nief, F.; Mathey, F. *Synlett* **1991**, 745−746.

(6) Nief, F.; Mathey, F. *J. Chem. Soc., Chem. Commun.* **1988**, 770−771.

(7) Carmichael, D. Unpublished.

(8) Holand, S.; Mathey, F.; Fischer, J.; Mitschler, A. *Organometallics* **1983**, *2*, 1234−1238. For rather different reactions involving thermolysis of phospholes, see also: Bitta, J.; Fassbender, S.; Reiss, G.; Ganter, C. *Organometallics* **2006**, *25*, 2394−2397, and references therein.

(9) Phospholyl ligands are more electron-withdrawing than their cyclopentadienyl analogues when coordinated to soft metal centers, so that loss of CO ligands is facilitated.[46,47]

(10) Neutral precursors such as [Co(η^5-phospholyl)(CO)$_2$][47] and [Mn(η^5-phospholyl)(CO)$_3$][63] have been shown to undergo useful displacement reactions with neutral ligands. Also for for the middle transition elements see: [M(η^5-phospholyl)(CO)$_2$X] (M = Mo[64] or W,[65] X = TMSn, I).

(11) Roberts, R. M. G.; Wells, A. S. *Inorg. Chim. Acta* **1987**, *126*, 67−70.

(12) Ogasawara, M.; Ito, A.; Yoshida, K.; Hayashi, T. *Organometallics* **2006**, *25*, 2715−2718.

(13) Suarez, A.; Downey, C. W.; Fu, G. C. *J. Am. Chem. Soc.* **2005**, *127*, 11244−11245.

(14) Shintani, R.; Fu, G. C. *Angew. Chem., Int. Ed.* **2003**, *42*, 4082−4085.

(15) Shintani, R.; Fu, G. C. *J. Am. Chem. Soc.* **2003**, *125*, 10778−10779.

(16) Shintani, R.; Fu, G. C. *Org. Lett.* **2002**, *4*, 3699−3702.

(17) Tanaka, K.; Qiao, S.; Tobisu, M.; Lo, M. M. C.; Fu, G. C. *J. Am. Chem. Soc.* **2000**, *122*, 9870−9871.

(18) Tanaka, K.; Fu, G. C. *J. Org. Chem.* **2001**, *66*, 8177−8186.

(19) Ogasawara, M.; Yoshida, K.; Hayashi, T. *Organometallics* **2001**, *20*, 3913−3917.

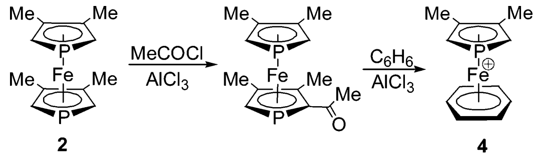
(20) Ganter, C.; Kaulen, C.; Englert, U. *Organometallics* **1999**, *18*, 5444−5446.

(21) Qiao, S.; Fu, G. C. *J. Org. Chem.* **1998**, *63*, 4168−4169. Carmichael, D.; Goldet, G.; Klankermayer, J.; Seeboth, N.; Ricard, L.; Stankevič, M. *Chem. Eur. J.* **2007**, *13*, 5492−5502.

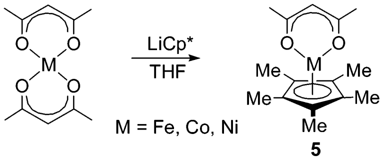
(22) Ganter, C.; Glinsböckel, C.; Ganter, B. *Eur. J. Inorg. Chem.* **1998**, 1163−1168.

10.1021/om0610952 CCC: \$37.00

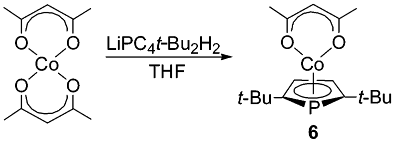
a simple access to phospholyl half-sandwich complexes containing the "softer" metals. One untried and promising method lies in adapting Bunel et al.'s approach to [M(η^5-Cp*)(acac)] (**5**) (eq 2),[27] so as to treat metal acetylacetonate complexes with single equivalents of metal phospholide reagents at low temperature (eq 3). Precedence shows that the easily accessible [Co(η^5-Cp*)(acac)] (**5**) offers a useful combination of high thermal stability and low reactivity toward phosphines,[28] and it was felt that a phospholyl-containing analogue might provide a good entry into the chemistry of phospholyl-substituted cobalt complexes. This work provides a structural proof of the complex [Co(η^5-PC_4H_2t-Bu_2)(acac)] (**6**) along with an *in situ* reactivity study that confirms that **6** opens up a simple and efficient route to phosphacobaltocenes.



eq 1



eq 2



eq 3

Preparation and Characterization of [Co(η^5-PC_4H_2t-Bu_2)(acac)], 6. Dropwise addition of a thf solution of [Li(PC_4H_2t-Bu_2)·2thf] (**7**) to anhydrous [Co(acac)$_2$] in thf at −78 °C gave an air-sensitive red solution which, after removal of solvent and extraction into pentane, furnished a crude, pale orange, air-sensitive solid in ca. 80% yield (eq 3). The complex was initially freed from traces of impurities by sublimation (8×10^{-3} mm, 40 °C) and a further, more prolonged, sublimation then furnished a small quantity of high-quality orange monocrystals. These were investigated by low-temperature X-ray diffraction, which confirmed their formulation as [Co(η^5-PC_4H_2t-Bu_2)(acac)] (**6**). As with the corresponding complex [Co(η^5-Cp*)(acac)] (**5**), no short intermolecular contacts are found in the unit cell (with the nearest intermolecular heavy atom contacts being: for Co(1), 3.744 Å to C2 and 3.938 Å to C17, and for P2 4.049 Å to C17 and 4.264 Å to C6), so that the molecule exists as a discrete monomer, having a rather encumbered structure wherein the acac plane is straddled by two methyl groups of each *tert*-butyl function (Figure 1).

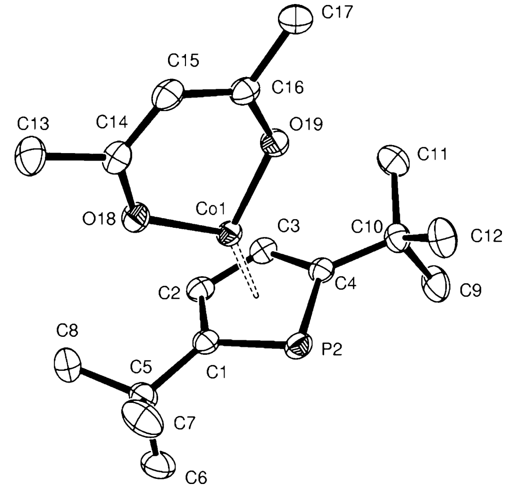


Figure 1. Molecular structure of [Co(η^5-PC_4H_2t-Bu_2)(acac)] (showing 50% probability ellipsoids), **6**. Selected bond lengths (Å): Co(1)−P(2), 2.345(1); Co(1)−O(18), 1.880(2); Co(1)−O(19), 1.879(1); Co(1)−C(1), 2.112(2); Co(1)−C(2), 2.091(2); Co(1)−C(3), 2.091(2); Co(1)−C(4), 2.108(2); P(2)−C(1), 1.783(2); C(1)−C(2), 1.432(2); C(2)−C(3), 1.400(3); C(3)−C(4), 1.424(2); P(2)−C(4), 1.783(2); C(13)−C(14), 1.505(3); C(14)−O(18), 1.281(2); C(14)−C(15), 1.388(3); C(15)−C(16), 1.395(3); C(16)−C(17), 1.500(3); C(16)−O(19), 1.280(2).

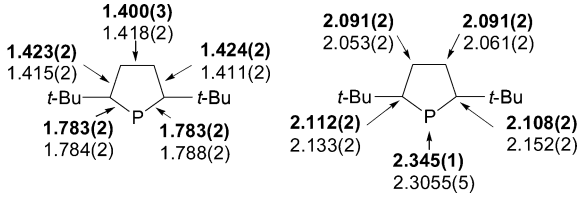


Figure 2. Comparison of bond lengths (Å) for the phospholyl ligand in [Co(η^5-2,5-PC_4t-Bu_2H_2)(acac)], **6** (bold), and [CoCp*-(2,5-PC_4t-Bu_2H_2)$^+$][BPh_4^-], **8**. Left: intracyclic separations. Right: distances to cobalt.

The M−P and P−C bonds in **6** combine such that the structural differences in the vicinity of the five-membered rings of **5** and **6** are small, being expressed principally as a simple increase in radial expansion of the phospholyl ring along the centroid−P vector of **6**. Generalized molecular orbital treatments of the 17 VE [$CpML_2$] system for cases where L is not π-accepting predict that the unpaired electron should prefer an M−Cp antibonding orbital of a′ symmetry,[28,29] and the relative orientation of the *tert*-butyl and acac groups is consistent with this configuration. Comparison of the distances in **6** with those obtained for the same phospholyl ligand in the more rotationally isotropic **8**[30] (Figure 2) also reveals evidence of a shortening of Co−C_α and C_β−C_β and a lengthening of the Co−P, Co−C_β, and C_α−C_β distances upon passing from **8** to **6** so as to generate the rare ene-2-phosphaallyl configuration[31] required by such a formulation. The observed distortions resemble those found upon comparing [Co(η^5-Cp*)(acac)][28] with the decamethylcobaltocenium cation[32] and are also similar in magnitude (though opposite in sign) to those occurring upon 1e reduction of **8**[30] to **9**.[33] Theoretically, the a′ symmetrical SOMO places

---

(23) Melaimi, M.; Mathey, F.; Le Floch, P. *J. Organomet. Chem.* **2001**, *640*, 197−199.

(24) Sava, X.; Ricard, L.; Mathey, F.; Le Floch, P. *Organometallics* **2000**, *19*, 4899−4903.

(25) Wang, L. S.; Hollis, T. K. *Org. Lett.* **2003**, *5*, 2543−2545.

(26) Le Floch, P. *Coord. Chem. Rev.* **2006**, *250*, 627−681.

(27) Bunel, E. E.; Valle, L.; Manriquez, J. M. *Organometallics* **1985**, *4*, 1680−1682.

(28) Smith, M. E.; Andersen, R. A. *J. Am. Chem. Soc.* **1996**, *118*, 11119−11128.

(29) Albright, T. A.; Burdett, J. K.; Whangbo, M. H. *Orbital Interactions in Chemistry*; Wiley: New York, 1985; p 370.

(30) Forissier, K.; Ricard, L.; Carmichael, D.; Mathey, F. *Organometallics* **2000**, *19*, 954−956.

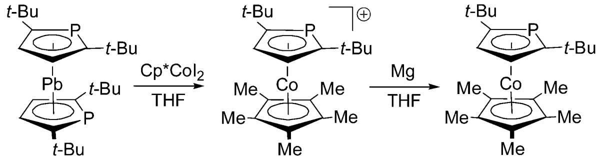
(31) Caliman, V.; Hitchcock, P. B.; Nixon, J. F. *J. Chem. Soc., Chem. Commun.* **1997**, 1739−1740.

(32) Heise, H.; Köhler, F. H.; Herker, M.; Hiller, W. *J. Am. Chem. Soc.* **2002**, *124*, 10823−10832.

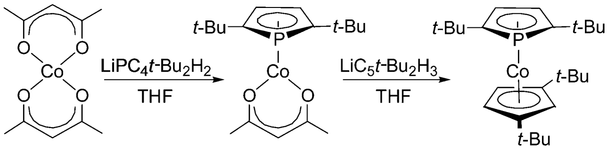
(33) (a) Burney, C.; Carmichael, D.; Forissier, K.; Green, J. C.; Mathey, F.; Ricard, L. *Chem.−Eur. J.* **2003**, *9*, 2567−2573. (b) There is evidence that the synthesis of unhindered phosphametallocenes containing the late transition metals is problematical,[52,66] so unhindered complexes were not envisioned at this stage.

finite unpaired electron spin density on the phosphorus atom and, consistently, no ^{31}P NMR signal was obvious between ±2000 ppm.

Synthesis of Phosphacobaltocenes. To date, the only route to phosphacobaltocenes[33] involves the metathesis of a 1,1′-diphosphaplumbocene[34] with a suitable Cp-derived cobalt(III) precursor, followed by a chemical reduction[33] of the intermediate phosphacobaltocenium salt[30] (eq 4).



8 **9** eq 4



6 **10** eq 5

This approach is both tedious and restrictive, inasmuch as it is only useful in cases where the requisite "[$CoCpX_2$]" derivative is available.[35] The displacement of the acac⁻ anion from **6** by a cyclopentadienide should provide a far more convenient and versatile access, particularly if performed as a one-pot procedure from [$Co(acac)_2$] (eq 5).

Rather than resynthesising the (only) known phosphacobaltocene [$Co(\eta^5\text{-}Cp^*)(\eta^5\text{-}PC_4H_2t\text{-}Bu_2)$] (**9**)[33b] using this methodology, the preparation of a nonsymmetrical complex **10** containing the di(*tert*-butyl)cyclopentadienyl ligand was attempted. Simple treatment of a cold THF solution of [$Co(acac)_2$] with phospholide **7** and subsequent addition of lithium 1,3-di-(*tert*-butyl)-cyclopentadienide (**12**), prior to extraction and crystallization was found to give large air-sensitive purple crystals of the anticipated phosphacobaltocene (eq 5) whose structure was established by physical measurements. The uncorrected[36] magnetic moment of 1.68 μ_B, estimated by Evans' method[37] at 296 K, lies close to the spin-only value for a single electron and resembles the values observed for **9** (1.69 μ_B),[33] **13** (1.62 μ_B), and other cobaltocenes. The plot of χ_m against $1/T$ was essentially linear for temperatures from 193 to 353 K (Figure 3). The 300 MHz ^1H NMR spectrum of **10** at 353 K is consistent with a fluxional structure (in both the presence and absence of 10 molar equiv of PMe_3) and shows three cyclopentadienyl C*H* protons in a region typical of cobaltocenes[38−40] (2 at −48 ppm; 1 at −66 ppm) and two phospholyl C*H* protons (−14 ppm) at relatively high frequency. The weakly paramagnetic phospholyl C*H* shifts and the observation of a broad ^{31}P NMR resonance (−16 ppm at 353 K) suggest a SOMO having a node at phosphorus, which is consistent with related observations made on **9**. Cooling (Figure 4) of the sample to ambient temperature produces five different C*H* proton resonances spread over a range from −7 to −100 pm, in accord with the anticipated[41−43] intermeshing of the phospholyl and Cp rings.

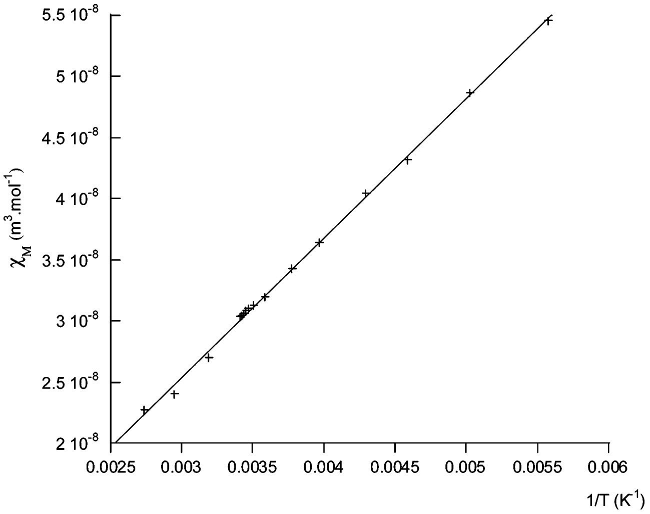


Figure 3. Variation of molar magnetic susceptibility in **10** as a function of reciprocal temperature in deuterotoluene.

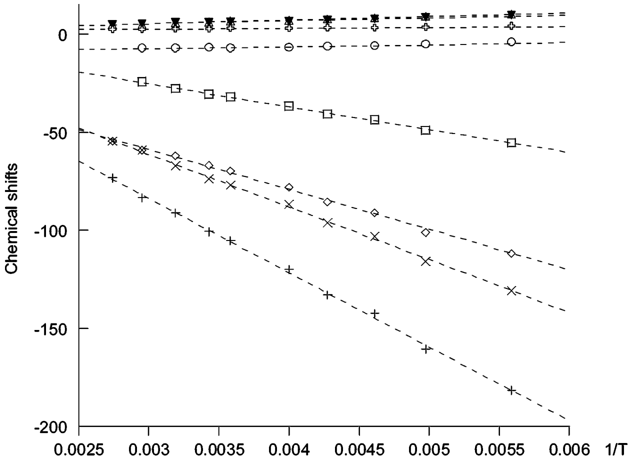


Figure 4. Variation of ^1H NMR chemical shifts (ppm) with reciprocal temperature (K^{-1}) for **10** (THF-d_8).

Table 1. Cyclic Voltammetry Data for Selected Cobaltocene−Cobaltocenium and Phosphacobaltocene−Phosphacobaltocenium Couples[a]

complex	$E_{1/2}$ (SCE)	ref
$CoCp^*_2$	−1.23[b]	this work
[$CoCp^*(1,3\text{-}C_5t\text{-}Bu_2H_3)$]	−1.02[c]	33
[$Co(1,3\text{-}C_5t\text{-}Bu_2H_3)_2$], **13**	−0.81[c]	this work
[$CoCp^*(2,5\text{-}PC_4t\text{-}Bu_2H_2)$], **9**	−0.74[c]	33
[$Co(1,3\text{-}C_5t\text{-}Bu_2H_3)(2,5\text{-}PC_4t\text{-}Bu_2H_2)$], **10**	−0.56[b]	this work

[a] All values obtained in THF at 304 K using a 3 M Bu_4NBF_4 electrolyte. [b] Measured by oxidation. [c] Measured by the reduction of the corresponding cation BF_4^- salt.

Cyclic voltammetry (Table 1) gave an oxidation wave for **10** at −0.56 V (in 3 M $n\text{-}Bu_4NBF_4$ in THF), which was reversible at scan rates of 50 mV s^{-1}. This value, when

---

(34) Forissier, K.; Ricard, L.; Carmichael, D.; Mathey, F. *Chem. Commun.* **1999**, 1273−1274.

(35) The most frequently used and reliable synthesis of this kind of complex involves oxidation and high-temperature pyrolysis steps, which are not necessarily compatible with functionalized cyclopentadienyl ligands.[1] Furthermore, nonhindered 1,1′-diphosphaplumbocenes are prone to reductive elimination of the corresponding 1,1′-biphospholes.[34]

(36) Deutsch, J. L.; Poling, S. M. *J. Chem. Educ.* **1969**, *46*, 167.

(37) Evans, D. F. *J. Chem. Soc.* **1959**, 2003−2005. Live, D. H.; Chan, S. I. *Anal. Chem.* **1970**, *42*, 791−792.

(38) Blümel, J.; Hebendanz, N.; Hudeczek, P.; Köhler, F. H.; Strauss, W. *J. Am. Chem. Soc.* **1992**, *114*, 4223−4230.

(39) Eicher, H.; Köhler, F. H. *Chem. Phys.* **1988**, *128*, 297−309.

(40) Köhler, F. H. *J. Organomet. Chem.* **1976**, *110*, 235−246.

(41) Abel, E. W.; Long, N. J.; Orrell, K. G.; Osborne, A. G.; Šik, V. *J. Organomet. Chem.* **1991**, *403*, 195−208.

(42) Bartsch, R.; Hitchcock, P. B.; Nixon, J. F. *J. Chem. Soc., Chem. Commun.* **1987**, 1146−1148.

(43) Kuhn, N.; Jendral, K.; Stubenrauch, S.; Mynott, R. *Inorg. Chim. Acta* **1993**, *206*, 1−3.

compared with the potential of −0.81 V for the corresponding cyclopentadienyl derivative **13**[44,45] under identical conditions, confirms that the phosphorus atom induces a large stabilization of the unpaired electron, which is similar to that found in **9** (+250 mV for **10** and +290 mV for **9**[33] shifts being observed respectively when formally replacing CH in the corresponding alicyclic cobaltocenes by P).

Discussion

Overall, the work presented here provides a much improved route to the previously rather inaccessible phosphacobaltocene class. Its simplicity suggests that developing the chemistry of bulky phospholyl ligands at cobalt centers is unlikely to pose significant experimental difficulties, and **6** should clearly be valuable for the rational synthesis of phospholyl cobalt compounds that do not contain a cyclopentadienyl ligand.[46,47] The physicochemical results of the study clearly confirm the well-established tenet[48] that the formal introduction of a phosphorus atom into a Cp ligand may be viewed as a simple perturbation, so that the reactivity patterns of **5** and **6** might reasonably be expected to be analogous. [Co(η^5-Cp*)(acac)] (**5**) has been used in wide-ranging studies over fields as disparate as molecular magnets[49] and chiral anion receptors,[50,51] so this chemistry should be well adapted for the preparation of rather sophisticated cobalt-phospholyl-containing complexes.

Compound **6** represents the first example of a simple cobalt-based phospholyl-containing radical species having fewer than 18 valence electrons and, as such, the influence of the *t*-Bu groups upon its stability is difficult to estimate with precision. In general, 19 and 20 VE phospholyl-containing species are isolable only when the phospholyl ligands are bulky. However, 17 VE phospholyl-containing compounds show acceptable stability even when relatively unhindered,[52] and in this light, it seems probable that **6** provides a prototype for a wider range of less hindered analogues.

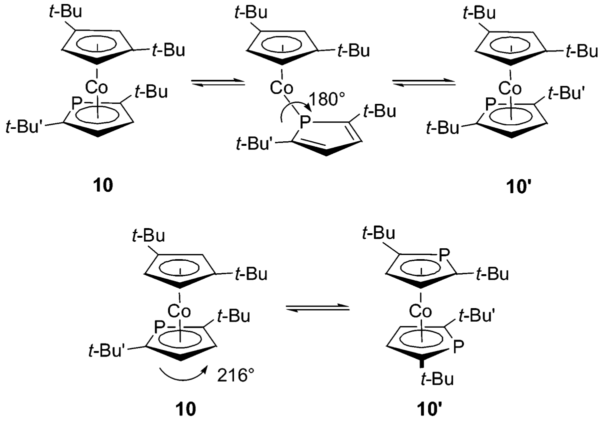


Figure 5. Two possible mechanisms for site exchange in **10**.

The choice of the *tert*-butyl-substituted phosphacobaltocene target **10** was conditioned by earlier studies, principally undertaken by Nixon and co-workers, wherein it was shown that heavily *tert*-butyl-substituted di- and triphospholyl ligands react with Co(II) and Ni(II) centers to produce diamagnetic hexaphospha complexes such as **11**[53] rather than the corresponding phosphanickelocenes and phosphacobaltocenes. The successful preparation of **10** establishes that neither nonsymmetrical substitution patterns nor tetra-*tert*-butyl configurations lead to diamagnetic complexes such as **11** *per se*, which reinforces Green's argument[54] that electronic effects are responsible for the differing behavior of monophospholyl and polyphospholyl ligands at late transition metal centers. Rather than showing instability, **10** is quite robust with respect to heating in solution. The data presently available concerning the equilibration of CH and *t*-Bu sites of **10** upon heating do not definitively exclude a decomplexation−rotation (or inversion)−recomplexation process (Figure 5, upper). However, because of its well-filled d shell,[55] pathways involving decoordination to an η^1-intermediate are likely to be at much higher energy in **10** than in Ti and Zr(IV) analogues, where they have been well established,[56,57] and the invariance of the exchange profile in the presence of PMe_3 suggests strongly that the coordination sphere of **10** is not significantly opened during the exchange process. It therefore seems likely that a simple rotational process operates in **10**.

Taken together, these new data imply that functionalized phosphacobaltocenes may be quite accessible synthetic targets. Given their easy oxidation to phosphacobaltocenium salts,[33] which are good candidates for new ligand platforms,[58] further research into these and related cobalt complexes is in progress.

---

[44] Nesmeyanov, A. N.; Leonova, E. V.; Kochetko, N. S.; Butyugin, S. M.; Meisner, I. S. *Izv. Akad. SSSR-Ser. Khim.* **1971**, 106.

[45] Okuda, J. *J. Organomet. Chem.* **1990**, *385*, C39−C42.

[46] Charrier, C.; Bonnard, H.; Mathey, F.; Neibecker, D. *J. Organomet. Chem.* **1982**, *231*, 361−367.

[47] Caffyn, A. J. M.; Carmichael, D.; Mathey, F.; Ricard, L. *Organometallics* **1997**, *16*, 2049−2054.

[48] Dillon, K. B.; Mathey, F.; Nixon, J. F. *Phosphorus, the Carbon Copy*; Wiley: Chichester, 1998.

[49] Hilbig, H.; Köhler, F. H. *Nouv. J. Chim.* **2001**, *25*, 1152−1162.

[50] Uno, M.; Komatsuzaki, N.; Shirai, K.; Takahashi, S. *J. Organomet. Chem.* **1993**, *462*, 343−345.

[51] Obviously, the compound is also a surrogate of [Co(Cp)X] species (X = halogen, Cp cyclopentadienyl or derivative), which have also found extensive uses including, for example, in the synthesis of cobalt complexes with unusual spin states: Brunker, T. J.; Cowley, A. R.; O'Hare, D. *Organometallics* **2002**, *21*, 3123−3138, and poly(π-complexes): Schneider, J. J.; Wolf, D.; Janiak, C.; Heinemann, O.; Rust, J.; Krüger, C. *Chem.−Eur. J.* **1998**, *4*, 1982−1991.

[52] For crystallographically proven examples see, for example, refs 67 and 68. The instability of unencumbered electron-excessive paramagnetic phospholyl complexes results principally from the possibility of reducing metal electron count through an η^5 to η^1 ring slip of the phospholyl ligand, whereby the ligand anion goes from being a formal 6e donor in a monomeric metallocene to a 4e donor in a $\mu^2-\eta^1_{(P)}$-bridged dimer.[66,69] The dimeric complex can then attain a diamagnetic closed-shell configuration directly (if the precursor is a formal 20 VE phosphametallocene) or through the formation of a metal−metal bond (if 19 VE). In such cases, the effect of the hindrance is to sterically disfavor the phospholyl bridging position and thereby confer a relative stabilization upon the electron-excessive phosphametallocene.[69] It is not clear how such a reduction in the number of electrons made available to a metal center by the phospholyl ligand should stabilize electron-deficient complexes, and this probably provides the explanation of the differing requirements for hindrance in electron-deficient and electron-excessive phospholyl-based complexes. Similar relative stabilities of the sandwich configuration as a function of overall metal electron count are seen in polyphospholyl complexes (even if the structural outcomes are different); compare the interaction of triphospholyl ligand precursors with Mn(II)[70] and Co(II)[71] halides.

[53] Bartsch, R.; Carmichael, D.; Hitchcock, P. B.; Meidine, M. F.; Nixon, J. F.; Sillett, G. J. D. *J. Chem. Soc., Chem. Commun.* **1988**, 1615−1617.

[54] Cloke, F. G. N.; Green, J. C.; Hanks, J. R.; Nixon, J. F.; Suter, J. L. *J. Chem. Soc., Dalton Trans.* **2000**, 3534−3536. Bruce and Rocha have subsequently presented a very similar analysis, see ref 72.

[55] Hollis, T. K.; Ahn, Y. J.; Tham, F. S. *Organometallics* **2003**, *22*, 1432−1436.

[56] Ahn, Y. J.; Rubio, R. J.; Hollis, T. K.; Tham, F. S.; Donnadieu, B. *Organometallics* **2006**, *25*, 1079−1083.

[57] Hollis, T. K.; Ahn, Y. J.; Tham, F. S. *Chem. Commun.* **2002**, 2996−2997.

[58] In addition to the more classical uses illustrated by refs 12−26, this kind of ligand may also show interesting redox-driven properties; see: Gudat, D.; Lewall, B.; Nieger, M.; Detmer, I.; Szarvas, L.; Saarenketo, P.; Marconi, G. *Chem.−Eur. J.* **2003**, *9*, 661−670.

Experimental Section

All operations were performed either using cannula techniques on Schlenk lines under an atmosphere of dry nitrogen or in a Braun Labmaster 130 drybox under dry purified argon. Li(2,5-PC$_4$*t*-Bu$_2$H$_2$)·2thf (**7**) was prepared as described previously,[59] and [Co-(η^5-C$_5$*t*-Bu$_2$H$_3$)$_2$] (**13**) was obtained according to Okuda[45] and purified by crystallization (pentane) followed by sublimation (110 °C, 5×10^{-3} mmHg). Li(1,3-C$_5$*t*-Bu$_2$H$_3$) was prepared by *n*-BuLi-induced deprotonation of 1,3-C$_5$*t*-Bu$_2$H$_4$[60] in hexane. Co(acac)$_2$ was used as purchased. THF and [D$_6$]benzene were distilled from sodium-benzophenone ketyl and pentane was distilled from sodium-benzophenone ketyl-tetraglyme; all were prepared under an atmosphere of dry nitrogen and stored over activated 4 Å molecular sieves prior to use. Chloroform and dichloromethane were distilled from P$_4$O$_{10}$ under nitrogen and also stored for short periods over activated 4 Å molecular sieves. The electrochemical measurements, calibrated against internal ferrocene and expressed relative to SCE, were made on a Digital DEA-1 apparatus at platinum electrodes under dry argon in THF using a 3 M Bu$_4$NBF$_4$ electrolyte. NMR measurements were made on a Bruker AVANCE 300 spectrometer and are referenced to internal capillary-contained TMS or external H$_3$PO$_4$ as appropriate. Variable-temperature measurements were calibrated against methanol (173−295 K) or ethyleneglycol (300−360 K) references.[61] Mass spectra were obtained under 70 eV electron impact using direct inlet methods on a Hewlett-Packard 5989B spectrometer.

***O,O*-Acetylacetonato-{η^5-2,5-di(*tert*-butyl)phospholyl}cobalt-(II), 6.** A solution of [Co(acac)$_2$] (354 mg, 1.33 mM) in THF (20 mL) was treated dropwise at −78 °C over 15 minutes with a THF (20 mL) solution of [Li(thf)$_2$(2,5-PC$_4$*t*-Bu$_2$H$_2$)] (464 mg, 1.33 mM), thereby causing a color change from brown to orange. The reaction was stirred for 30 min and brought slowly to room temperature. The volatiles were removed, and the resulting solid was extracted with pentane and filtered through a bed of dry Celite. Evaporation to dryness gave an orange powder (451 mg, 88%), from which crystals suitable for X-ray diffraction were obtained by sublimation (40 °C, 10^{-3} mmHg), 24 mg, 5%. ^{1}H NMR: 6.6 (br), −18.8 ppm (br). MS: 353 (M$^+$) 100%, 338 (M$^+$ − CH$_3$) 86%, 282 (M$^+$ − CH$_3$ − *t*-Bu + H) 67%, 158 (M$^+$ − phospholyl) 34%.

{η^5-1,3-Di(*tert*-butyl)cyclopentadienyl}{η^5-2,5-di(*tert*-butyl)-phospholyl}cobalt(II), 10. As above, a solution of [Co(acac)$_2$] (261 mg, 1.02 mM) in THF was treated with [Li(PC$_4$H$_2$*t*-Bu$_2$)·2thf] (356 mg, 1.02 mM), stirred at −78 °C for 30 min, and warmed to room temperature for 15 min. The solution was recooled to −78 °C and further treated with a THF solution of Li(1,3-C$_5$*t*-Bu$_2$H$_3$) (184 mg, 1.02 mM). After stirring further for 30 min at −78 °C, the solution was warmed to ambient temperature, stirred for a further 45 min, and then evaporated to dryness. The purple air-sensitive solution was extracted with pentane (3 × 10 mL), concentrated to ca. 1 mL, and cooled to −4 °C overnight. Purple crystals were separated from the mother liquor and dried *in vacuo*, 290 mg, 66%. μ_{eff}: 1.68 μ_{B} (296 K, toluene). $E_{1/2(\mathrm{ox})}$: −0.56 V (THF). ^{31}P NMR (296 K, C$_6$D$_6$): −45 ppm. ^{1}H NMR (296 K, C$_6$D$_6$): 5.8 (2 × *t*-Bu), 2.7 (2 × *t*-Bu), −7.2, (PCC*H*), −31.0, (PCC*H*), −67.0, (*t*-BuCHC*H*), −74.2, (*t*-BuC*H*C*t*-Bu), −100.7, (*t*-BuCHC*H*) ppm. MS: 431 (M$^+$) 100%, 359 (M$^+$ − CH$_3$ − *t*-Bu) 46%, 287 (M$^+$ − 2CH$_3$ − 2*t*-Bu) 14%.

Crystallographic Data. For **6** C$_{17}$H$_{24}$CoO$_2$P, by sublimation. $M = 353.29$, triclinic, space group $P\bar{1}$, $a = 9.380(5)$ Å, $b = 10.174(5)$ Å, $c = 10.251(5)$ Å, $\alpha = 68.120(5)°$, $\beta = 85.680(5)°$, $\gamma = 79.930(5)°$, $U = 839.8(8)$ Å^3, $Z = 2$, $D_c = 1.313$ g cm^{-3}, $F(000) = 374$. Monochromated Mo K$_\alpha$ radiation $\lambda = 0.71070$ Å, $\mu = 1.051$ cm^{-1}, $T = 150$ K. Of 5125 independent reflections with h −13 to 12° k −14 to 14°, l −14 to 10° taken from an orange plate of *ca.* 0.18 × 0.16 × 0.12 mm and collected on a Kappa CCD diffractometer, 4363 with intensity $>2\sigma(I)$ were refined on F^2 using direct methods in SHELXL. $wR_2 = 0.0968$, $R_1 = 0.0379$, GOF = 1.001. Full data have been deposited with the Cambridge Crystallographic Data Centre under reference CCDC 192724. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html.

Acknowledgment. Financial support for this work from CNRS, Ecole Polytechnique (Gaspard Monge grants to N.S. and Y.C.), and the Ministère des Affaires Etrangères (grant to K.F.) is gratefully acknowledged.[62]

Supporting Information Available: Crystallographic data. This material is available free of charge via the Internet at http://pubs.acs.org.

OM0610952

---

(59) Carmichael, D.; Ricard, L.; Mathey, F. *J. Chem. Soc., Chem. Commun.* **1994**, 1167.

(60) Riemschneider, R. *Z. Naturforsch., B* **1963**, *18*, 641.

(61) Piccinni-Leopardi, C.; Fabre, O.; Reisse, J. *Org. Magn. Reson.* **1976**, *8*, 233−236.

(62) Bitta, J.; Fassbender, S.; Reiss, G.; Ganter, C. *Organometallics* **2006**, *25*, 2394−2397.

(63) Deschamps, B.; Ricard, L.; Mathey, F. *Organometallics* **1999**, *18*, 5688−5690.

(64) Carmichael, D.; Ricard, L.; Mathey, F. *J. Chem. Soc., Chem. Commun.* **1994**, 2459−2460.

(65) Holand, S.; Mathey, F.; Fischer, J. *Polyhedron* **1986**, *5*, 1413−1421.

(66) Arliguie, T.; Ephritikhine, M.; Lance, M.; Nierlich, M. *J. Organomet. Chem.* **1996**, *524*, 293−297.

(67) Sava, X.; Ricard, L.; Mathey, F.; Le Floch, P. *J. Organomet. Chem* **2003**, *671*, 120−125.

(68) Sava, X.; Ricard, L.; Mathey, F.; Le Floch, P. *Inorg. Chim. Acta* **2003**, *350*, 182−186.

(69) Burney, C.; Carmichael, D.; Forissier, K.; Green, J. C.; Mathey, F.; Ricard, L. *Chem.−Eur. J.* **2005**, *11*, 5381−5390.

(70) Clark, T.; Elvers, A.; Heinemann, F. W.; Hennemann, M.; Zeller, M.; Zenneck, U. *Angew. Chem., Int. Ed.* **2000**, *39*, 2087.

(71) Bartsch, R.; Hitchcock, P. B.; Nixon, J. F. *J. Chem. Soc., Chem. Commun.* **1988**, 819.

(72) Bruce, K. D. V.; Rocha, W. R. *Organometallics* **2004**, *23*, 5308−5313.