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Monophospholyl Analogs of Cobaltocenium, Rhodocenium, and Iridocenium Cations. Molecular Structures of $[MCp^*(\eta^5\text{-}PC_4H_2tBu_2)]^+BPh_4^-$ (M = Co, Rh)

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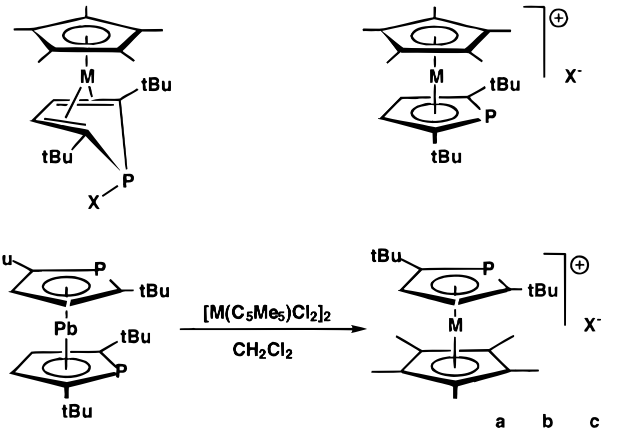
*Summary: Monophosphametallocenium cations of the cobalt group are easily prepared through metathesis of bis(η^5-2,5-di-tert-butylphospholyl)lead (**1**) with $[MCp^*X_2]_2$ (M = Co, Rh, Ir). Crystal structure analyses confirm their metallocene structures, and electrochemical studies show that $[CoCp^*(PC_4H_2tBu_2)]^+$ (**2**) undergoes reversible reduction to a long-lived product at a potential of −0.74 V (vs SCE).*

We have recently been exploring the specific preparation of η^5-phospholyl complexes by using a sterically hindered phosphole which incorporates *tert*-butyl groups to minimize redox reactions and η^1-coordination. This ligand has allowed the preparation of a number of previously inaccessible transition-metal[1] and p-block[2] derivatives. The p-block complexes should, in principle, be better phospholyl ligand transfer reagents for redox-sensitive metal centers than the corresponding alkali-metal salts,[3] and the 1,1′-diphosphaplumbocene **1** seems to be particularly attractive, because of the ease with which any PbX_2 byproducts can be removed.[2a] As part of a project directed toward the eventual synthesis of paramagnetic phosphametallocenes, we evaluated the reactions of **1** with $[MCp^*X_2]_2$ (M = Co, X = I; M = Rh, Ir; X = Cl).

Stirring dichloromethane solutions of $[Pb(PC_4tBu_2H_2)_2]$ (**1**) with $[CoCp^*I_2]_2$ at room temperature followed by filtration, metathesis of the crude $[CoCp^*(PC_4H_2tBu_2)]^+I^-$ with KPF_6, $NaBF_4$, or $NaBPh_4$ in MeOH, and crystallization from chloroform/methanol to remove traces of 2,2′,5,5′-tetra-*tert*-butyl-1,1′-biphosphole gave yellow, essentially air-stable, crystals of $[CoCp^*(PC_4H_2tBu_2)]^+X^-$ (**2**-X) in good yield. The corresponding rhodium and iridium complexes $[MCp^*Cl_2]_2$ were converted into colorless, air-stable $[MCp^*(PC_4H_2tBu_2)]^+X^-$ (**3**, M = Rh; **4**, M = Ir) under similar conditions and purified analogously.[4]

In principle, two structural forms may be written for **2**−**4** (Chart 1) but all available solution data indicate that these complexes exist as metallocene cations rather than cyclopentadienyl(η^4-phosphole)metal(I) complexes. Thus, in being recovered unchanged from neat iodomethane after 7 days at 25 °C, [**2**-BPh_4] shows the classically low nucleophilicity expected from sp^2-hybridized phosphorus.[5] In addition, the complexes are soluble and stable in polar media (MeOH, MeCN) and show ^{31}P and ^{13}C NMR parameters which are insensitive to the nature of X (Cl, I, BF_4, BPh_4, PF_6). The large $^1J_{PC}$ coupling constants observed in each of the compounds are typical of aromatic phospholyl ligands,[6] and the isoelectronic rhodocenium (**3**) and ruthenocene (**5**)[1a] complexes have ^{13}C NMR spectra which are very similar in form. The differing charge upon moving from **5** to **3** induces low-field shifts at each of the rhodium-bound carbon atoms whose magnitudes (phospholyl, P**C**=C +24.7 ppm, PC=**C** +15.4 ppm; Cp*, Me**C** +16.4 ppm) suggest that both rings perceive the metal electron density to a similar degree.

Chart 1



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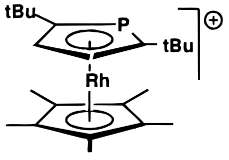
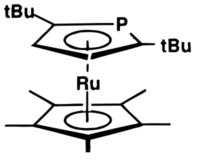
a b c
2 M = Co, X = PF_6, BF_4, BPh_4
3 M = Rh, X = PF_6, BF_4, BPh_4
4 M = Ir, X = PF_6, BF_4, BPh_4



3 BPh_4



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A solid-state cationic metallocene formulation was confirmed by X-ray diffraction studies on **2**-BPh_4 and

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[1] (a) Carmichael, D.; Ricard, L.; Mathey, F. *J. Chem. Soc., Chem. Commun.* **1994**, 1167. (b) Carmichael, D.; Ricard, L.; Mathey, F. *J. Chem. Soc., Chem. Commun.* **1994**, 2459. (c) Caffyn, A. J. M.; Carmichael, D.; Mathey, F.; Ricard, L. *Organometallics* **1997**, *16*, 2049.

[2] (a) Forissier, K.; Ricard, L.; Carmichael, D.; Mathey, F. *Chem. Commun.* **1999**, 1273. (b) Schnepf, A.; Stösser, G.; Carmichael, D.; Mathey, F.; Schnöckel, H. *Angew. Chem., Int. Ed.* **1999**, *38*, 1646.

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10.1021/om990820o CCC: $19.00

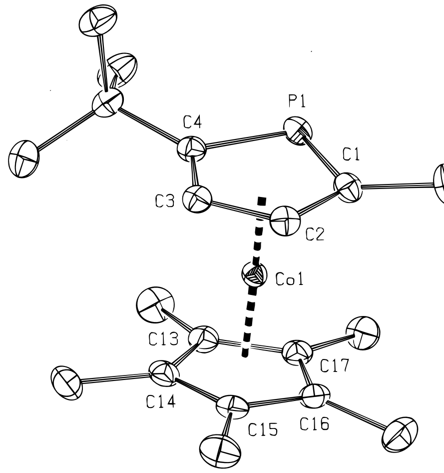

Figure 1. Structure of the cation in **2**-BPh_4. Selected bond lengths (Å) and angles (deg): P(1)−C(1), 1.788(2); P(1)−C(4), 1.784(2); C(1)−C(2), 1.411(2); C(2)−C(3), 1.418(2); C(3)−C(4), 1.415(2); C(13)−C(14), 1.429(2); C(14)−C(15), 1.423(3); C(15)−C(16), 1.436(2); C(16)−C(17) 1.424(2); C(13)−C(17), 1.437(2); Co(1)−P(1), 2.3055(5); Co(1)−C(1), 2.152(2); Co(1)−C(2), 2.061(2); Co(1)−C(3), 2.053(2); Co(1)−C(4), 2.133(2); C(1)−P(1)−C(4), 90.35(8); P(1)−C(1)−C(2), 111.5(1); C(1)−C(2)−C(3), 113.3(2); C(2)−C(3)−C(4), 113.2(2); C(3)−C(4)−P(1), 111.6(1).

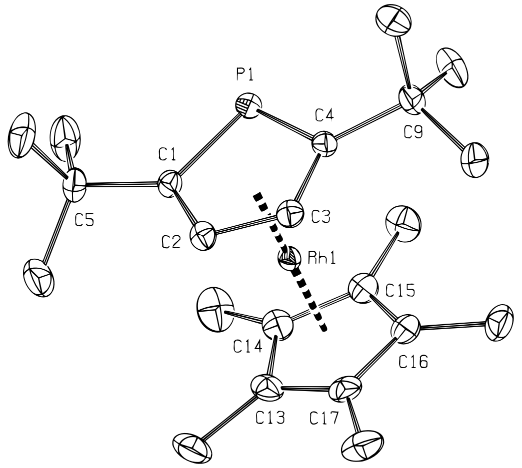

Figure 2. Structure of the cation in **3**-BPh_4. Selected bond lengths (Å) and angles (deg): P(1)−C(1), 1.788(2); P(1)−C(4), 1.788(2); C(1)−C(2), 1.421(3); C(2)−C(3), 1.433(2); C(3)−C(4), 1.425(3); C(13)−C(14), 1.438(3); C(14)−C(15), 1.443(3); C(15)−C(16), 1.430(3); C(16)−C(17), 1.438(3); C(13)−C(17), 1.431(3); Rh(1)−P(1), 2.4243(5); Rh(1)−C(1), 2.259(2); Rh(1)−C(2), 2.200(2); Rh(1)−C(3), 2.1948(2); Rh(1)−C(4), 2.260(2); C(1)−P(1)−C(4), 90.5(1); P(1)−C(1)−C(2), 111.8(1); C(1)−C(2)−C(3), 113.1(2); C(2)−C(3)−C(4), 112.7(2); C(3)−C(4)−P(1), 111.9(1).

3-BPh_4, which both show discrete well-separated ions[7] (Figures 1 and 2).

The cations have planar phospholyl rings and well-equalized C−C bond lengths indicative of high aromaticity;[8] lengths and angles in **2** are comparable with those of other (2,5-di-*tert*-butylphospholyl)cobalt complexes and fall within the normal ranges.[1c] It is noteworthy that there is slight evidence for greater bond length equalization in the CC phospholyl framework for the Co than for the Rh compound and also that all bonds in the phospholyl ligand of the rhodium compound are slightly elongated by comparison with those of the cobalt complex; this effect is mirrored in the Cp* portion of the molecule. Predictably[9] the M−Cp distances in **3** and the neutral ruthenocene analogue **5**[1a] are similar, but the M−phospholyl distance is slightly elongated in **3**.

Electrochemical studies on the cobaltocenium complex **2**-PF_6 reveal a first-reduction half-wave potential at −0.74 V (vs SCE in *n*-Bu_4NBF_4−THF) which is essentially reversible at 50 mV s^{-1} and insensitive to doping with water. A second reduction observed at −1.95 V is irreversible even at scan rates of 250 mV s^{-1}. No oxidation wave could be found within the THF window. The diminution of approximately 0.45 V in the reduction potential upon replacement of Cp by the

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(4) Synthesis of **2c**: finely ground $[CoCp^*I_2]_2$ (0.150 g, 0.170 mmol) was added at room temperature to a dichloromethane (10 mL) solution of bis(η^5-2,5-di-*tert*-butylphospholyl)lead (**1**; 0.100 g, 0.167 mmol). After 15 min of stirring, the green reaction mixture was evaporated to dryness and redissolved in methanol (35 mL) and the solution was filtered through Celite and treated with $NaBPh_4$ (0.115 g, 0.336 mmol). The precipitate was collected on a frit and recrystallized from chloroform/methanol to give yellow crystals of **2c**. Yield: 0.101 g, 77%. ^1H NMR ($CDCl_3$): δ 7.42 (s, br, 8H, C*H*), 7.04 (t, ^3J(H−H) = 7.1 Hz, 8H, C*H*), 6.91 (d, ^3J(H−H) = 7.1 Hz, 4H, C*H*), 5.45 (d, ^3J(P−H) = 4.0 Hz, 2H, PCC*H*), 1.87 (s, br, 15H, CCH_3), 1.14 (s, br, 18H, C$(CH_3)_3$), ^{13}C NMR ($CDCl_3$): δ 164.7 (q, ^1J(B−C) = 49.7 Hz, B*C*), 139.8 (d, ^1J(P−C) = 67.1 Hz, P*C*), 136.9 (s, *Ph*), 126.2 (s, *Ph*), 122.4 (s, *Ph*), 99.4, (s, P*C*), 92.2 (d, ^2J(P−C) = 7.6 Hz, Me*C*), 94.1 9d, ^2J(P−C) = 6.1 Hz, PC*C*), 35.8 (d, ^2J(P−C) = 13.4 Hz, Me_3C), 32.4 (d, ^3J(P−C) = 6.1 Hz, Me_3C), 12.5 (s, *Me*C). ^{31}P NMR ($CDCl_3$): δ −22.3. EI-MS: *m*/*z* 389 (MH^+ − $HBPh_4$; 100%), 164 ($tBuC_4H_2tBu^+$; 82%). Synthesis of **3c**: similarly, powdered $[RhCp^*Cl_2]_2$ (0.150 g, 0.241 mmol) and bis(η^5-2,5-di-*tert*-butylphospholyl)lead (**1**; 0.145 g, 0.243 mmol) in dichloromethane (15 mL) were stirred at room temperature for 20 min, redissolved in methanol, filtered, and treated with $NaBPh_4$ (0.166 g, 0.485 mmol) to give colorless **3c** upon recrystallization from chloroform/methanol. Yield: 0.204 g, 56%. ^1H NMR ($CDCl_3$): δ 7.42 (s, br, 8H, C*H*), δ 7.04 (t, ^3J(H−H) = 7.1 Hz, 8H, C*H*), 6.91 (d, ^3J(H−H) = 7.1 Hz, 4H, C*H*), 5.45 (d, ^3J(P−H) = 4.0 Hz, 2H, PCC*H*), 1.87 (s, br, 15H, CCH_3), 1.14 (s, br, 18H, C$(CH_3)_3$). ^{13}C NMR ($CDCl_3$): δ 164.7 (q, ^1J(B−C) = 49.7 Hz, B*C*), 141.4 (dd, ^1J(Rh−C) = 7.8 Hz, ^1J(P−C) = 69.6 Hz, P*C*), 136.9 (s, *Ph*), 126.1 (s, *Ph*), 122.4 (s, *Ph*), 104.1 (d, ^1J(Rh−C) = 7.6 Hz, Me*C*), 94.1 (pseudo-t, ^1J(Rh−C) = ^2J(P−C) = 7.6 Hz, PC*C*), 35.2 (d, ^2J(P−C) = 12.6 Hz, Me_3C), 32.4 (d, ^3J(P−C) = 6.1 Hz, Me_3C), 12.3 (s, *Me*C). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ −6.7 (d, ^1J(Rh−P) = 18.3 Hz). EI-MS: *m*/*z* 433 (MH^+ − $HBPh_4$; 100%), 164 ($tBuC_4H_2tBu^+$; 94%). Synthesis of **4c**: $[IrCp^*Cl_2]_2$ (0.050 g, 0.06 mmol) and **1** (0.040 g, 0.07 mmol) in dichloromethane (15 mL) were likewise converted by $NaBPh_4$ (0.046 g, 0.13 mmol) into colorless needlelike crystals of $[Cp^*Ir(PC_4H_2Bu^t_2)]^+$-$[BPh_4]^-$ (**4c**) from chloroform/methanol. Yield: 0.050 g, 50%. ^1H NMR ($CDCl_3$): δ 7.45 (m, br, 8H), 7.00 (m, 12H), 5.48 (d, ^3J(P−H) = 4.1 Hz, 2H, PCC*H*), 2.07 (s, 15H, CCH_3), 1.17 (s, 18H, C$(CH_3)_3$). ^{13}C NMR ($CDCl_3$): δ 164.8 (q, ^1J(B−C) = 48.9 Hz, B*C*), 136.9 (s, *Ph*), 129.0 (d, ^1J(P−C) = 68.7 Hz, P*C*), 126.2 (s, *Ph*), 122.4 (s, *Ph*), 97.8 (s, Me*C*), 87.4 (d, ^2J(P−C) = 6.1 Hz, PC*C*), 34.5 (d, ^2J(P−C) = 10.7 Hz, Me_3C), 32.2 (d, ^3J(P−C) = 7.6 Hz, Me_3C), 11.9 (s, *Me*C). ^{31}P NMR (C_6D_6): δ −40.3. EI-MS: *m*/*z* 523 (MH^+ − $HBPh_4$; 79%), 164 ($tBuC_4H_2tBu^+$; 100%).

(5) For example: Mathey, F.; Mitschler, A.; Weiss, R. *J. Am. Chem. Soc.* **1978**, *100*, 5748.

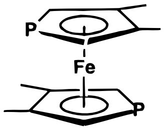
(6) Mathey, F. *Coord. Chem. Rev.* **1994**, *37*, 1.

(7) Crystal data for **2c**: $C_{46}H_{55}BCoP$; M_r = 708.61; triclinic; space group *P*1; *a* = 11.1692(5) Å, *b* = 11.9323(5) Å, *c* = 16.2789(7) Å, α = 78.111(2)°, β = 71.694(2)°, γ = 72.959(2)°, *V* = 1953.75(15) $Å^3$; *Z* = 2; *D* = 1.205 g cm^{-3}; μ = 0.511 cm^{-1}; *F*(000) = 756; crystal dimensions 0.22 × 0.10 × 0.06 mm; 14 399 reflections collected, 6862 of which with $I > 2\sigma(I)$; goodness of fit on F^2 1.021; R1 = 0.0408 ($I > 2\sigma(I)$); wR2 = 0.0894 (all data); maximum/minimum residual density 0.331(0.053)/−0.380(0.053) e $Å^{-3}$. Crystal data for **3c**: $C_{47}H_{56}BCl_3PRh$; M_r = 869.94; triclinic; space group $P\bar{1}$; *a* = 10.8262(2) Å, *b* = 12.1038(3) Å, *c* = 17.5262(3) Å, α = 88.2620(1)°, β = 86.9715(1)°, γ = 72.9101(1)°, *V* = 2191.87(8) $Å^3$; *Z* = 2; *D* = 1.318 g cm^{-3}; μ = 0.640 cm^{-1}; *F*(000) = 904; crystal dimensions 0.18 × 0.18 × 0.14 mm; 14733 reflections collected, 9182 of which with $I > 2\sigma(I)$; goodness of fit on F^2 1.103; R1 = 0.0310 ($I > 2\sigma(I)$); wR_2 = 0.0869 (all data); maximum/minimum residual density 0.953(0.088)/−0.874(0.088) e $Å^{-3}$. All data were collected on a KappaCCD diffractometer at 150.0(1) K using Mo Kα radiation (λ = 0.710 73 Å). Full details are given in the Supporting Information.

(8) Schleyer, P. v. R.; Freeman, P. K.; Jiao, H.; Goldfuss, B. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 337.

(9) For instance, no difference between $Fe(Cp^*)_2$ and $Co(Cp^*)_2^+$: Dixon, D. A.; Miller, J. S. *J. Am. Chem. Soc.* **1987**, *109*, 3656.

phospholyl ligand (for [Cp*CpCo] $E_1 = -1.17$ V; DMF, n-Bu$_4$NBF$_4$)[10] is broadly in accord with earlier data obtained by Lemoine et al. indicating a 0.6 V difference in reduction potential between ferrocene and the diphosphaferrocene derivative **6**.[11a−c] It also concurs with more recent results showing that replacement of a *t*BuC group by P in the multiphosphaferrocene couple **7** and **8** lowers the reduction potential by ca. 350 mV.[11d]



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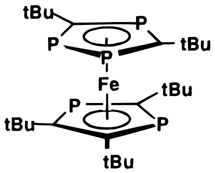

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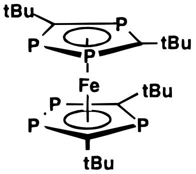

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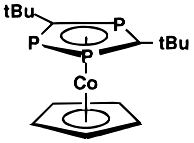

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In an important recent contribution, Zenneck and colleagues have reported a neutral triphosphacobaltocene derivative **9**,[12] but no other simple phospholyl-containing metallocene complexes of the group IX elements appear to be known.[13] Our studies confirm that monophosphametallocenes of the cobalt group are also viable synthetic targets and provide a straightforward access to their precursors. Full details concerning the chemical reduction of these phosphametallocenium ions and the structures and properties of mono- and diphosphacobaltocenes will be presented in due course.

Acknowledgment. We thank Dr P. le Floch (Ecole Polytechnique) for some technical assistance with the cyclic voltammetry measurements and Ecole Polytechnique (grant to K.F.) and the CNRS for funding.

Supporting Information Available: Crystal structure data for **2**-BPh$_4$ and **3**-BPh$_4$. This material is available free of charge via the Internet at http://pubs.acs.org.

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(11) (a) Lemoine, P.; Gross, M.; Braunstein, P.; Mathey, F.; Deschamps, B.; Nelson, J. H. *Organometallics* **1984**, *3*, 1303, (b) Lemoine, P.; Gross, M.; Braunstein, P.; Mathey, F.; Deschamps, B.; Nelson, J. H. *J. Organomet. Chem.* **1985**, *295*, 189. Roman, E.; Leiva, A. M.; Casasempere, M. A.; Charrier, C.; Mathey, F.; Garland, M. T.; Le Marouille, J. Y. *J. Organomet. Chem.* **1986**, *309*, 323. (d) Bartsch, R.; Datsenko, S.; Ignatiev, N. V.; Müller, C.; Nixon, J. F.; Pickett, C. J. *J. Organomet. Chem.* **1997**, *529*, 375. (e) Weber, L.; Sommer, O.; Stammler, H.-G.; Neumann, B.; Kölle, U. *Chem. Ber.* **1995**, *128*, 665. (f) For further electrochemistry of phospholyl complexes, see also: Feher, R.; Kohler, F. H.; Nief, F.; Ricard, L.; Rossmayer, S. *Organometallics* **1997**, *16*, 4610 and references therein.

(12) (a) Envers, A.; Heinemann, F.; Kummer, S.; Wrackmeyer, B.; Zenneck, U. Lecture LF3-3 to XIVth ICPC, Cincinnati, OH, July 12−17, 1998. After submission, two fuller descriptions have appeared: (b) Envers, A.; Heinemann, F.; Wrackmeyer, B.; Zenneck, U. *Chem. Eur. J.* **1999**, *5*, 3143. (c) Envers, A.; Heinemann, F.; Kummer, S.; Wrackmeyer, B.; Zeller, M.; Zenneck, U. *Phosphorus, Sulfur Silicon Relat. Elem.* **1999**, *144−6*, 725.

(13) (a) An undetected hexaphosphacobaltocene was suggested as a conceivable intermediate in the synthesis of a triphospholyl(triphosphadiene)cobalt(I) compound: Bartsch, R.; Hitchcock, P. B.; Nixon, J. F. *J. Chem. Soc., Chem. Commun.* **1988**, 819. (b) Other reactions of triphospholides with Co and Rh(III) precursors have given complex redox products: Nixon, J. F. *Coord. Chem. Rev.* **1995**, *145*, 201. (c) Cobalt triple-decker monophospholyl compounds: Chase, K. J.; Bryan, R. F.; Woods, M. K.; Grimes, R. N. *Organometallics* **1991**, *10*, 2631. (d) Diazacobaltocenium: Kuhn, N.; Köckerling, M.; Stubenrauch, S.; Bläser, D.; Boese, R. *J. Chem. Soc., Chem. Commun.* **1988**, 819. See also: (e) Kuhn, N.; Köckerling, M.; Stubenrauch, S.; Bläser, D.; Boese, R. *Z. Naturforsch., B* **1999**, *54B*, 424. (f) Borole analogues of cobaltocenium salts: Herberich, G. E. In *Comprehensive Organometallic Chemistry II*; Wilkinson, G., Stone, F. G. A.; Abel, E. W., Eds.; Pergamon: Oxford, U.K., 1995; Vol. 1, p 197.