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## Communications

### Biphosphinine Rhodium and Cobalt(−1) Complexes

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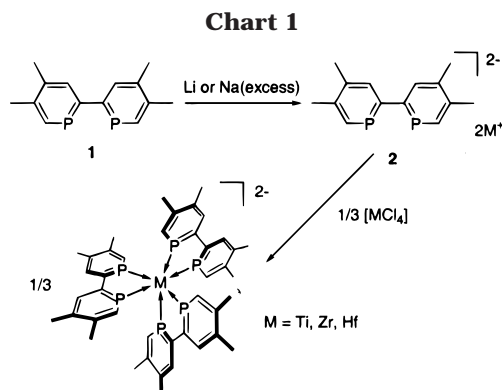
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**Summary:** The 4,4',5,5'-tetramethyl-2,2'-biphosphinine (tmbp) dianionic sodium salt **2** reacts with  $[M(acac)_3]$  ( $M = Co, Rh$ ) precursors to yield the anionic  $[M(tmbp)_2]^-$  cobalt (**3**,  $M = Co$ ) and rhodium (**4**,  $M = Rh$ ) complexes. Trapping of these two species with  $Ph_3SnCl$  affords  $[M(tmbp)SnPh_3]$  complexes (**5**,  $M = Co$ ) and (**6**,  $M = Rh$ ).

For several years now, we have been interested in the chemistry of 2,2'-biphosphinines, the phosphorus equivalents of 2,2'-bipyridines. Our studies aim at developing the use of these strong  $\pi$ -acceptor ligands for the stabilization of highly reduced transition metal complexes.<sup>1</sup> In 1999, we reported on syntheses of the anion radical and dianion of 4,4',5,5'-tetramethyl-2,2'-biphosphinine (tmbp) and showed that their reactions with halide salts of metals (W, Ru, and group 10 metals) proved to be a convenient way to prepare the corresponding zerovalent complexes.<sup>2</sup> More recently, using the same approach, we synthesized the first anionic homoleptic biphosphinine complexes  $[M(tmbp)_3]^{2-}$  with group 4 metals ( $M = Ti, Zr, Hf$ ) (Chart 1).<sup>3</sup>

As part of a continuing program aimed at expanding this methodology to the synthesis of other anionic



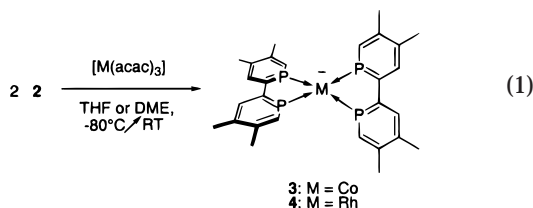
complexes, we investigated the reactivity of these anions toward Co and Rh precursors to see whether anionic Co and Rh(−1) complexes could be obtained. In this communication, we wish to report on these results.

Two strategies are available for the synthesis of the Rh(−1) complex **4**. The first one involves reaction of 2 equiv of the monoanion radical ( $M = Li$  or  $Na$ ) with 1 equiv of a Rh(I) precursor such as  $[Rh(COD)Cl]_2$ . The second requires the condensation of 2 equiv of dianion **2** with 1 equiv of a Rh(III) precursor,  $[Rh(acac)_3]$ . This latter method turned out to be the more successful and was then subsequently transposed to the synthesis of the Co(−1) complex, through the reaction of **2** with  $[Co(acac)_3]$  (eq 1).<sup>4</sup>

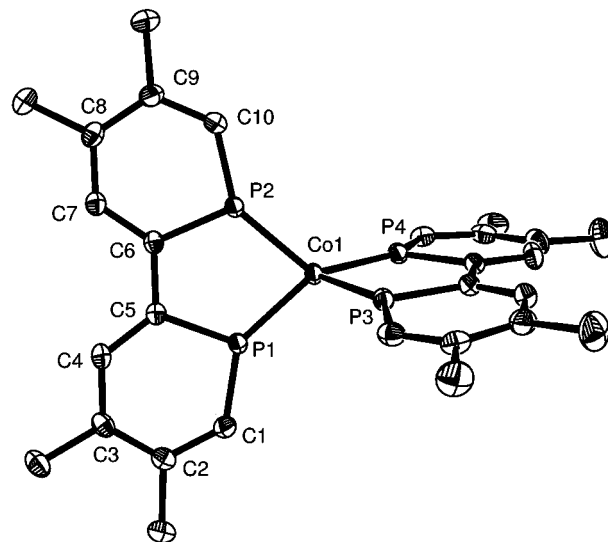
(1) (a) Mathey, P.; Le Floch, P. *Chem. Ber.* **1996**, *129*, 263. (b) Rosa, P.; Ricard, L.; Le Floch, P.; Mathey, F.; Sini, G.; Eisenstein, O. *Inorg. Chem.* **1998**, *37*, 3154.

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(3) Rosa, P.; Mézailles, N.; Ricard, L.; Mathey, F.; Le Floch, P. *Angew. Chem., Int. Ed.* **2000**, *39*, 1821.



It must be noted that **3** is the first example of a  $\eta^1$ -phosphinine cobalt complex. In both cases, the reduced complexes were univocally formed and no side product was detected in the  $^{31}\text{P}$  NMR spectra of the crude mixture. Unfortunately,  $[\text{Na}(\text{acac})]$  salts could not be totally removed from the crude mixture by precipitation, and **3** and **4** could not be recovered as analytically pure substances. NMR experiments ( $^{31}\text{P}$ ,  $^1\text{H}$ , and  $^{13}\text{C}$ ) were carried out on crude mixtures in both cases. We found that addition of the (2.2.2) cryptand resulted in nearly quantitative precipitation of **3** and **4** as a powder (contaminated by traces of acac salts). To gain more structural information, X-ray crystallographic studies were carried out. Suitable crystals were obtained by heating poorly soluble  $[\text{Na}(2.2.2)]$  salts of **3** and **4** in THF or DME overnight.<sup>5,8,9</sup> Both complexes adopt a nearly tetrahedral geometry as reported for other group 9  $d^{10}$  complexes.<sup>5–7</sup> Nevertheless the presence of different conformations in the solid points toward a fluxional behavior for **3** and **4** in solution. Thus, two independent molecules ( $\theta = 78^\circ$  and  $83^\circ$ ), differing from each other by the twist angle between the planes of the ligands, are contained in the unit cell of the Co complex **3**<sup>8</sup> and three molecules ( $\theta = 59^\circ$ ,  $63^\circ$ ,  $87^\circ$ ) in the case of its Rh counterpart **4**.<sup>9</sup> This situation is not maintained in solution since the  $^{31}\text{P}$  NMR spectra of **4** (doublet at  $\delta = 194.1$  ppm with  $^1J(^{31}\text{P} - ^{103}\text{Rh}) = 191$  Hz) and **3** (broad singlet at  $\delta = 209.4$  ppm) show only a single resonance pointing toward magnetic equivalence of the four P atoms. An ORTEP view of one molecule of **3** ( $\theta = 78^\circ$ )



**Figure 1.** ORTEP drawing of one molecule of **4**. Selected bond distances (Å) and angles (deg): Co(1)–P(1) = 2.1063(7), Co(1)–P(3) = 2.0841(7), Co(1)–P(2) = 2.0988(6), Co(1)–P(4) = 2.1097(5), P(1)–C(1) = 1.730(2), C(1)–C(2) = 1.391(2), C(2)–C(3) = 1.414(2), C(3)–C(4) = 1.391(2), C(4)–C(5) = 1.397(2), C(5)–C(6) = 1.454(2), C(6)–P(2) = 1.737(2); C(1)–P(1)–C(5) = 101.91(7), P(1)–Co(1)–P(2) = 83.82(2), P(2)–Co(1)–P(4) = 122.32(2), P(1)–Co(1)–P(3) = 112.44(2), P(1)–Co(1)–P(4) = 133.23(2), P(2)–Co(1)–P(3) = 126.25(2).

is presented in Figure 1. In both cases a significant electronic transfer from the metal to the  $\pi^*$  LUMO of the ligand is observed. This phenomenon is evidenced by the shortening of the C–C bridge bond between each phosphinine unit (average 1.456 vs 1.490(8) Å in *cis*-**1**) and by the lengthening of the internal P=C bond (average 1.763 vs 1.736(4) Å in *cis*-**1**), in good agreement with the shape of the biphosphinine LUMO.<sup>1b</sup> Accordingly, the Rh–P bond lengths in **4** appear to be rather short (from average 2.219 Å) compared to values reported for phosphinine Rh(+1) complexes (average 2.26 Å).<sup>10</sup>

Though a significant part of the charge resides on ligands, main-group electrophiles react at the metal

(4) Preparation of **3**: Biphosphinine **1** (0.1 g, 0.4 mmol) was reacted, in a glovebox, at room temperature with excess sodium (0.23 g, 10 mmol) in THF or DME (10 mL). After 3 h, excess sodium was removed and  $[\text{Co}(\text{acac})_3]$  (71 mg, 0.2 mmol) was added at  $-78^\circ\text{C}$ . The resulting solution was then slowly warmed to room temperature. After 3 h, Na(acac) salts were separated by filtration (glovebox), and cryptand (2.2.2) (75 mg, 0.2 mmol) was added to the filtrate to precipitate complex **3**. After drying, complex **3** was recovered as a very oxygen sensitive dark red powder. Elemental data could not be obtained due to traces of Na(acac) salt. Preparation of **4**: Synthesis of **4** was carried out following the procedure described above for **3** using **1** (0.1 g, 0.4 mmol), Rh(acac)<sub>3</sub> (70 mg, 0.2 mmol), and cryptand (2.2.2) (75 mg, 0.2 mmol). After washing with hexanes, complex **4** was recovered as a very oxygen sensitive black powder. Suitable crystals of **3** and **4** were obtained as follows. In the glovebox, 15 mg of powder was placed in a glass tube and was then subsequently covered with THF or DME. The tube was sealed under vacuum and then heated at  $80^\circ\text{C}$  overnight. The tube was broken in the glovebox, and crystals were protected with paratone oil for handling and then submitted to X-ray diffraction analysis.

(5) For references on the synthesis of anionic group 9 complexes incorporating alkene ligands, see: (a) Jonas, K.; Mynott, R.; Krüger, C.; Sekulowski, J. C.; Tsay, Y.-H. *Angew. Chem., Int. Ed. Engl.* **1976**, *15*, 767. (b) Jonas, K.; Schieferstein, L.; Krüger, C.; Tsay, Y. H. *Angew. Chem., Int. Ed. Engl.* **1979**, *18*, 550. (c) Jonas, K.; Krüger, C. *Angew. Chem., Int. Ed. Engl.* **1980**, *19*, 520. (d) Jonas, K. *Pure Appl. Chem.* **1984**, *56*, 63. (e) Jonas, K. *Angew. Chem., Int. Ed. Engl.* **1985**, *24*, 295.

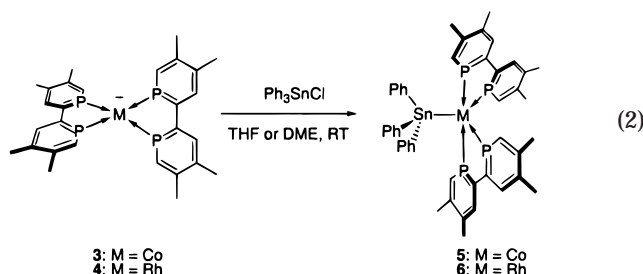
(6) For pertinent references on the synthesis of anionic group 9 complexes incorporating CO ligands and isonitriles, see: (a) Hieber, W.; Schulten, H. *Z. Anorg. Allg. Chem.* **1937**, *232*, 17. (b) Devasagayaram, A.; Achyutha Rao, S.; Periasamy, M. *J. Organomet. Chem.* **1991**, *387–391*, 403. (c) Warnock, G. F.; Cooper, N. J. *Organometallics* **1989**, *8*, 1826. (d) Leach, P. A.; Geib, S. J.; Corella, J. A.; Warnock, G. F.; Cooper, N. J. *J. Am. Chem. Soc.* **1994**, *116*, 8566. (e) Beck, W. *Angew. Chem., Int. Ed. Engl.* **1991**, *30*, 168.

(7) For pertinent references on the synthesis of anionic group 9 complexes incorporating phosphine ligands, see: (a) Hieber, W.; Duchatsch, H. *Chem. Ber.* **1965**, *98*, 2933. (b) Kruck, Th.; Derner, N.; Lang, W. *Z. Naturforsch.* **1966**, *21b*, 1020. (c) Schönberg, H.; Boulmaaz, S.; Wörle, M.; Liesum, L.; Schweiger, A.; Grützmacher, H. *Angew. Chem., Int. Ed.* **1998**, *37*, 1423. (d) Boulmaaz, S.; Mlaker, M.; Loss, S.; Schönberg, H.; Deblon, S.; Wörle, M.; Nesper, R.; Grützmacher, H. *J. Chem. Soc., Chem. Commun.* **1998**, 2623. (e) Collman, J. P.; Vastine, F. D.; Roper, W. R. *J. Am. Soc.* **1966**, *88*, 5035. (f) Collman, J. P.; Vastine, F. D.; Roper, W. R. *J. Am. Chem. Soc.* **1968**, *90*, 2282.

(8) Structure of **3**: Deep red cubic crystals were grown from a hot ( $80^\circ\text{C}$ ) THF solution of the complex. Crystal data:  $\text{C}_{28}\text{H}_{32}\text{P}_4\text{Co} \cdot \text{C}_{18}\text{H}_{36}\text{O}_6\text{N}_2\text{Na}$ , triclinic,  $P1$ ,  $a = 12.789(5)$  Å,  $b = 18.760(5)$  Å,  $c = 20.143(5)$  Å,  $\alpha = 91.210(5)^\circ$ ,  $\beta = 93.630(5)^\circ$ ,  $\gamma = 93.530(5)^\circ$ ,  $V = 4812(3)$  Å<sup>3</sup>,  $Z = 4$ ,  $D_{\text{calc}} = 1.312$  g cm<sup>-3</sup>, Mo K $\alpha$  radiation,  $\lambda = 0.71069$  Å,  $T = -150.0$  K,  $\theta_{\text{max}} = 27.50^\circ$ , 34 137 measured reflections, 21 921 independent reflections, 18 341 reflections used,  $R_{\text{int}} = 0.0314$  ( $>2\sigma$ ),  $wR2 = 0.0788$ ,  $R1 = 0.0323$ , GOF = 1.026, difference peak/hole =  $0.400(0.049)/-0.322(0.049)$  e Å<sup>-3</sup>.

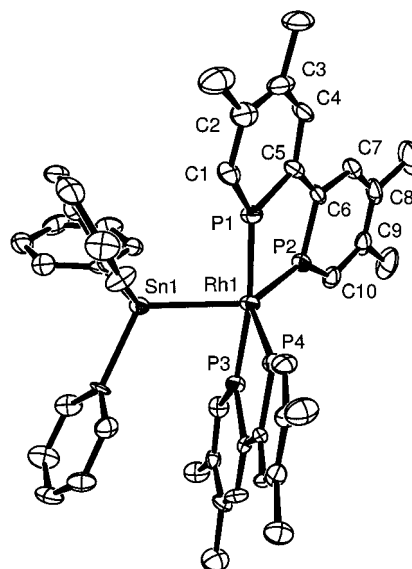
(9) Structure of **4**: Deep red plates were grown from a hot ( $80^\circ\text{C}$ ) DME solution of the complex. Crystal data:  $\text{C}_{28}\text{H}_{32}\text{P}_4\text{Rh} \cdot \text{C}_{18}\text{H}_{36}\text{O}_6\text{N}_2\text{Na}$ , triclinic,  $P1$ ,  $a = 13.159(3)$  Å,  $b = 13.579(3)$  Å,  $c = 41.546(8)$  Å,  $\alpha = 81.428(1)^\circ$ ,  $\beta = 85.187(1)^\circ$ ,  $\gamma = 88.475(1)^\circ$ ,  $V = 7314.1(3)$  Å<sup>3</sup>,  $Z = 6$ ,  $D_{\text{calc}} = 1.355$  g cm<sup>-3</sup>, Mo K $\alpha$  radiation,  $\lambda = 0.71069$  Å,  $T = -150.0$  K,  $\theta_{\text{max}} = 24.11^\circ$ , 30 133 measured reflections, 22 243 independent reflections, 15 658 reflections used,  $R_{\text{int}} = 0.0603$  ( $>2\sigma$ ),  $wR2 = 0.1403$ ,  $R1 = 0.0540$ , GOF = 1.008, difference peak/hole =  $0.582(0.152)/-0.634(0.152)$  e Å<sup>-3</sup>.

center. Thus reaction of  $\text{Ph}_3\text{SnCl}$  with **3** and **4**, in THF at room temperature, yielded the expected  $[\text{M}(\text{tmbp})_2(\text{SnPh}_3)]$  complexes **5** ( $\text{M} = \text{Co}$ ) and **6** ( $\text{M} = \text{Rh}$ ),<sup>11</sup> respectively, whose formulation was unambiguously established on the basis of NMR and elemental analyses data (eq 2).



Further information on the structure of complex **6** was given by an X-ray structural study. An ORTEP view of **6** is presented in Figure 2 along with the more relevant bond distances and angles.<sup>12</sup> As generally observed for penta-coordinated metal complexes, **6** shows a fluxional behavior. Thus, whereas the  $^{31}\text{P}$  NMR signal of **6** attests the presence of four equivalent P atoms (sharp doublet of pseudo triplet at  $\delta = 196.3$  with  $^1J(^{31}\text{P}-^{103}\text{Rh}) = 142$  Hz and  $^2J(^{31}\text{P}-^{117}\text{Sn}/^{119}\text{Sn}) = 66$  Hz) even at low temperature ( $-50^\circ\text{C}$ ), **6** adopts a distorted trigonal bipyramidal geometry in the solid state. The  $\text{SnPh}_3$  group and two P atoms of two different biphosphinines (P2 and P4) are located on equatorial sites, while the two others (P1 and P3) occupy axial sites.

In summary, we have established that the reaction of biphosphinine dianion **3** with  $[\text{M}(\text{acac})_3]$  complexes



**Figure 2.** ORTEP drawing of one molecule of **6**. Selected bond distances (Å) and angles (deg):  $\text{Rh}(1)-\text{P}(1) = 2.243(2)$ ,  $\text{Rh}(1)-\text{P}(2) = 2.236(2)$ ,  $\text{Rh}(1)-\text{P}(3) = 2.240(2)$ ,  $\text{Rh}(1)-\text{P}(4) = 2.263(2)$ ,  $\text{Rh}(1)-\text{Sn} = 2.6140(7)$ ,  $\text{P}(1)-\text{C}(1) = 1.716(7)$ ,  $\text{C}(1)-\text{C}(2) = 1.38(1)$ ,  $\text{C}(2)-\text{C}(3) = 1.40(1)$ ,  $\text{C}(3)-\text{C}(4) = 1.37(1)$ ,  $\text{C}(4)-\text{C}(5) = 1.42(1)$ ,  $\text{C}(5)-\text{P}(1) = 1.744(7)$ ,  $\text{C}(5)-\text{C}(6) = 1.452(8)$ ;  $\text{C}(1)-\text{P}(1)-\text{C}(5) = 104.4(4)$ ,  $\text{P}(1)-\text{Rh}(1)-\text{P}(2) = 80.05(7)$ ,  $\text{P}(3)-\text{Rh}(1)-\text{P}(4) = 80.81(6)$ ,  $\text{P}(1)-\text{Rh}(1)-\text{P}(3) = 170.72(6)$ ,  $\text{P}(2)-\text{Rh}(1)-\text{P}(4) = 131.79(6)$ ,  $\text{P}(1)-\text{Rh}(1)-\text{P}(4) = 106.35(7)$ ,  $\text{P}(1)-\text{Rh}(1)-\text{Sn} = 89.81(5)$ ,  $\text{P}(3)-\text{Rh}(1)-\text{Sn} = 83.30(5)$ ,  $\text{P}(2)-\text{Rh}(1)-\text{Sn} = 130.63(5)$ ,  $\text{P}(4)-\text{Rh}(1)-\text{Sn} = 97.49(5)$ .

( $\text{M} = \text{Co}$ ,  $\text{Rh}$ ) provided the corresponding Co and Rh(–I) complexes as isolable species. Further investigations will now focus on the reactivity of these species toward electrophiles as well as on the extension of this approach to the synthesis of other reduced complexes.

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**Supporting Information Available:** Text giving experimental details and characterization data for the compounds prepared in this paper and tables of atomic coordinates and equivalent isotropic displacement parameters, bond lengths and bond angles, anisotropic displacement parameters, hydrogen coordinates, and equivalent isotropic parameters. This material is available free of charge via the Internet at <http://pubs.acs.org>.

(10) For relevant references on Rh–phosphinine bond distances, see: (a) Breit, B.; Winde, R.; Harms, K. *J. Chem. Soc., Perkin Trans. 1997*, 1, 2681. (b) Mézailles, N.; Avarvari, N.; Ricard, L.; Mathey, F.; Le Floch, P. *Inorg. Chem.* **1998**, 37, 5313. (c) Avarvari, N.; Mézailles, N.; Ricard, L.; Le Floch, P.; Mathey, F. *Science* **1998**, 281, 1587.

(11) Preparation of **5**: Triphenyltin chloride (77 mg, 0.2 mmol) was added at room temperature to a solution of complex **3** prepared as above (in THF) from **1** (0.1 g, 0.4 mmol) and  $[\text{Co}(\text{acac})_3]$  (71 mg, 0.2 mmol). The resulting mixture was stirred for 1 h and then taken to dryness. Complex **5** was extracted in  $\text{CH}_2\text{Cl}_2$  (20 mL) and filtrated. After evaporation of the solvent complex **5** was recovered as a violet powder. Yield: 91 mg (50%). Anal. Calcd for  $\text{C}_{46}\text{H}_{47}\text{CoP}_4\text{Sn}$ : C, 61.29; H, 5.26. Found: C, 60.96; H, 5.20. Preparation of **6**: Synthesis of complex **6** was carried out following the same procedure from **1** (0.1 g, 0.4 mmol),  $[\text{Rh}(\text{acac})_3]$  (70 mg, 0.2 mmol), and  $\text{Ph}_3\text{SnCl}$  (77 mg, 0.2 mmol) in DME. Yield: 125 mg (65%). Anal. Calcd for  $\text{C}_{46}\text{H}_{47}\text{P}_4\text{RhSn}$ : C, 58.21; H, 5.29. Found: C, 58.10; H, 5.09.

(12) Structure of **6**. Crystals were grown by slow diffusion of hexane into a  $\text{CHCl}_3$  solution of the complex. Crystal data:  $\text{C}_{46}\text{H}_{47}\text{P}_4\text{RhSn} \cdot 1/2\text{DME}$ , monoclinic,  $C2/c$ ,  $a = 32.9410(10)$  Å,  $b = 12.4230(10)$  Å,  $c = 22.7740(10)$  Å,  $\alpha = 90.0000(10)^\circ$ ,  $\beta = 107.740(10)^\circ$ ,  $\gamma = 90.0000(10)^\circ$ ,  $V = 8876.5(9)$  Å<sup>3</sup>,  $Z = 8$ ,  $D_{\text{calcd}} = 1.482$  g cm<sup>–3</sup>, Mo K $\alpha$  radiation,  $\lambda = 0.71069$ ,  $T = -150.0$  K,  $\theta_{\text{max}} = 22.21^\circ$ , 12 582 measured reflections, 5450 independent reflections, 3982 reflections used,  $R_{\text{int}} = 0.0889$  ( $>2\sigma$ ),  $wR2 = 0.0865$ ,  $R1 = 0.0593$ ,  $\text{GOF} = 1.033$ , difference peak/hole =  $0.513(0.092)/-0.634(0.092)$  e Å<sup>–3</sup>.

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