An Unusual Heterobimetallic Compound with a Rhodium(I)–η^4-Arene Interaction

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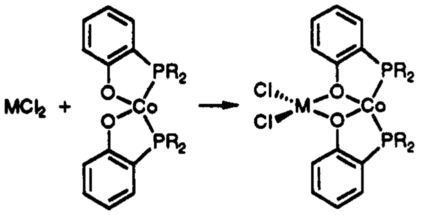
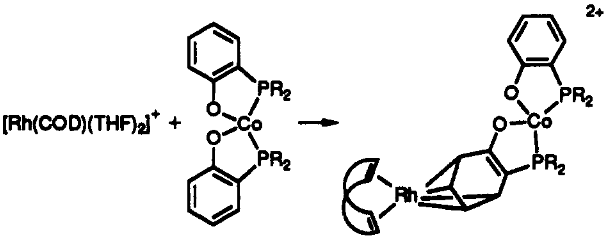
Summary: The synthesis, structure, and spectroscopic properties of the unusual heterobimetallic complex $[(cod)RhCo(TMPP\text{-}O)_2][BF_4]_2$ *(1) are described (cod = 1,5-cyclooctadiene; TMPP = tris(2,4,6-trimethoxyphenyl)phosphine; TMPP-O =* $[P(C_6H_2(OMe)_3)_2(C_6H_2(OMe)_2O)]^-$*). The structure of 1 consists of a six-coordinate Co(III) center in which the phenoxide oxygens are in a trans disposition, with a Rh(I) center being coordinated to the diene molecule in two cis positions and in an* η^4 *bonding mode to one of the demethylated phenyl rings of the TMPP ligand.*

The chemistry of tris(2,4,6-trimethoxyphenyl)phosphine (TMPP)[1] with 3d elements produces bis(phosphino-phenoxide) complexes of general formula $M(TMPP\text{-}O)_2$ (M = Co, Ni; TMPP-*O* = $[P(C_6H_2(OMe)_3)_2(C_6H_2(OMe)_2O)]^-$).[2] In the case of Co(II), the two phenoxide oxygens assume a cis orientation and thus the molecule is poised to coordinate a second metal center as illustrated by the reaction in eq 1.[3] After recently establishing that



(1)

compounds of the type $Cl_2MCo(\mu,\eta^2\text{-}(TMPP\text{-}O)_2)$ (M = Co, Mn)[3] were accessible, we became intrigued by the possibility of preparing organometallic heterodinuclear compounds with both early–late and late–late transition-metal combinations. To this end, the reaction between $Co(TMPP\text{-}O)_2$ and the diene complex $[Rh(COD)(THF)_2]^+$ was investigated, the idea being that the electron-deficient cationic species would preferentially bind the phenoxide oxygens in lieu of THF ligands. The chloro-bridged dimer $[Rh(cod)Cl]_2$[4] was treated with excess $AgBF_4$ to give the activated Rh(I) compound $[Rh(cod)(THF)_2][BF_4]$, which was then reacted with $Co(TMPP\text{-}O)_2$ in acetone at room temperature to give a dark brown solution after 10 min. Subsequent removal of the solvent followed by washing with diethyl ether gave the title compound $[(cod)RhCo(TMPP\text{-}O)_2][BF_4]_2$ (1), as depicted in eq 2. The sample was recrystallized by slow diffusion of hexanes into an acetone solution of 1 (yield 73% relative to $Co(TMPP\text{-}O)_2$).[5]



(2)

A single-crystal X-ray study revealed the identity of the product as $[(cod)Rh^{I}–Co^{III}(TMPP\text{-}O)_2]^{2+}$ (1), in which the Rh(I) atom is involved in an η^4 interaction with a phenyl ring from one of the coordinated phosphine–phenoxide ligands. The ORTEP representation of the cation in Figure 1 and, more clearly, the PLUTO drawing in Figure 2 indicate that the Co(III) center is coordinated to four oxygen and two phosphorus atoms to give an overall pseudooctahedral environment.[6] The phosphorus and the methoxy oxygen atoms are mutually cis, whereas the phenoxide groups are disposed in a trans fashion. The average Co–P bond distance of 2.166[4] Å (versus 2.198(2) Å) and the metal–ether interactions (2.064[8] versus 2.313(4) Å) are shorter than in the Co(II) structure $Cl_2Co_2(\mu,\eta^2\text{-}(TMPP\text{-}O)_2)$[3], as expected for a more electrophilic metal center. The Co–O distances for the oxygen atoms from the phenoxide groups are also shorter than those found in the aforementioned structure, being 1.889[7] Å compared to 1.927(4) Å; this value is also in agreement with the Co^{III}–O bond distance of 1.899(2) Å reported for the macrocyclic carboxylato–Co(III) complex $[Co(L^3\text{-}H)][ClO_4]_2$.[7] The angles about the Co(III) center define a quasi-octahedral geometry with the O(9)–Co(1)–O(18) bond angle being 174.1(3)° and the P(1)–Co(1)–P(2) angle 101.6(1)°.

We now turn to the most unusual feature of the present structure, viz. the binding mode of the Rh atom. The Rh(I) center is ligated to a cod ligand in the usual configuration and further, in an η^4 fashion, to one of the demethylated phenyl rings of the phosphine. This constitutes the first example of the TMPP phosphine ligand participating in this type of bonding; furthermore, to our

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[†] Camille and Henry Dreyfus Teacher-Scholar 1991–1995. Fellow of the Alfred P. Sloan Foundation 1992–1994.

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(5) Anal. Calcd for $RhCoP_2C_{60}O_{18}H_{72}B_2F_8$: C, 48.71; H, 4.87. Found: C, 48.81; H, 5.24.

(6) The compound crystallizes in the monoclinic space group $P2_1/n$ with cell dimensions a = 15.890(4) Å, b = 17.209(5) Å, c = 27.705(9) Å, β = 74.57(2)°, V = 7303(4) Å^3, Z = 4, d_{calcd} = 1.445 g/cm^3, and μ(Mo Kα) = 5.771 cm^{-1}. A Nicolet P3/F upgrade to a Siemens/P3V diffractometer was used to collect 11 731 unique data in the 5–47° 2θ range using the ω-scan mode at −90 ± 2 °C; 5797 data with $F_o^2 \geq 2.2\sigma(F_o)^2$ were used to refine 870 parameters to convergence, giving residuals of R = 0.075 and R_w = 0.076 and a quality-of-fit indicator of 1.607. The final difference Fourier map showed the highest peak to be 1.12 e$^-$/Å^3, and the final shift/esd was 0.01.

(7) Hambley, T. W.; Lawrance, G. A.; Maeder, M.; Wilkes, E. N. *J. Chem. Soc., Dalton Trans.* **1992**, 1283.

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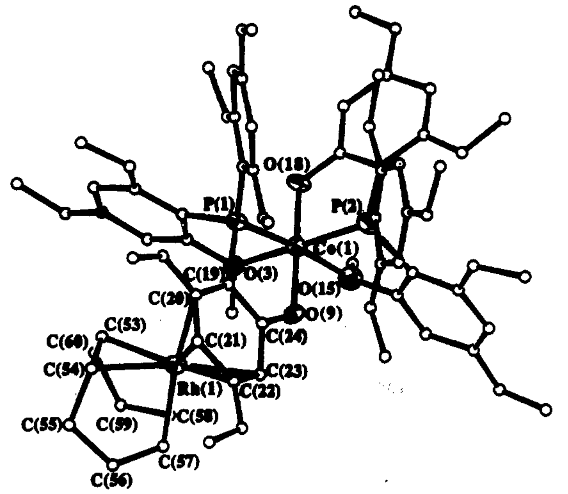

Figure 1. ORTEP representation of the molecular cation in 1, [(cod)RhCo(TMPP-*O*)$_2$]$^{2+}$. All phenyl group and cod carbon atoms are represented as small circles for clarity, whereas all other atoms are represented by their 40% probability ellipsoids. Important bond distances (Å) and angles (deg) are as follows: Rh(1)–C(20), 2.33(1); Rh(1)–C(21), 2.35(1); Rh(1)–C(22), 2.27(1); Rh(1)–C(23), 2.21 (1); Rh(1)–C(53), 2.14(1); Rh(1)–C(54), 2.17(1); Rh(1)–C(57), 2.11(1); Rh(1)–C(58), 2.13(1); Co(1)–P(1), 2.164(3); Co(1)–P(2), 2.168(4); Co(1)–O(9), 1.902(7); Co(1)–O(18), 1.875(6); Co(1)–O(3), 2.044(8); Co(1)–O(15), 2.083(7); C(20)–Rh(1)–C(21), 35.8(4); C(20)–Rh(1)–C(23), 76.2(4); C(21)–Rh(1)–C(22), 36.5(4); C(22)–Rh(1)–C(23), 37.5(4); C(53)–Rh(1)–C(54), 38.0(5); C(53)–Rh(1)–C(57), 97.2(5); C(53)–Rh(1)–C(58), 82.3(5); C(54)–Rh(1)–C(57), 81.5(5); C(54)–Rh(1)–C(58), 91.4(5); C(57)–Rh(1)–C(58), 38.8(5); O(9)–Co(1)–O(18), 174.1(3); P(1)–Co(1)–P(2), 101.6(1); P(1)–Co(1)–O(3), 83.0(2); P(1)–Co(1)–O(15), 173.9(2); O(15)–Co(1)–O(18), 89.9(3).

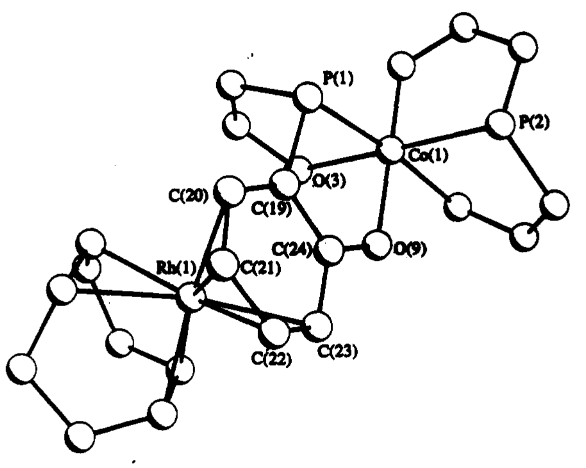

Figure 2. Skeletal PLUTO drawing of 1 emphasizing the immediate coordination spheres of the metal atoms.

knowledge, there are no documented examples of Rh(I) complexes coordinated to a phenyl ring in an η^4 fashion.[8] The four Rh$^{\mathrm{I}}$–C(phenyl) bonds range from 2.21(1) to 2.35(1) Å with an average of 2.29[1] Å, a distance that falls at the short end of the range reported for η^6-phenyl interactions.[8,9] This value is in accord, however, with typical values for complexes of Rh possessing η^4 ligands.[8] The average ring carbon–carbon distance for the coordinated η^4-arene ring is longer than those found for the other three phenyl groups involved in a metallacycle (1.43[1] versus 1.38[2], 1.39[2], and 1.37[2] Å), but the six C–C distances within the Rh η^4 ring are not significantly different from one another, which argues against a localized bonding picture. For the purposes of electron counting, we view the TMPP ligand as a diene contributing 4 e$^-$, which leads to an overall 16-e$^-$ count for the complex. It is interesting to note that most [(η^4-diene)Rh$^{\mathrm{I}}$(arene)]$^+$ complexes are 18-e$^-$ complexes,[10] although it has been suggested on the basis of ^{1}H NMR data, e.g. for [(η^4-cod)Rh$^{\mathrm{I}}$(η^n-C$_7$H$_8$)]$^+$ (n = 4, 6),[11] that these molecular cations may adopt either the 16-e$^-$ or the 18-e$^-$ configuration depending on the hapticity of the arene ring (η^4 versus η^6).

Oxidation of Co$^{\mathrm{II}}$ to Co$^{\mathrm{III}}$ in the reaction leading to the title compound is attributed to the excess Ag$^+$ in the reaction leading to [Rh(cod)(THF)^2]$^+$. The cis to trans phenoxide isomerization that accompanies the oxidation from Co$^{\mathrm{II}}$ to Co$^{\mathrm{III}}$ is compatible with our observation of an irreversible oxidation feature in the cyclic voltammogram of Co$^{\mathrm{II}}$(TMPP-*O*)$_2$ ($E_{\mathrm{p,a}}$ = +0.51 V vs Ag/AgCl).[12] Surprisingly, the ^{1}H NMR spectrum of the product in acetone-d_6 or acetonitrile-d_3 exhibits the expected pattern for an η^3-TMPP ligand coordinated to a diamagnetic metal center, viz. six meta protons and eight methoxy groups, indicating that the two phosphine ligands are equivalent in solution. ^{31}P NMR spectroscopy confirms the structural equivalence of the phosphine ligands in solution, as only one signal is observed at δ +5.6 ppm. These results indicate lability of the Rh(cod)$^+$ moiety in coordinating solvents.[13,14] If the ^{1}H NMR experiment is carried out in a noncoordinating solvent such as CD$_2$Cl$_2$, however, the result is quite different, in this case, 16 methoxy and 12 meta resonances are observed, attributable to two inequivalent phosphine groups, thereby suggesting that the Rh(cod)$^+$ fragment remains bound in this solvent and that the structure is similar to the one assumed in the solid state.[15]

The present finding is relevant to recent work by Alper et al., who reported that a zwitterionic Rh(I) complex comprised of a Rh(cod)$^+$ unit attached to an η^6-phenyl substituent on a BPh$_4^-$ anion is a regioselective olefin

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(11) Green, M.; Kuc, T. A. *J. Chem. Soc., Dalton Trans.* 1972, 832.

(12) Chemical oxidation of Co$^{\mathrm{II}}$(TMPP-*O*)$_2$ to produce [Co$^{\mathrm{III}}$(TMPP-*O*)$_2$]$^+$ was achieved in low yield with [Cp$_2$Fe][BF$_4$] in acetone.

(13) For NMR studies of TMPP compounds, see for example: Haefner, S. C.; Dunbar, K. R.; Bender, C. *J. Am. Chem. Soc.* 1991, *113*, 9540.

(14) ^{1}H NMR (acetone-d_6; δ, ppm): 3.01 (s), 3.31 (s), 3.49 (s), 3.58 (s), 3.61 (s), 3.84 (s), 3.90 (s), 4.17 (s) (8 CH$_3$O–), 5.43 (s), 5.67 (s), 5.78 (s), 5.94 (s), 6.30 (s), 6.89 (s) (6 meta H). ^{31}P NMR (CD$_3$CN; δ, ppm): +5.6, corresponding to [Co$^{\mathrm{III}}$(TMPP-*O*)$_2$]$^+$.

(15) ^{1}H NMR (CD$_2$Cl$_2$; δ, ppm): 2.87 (s), 3.05 (s), 3.32 (s), 3.33 (s), 3.45 (s), 3.53 (s), 3.54 (s), 3.62 (s), 3.64 (s), 3.80 (s), 3.87 (s), 3.89 (s), 4.01 (s), 4.02 (s), 4.09 (s), 4.71 (s) (16 CH$_3$O–) and 12 multiplets between 5 and 7 ppm (12 meta H) corresponding to [(cod)RhCo(TMPP-*O*)$_2$]$^{2+}$. Unfortunately, the low solubility of 1 in CD$_2$Cl$_2$ thwarted efforts to observe a ^{31}P NMR signal.

hydroformylation catalyst under mild conditions.[16] In the present case, the title compound is not zwitterionic, but the high lability in donor solvents of the Rh(I) moiety releases a reactive "Rh(cod)$^+$" fragment for substrate binding; thus, it should also be a reactive precursor. In noncoordinating solvents, the (η^4-$C_6H_2O(OMe)_2$)–Rh(cod)$^+$ unit remains intact, but the presence of a Co(III) center with weak ether interactions leaves open the possibility for coordinative unsaturation at that center which may promote additional interesting reactivity patterns related to the synergistic effect of the nearby Rh(I) center.

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Supplementary Material Available: Tables giving details of the crystal structure determination, positional and thermal parameters, and bond distances and angles for 1 (24 pages). Ordering information is given on any current masthead page.

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