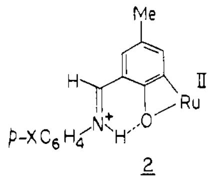
Volume 29
Number 25
December 12, 1990

Inorganic Chemistry

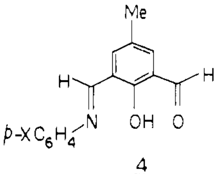
Communications

Ruthenium(II) Phenolates. Synthesis and Characterization of A Novel Four-Membered Metallacycle

Ruthenium phenolates constitute a small family of interesting complexes.[1] While 4-methyl-2,6-diformylphenol (**1**) was studied as a potential binucleating ligand for the metal, complexes of composition Ru(p-XC_6H_4L)(CO)($(PPh_3)_2$Cl, incorporating **2**, were discovered. The X = Me complex **3**, described here, is representative of the family.[2]



2



4

Reaction of $Ru(PPh_3)_3Cl_2$ (100 mg, 0.10 mmol), **1** (26 mg, 0.15 mmol), and p-$MeC_6H_4NH_2$ (17 mg, 0.15 mmol) in boiling ethanol (30 mL) for 0.5 h (the reaction does not proceed in the absence of the amine) affords a violet solution, which, upon cooling, deposits **3** as dark violet crystals in nearly quantitative yield.[3] The same results are obtained when **1** + p-$MeC_6H_4NH_2$ is replaced by an equivalent amount of the preformed Schiff base **4** (40 mg, 0.15 mmol), which is thus the active reagent in the synthesis. Benzene can replace ethanol as the solvent without loss of synthetic efficacy.

The X-ray structure[4,5] of **3** is shown in Figure 1. The ruthenium coordination sphere is distorted octahedral. The unprecedented four-membered metallacycle incorporating the phenolato function is excellently planar, and indeed, the entire p-MeC_6H_4L ligand is a good plane (mean deviation 0.038 Å). The coordinated carbonyl function is located cis to C37, to which the aldehyde function was attached before decarbonylative orthometalation. The ruthenium(II)–O(phenolato) distance in the four-membered chelate ring of **3** is significantly longer than those in five-membered rings.[6-8] The distance is even longer than that of Ru(II)–O(H_2O), 2.122 (16) Å.[9] The azomethine H atoms were located in calculated positions,[4] and the N–H···O1 hydrogen bonding is found to be highly unsymmetrical. Complex **3** is a zwitterion in which the positive and negative charges reside on the protonated azomethine function and on the metal coordination sphere, respectively.

All protons in **3** have been observed by ^1H NMR spectroscopy in $CDCl_3$ at 270 MHz. The metalated ring proton singlets are shifted upfield: H42, 5.885 ppm; H40, 6.025 ppm. The C_6H_4 proton doublets (J = 9.00 Hz) are 7.258 ppm for H46 and H50 and 6.976 ppm for H47 and H49. The singlet $C51H_3$ and $C42H_3$ signals occur at 1.702 and 2.401 ppm, respectively. The protonated azomethine singlets are 7.584 ppm for C44H and 13.194 ppm for NH. The latter signal is very broad and disappears on D_2O treatment. The triphenylphosphine protons give rise to two complex signals centered at 7.220 and 7.700 ppm.

The following rationale is tentatively proposed for the formation of **3**. Decarbonylation of aldehydes by transition-metal complexes normally proceeds as symbolized in eq 1, where [M] = ligated

$$[M^z] + RCHO \xrightarrow{oa} [M^{z+2}](R)(CO)H \xrightarrow{re} [M^z](CO) + RH \qquad (1)$$

metal, z = metal oxidation state, oa = oxidative addition, and re = reductive elimination.[10] In the synthesis of **3** and **4** the co-

---

(1) Bag, N.; Lahiri, G. K.; Bhattacharya, S.; Falvello, L. R.; Chakravorty, A. *Inorg. Chem.* **1988**, *27*, 4396–4402 and references therein.

(2) The complexes synthesized and characterized have X = Me, H, OMe, Cl, CO_2Et, and NO_2. Compounds in which the p-XC_6H_4 function is replaced by aliphatic groups (Me, Et, ^nBu) have also been prepared.

(3) Anal. Calcd for $RuC_{52}H_{44}NO_2P_2Cl$ ($Ru(MeC_6H_4L)(CO)(PPh_3)_2Cl$): C, 68.38; H, 4.82; N, 1.53. Found: C, 68.49; H, 4.79; N, 1.49. The solid is diamagnetic and nonelectrolytic in MeCN solution. UV–vis (CH_2Cl_2): λ 530 nm (ε 4560), 405 (11 430), 320 (7700). IR: ν(CO) 1895 cm^{-1}.

(4) **3** ($C_{52}H_{44}NO_2P_2ClRu$; MW 913.3) crystallized in the triclinic space group $p\bar{1}$ with a = 9.967 (2) Å, b = 12.018 (4) Å, c = 21.207 (8) Å, α = 80.64 (3)°, β = 76.62 (2)°, γ = 66.20 (2)°, V = 2254.4 (13) $Å^3$, and Z = 2. Data collection ($2° < 2\theta < 62°$) on a 0.14 × 0.10 × 0.38 mm^3 crystal was done by the ω-scan method on a Nicolet R3m/V diffractometer with graphite-monochromated Mo Kα radiation (λ = 0.710 73 Å) at 22 °C. Full-matrix least-squares refinement of the model based on 6308 reflections chosen ($F > 6.0\sigma(F)$) from 7927 independent reflections converged to a final $R(F_o)$ = 4.86%, $R_w(F_o^2)$ = 6.77%, and GOF = 1.60. The largest difference Fourier peak was 0.24 e $Å^{-3}$ near the metal atom. The benzene rings (C19–C36) of one of the PPh_3 ligands were disordered and were refined as such. All non-hydrogen atoms except the disordered rings were refined anisotropically. The hydrogen atoms except those in the disordered PPh_3 ligand and those attached to C3, C10, C11, C12, and C51 were located and subsequently refined, and the rest were affixed. The weighting scheme used was $w = 1/[\sigma^2(F) + 0.0005F^2]$. All calculations were done on a MicroVAX II computer using SHELXTL-PLUS program package.[5]

(5) Sheldrick, G. M. *SHELXTL-PLUS 88, Structure Determination Software Programs*; Nicolet Instrument Corp.: 5225-2 Verona Rd., Madison, WI 53711, 1988.

(6) Bag, N.; Basu, P.; Lahiri, G. K.; Chakravorty, A. Unpublished resulted on catecholatobis(2-((3-methylphenyl)azo)pyridine)ruthenium(II): Ru(II)–O(phenolato), 2.040 (12) Å.

(7) Pizzotti, M.; Crotti, C.; Demartin, F. *J. Chem. Soc., Dalton Trans.* **1984**, 735–737.

(8) Structures of a number of ruthenium(II) semiquinonates are known, the average Ru–O distance being 1.99 Å. (a) Bhattacharya, S.; Boone, S. R.; Fox, G. A.; Pierpont, C. G. *J. Am. Chem. Soc.* **1990**, *112*, 1088–1096. (b) Lever, A. B. P.; Auburn, P. R.; Dodsworth, E. S.; Haga, M.; Liu, W.; Melnik, M.; Nevin, A. *J. Am. Chem. Soc.* **1988**, *110*, 8076–8084. (c) Boone, S. R.; Pierpont, C. G. *Inorg. Chem.* **1987**, *26*, 1769–1773.

(9) Bernhard, P.; Burgi, H. B.; Hauser, J.; Lehmann, H.; Ludi, A. *Inorg. Chem.* **1982**, *21*, 3936–3941.

0020-1669/90/1329-5013$02.50/0

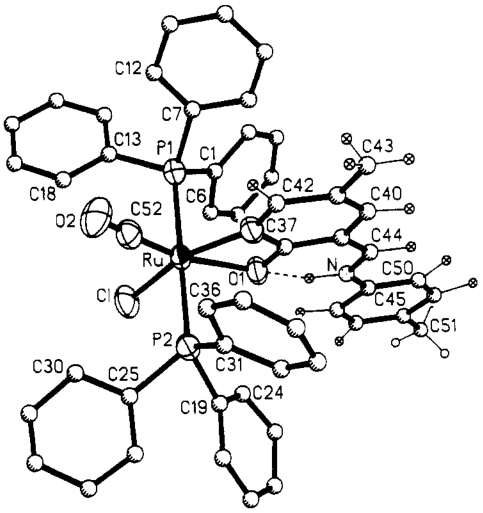


Figure 1. Perspective view of complex **3**. Selected bond distances (Å) and angles (deg): Ru–Cl, 2.500 (2); Ru–P1, 2.386 (2); Ru–P2, 2.388 (2); Ru–O1, 2.235 (4); Ru–C37, 2.043 (6); Ru–C52, 1.800 (7); C52–O2, 1.157 (8); C38–O1, 1.314 (6); C44–N, 1.311 (8); N–H1N, 0.985 (11); O1···H1N, 1.753 (12); Cl–Ru–P1, 91.3 (1); Cl–Ru–P2, 89.2 (1); Cl–Ru–O1, 93.0 (1); Cl–Ru–C37, 156.9 (2); Cl–Ru–C52, 103.7 (2); P1–Ru–P2, 179.5 (1); P1–Ru–O1, 87.7 (1); P1–Ru–C37, 89.6 (2); P1–Ru–C52, 90.6 (2); P2–Ru–O1, 92.2 (1); P2–Ru–C37, 89.9 (2); P2–Ru–C52, 89.4 (2); O1–Ru–C37, 64.0 (2); O1–Ru–C52, 163.2 (2); C37–Ru–C52, 99.3 (3); N–H1N–O1, 143.8 (3). One PPh_3 ligand is disordered, each benzene ring appearing in two ways—of these only one set (C19–C36) is shown. The PPh_3 hydrogens are not shown for clarity.

ordinated (R) group in the ruthenium(IV) intermediate formed after oxidative addition is a stable ortho-metalated phenolato chelate ring. Reductive elimination therefore proceeds by the alternative route of H^+ elimination assisted by the azomethine nitrogen, which is thus obligatory for the reaction. The result is **2**. Base-promoted reductive H^+ elimination ($Ru^{IV}H + B \rightarrow Ru^{II} + HB^+$) from organometallic ruthenium(IV) hydride species has been documented elsewhere.[11]

The complex **3** can be deprotonated by base, and it forms multinuclear complexes with other metal ions such as copper(II), possibly via phenolato and azomethine nitrogen coordination. The reaction and properties of $Ru(p\text{-}XC_6H_4L)(CO)(PPh_3)_2Cl$ and cognate osmium complexes are under scrutiny.

Acknowledgment. We are grateful to the Department of Science and Technology, New Delhi, for establishing a National Single-Crystal Diffractometer Facility at the Department of Inorganic Chemistry, Indian Association for the Cultivation of Science. Financial support received from the Council of Scientific and Industrial Research is also acknowledged.

Supplementary Material Available: Tables of positional parameters, thermal parameters, bond distances, and bond angles of **3** and a figure showing the nature of PPh_3 disorder (8 pages); a table of structure factors (29 pages). Ordering information is given on any current masthead page.

---

(10) (a) Doughty, D. H.; Pignolet, L. H. *Homogeneous Catalysis with Metal Phosphine Complexes*; Pignolet, L. H., Ed.; Plenum Press: New York, 1983; pp 343-375. (b) Sonnenfroh, D. M.; Farrar, J. M. *J. Am. Chem. Soc.* **1986**, *108*, 3521-3522. (c) Anton, A. B.; Avery, N. R.; Toby, B. H.; Weinberg, W. H. *J. Am. Chem. Soc.* **1986**, *108*, 684-694.

(11) (a) Ashworth, T. V.; Singleton, E. *J. Chem. Soc., Chem. Commun.* **1976**, 705-706. (b) Seddon, E. A.; Seddon, K. R. *The Chemistry of Ruthenium*; Elsevier: New York, 1984; pp 139-149.

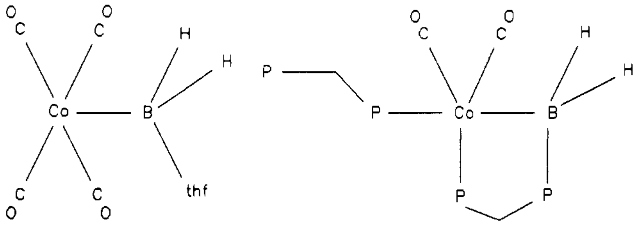
Department of Inorganic Chemistry
Indian Association for the
Cultivation of Science
Calcutta 700032, India

Nilkamal Bag
Suranjan Bhanja Choudhury
Amitava Pramanik
Goutam Kumar Lahiri
Animesh Chakravorty*

Received June 28, 1990

A Bridged Cobaltaborane Complex: First Structural Characterization of a Transition-Metal-BH_2 Bond

Transition-metal complexes containing $M-BH_2$ units have proved to be elusive, despite intensive research in transition-metal–borane chemistry.[1] The first such complex $[(CO)_4CoBH_2\cdot THF]$ (**1**) has recently been characterized by Fehlner and co-workers using spectroscopic methods at low temperature, but it decomposes rapidly at room temperature.[2] This paper reports a diphosphine-bridged derivative of **1**, that is stable at room temperature and has been characterized crystallographically.



1

2, PP = dppm

The new complex $[(CO)_2(\eta^1\text{-dppm})Co(\mu\text{-dppm})BH_2]$ (**2**), dppm = $Ph_2PCH_2PPh_2$, was prepared in one step but in low yield by reduction of cobalt(II) chloride or bromide with $NaBH_4$ in the presence of dppm and CO.[3] The major product of this reaction is $[Co_2(CO)_4(\mu\text{-dppm})_2]$ (**3**),[4] and the yellow complex **2** was separated from the black complex **3** by handpicking crystals.[3] Complex **2** is air-stable and was fully characterized by spectroscopic methods[5] and by an X-ray structure determination.[6] The structure of **2** is shown in Figure 1. It contains a distorted trigonal-bipyramidal (TBP) cobalt center with the monodentate dppm and boron ligands in axial positions and two carbonyls and a phosphorus donor of the μ-dppm ligand in equatorial positions. The major distortion probably arises from the steric interaction between the axial dppm ligand and the equatorially bonded ligands. This gives rise to the displacement of the equatorially bonded atoms away from P(4). Thus, the angles P(1)CoP(2) = 101.91 (3)°, BCoC(3) = 82.4 (2)°, and BCoC(4) = 75.5 (2)° are considerably distorted from the idealized 90° for a trigonal bipyramid.

---

(1) For example: (a) Fehlner, T. P. *New J. Chem.* **1988**, *12*, 307. (b) Housecroft, C. E. *Polyhedron* **1987**, *6*, 1935. (c) Coffy, T. J.; Medford, G.; Plotkin, J.; Long, G. J.; Huffman, J. C.; Shore, S. G. *Organometallics* **1989**, *8*, 2404. (d) Kennedy, J. D. *Prog. Inorg. Chem.* **1984**, *32*, 519; **1984**, *34*, 211.

(2) Basil, J. D.; Aradi, A. A.; Bhattacharyya, N. K.; Rath, N. P.; Eigenbrot, C.; Fehlner, T. P. *Inorg. Chem.* **1990**, *29*, 1260.

(3) A solution of $NaBH_4$ (0.12 g) in EtOH (15 mL) was added to a CO-saturated solution of $CoBr_2\cdot 6H_2O$ (0.44 g) and dppm (1.00 g) in C_6H_6/EtOH (30 mL, 1:1) over 30 min. The mixture was stirred for 4 h, and then the solvents were removed and the product was washed with EtOH and recrystallized from CH_2Cl_2/EtOH. The large yellow crystals of **2** were separated by hand from black crystals of **3**.

(4) Elliot, D. J.; Holah, D. G.; Hughes, A. N. *Inorg. Chim. Acta* **1988**, *142*, 195.

(5) Spectroscopic data (labeling defined in Figure 1) is as follows. IR: ν(CO) = 1925 (m), 1865 (s) cm^{-1}; ν(BH) = 2380 (w), 2310 (w) cm^{-1}. NMR in CD_2Cl_2: $\delta(^{31}P) = -33.0$ [d, $^2J(P^1P^3) = 28$ Hz, P^1], 47.1 [br, P^3], 15.7 [d, $^2J(P^2P^4) = 155$ Hz, P^2], 44.5 [d, $^2J(P^2P^4) = 155$ Hz, P^4]; $\delta(^{11}B) = -25.9$ (br s). FAB-MS: found, m/z = 898, 884, 870, 841; calcd for $C_{52}H_{46}BCoO_2P_4$, m/z 896, 883 (P – BH_2), 868 (P – CO), 840 (P – 2CO). There was excellent agreement between the observed and calculated (for P – 2CO + H) envelope structures at m/z = 841, thus proving the presence of a single boron atom. EI-MS: confirms ^{11}B and ^{10}B at m/z = 11 and 10 in required ratio.

(6) Crystal data for $C_{52}H_{46}BCoO_2P_4\cdot 0.5CH_2Cl_2$ (**2**): fw 937.2; monoclinic, space group $P2_1/c$; $a = 19.520$ (7), $b = 10.943$ (3), $c = 24.625$ (14) Å, $\beta = 112.75$ (4)°; $V = 4850.7$ Å^3; $Z = 4$; calculated density = 1.284 g cm^{-3}; ambient temperature; graphite-monochromated Mo Kα radiation; ω-scan technique from $0° \leq 2\theta \leq 48°$; octants measured $\pm h,k,l$, total reflections 8505; $R = 0.054$, $R_w = 0.072$; goodness of fit 1.657 for 583 variables and 5362 reflections with $I \geq 3\sigma(I)$. All calculations were carried out by using an AT&T 6386 WGS computer with a PC version of NRCVAX. NRCVAX: Gabe, E. J.; Lee, F. L.; Le Page, Y. In *Crystallographic Computing 3: Data Collection, Structure Determination, Proteins and Data Bases*; Sheldrick, G. M., Kruger, C., Eds.; Clarendon Press: Oxford, England, 1985; p 167.

0020-1669/90/1329-5014$02.50/0