Organometallic Chemistry

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Formation of an Unsymmetrical Dinuclear Ruthenium Complex with μ-H, μ-OH, and μ-κ^2-CO_2 Bridges and Multiple Reactive Sites**

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Hydrido ruthenium species and their organometallic derivatives play important roles as chemically active intermediates in the key steps of numerous catalytic reactions.[1] Judicious design and syntheses of model compounds for these processes have contributed to the rapid development of organoruthenium chemistry. We have exploited some versatile hydrido (phosphine) transition-metal compounds to obtain useful highly reactive catalysts[1,2] and to investigate the structural characteristics and chemical reactivities of organometallic intermediates derived from them through the incorporation of organic substrates, such as alkenes, alkynes, nitriles, and allylic compounds.[3] In the course of these studies, we treated ethanol solutions of some chloro(carbonyl)(phosphine) ruthenium(II) complexes $[RuCl_2(CO)_n(PR_3)_m]$ with a large excess of concentrated aqueous KOH solution, and from the reactions of the PMe_3 complexes, we succeeded in isolating and characterizing of an unprecedented dinuclear ruthenium complex with μ-H, μ-OH, and μ-κ^2-CO_2 bridges.[4] In contrast to this result, Lavigne and co-workers have described that reactions of the halo(carbonyl)ruthenium(II) complex $[RuCl_2(CO)_3(thf)]$ with methanolic solutions of KOH result in the formation of a hydroxycarbonyl species $[RuCl_2(CO)_2\{C(O)OH\}]^-$, and that subsequent thermal decarboxylation gives a transient hydride "$[RuCl_2(H)(CO)_2]^-$".[5] Our isolated dinuclear species is bridged not only by hydrido but also by hydroxo and κ^2-*O,C*- carbon dioxide ligands. Herein we report the synthesis of this complex and its chemical reactivity towards neutral monodentate donor molecules (i.e. Lewis bases), protic acids, and molecular iodine.

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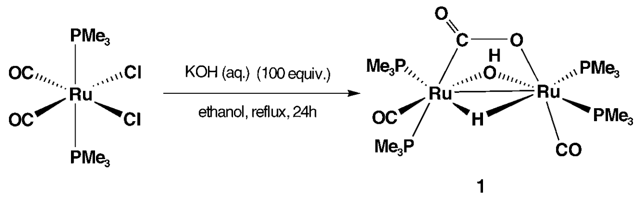
Treatment of *cis,cis,trans*-[RuCl$_2$(CO)$_2$(PMe$_3$)$_2$] with 100 equivalents of KOH (10 M aqueous solution) in refluxing ethanol was found to afford [{Ru(CO)(PMe$_3$)$_2$}$_2$(μ-H)(μ-OH){μ-κ^2-C(O)O}] (**1**) as yellow brown powder in 59% yield (Scheme 1). The structural assignment of **1** was performed by an X-ray diffraction study of single crystals grown from benzene/hexane (Figure 1).[6]



Scheme 1. Synthesis of **1**.

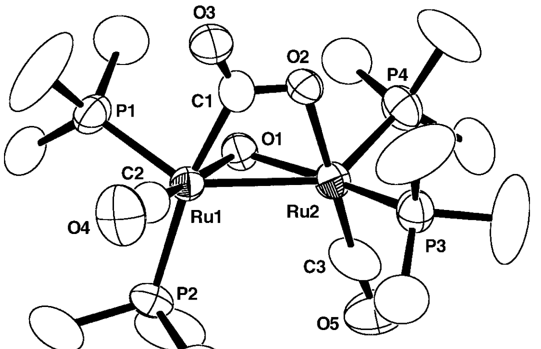


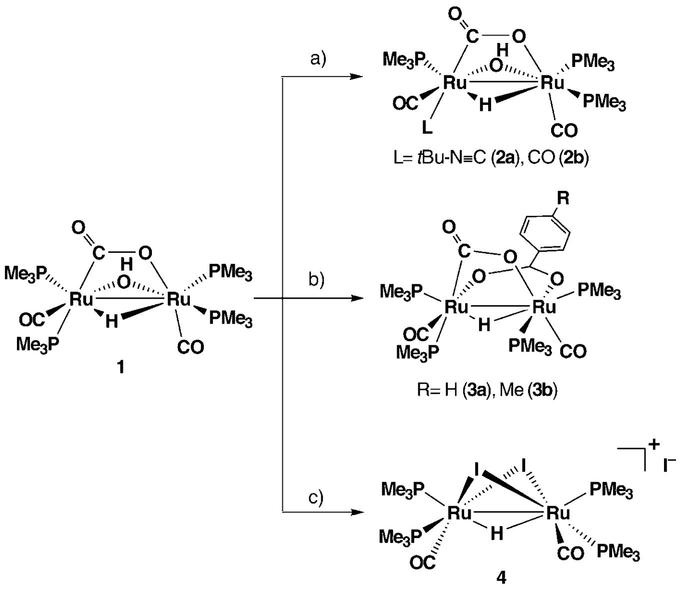
Figure 1. ORTEP diagram of complex **1** (thermal ellipsoids set at 50% probability). Selected bond lengths [Å] and angles [°]: Ru1-Ru2 2.788(1), Ru1-P1 2.282(2), Ru1-P2 2.402(2), Ru2-P3 2.273(3), Ru2-P4 2.312(3), Ru1-O1 2.089(5), Ru2-O1 2.089(5), Ru1-C1 2.089(9), Ru2-O2 2.105(5), O2-C1 1.320(10), O3-C1 1.248(10); O2-C1-O3 119.3(8).

The molecule consists of two [Ru(CO)(PMe$_3$)$_2$] units bridged by hydrido, hydroxo, and additionally κ^2-*O,C*-carbon dioxide ligands, resulting in an asymmetric dinuclear structure. Although some other dinuclear complexes containing CO$_2$ in a similar unsymmetrical bridging mode have been reported,[7] such a triply bridged dinuclear species is unprecedented. The geometry around each ruthenium atom is approximately octahedral. The coordinated carbon and oxygen atoms in the κ^2-*O,C*-CO$_2$ ligand are *trans* to a PMe$_3$ ligand (P2 of Ru1) and the CO ligand (of Ru2), respectively. The CO ligand of Ru1 and the PMe$_3$ (P3) ligand of Ru2 conform to the "A-frame" structure imposed by the bridging hydroxo group. Moreover, two positions *trans* to the bridging hydrido group are occupied by two PMe$_3$ ligands. Compound **1** has 34 cluster valence electrons with a typical Ru–Ru single bond of 2.788(1) Å.[8] The hydrido atom was located in a difference electron density map, but unfortunately its position was not refined. Bond lengths between the bridging hydroxo oxygen atom and two ruthenium atoms (Ru1-O1 2.089(5), Ru2-O1 2.089(5)) fall within the range of normal hydroxo bridge bonds in dinuclear complexes.[9] Whereas the Ru1-C1 bond length (2.089(9) Å) is comparable to that found in the only other structurally characterized metallacyclic CO$_2$-bridged diruthenium complex [{Ru(CO)$_2$}$_2${μ-κ^2-C(O)O}{μ-(*i*PrO)$_2$PN(Et)P(O*i*Pr)$_2$}$_2$],[7a] but the Ru2-O2 bond (2.105(5) Å) of **1** is shorter. The C–O bond length of 1.248(10) Å for the noncoordinated carboxyl oxygen atom (O3), that is, the carbonyl oxygen, is shorter than the other C–O bond (C1–O2 1.320(10) Å) in the CO$_2$ ligand. The Ru1-P2 bond (2.402(2) Å) is the longest of the Ru–P bonds in **1**. The O···O separation of 2.758(8) Å between the hydroxo oxygen (O1)and neighboring non-coordinated carbonyl oxygen (O3) atoms indicates the presence of intermolecular hydrogen bonding.

The IR spectrum of **1** shows two ν(CO) bands at 1920 and 1906 cm^{-1}, together with a broad ν(OH) band near 3390 cm^{-1} which arises from the intermolecular hydrogen-bonding. The ^{31}P{^{1}H} NMR spectrum displays four non-equivalent signals at $\delta = 16.1$, 3.81, 0.21, and −18.4 ppm with multiple mutual couplings. In the ^{1}H NMR spectrum, a diagnostically split signal for the bridging hydrido atom which couples with these phosphorus atoms is observed at $\delta = -11.2$ ppm, in addition to a broad signal ($\delta = -0.61$ ppm) for the hydroxo proton. The latter signal diminished on addition of D$_2$O to the NMR sample. In the ^{13}C{^{1}H} NMR spectrum, the bridging CO$_2$ carbon atom resonated at $\delta = 205$ ppm and shows a large *trans*-phosphine coupling, in addition the spectrum also shows two lowfield resonances for the CO ligands. The FAB-MS spectrum supported the formulation of **1**.

While a similar reaction of the isomeric *trans,trans,trans*-[RuCl$_2$(CO)$_2$(PMe$_3$)$_2$] failed to afford **1**, the use of another related ruthenium complex *trans*-[RuCl$_2$(CO)(PMe$_3$)$_3$] gave rise to **1** in a low yield (4%). Thus, employment of *cis,cis,trans*-[RuCl$_2$(CO)$_2$(PMe$_3$)$_2$] was essential for the successful isolation of the triply bridged diruthenium complex **1**, as the use of *cis,cis,trans*-stereoisomers with other phosphines PR$_3$ did not yield similar dinuclear complexes with the exception of R$_3$ = Me$_2$Ph, where formation of the corresponding dinuclear compound was detected in the solution, but it could not be isolated owing to its high instability. Use of a large excess of highly concentrated aqueous KOH solution was also a crucial factor in the successful formation of **1**. A reasonable mechanistic rationalization for the formation of **1** would involve initial generation of the five-coordinated hydroxycarbonyl species [RuCl{C(O)OH}(CO)(PMe$_3$)$_2$], followed by its intermolecular unsymmetrical association as a dimer through two hydroxycarbonyl groups. Decarboxylation of one group and deprotonation of the other group would afford the μ-H and asymmetric μ-κ^2-*O,C*-CO$_2$ bridges, respectively.[10] A similar formation mechanism has been suggested by Lavigne and co-workers in the reaction of [RuCl$_2$(CO)$_3$(thf)] with Et$_4$NOH to form polymeric carbonyl- and chloride-bridged diruthenium polyanions.[5b]

To examine the chemistry of the reactive sites in **1**, its reactivities toward neutral monodentate donor molecules were tested (Scheme 2). Treatment of **1** with excess *t*BuNC or CO in benzene gave rise to [{Ru$_2$(CO)$_2$(PMe$_3$)$_3$(L)}(μ-H)(μ-OH){μ-κ^2-C(O)O}] (L = *t*BuNC (**2a**) and CO (**2b**)), respectively. Both ^{31}P{^{1}H} NMR spectra of **2a** and **2b** show a disappearance of the highest-field signal ($\delta = -18.4$ ppm) of



Scheme 2. Reactions of **1** with various reagents. a) *t*BuNC or CO, b) benzoic acid or *p*-toluic acid, c) I_2.

the four observed for **1**, and in the ^1H NMR spectrum the resonances of the hydrido ligands were detected as doublet of doublet of doublet signals ($\delta = -11.0$ (**2a**), -10.9 ppm (**2b**)). Furthermore, the IR spectra of **2a** and **2b** show additional strong bands arising from ν(CN) at 2148 and ν(CO) at 2018 cm^{-1}.

Yellow crystals of **2a** were obtained and the molecular structure was determined by single-crystal X-ray structural analysis.[11] Complex **2a** has a similar framework to **1**, despite the use of excess *t*BuNC only the PMe_3 ligand situated *trans* to the bridging CO_2 carbon atom is selectively displaced by a *t*BuNC ligand. In contrast to this result, some hydrido-bridged dinuclear complexes have been reported to react with *t*BuNC to give μ-formimidoyl derivatives.[12] Moreover, it is noted that treatment of **1** with CO gas also resulted in displacement of the PMe_3 ligand at the same position (based on the $^{31}P\{^1H\}$ and ^1H NMR spectra) to give **2b**.

The reaction of **1** with benzoic acid as a protic acid was carried out to give $[\{Ru(CO)(PMe_3)_2\}_2(\mu\text{-}H)(\mu\text{-}\kappa^2\text{-}O_2CPh)\{\mu\text{-}\kappa^2\text{-}C(O)O\}]$ (**3a**) in 49 % yield (Scheme 2). The $^{31}P\{^1H\}$ NMR spectrum shows similar signal pattern arising from four non-equivalent phosphorus atoms, indicating the framework of **3a** is analogous to that of **1**. In the ^1H NMR spectrum, the aryl protons, the methyl protons of the PMe_3 groups, and the hydride are detected but there is no signal from the hydroxo proton. The *p*-toluic derivative $[\{Ru(CO)(PMe_3)_2\}_2(\mu\text{-}H)(\mu\text{-}\kappa^2\text{-}O_2CC_6H_4Me)\{\mu\text{-}\kappa^2\text{-}C(O)O\}]$ (**3b**) was also isolated in 77 % yield from reaction with *p*-toluic acid under the same conditions, and the molecular structure of the monohydrate of **3b** was revealed by X-ray crystallographic analysis.[13] Complex **3b** consists of two $[Ru(CO)(PMe_3)_2]$ units connected by hydrido, κ^2-*O*,*C*-CO_2, and a new arylcarboxylato bridge. During this reaction, the configuration of the dinuclear structure remains intact. The bond lengths of **3b** are comparable to those of **1**, except for the elongation of the Ru–Ru bond to 3.0160(5) Å, which is still within the range of typical Ru–Ru single bonds.[8] FAB-MS and elemental analyses confirm the formulation.

When **1** was treated with $HBAr^F_4$ ($Ar^F_4 = 3{,}5\text{-}C_6H_3(CF_3)_2$) at −78 °C, four new signals were detected in the $^{31}P\{^1H\}$ NMR spectrum, these are at $\delta = 17.1$, 5.36–4.39 ppm (overlap of two signals), and $\delta = -14.0$ ppm, and the ^1H NMR spectrum showed the multiplet hydride signal at $\delta = -11.4$ ppm along with methyl protons of PMe_3 and aryl protons of BAr^F_4. The ESI-MS spectrum exhibited a parent peak at *m*/*z* 626 ascribed to $[\mathbf{1}+H]^+$. Although complete purification of this product was unsuccessful due to its low stability in solution, these data probably indicate generation of an H_2O-bridged species $[\{Ru(CO)(PMe_3)_2\}_2(\mu\text{-}H)(\mu\text{-}OH_2)\{\mu\text{-}\kappa^2\text{-}C(O)O\}]BAr^F_4$ (**3′**), which would be the intermediate leading to **3a** and **3b**. Unfortunately, the μ-OH_2 protons were not detectable even at −60 °C in the ^1H NMR spectrum.

Treatment of **1** with I_2 at room temperature for 23 h afforded $[\{Ru(CO)(PMe_3)_2\}_2(\mu\text{-}H)(\mu\text{-}I)_2]I$ (**4**) in 66 % yield (Scheme 2). The $^{31}P\{^1H\}$ NMR spectrum exhibited only two multiplet signals, indicating a higher symmetry in **4** than **1**. A triplet of triplet signal of the hydrido ligand of **4** supports the presence of two pairs of PMe_3 ligands. Cooling the acetone solution of **4** afforded yellow crystals suitable for X-ray diffraction analysis.

The crystal structure of **4** (Figure 2)[14] which has a crystallographic two-fold axis verified the presence of two $\{Ru(CO)(PMe_3)_2\}$ units symmetrically bridged by two iodide and one hydrido ligands, accompanied by a counterion I^-. The hydrido atom was located in a difference electron density map, but unfortunately its position was not refined, however its presence was confirmed by the ^1H NMR spectrum (see Supporting Information). The Ru1–Ru1* distance of 2.8955(8) Å,which clearly indicates the presence of a metal–metal single bond,[8] is slightly longer than that of similar complex $[\{Ru(CO)(PPh_3)_2\}_2(\mu\text{-}H)(\mu\text{-}Cl)_2]BF_4$ (2.842(1) Å).[15] The cationic structure of $[\{Ru(CO)(PMe_3)_2\}_2(\mu\text{-}H)(\mu\text{-}I)_2]^+$ was also confirmed by the observation of the parent ion $[M-1]^+$ at *m*/*z* 817 in the positive ESI mass spectrum (acetone).

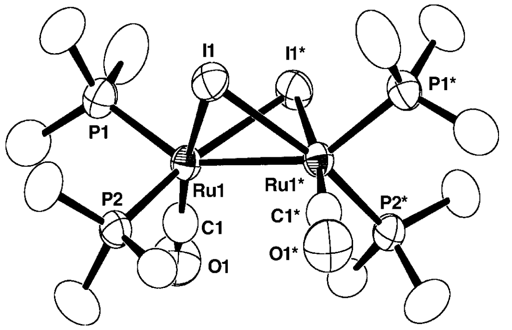


Figure 2. ORTEP diagram of complex **4** (thermal ellipsoids set at 50% probability). Selected bond lengths [Å]: Ru1-Ru1* 2.8955(8), Ru1-I1 2.7644(5), Ru1*-I1 2.7817(5), Ru1-P1 2.338(2), Ru1-P2 2.293(2).

Interestingly, when **1** was treated with molecular iodine I_2 in dilute acetone solutions for only 30 min, the intermediate $[\{Ru(CO)(PMe_3)_2\}_2(\mu\text{-}H)(\mu\text{-}OH)(\mu\text{-}I)]I$ (**4′**) was detected with a small amount of **4** on the basis of NMR spectroscopy and ESI mass spectra. This result indicates that the mechanism of formation in the initial I_2 oxidation involves the release of CO_2 in **1** and coordination of I^- to the resulting vacant site generating the intermediate **4′**. Further reaction of the bridging OH group of **4′** with another mole of I_2 would proceed to produce **4**. However, isolation of **4′** failed owing to its facile conversion into **4** during the separation procedures.

In conclusion, we have isolated the novel dinuclear species **1** that is bridged by hydrido, hydroxo, and κ^2-*O*,*C*-CO_2, and which has multiple reactive sites. With *t*BuNC and CO **1** undergoes simple ligand replacement of one PMe_3 molecule to give **2a** and **2b**, respectively. The reactions with protic acids (benzoic and *p*-toluic acid) afford arylcarboxylato bridging complexes (**3a** and **3b**) in reactions that proceed through the selective protonation on the hydroxo ligand. A similar result was also observed in the reaction with $HBAr^F{}_4$. On the other hand, for the reaction of **1** with I_2, oxidative addition occurred to afford the decarboxylated complex **4** via the intermediate **4′**. Further investigations on other chemical reactivities of **1** are underway.

Experimental Section

Details on the syntheses as well as full spectroscopic characterization of **1**–**4** are given in the Supporting Information.

1: An aqueous 10 M KOH solution (76 mL, 760 mmol) was added to an ethanol solution (230 mL) of *cis*,*cis*,*trans*-$[RuCl_2(CO)_2(PMe_3)_2]$ (2.9 g, 7.6 mmol). The mixture was heated under reflux for 24 h and the resulting red brown solution was concentrated to one-third of its original volume to produce red brown oil. The supernatant colorless solution was then removed and the oily product was dried in vacuo. The residue was extracted with benzene and addition of hexane precipitated a yellow brown powder of **1** (1.4 g, 59 %). ^{1}H NMR (C_6D_6, 400 MHz): $\delta = 1.51$ (d, $J = 9.4$ Hz, PMe_3), 1.30 (d, $J = 9.9$ Hz, PMe_3), 1.26 (d, $J = 9.8$ Hz, PMe_3), 1.15 (d, $J = 6.0$ Hz, PMe_3), −0.61 (s, μ-OH), −11.2 ppm (m, μ-H); ^{31}P{^{1}H} NMR (C_6D_6; 162 MHz): $\delta =$ 16.1 (d, $J = 26$ Hz, PMe_3), 3.81 (dd, $J = 11, 41$ Hz, PMe_3), 0.21 (dd, $J =$ 26, 41 Hz, PMe_3), −18.4 ppm (d, $J = 11$ Hz, PMe_3); ^{13}C{^{1}H} NMR (C_6D_6; 100 MHz): $\delta = 207$ (dd, $J = 7.9$, 16 Hz, CO), 205 (br, d, $J =$ 102 Hz, CO_2), 204 (t, $J = 14$ Hz, CO), 20.3 (d, $J = 31$ Hz, PMe_3), 19.4 (d, $J = 27$ Hz, PMe_3), 18.9 (d, $J = 16$ Hz, PMe_3), 15.8 ppm (d, $J =$ 27 Hz, PMe_3). IR (KBr, pellet): $\tilde{\nu} = \nu$(OH) 3390 (br); ν(C≡O) 1920 (s), 1906 (s); 951 (m) cm^{-1}. FAB-MS (*m*/*z*): 626 ($[M+1]^+$), 581 ($[M-CO_2-1]^+$), 505 ($[M-CO_2-PMe_3-1]^+$). Elemental analysis (%) calcd for $C_{15}H_{38}O_5P_4Ru_2$: C 28.97, H 6.60; found: C 28.85, H 6.13.

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[6] a) Crystal data for **1**: $C_{15}H_{37}O_5P_4Ru_2$ ($M_r = 623.49$); monoclinic, $P2_1/n$ (No. 14), $a = 11.663(5)$, $b = 12.589(3)$, $c = 18.762(2)$ Å, $\beta = 103.024(2)°$, $V = 2683(1)$ Å^3, $Z = 4$, $\rho_{calcd} = 1.543$ g cm^{-3}, R (Rw) = 0.133 (0.137), GOF = 1.19 for 235 variables and 5947 unique reflections (all data).[6b] For crystallographic details, see Supporting Information; b) CCDC-268894 to 268897 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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[10] A probable mechanistic scheme is given in the Supporting Information.

[11] Crystal data for **2a**: $C_{17}H_{37}NO_5P_3Ru_2$ ($M_r = 630.54$); cubic, $Pa\bar{3}$ (No. 205), $a = 26.0919(3)$ Å, $V = 17763.0(4)$ Å^3, $Z = 24$, $\rho_{calcd} =$ 1.415 g cm^{-3}, R (Rw) = 0.073 (0.096), GOF = 1.90 for 253 variables and 6787 unique reflections (all data).[6b] For ORTEP diagram and crystallographic details, see Supporting Information.

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[13] Crystal data for **3b**·H_2O: $C_{23}H_{35}O_7P_4Ru_2$ ($M_r = 749.56$); monoclinic, $P2_1/c$ (No. 14), $a = 17.586(2)$, $b = 11.408(2)$, $c =$ 17.5779(3) Å, $\beta = 103.0707(4)°$, $V = 3435.0(8)$ Å^3, $Z = 4$, $\rho_{calcd} =$ 1.449 g cm^{-3}, R (Rw) = 0.075 (0.101), GOF = 0.91 for 337 variables and 7523 unique reflections (all data).[6b] For ORTEP diagram and crystallographic details, see Supporting Information.

[14] Crystal data for **4**: $C_{14}H_{37}O_2P_4Ru_2I_3$ ($M_r = 944.19$); monoclinic, $C2/c$ (No. 15), $a = 14.661(1)$, $b = 18.278(2)$, $c = 14.1796(4)$ Å, $\beta = 108.356(1)°$, $V = 3606.3(5)$ Å^3, $Z = 4$, $\rho_{calcd} = 1.739\ g\,cm^{-3}$, R (Rw) = 0.061 (0.089), GOF = 1.32 for 114 variables and 4045 unique reflections (all data).[6b] For crystallographic details, see Supporting Information.

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