Agostic Interaction in Formally Five-coordinate Hydridobis[1,3-bis(diphenylphosphino)propane]ruthenium(II) Ion

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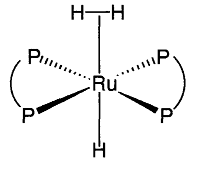
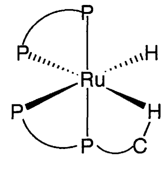
The molecular structures of $[RuH(dppp)_2]^+$ (**1**) and $[RuH\{OC(CH_3)_2\}(dppe)_2]^+$ (**2**) ions in the PF_6^- salts were determined by the X-ray crystallography. **1** involves the agostic interaction between the *ortho* C–H bond of a phenyl group of the dppp ligands and the formally unsaturated Ru center, and takes the *cis* geometry, where the terminal hydride and the agostic C–H moiety occupy the adjacent sites to each other. **2** adopts a typical octahedral six-coordinate structure with a coordinating acetone molecule *trans* to the hydride.

We have investigated the solution behavior and reactivity of the formally five-coordinate complexes $[RuH(P\text{–}P)_2]PF_6$ (P–P = diphosphine) with various diphosphine ligands.[1,2] These complexes react readily with H_2 gas in solution to give rise to the molecular hydrogen complexes $[RuH(\eta^2\text{-}H_2)(P\text{–}P)_2]^+$,[2–4] one of the representatives of so called "σ complexes."[5] Agostic interaction,[5,6] the intramolecular coordination of a C–H moiety in a ligand to unsaturated metal center with its σ-bond electron pair, provides another class of σ complexes. The occurrence of agostic interaction was demonstrated for several $[RuH(P\text{–}P)_2]PF_6$ through ^1H NMR and hydrogen isotope exchange studies.[1] In spite of great interest in the structure of this series of complexes, however, structurally characterized $[RuH(P\text{–}P)_2]^+$ type complexes have been seriously limited in number, and no direct evidence for the agostic interaction in the solid state has been obtained. In contrast, a considerable number of metal complexes of the type $[M(CO)(P\text{–}P)_2]^{n+}$ has been revealed to include the agostic interaction by X-ray studies.[7]



η^2-H_2 complex



Agostic interaction

First, we determined the molecular structure of $[RuH(dppp)_2]^+$ ion (**1**)[8,9] in its PF_6^- salt by X-ray structure analysis. $[RuH(dppp)_2]PF_6$ (**1PF$_6$**) was prepared by a reaction of dppp with $[RuH(NH_2NMe_2)_3(cod)]PF_6$[9] (2:1 molar ratio) in acetone under argon at room temperature. The slow diffusion of hexane into the concentrated deep dark red reaction mixture for several days afforded **1PF$_6$** as blackish brown crystals of good quality for diffraction study.[10]

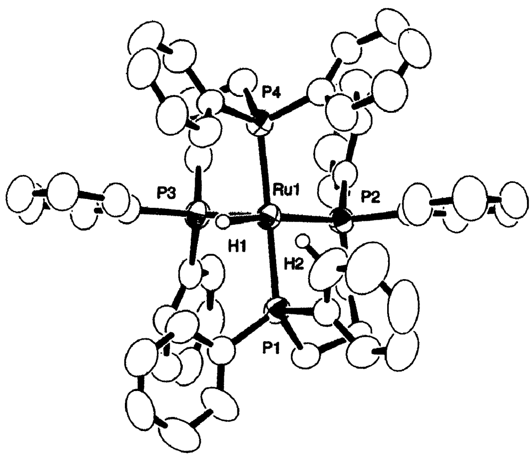


Figure 1. An ORTEP view of $[RuH(dppp)_2]^+$ ion (**1**) in the PF_6^- salt. Selected bond lengths or atomic distances (Å) and angles (°): Ru1–H1 = 1.65, Ru1--H2 = 2.75, Ru1--C2 = 3.282(8), Ru1–P1 = 2.348(2), Ru1–P2 = 2.432(2), Ru1–P3 = 2.215(2), Ru1–P4 = 2.338(2), P1–Ru1–P2 = 90.57(5), P3–Ru1–P4 = 89.24(6), P2–Ru1–H1 = 172.2, P3–Ru1–H1 = 85.2, P2–Ru1–P3 = 99.06(5), Ru1–P1–C1 = 102.1(2).

An ORTEP view of the complex ion **1** is given in Figure 1 together with representative bond lengths, atomic distances, and bond angles.[10] Figure 1 shows that **1** involves the agostic interaction between the Ru center and the *ortho* C–H bond in a phenyl group of one of the dppp ligands with the Ru1--H2 and Ru1--C2 distances at 2.75 and 3.282(8) Å, respectively. Due to the attractive interaction between the Ru and the C–H moiety, an evident bond angle deformation was brought about around the P1 atom (Ru1–P1–C1 = 102.1(2)°). Thus, the Ru center is regarded to take a distorted octahedral geometry, where the sixth site is occupied by the agostic C–H group. The position of the hydride ligand was located (not refined) unequivocally in the difference Fourier map (Ru1–H1 = 1.65 Å) at the *cis* position with regard to the agostic site. To the best of our knowledge, this is the first example of establishing the agostic C–H group in the crystalline state for $[RuH(P\text{–}P)_2]^+$ complexes.

It was indicated by the ^1H NMR measurements that for $[RuH(P\text{–}P)_2]^+$ complexes (P–P = dppb,[8] (*R*,*R*)-diop[8]) the agostic interaction occurs with the methylene C–H group of a diphosphine at lower temperatures, not with the *ortho* C–H moiety of a phenyl group.[1] No clear ^1H NMR evidence for the agostic interaction has, however, been obtained for the dppp complex **1**.

In **1PF$_6$**, the four Ru–P bond lengths are evidently affected by the corresponding *trans* ligands. The Ru1–P2 bond *trans* to the hydride is the longest (2.432(2) Å), reflecting the strong *trans* influence of H^-, while the other two, *trans* to a P atom, are at intermediate lengths (Ru1–P1 = 2.348(2), Ru1–P4 = 2.338(2) Å). The significantly short Ru1–P3 distance (2.215(2) Å) suggests that the *trans* influence of agostic interaction of a C–H group is quite weak.

The structure of **1** is significantly different from that of dcpe analog, $[RuH(dcpe)_2]BPh_4$.[11] The latter has the true square-

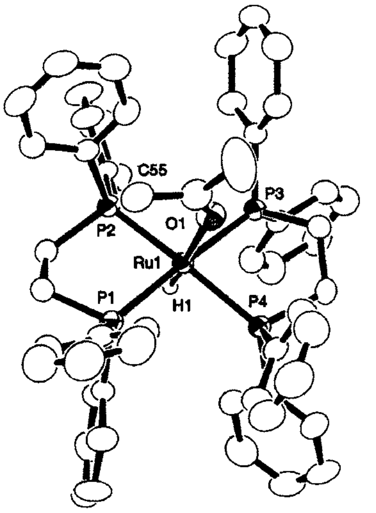


Figure 2. An ORTEP view of $[RuH\{OC(CH_3)_2\}(dppe)_2]^+$ ion (**2**) in the PF_6^- salt. Selected bond lengths (Å) and angles (°): Ru1–H1 = 1.45, Ru1–P1 = 2.348(1), Ru1–P2 = 2.319, Ru1–P3 = 2.344(1), Ru1–P4 = 2.382(1), Ru1–O1 = 2.286(3), P1–Ru1–P2 = 83.87(4), P3–Ru1–P4 = 81.47(4), O1–Ru1–H1 = 171.5, P2–Ru1–H1 = 79.4, P1–Ru1–O1 = 101.20(8), P2–Ru1–O1 = 99.10(8), P3–Ru1–O1 = 83.25(8), P4–Ru1–O1 = 89.19(8).

based pyramidal geometry, in which the hydride occupies the apical site, and no agostic interaction with a C–H moiety is involved.[11] The complex of *R*,*R*'-Me-DuPHOS was also reported to adopt a similar square-based pyramidal structure.[12]

These facts prompted us to examine the structure of $[RuH(dppe)_2]^+$ ion. The complex obtained by a reaction of dppe with $[RuH(NH_2NMe_2)_3(cod)]PF_6$ in acetone was markedly different in color from **1PF₆** and other analogs. **1PF₆** and others are in common very deeply colored (deep brown to almost black), while the dppe complex obtained here is pale beige. The X-ray structure determination[13] revealed that the dppe complex adopts an octahedral structure with an acetone molecule coordinating to the Ru center with the oxygen atom. Shown in Figure 2 is an ORTEP view of $[RuH\{OC(CH_3)_2\}(dppe)_2]^+$ ion (**2**), where no agostic interaction is possible. The acetone occupies the coordination site *trans* to the terminal hydride.

On the basis of the results described above or reported in literature,[11,12] it is supposed that diphosphine ligands which form five-membered chelate rings such as dppe and dcpe afford preferentially the $[RuH(P\text{–}P)_2]^+$ unit of a square-based pyramidal geometry with the hydride at the apex. Although small molecules can easily be coordinated to the vacant site *trans* to the hydride, the agostic interaction with a C–H bond of the phosphine ligands seems to be of little importance in these complexes. In contrast, the dppp complex **1PF₆** involves the agostic interaction with an *ortho* C–H bond of the diphosphine. The differences in the solid state structures might be ascribed to the larger bite angle of dppp chelates (89.2—90.6° for dppp, 81.5—83.9° for dppe). In order to obtain further insight into the effects of the bite angles of diphosphine chelates, the steric congestion around P atoms, and the flexibility of chelate backbones on the occurrence of agostic interaction, the structure determinations of other $[RuH(P\text{–}P)_2]^+$ type complexes are now in progress.

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8 Abbreviations of diphosphines: dppp = 1,3-bis(diphenylphosphino)propane, dppe = 1,2-bis(diphenylphosphino)ethane, dppb = 1,4-bis(diphenylphosphino)butane, diop = 2,2-dimethyl-4,5-bis(diphenylphosphinomethyl)-1,3-dioxolane, dcpe = 1,2-bis(dicyclohexylphosphino)ethane, *R*,*R*'-Me-DuPHOS = 1,2-bis[(2*R*,5*R*)-2,5-dimethylphospholano]benzene.

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10 Crystallographic data for **1PF₆•(CH₃)₂CO**: $C_{57}H_{59}F_6OP_5Ru$, M = 1130.02, crystal dimensions 0.3 × 0.5 × 0.8 mm, monoclinic, space group $P2_1/c$ (#14), deep brown crystal, a = 13.472(5) Å, b = 15.460(4) Å, c = 26.455(4) Å, β = 92.51(2)°, V = 5504(2) Å^3, Z = 4, D_{calcd} = 1.363 g/cm^3, F(000) = 2328.00, μ(Mo Kα) = 4.89 cm^{-1}, R = 0.053, R_w = 0.048 for 7080 reflections with $I > 3\sigma(I)$, GOF = 2.70.

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13 Crystallographic data for **2PF₆**: $C_{55}H_{55}F_6OP_5Ru$, M = 1101.02, crystal dimensions 0.80 × 0.25 × 0.20 mm, monoclinic, space group $P2_1/c$ (#14), pale beige crystal, a = 12.132(3) Å, b = 22.272(4) Å, c = 19.502(2) Å, β = 107.10(1)°, V = 5036(1) Å^3, Z = 4, D_{calcd} = 1.363 g/cm^3, F(000) = 2264.00, μ(Mo Kα) = 5.32 cm^{-1}, R = 0.045, R_w = 0.029 for 6722 reflections with $I > 3\sigma(I)$, GOF = 1.93.