Novel Dihydridoruthenium(II) Complexes with Chelating Diphosphine Ligands, $RuH_2(CO)(diphosphine)(PPh_3)$ (diphosphine = dppe, dppp, dppb, and dppf)

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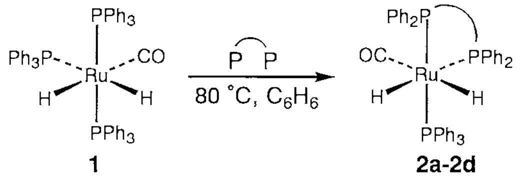
Ligand exchange of $[RuH_2(CO)(PPh_3)_3]$ with some diphosphine ligands affords a series of $[RuH_2(CO)(diphosphine)(PPh_3)]$ (diphosphine = dppe, dppp, dppb, and dppf). The X-ray structure analysis of $[RuH_2(CO)(dppp)(PPh_3)]$ reveals its distorted octahedral structure. The diphosphine ligand complexes react with styrene to generate ruthenium(0) species, which successively proceed with the intramolecular C-H addition to give the cyclometallated aryl(hydrido)ruthenium(II) species.

Hydrogen transfer from a dihydridoruthenium(II) complex $[RuH_2(CO)(PPh_3)_3]$ (**1**) to an olefin is a convenient way to generate a nascent ruthenium(0) species.[1] Successive C-H bond addition of a substrate to the ruthenium(0) center is one of the key-steps of the C-H/olefin coupling reactions.[2] In this regard, our recent study has demonstrated that *trans*-addition of a C-H bond of certain aromatic bases occurs on the active ruthenium(0) species; the aryl and the hydride ligands are located mutually *trans* in the resulting aryl(hydrido)ruthenium(II) complex.[3] This unusual *trans*-addition arises from quick realignment of the ligands on the ruthenium(II) center after ordinary *cis*-addition. The realignment is considered to be caused by the movement of the two PPh_3 ligands from *cis* to *trans* because of the steric repulsion between them.[4]

If a chelating diphosphine ligand is coordinated to the ruthenium(0) center, two phosphorus atoms remain on the *cis* coordination sites. Such a constraint on the coordination geometry must keep the aryl(hydrido)ruthenium(II) species from the realignment of the ligands. From this point of view, here we report preparation and reaction of a series of dihydridoruthenium(II) complexes $[RuH_2(CO)(diphosphine)(PPh_3)]$ as precursors of ruthenium(0) species with chelating diphosphine ligands, which are immediately altered to the corresponding cyclometallated aryl(hydrido)ruthenium(II) species. The X-ray structure of the dppp complex $[RuH_2(CO)(dppp)(PPh_3)]$ is also discussed.

The dihydridoruthenium(II) complexes with chelating diphosphines such as 1,2-bis(diphenylphosphino)ethane (dppe for **2a**), 1,3-bis(diphenylphosphino)propane (dppp for **2b**), 1,4-bis(diphenylphosphino)butane (dppb for **2c**), and 1,1'-bis(diphenylphosphino)ferrocene (dppf for **2d**) were prepared by means of ligand exchange between **1** and the equimolar amount of the diphosphine ligands at 80 °C in benzene. The yields varied with the diphosphine ligands.[5] When dppe was used for the preparation of **2a**, a considerable amount of a five-coordinate ruthenium(0) complex $[Ru(CO)(dppe)_2]$ was recognized as a byproduct in the reaction mixture. The dppb complex **2c** was so soluble in common organic solvent that the isolated yield of **2c** was low. Any experiment aimed for the ligand exchange of **1** with (*R*)-binap ((*R*)-2,2'-bis(diphenylphosphino)-1,1'-binaphthyl) resulted in failure at all.



All **2a–2d** showed three ^{31}P- and two hydrido proton-signals in their NMR spectra.[6] In each complex, two of the three ^{31}P-signals were coupled with a remarkably large J_{PP} value (229–242 Hz) and, in addition, one of the two hydrido signals had a large J_{HP} value (71–74 Hz). These spectroscopic data are consistent with the octahedral six-coordinate structure where the two of the three PPh_3 ligands of **1** are replaced with the diphosphine ligand. The ^{31}P-signals of the dppe complex **2a** were shifted notably to the lower field than those of **2b–2d** (δ 79.4–57.9 for **2a** while 57.8–26.7 for the others). This may indicate that the octahedral structure of **2a** is more distorted than those of the other three complexes.

The X-ray structure analysis of the dppp complex **2b** confirms the six-coordinate octahedral structure where the chelating dppp and the PPh_3 ligands coordinate on three meridional sites and one of the two hydrido ligands is situated *trans* to the CO ligand.[7] The arrangement of the ligands in **2b** is distorted because of the steric repulsion between the dppp and PPh_3 ligands (Figure 1). The P1–Ru1–P2 angle for the chelating dppp is 92.14(9)°, much closer to the ideal 90° than the other P2–Ru1–P3 value (102.11(9)°), suggesting that the chelation ties two phosphorus

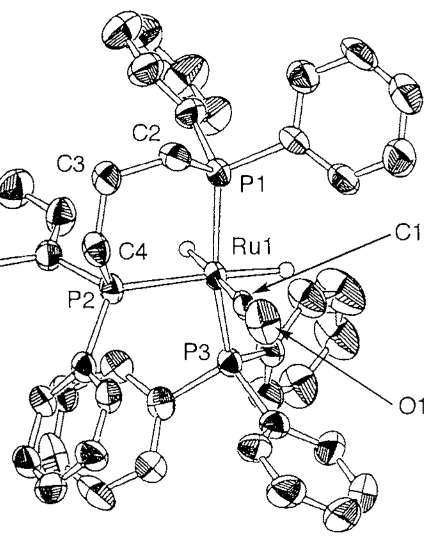
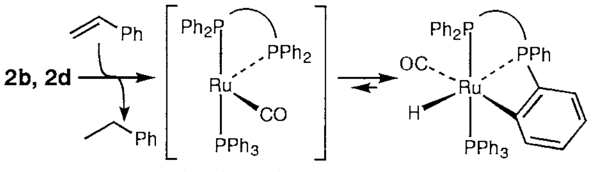


Figure 1. The molecular structure of **2b**. Hydrogen atoms are omitted for clarity except for the hydrides. Selected bond lengths (Å) and angles (°): Ru1–P1, 2.309(3); Ru1–P2, 2.363(2); Ru1–P3, 2.326(3); Ru1–C1, 1.93(1); O1–C1, 1.11(1); P1–Ru1–P2, 92.14(9); P1–Ru1–P3, 160.67(9); P2–Ru1–P3, 102.11(9); P1–Ru1–C1, 91.9(3); P2–Ru1–C1, 90.7(3); P3–Ru1–C1, 100.8(3); Ru1–C1–O1, 176.5(9).

atoms compactly. The P1–Ru1–P3 angle between the *trans*-phosphorus atoms is 160.67(9)° and significantly smaller than 180°. As a result of the strong trans influence of the hydride, the Ru1–P2 length (2.363(2) Å) is longer than the other Ru–P lengths. The six-membered dppp chelate is revealed to be a chair conformation. According to the chair conformation of the chelate ring, the dppp chelate is almost symmetrical about a mirror plane through the ruthenium atom and the C3 atom.

In order to investigate the reactivity of **2a**–**2d** to olefins generating a nascent ruthenium(0) species, some preliminary experiments were examined in sealed NMR tubes. When **2b** reacted with styrene in C_6D_6 at 110 °C, all the starting **2b** was converted into a single product within 3 h. In the hydride region of the ^{1}H-NMR spectrum of the reaction mixture, the new product **3b** showed a signal coupled with three inequivalent phosphorus atoms.[8] One relatively large J_{HP} value and the other two small ones indicated the hydrido ligand coordinated *trans* to one phosphorus atom and *cis* to the other two. The large coupling constant (J_{PP} = 273.4 Hz) between the two phosphorus atoms observed at the lower field in the ^{31}P-NMR spectra indicated that they occupied mutually *trans* coordination sites. One ^{31}P-signal split with two small coupling constants was significantly shifted up-field. These NMR spectroscopic data of **3b** are consistent with the cyclometallated structure shown in the following scheme. The dppf complex **2d** also reacted with styrene to afford a similar cyclometallated complex **3d** although **2d** was less reactive to styrene than **2b**. The complexes **3b** and **3d** are apparently derived from the coordinatively unsaturated ruthenium(0) species [Ru(CO)(diphosphine)(PPh_3)] via intramolecular C-H addition of the phenyl group. Roper[9] reported that another coordinatively unsaturated [Ru(CO)(PPh_3)$_3$] allowed comparable intramolecular C-H addition to give [RuH($C_6H_4PPh_2$)(CO)(PPh_3)$_2$]. Two other examples of the intramolecular C-H addition were reported by Wilkinson[10] and Pez,[11] giving an ethylene-coordinated [RuH($C_6H_4PPh_2$)(C_2H_4)(PPh_3)$_2$] and an anionic [RuH_2($C_6H_4PPh_2$)(PPh_3)$_2$]$^-$, respectively. Our reaction is classified as the same type as these ones.



a ruthenium(0) species **3b, 3d**

Although the reason has not been clarified so far, the reactivity of the dihydridoruthenium(II) complexes to styrene depends on the chelating diphosphine ligands. The complexes **2a** and **2c** were far less reactive than **2b**. Only 4% of the starting **2c**, for example, was consumed after 72 h when it was treated with styrene. The NMR spectra of the reaction mixture showed the production of several species that were too complicated to be identified and assigned.

Unfortunately, the ruthenium(0) species derived from the dppp complex **2b** failed in C-H addition of *N*-benzylideneaniline at 70 °C. The reaction between **2b** and styrene proceeded slowly; about half of the starting **2b** was consumed after 12 h (49% remained). The resulting ruthenium(0) species did not activate the C-H bond of the *N*-base but the C-H bond of the coordinating phosphine ligand to give **3b**. The relative yield of **3b** was 33% (65% of the reacted **2b**) based on the NMR spectra. Consequently, when **2b** was applied to catalytic C-H/olefin coupling between acetophenone and styrene,[12] only a trace amount of the coupling product was recognized in the ^{1}H-NMR spectrum of the reaction mixture. These facts indicate that the intramolecular C-H addition on the dppp-coordinating ruthenium(0) center proceeds in preference to the intermolecular C-H addition of the substrates. The cyclometallated **3b** is too stable for the substrate to reverse the intramolecular C-H addition and reproduce the ruthenium(0) center. Further investigation on C-H addition of a variety of organic substrates on the ruthenium(0) species with these chelating phosphines is in progress.

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5 Yield: **2a**, 16%; **2b**, 68%; **2c**, 15%; **2d**, 78%; IR data (KBr): **2a**, 1935 vs ν(C≡O); **2b**, 1935 vs ν(C≡O); **2c**, 1942 vs ν(C≡O); **2d**, 1945 vs ν(C≡O).

6 Selected NMR data ($CDCl_3$): **2a**: ^{1}H δ -7.67 (ddt, *J* = 71.8, 19.8, and 5.1 Hz, RuH), -7.90 (dq, *J* = 23.5 and 5.1 Hz, RuH), ^{31}P{^{1}H} δ 79.4 (d, $^2J_{PP}$ = 234.4 Hz), 64.0 (d, $^2J_{PP}$ = 14.7 Hz), 57.9 (dd, $^2J_{PP}$ = 234.4 and 14.7 Hz); **2b**: ^{1}H δ -6.94 (ddt, *J* = 30.1, 16.1, and 5.9 Hz, RuH), -7.70 (ddt, *J* = 72.6, 20.5, and 5.9 Hz, RuH), ^{31}P{^{1}H} δ 57.2 (dd, $^2J_{PP}$ = 229.5 and 19.5 Hz), 36.5 (dd, $^2J_{PP}$ = 229.5 and 24.4 Hz), 26.7 (dd, $^2J_{PP}$ = 24.4 and 19.5 Hz); **2c**: ^{1}H δ -7.34 (dq, *J* = 25.7 and 5.9 Hz, RuH), -8.45 (ddt, *J* = 71.9, 25.3, and 5.9 Hz, RuH), ^{31}P{^{1}H} δ 57.8 (dd, $^2J_{PP}$ = 231.9 and 17.1 Hz), 51.5 (dd, $^2J_{PP}$ = 231.9 and 17.1 Hz), 34.6 (t, $^2J_{PP}$ = 17.1 Hz); **2d**: ^{1}H δ -6.73 (dq, *J* = 26.0 and 5.5 Hz, RuH), -8.84 (dddd, *J* = 73.4, 32.0, 26.0, and 5.5 Hz, RuH), ^{31}P{^{1}H} δ 57.2 (dd, $^2J_{PP}$ = 241.7 and 13.0 Hz), 49.3 (dd, $^2J_{PP}$ = 241.7 and 21.2 Hz), 39.7 (dd, $^2J_{PP}$ = 21.2 and 13.0 Hz).

7 Crystal data for **2b**: $C_{46}H_{43}OP_3Ru$, *FW* = 805.84, triclinic, space group $P\bar{1}$ (# 2), *a* = 12.658(5), *b* = 15.871(7), *c* = 10.655(3) Å, α = 91.68(3)°, β = 97.81(3)°, γ = 109.73(3)°, *V* = 1989(1) Å^3, *Z* = 2, D_{calc} = 1.345 gcm^{-3}, *F*(000) = 832.00, μ(Mo*K*α) = 5.49 cm^{-1}, *T* = 293 K. Of 9112 unique reflections measured, 4365 ($I > 3\sigma(I)$) were used in refinement with 460 variables. *R* (R_w) = 0.074 (0.089), GOF = 1.87.

8 Selected NMR data ($CDCl_3$): **3b**: ^{1}H δ -6.26 (ddd, $^2J_{HP}$ = 107.8, 23.1, and 17.2 Hz, RuH), ^{31}P{^{1}H} δ 39.8 (dd, $^2J_{PP}$ = 273.4 and 22.0 Hz), 25.8 (dd, $^2J_{PP}$ = 273.4 and 24.1 Hz), 4.12 (dd, $^2J_{PP}$ = 24.1 and 22.0 Hz); **3d**: ^{1}H δ -7.94 (ddd, $^2J_{HP}$ = 108.2, 28.2, and 20.5 Hz, RuH), ^{31}P{^{1}H} δ 38.4 (dd, $^2J_{PP}$ = 307.6 and 9.8 Hz), 36.1 (dd, $^2J_{PP}$ = 307.6 and 19.5 Hz), 1.3 (dd, $^2J_{PP}$ = 19.5 and 9.8 Hz).

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12 Catalytic reaction conditions: **2b** : acetophenone : styrene = 1 : 2.5 : 4.3, in C_6D_6 at 110 °C for 12 h.