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Agostic Interaction and Hydrogen Exchange in Coordinatively Unsaturated Ruthenium Complexes

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Summary: The agostic interaction in coordinatively unsaturated ruthenium complexes [$RuH(P\text{-}P)_2$]PF_6 *(P-P = 1,4-bis(diphenylphosphino)butane (dppb) and 2,3-O-isopropylidene-2,3-dihydroxy-1,4-bis(diphenylphosphino)butane (diop)) was investigated by* ^1H *NMR studies. The hydrogen exchange between the agostic hydrogen in the phosphine ligand and the terminal hydride in each of complexes is reported.*

The coordination of C-H σ bonds to the transition metal centers, i.e. agostic interactions,[1] has attracted considerable attention in recent years.[2] It was proposed that the "agostic" M←H-C bonds are similar in bonding character to η^2-type coordination of a dihydrogen ligand to a transition metal (three-center 2-electron bond). It was demonstrated recently that some coordinatively unsatured 16-electron complexes, which are the precursors of molecular hydrogen complexes, involve agostic interactions.[3,4] Although agostic interactions are considered as intermediates on the way to oxidative additions of hydrocarbons, few cases are known as the examples of actual C-H bond activation, especially of aliphatic C-H groups.

We report herein that, in the formally five-coordinate complexes [RuH(dppb)$_2$]PF_6[5] (1) and [RuH(diop)$_2$]PF_6[6] (2), the interaction between an aliphatic C-H group of the phosphine ligand and the ruthenium center is detected at low temperatures and that the agostic hydrogen exchanges with the terminal hydride (Ru-H) at a considerable rate even at a temperature as low as -60 °C.

The high field region of variable temperature ^1H NMR spectra of 1 is shown in Figure 1. At 0 °C, a single broad peak was observed in the hydride region. In contrast, two distinct peaks emerged at -30 °C, and as the temperature is decreased further, they turn into two sharp resonances with equal intensities. The average chemical shift of the two resonances observed at -30 °C (ca. δ -8.8) is considerably shifted from that of the single peak found at 0 °C (δ -14.7). This may suggest that an intrinsic structural change occurs between 0 and -30 °C. The behavior of complex 1 above 0 °C will be reported separately.[7] The signal at δ -10.6, which reveals the clear couplings with four phosphorus nuclei (dq, J_{PH} = 25, 77 Hz) at -90 °C, is ascribed to the terminal hydride (Ru-H), while the other at δ -7.0, showing no coupling with phosphorus at the same temperature, is assigned to the hydrogen in a C-H moiety interacting with the ruthenium center (agostic interaction). The ^{31}P NMR spectrum of 1 at -90 °C showed the presence of four inequivalent phosphorus nuclei in 1,[8] suggesting a nonsymmetrical structure of the complex. Consistent with this assumption, the ^{13}C NMR spectrum of 1 has eight resonances in the methylene region.[9] These NMR characteristics indicate that the agostic hydrogen occupies the coordination site adjacent to the terminal hydride.

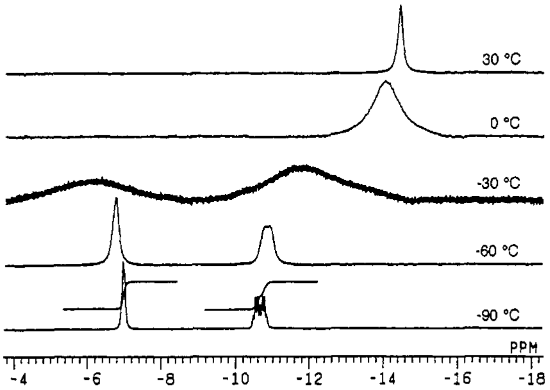

Figure 1. Variable temperature ^1H NMR spectra of [RuH(dppb)$_2$]PF_6 (1) in the high field region at 400 MHz in CD_2Cl_2.

There are two possible C-H hydrogens in a dppb ligand that interact with the ruthenium center in 1; an *o*-hydrogen of the phenyl group and a methylene proton. We assumed that the agostic hydrogen would present spin couplings with some other hydrogens such as the *m*-hydrogen or neighboring methylene protons. Thus, these two possibilities of agostic C-H could be distinguished on the basis of the chemical shift and the number of cross peaks in the ^1H-^1H COSY spectrum of 1. The ^1H-^1H COSY spectrum of 1 at -90 °C (Figure 2) reveals three distinct cross peaks between the agostic C-H resonance (δ -7.0) and the methylene signals of a coordinating dppb (ca. δ 0.8, 1.2, and 3.1). These facts strongly support that the agostic hydrogen should be ascribed to an α-methylene proton of dppb, which shows spin couplings with a geminal hydrogen and two inequivalent adjacent β-methylene hydrogens. It is demonstrated, therefore, that complex 1 involves the coordination of an α-methylene C-H moiety, not an *ortho*

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[8] $^{31}P\{^1H\}$ NMR of 1 at -90 °C [CD_2Cl_2, H_3PO_4 (85%) as external standard]: δ -13.4 (t, 1 P, J = 30 Hz), 37.9 (m, 2 P), 79.1 (t, 1 P, J = 10 Hz). This ^{31}P NMR spectrum is explained as an ABMX pattern.

[9] ^{13}C NMR of 1 in the methylene region at -90 °C [CD_2Cl_2, CD_2Cl_2 (δ 53.7) as internal standard]: δ 22.3 (J_{C-H} = 131 Hz), 23.7 (J_{C-H} = 128 Hz), 24.2 (J_{C-H} = 127 Hz), 27.9 (J_{C-H} = 119 Hz), 30.0 (J_{C-H} = 128 Hz), 36.2 (J_{C-H} = 127 Hz), 40.0 (J_{C-H} = 128 Hz), 46.6 (J_{C-H} = 129 Hz).

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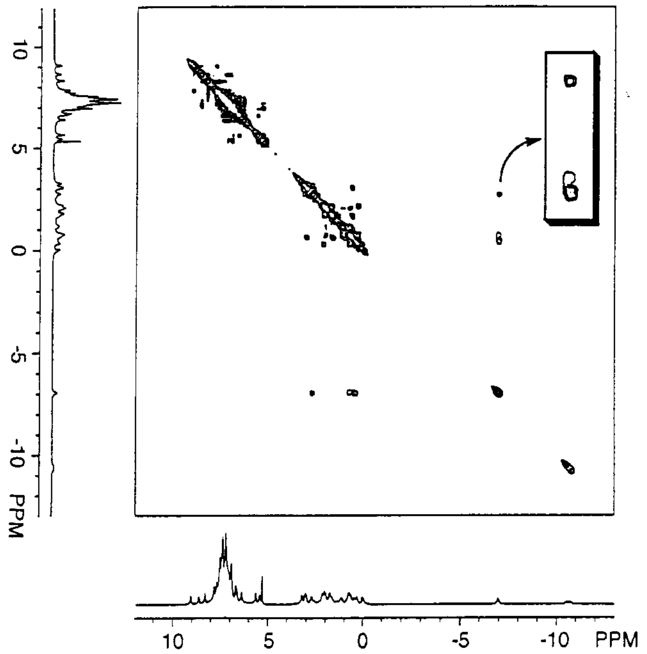

Figure 2. ^1H–^1H COSY spectrum of [RuH(dppb)$_2$]PF$_6$ (1) at −90 °C in CD_2Cl_2 at 400 MHz.

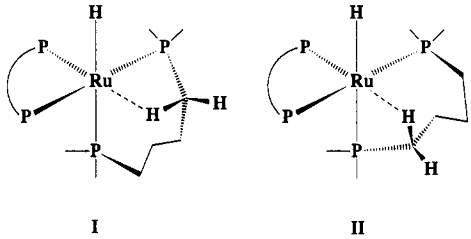

Figure 3. Two possible structures for the complex 1 at −90 °C.

phenyl proton, of dppb at the sixth coordination site of the ruthenium center to give rise to the agostic interaction at low temperatures. The two possible structures **I** and **II** for complex 1 are shown in Figure 3.

Among the ^{13}C NMR signals of the CH_2 groups of 1,[9] the resonance at δ 27.9 showed a smaller value of J_{CH} and was assigned to the signal of the agostic carbon, consistent with the coordination of the methylene C–H group in 1. Although two hydrogens of each methylene group of dppb are inequivalent in either structure **I** or **II**, the proton-coupled ^{13}C NMR spectrum of 1 reveals eight pseudo-triplets, instead of eight dd signals, in the methylene region. This is probably due to the broadening of the signals resulting from the coupling with ^{31}P nuclei and/or the similarity between the two geminal J_{CH} values. It is noteworthy that, in the ^{13}C NMR spectrum of 1 obtained under selective decoupling at the agostic hydrogen (δ −7.0), only the one resonance at δ 27.9 turned into a doublet. This observation confirms the above-mentioned assignment.

All these NMR characteristics were observed for the tetraphenylborate analogue [RuH(dppb)$_2$]BPh$_4$. This fact indicates that the anions, PF_6^- in 1 and BPh_4^- in [RuH(dppb)$_2$]BPh$_4$, have no interaction with the ruthenium center.

Similar ^1H and ^{31}P NMR characteristics were observed for the diop complex 2. As expected, the ^1H–^1H COSY spectrum of 2 showed two cross peaks between the agostic C–H signal (δ −4.1) and the aliphatic signals of a coordinating diop ligand (ca. δ 3.1 and 3.4). In contrast, no agostic interaction could be detected for analogous five-coordinate complexes of dppe,[5a,b,10] dppp,[5a,b,11] dpbp,[12] and binap.[6b,13] In the case of the dppe and dppp complexes, the smaller size of the chelate rings prevents a C–H bond in a methylene unit from coordinating to the ruthenium center, whereas dppb and diop ligands provide a flexible seven-membered chelate upon coordination. As to the complexes of dpbp and binap, the ligands have no aliphatic C–H groups in themselves, although these diphosphines form seven-membered chelate rings.

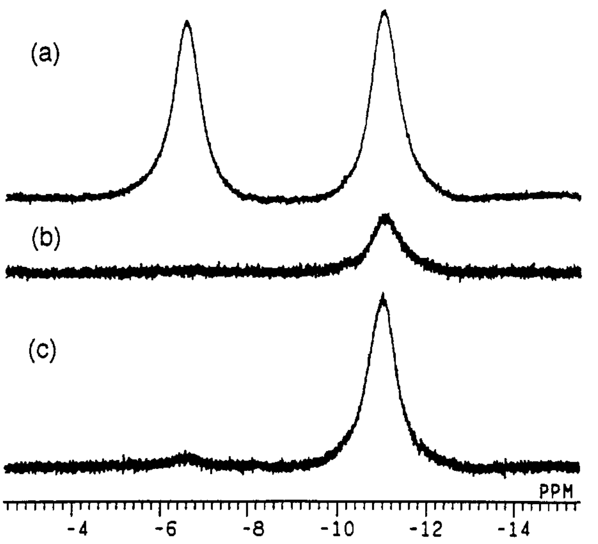

Figure 4. ^1H NMR (400-MHz) spectra of 1 in the high field region at −45 °C in CD_2Cl_2: (a) nonirradiated conditions; (b) irradiated at the agostic hydrogen (ca. δ −7); (c) irradiated at the α-hydrogen in the methylene group (ca. δ 1).

As shown in Figure 1, the Ru–H resonance no longer showed the coupling with phosphorus atoms above −60 °C and coalesced with the signal of the terminal hydride at −30 °C. This suggests a possibility of an exchange between agostic hydrogen and the hydride. Indeed, a spin saturation transfer was observed among the Ru–H, C–H (agostic at δ −7.0), and C–H (methylene at δ ca. 1) groups. At −45 °C, the signal at ca. δ −12 (Ru–H) almost disappeared upon irradiation of the agostic hydrogen at ca. δ −7. Further, the irradiation of the α-hydrogen in the methylene group at ca. δ 1 resulted in the complete disappearance of the signal due to the agostic C–H group and a considerable reduction of signal intensity for the Ru–H resonance (see Figure 4). These observations indicate the occurrence of rapid hydrogen exchanges among the Ru–H, agostic C–H, and noncoordinating methylene protons of dppb ligands even at −45 °C. The exchange rate between the agostic hydrogen and the terminal hydride was measured in the temperature range −55 to −65 °C by the spin saturation transfer method.[14,15] It was revealed that under these temperatures, the exchange proceeds once every 2–3 s.

The hydrogen exchanges between the terminal hydride and the C–H groups of the ligand in some transition metal

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[10] dppe = 1,2-bis(diphenylphosphino)ethane.

[11] dppp = 1,3-bis(diphenylphosphino)propane.

[12] (a) dpbp = 2,2′-bis(diphenylphosphino)-1,1′-biphenyl. (b) Ogasawara, M.; Saburi, M. Unpublished results.

[13] (a) binap = 2,2′-bis(diphenylphosphino)-1,1′-binaphthyl. (b) Tsukahara, T.; Kawano, H.; Ishii, Y.; Takahashi, T.; Saburi, M.; Uchida, Y.; Akutagawa, S. *Chem. Lett.* **1988**, 2055.

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complexes were observed in several cases using deuterium as the probe.[2b,16] Crabtree and co-workers reported either dissociative or nondissociative interaction of a C–H moiety in quinoline derivatives with iridium complexes and suggested the relationship between these hydrogen exchanges and agostic interactions.[17] However, there has been no direct evidence of the agostic interaction participating in C–H activation. Our results are the first example of the observation of the intramolecular hydrogen exchange involving the agostic hydrogen.

Experimental Section. the following complexes were prepared by literature methods: [RuH(dppb)$_2$]PF$_6$,[5a] [RuH(diop)$_2$]PF$_6$.[6b] Preparation of NMR samples was carried out under argon (not dinitrogen) atmosphere using air-free CD$_2$Cl$_2$ as a solvent. ^{1}H (400-MHz), ^{13}C (101-MHz), and ^{31}P (162-MHz) NMR spectra were recorded on a JEOL JNM-GX400 spectrometer. The T_1 experiments were performed with a 180°–τ–90° pulse sequence by the inversion-recovery method.

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Supplementary Material Available: ^{13}C NMR spectra of 1 (^{1}H coupled, decoupled, and selective decoupled with the agostic hydrogen), variable temperature ^{1}H NMR spectra of **2**, ^{1}H–^{1}H COSY spectrum of **2**, and ^{31}P NMR data for **2** (2 pages). Ordering information is given on any current masthead page.

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(15) The exchange rate k between these two resonances was calculated from T_1 (of terminal hydride), I (signal intensity of Ru–H under the nonirradiated conditions), and I' (signal intensity of Ru–H under the conditions irradiated at agostic resonance) according to the following equation; $1/k = T_1 I'/(I - I')$. At −55 °C, T_1 = 120 ms, k = 0.67 s^{-1}; at −60 °C, T_1 = 147 ms, k = 0.37 s^{-1}; at −65 °C, T_1 = 171 ms, k = 0.29 s^{-1}.

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