Attenuation of Intramolecular Ru−H···H−N Dihydrogen Bonding in Aminocyclopentadienyl Ruthenium Hydride Complexes Containing Phosphite Ligands

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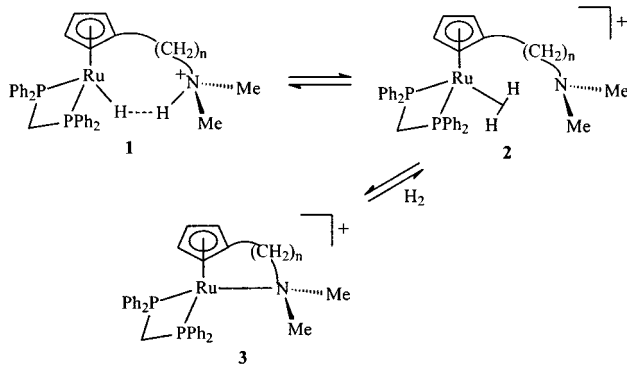
Replacement of the dppm ligand in (η^5-$C_5H_4(CH_2)_2NMe_2H^+$)Ru(dppm)H with two less donating triphenyl phosphite ligands reduces the strength of the intramolecular Ru−H···H−N dihydrogen bond to such an extent that it is hardly evidenced by NMR measurements. Unlike its dihydrogen-bonded dppm analogue, the triphenyl phosphite complex (η^5-$C_5H_4(CH_2)_2NMe_2H^+$)Ru($P(OPh)_3$)$_2$H shows no catalytic activity for reduction of carbon dioxide to formic acid.

Introduction

The unconventional hydrogen bond (dihydrogen bond) between a transition metal hydride and a hydrogen bond donor containing an O−H or an N−H group might be regarded as intermediates in hydride protonation to generate a η^2-H_2 ligand and the reverse reaction, heterolytic splitting of dihydrogen.[1] It is also recognized for activating the M−H bond for reactions such as H/D exchange, proton transfer, and substitution.[1] The importance of dihydrogen bonding for controlling the reactivity and stereochemistry of organometallic hydride complexes has been well-demonstrated also.[2]

We have recently synthesized and characterized the intramolecularly Ru−H···H−N dihydrogen-bonded complex (η^5-$C_5H_4(CH_2)_nNMe_2H^+$)Ru(dppm)H (n = 2 or 3) (**1**), which shows rapid and reversible hydride/proton exchange via the intermediacy of a η^2-dihydrogen tautomer, [(η^5-$C_5H_4(CH_2)_nNMe_2$)Ru(dppm)(H_2)]$^+$ (**2**) (Scheme 1).[3] Sabo-Etienne, Chaudret, and co-workers have, however, reported that in the triphenylphosphine analogue of **1** an exchange process between the hydride and the ammonium proton does not involve proton transfer within the dihydrogen bond.[4] The Ru−H···H−N dihydrogen bond in **1** is the key feature in the catalytic hydrogenation of CO_2 to formic acid. A theoretical study of this catalytic reaction with **1** has recently been reported.[5]

Scheme 1



Continuing our studies of dihydrogen bonding in aminocyclopentadienyl ruthenium hydride complexes and the catalytic activity of these complexes in CO_2 hydrogenation, we chose to study the influence of decreased basicity of the metal center on the strength of the Ru−H···H−N dihydrogen bond and the efficiency of CO_2 hydrogenation. The basicity of the metal center in the aminocyclopentadienyl ruthenium complex was decreased by replacement of the dppm ligand of **1** or **3**

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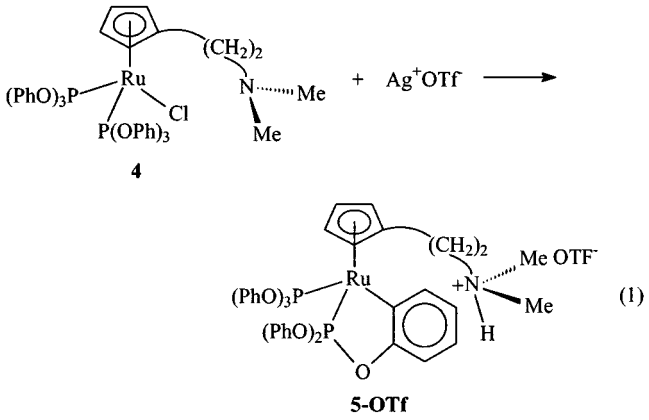
with triphenyl phosphite. We used the less donating phosphite because we anticipated that usage of more donating monodentate phosphine PR_3 might result in the formation of a dihydride complex instead of the Ru−H···H−N dihydrogen-bonded species analogous to **1**. It is well-known that the final thermodynamic products of protonation of ruthenium cyclopentadienyl hydride complexes $(\eta^5\text{-}C_5R_5)Ru(PR_3)_2H$ containing more basic PR_3 ligands adopt the dihydride form *trans*-$[(\eta^5\text{-}C_5R_5)\text{-}Ru(PR_3)_2(H)_2]^+$,[6] although the kinetic products may be η^2-dihydrogen complexes.[7]

Results and Discussion

We intended to prepare the triphenyl phosphite analogue of **3** (see Scheme 1) and then react the complex with pressurized H_2 to obtain $(\eta^5\text{-}C_5H_4(CH_2)_2NMe_2H^+)\text{-}Ru(P(OPh)_3)_2H$, the phosphite analogue of **1**, with which we would study the strength of its Ru−H···H−N interaction. Comparisons in terms of H-bond strength and reactivity of this complex with those of **1** could then be made. We reacted the chloro complex $(\eta^5\text{-}C_5H_4(CH_2)_2\text{-}NMe_2)Ru(P(OPh)_3)_2Cl$ (**4**) with AgOTf, anticipating that removal of the chloro ligand would create a vacant site, which would be occupied by the amine sidearm, thus producing the desired complex. But apparently, instead of sidearm coordination, proximal generation of a vacant coordination site at the cationic ruthenium center induced cyclometalation of one of the triphenyl phosphite ligands and produced the orthometalated complex $[(\eta^5\text{-}C_5H_4(CH_2)_2NMe_2H^+)Ru(P(OPh)_3)(\eta^2\text{-}P(OPh)_2OC_6H_4)]\text{-}OTf^-$ (**5-OTf)** (eq 1). Formation of **5-OTf** is not too



(1)

surprising, since it is known that the unsubstituted Cp complex $(\eta^5\text{-}C_5H_5)Ru(PPh_3)(P(OPh)_3)Cl$ reacts with AgOTf in the presence of piperidine at room temperature to give the orthometalated complex $(\eta^5\text{-}C_5H_5)(PPh_3)(\eta^2\text{-}P(OPh)_2OC_6H_4)$.[8] Orthometalated Cp ruthenium and osmium complexes are well-documented.[8,9] Complex **5-OTf** was characterized by NMR spectroscopy. The $^{31}P\text{-}\{^1H\}$ NMR spectrum showed two doublets corresponding to the two inequivalent phosphites at δ 144.2 and 172.9 ppm (J(PP) = 89 Hz). The sharp AX pattern indicates that there is no interconversion of the two phosphites at room temperature by reversible metalation/demetalation of ortho-hydrogens on the two different phosphites. It was known from variable-temperature ^{31}P NMR spectroscopic study that interconversion of the phosphines is facile in the orthometalated iridium complex $IrH(C_2Ph)(P^tBu_2Ph)(\eta^2\text{-}C_6H_4P^tBu_2)$.[10] The doublet signal at δ 111.2 ppm (J(CP) = 16.1 Hz) in the ^{13}C NMR spectrum of **5-OTf** is diagnostic of a metalated ortho-carbon atom Ru−C. Signals with similar chemical shifts and P−C coupling constants also appear in the ^{13}C NMR spectra of similar orthometalated Ru(II) complexes.[8,9a] The amine group in the sidearm was protonated. Evidence for amine protonation was provided by the ^1H NMR spectrum of **5-OTf**; it showed the protons of the two *N*-methyl groups, which are diastereotopic, as two doublets at δ 2.60 (J(HH) = 4.4 Hz) and 2.70 (J(HH) = 4.3 Hz) ppm. The doublets were downfield-shifted from the *N*-methyl proton signal of the free ligand $C_5H_5(CH_2)_2NMe_2$ (δ 2.27 ppm). Similar downfield shifts of the *N*-methyl protons have been observed in **1** and its chloro analogue $(\eta^5\text{-}C_5H_4(CH_2)_nNMe_2H^+)Ru\text{-}(dppm)Cl$,[3] as well as molybdenum[11] and rhodium[12] complexes containing similar ligands. Protonation of the amine group in **5-OTf** was also supported by observation of the broad signal of N−H at δ 8.20 ppm. Although **5-OTf** is well-characterized by NMR spectroscopy, it is difficult to obtain good elemental analysis results, due to difficulty in completely removing the silver salts from the complex, which is a sticky semisolid. We attempted to purify **5-OTf** by column chromatography using neutral alumina, but the product collected was the deprotonated form of **5-OTf**, i.e., $(\eta^5\text{-}C_5H_4(CH_2)_2NMe_2)\text{-}Ru(P(OPh)_3)(\eta^2\text{-}P(OPh)_2OC_6H_4)$ (**6**). The $^{31}P\{^1H\}$ NMR spectrum of **6** is similar to that of **5-OTf**, showing two doublets at δ 144.3 (J(PP) = 99.9 Hz) and 170.9 (J(PP) = 99.9 Hz) ppm. The ^{13}C NMR spectrum of **6**, similar to that of **5-OTf**, also contains a doublet in the downfield region at δ 111.1 ppm (J(CP) = 16.0 Hz), due to Ru−C. However, the ^1H NMR spectrum of **6**, shows, instead of a pair of downfield-shifted doublets for the *N*-methyl protons, a relatively upfield singlet, which integrates to 6 hydrogens, at δ 2.03 ppm. No N−H signal is observable in the downfield region. Acidification of **6** with $HBF_4{\cdot}OEt_2$ gives pure $[(\eta^5\text{-}C_5H_4(CH_2)_2NMe_2H^+)\text{-}Ru(P(OPh)_3)(\eta^2\text{-}P(OPh)_2OC_6H_4)]BF_4^-$ **(5-BF$_4$)**, whose NMR spectroscopic data are identical to those of **5-OTf**. Complex **6** can also be prepared by refluxing **4** with sodium methoxide in methanol. Similar orthometalation has been achieved for $(\eta^5\text{-}C_5H_5)Ru(P(OPh)_3)_2Cl$ by refluxing the complex with methoxide ion in methanol.[9a] However, the complexes $(\eta^5\text{-}C_5H_5)Ru(PPh_3)_2Cl$ and $(\eta^5\text{-}C_5H_5)Ru(PPh_3)(P(OPh)_3)Cl$ cannot be orthometalated under the same experimental conditions.[8]

Study of reactivity of **5-BF$_4$** and **6** toward pressurized dihydrogen gave interesting results. Complex **5-BF$_4$** reacted, as expected, with H_2 (10 atm) in chlorobenzene

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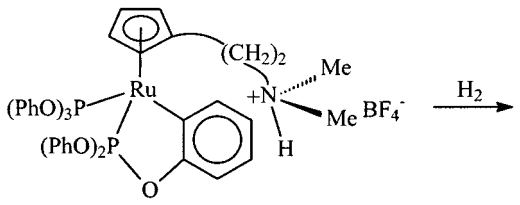
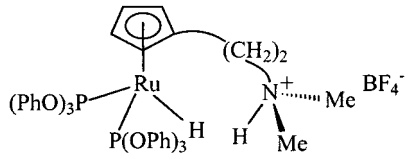


5-BF$_4$



7 (2)

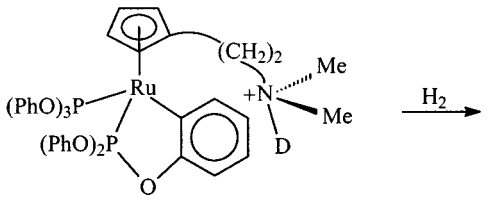
at room temperature to yield our target complex [(η^5-$C_5H_4(CH_2)_2NMe_2H^+$)Ru(P(OPh)$_3$)$_2$H]BF_4^- (**7**) (eq 2). Under identical experimental conditions, **6** is, however, inert to H_2. We expect **6**, in analogy with **5-BF$_4$**, to react with H_2, forming the deprotonated form of **7**, i.e., (η^5-$C_5H_4(CH_2)_2NMe_2$)Ru(P(OPh)$_3$)$_2$H (**8**). It was later found that **8** could be obtained by deprotonation of **7** with aqueous KOH in THF.

In the ^{1}H NMR spectrum of **7**, the hydride signal is a sharp triplet (J(HP) = 26.0 Hz) at δ −11.83 ppm. Similar to its precursor **5-BF$_4$**, complex **7** shows a downfield-shifted signal (δ 2.61 ppm) for its *N*-methyl protons, but the signal is a singlet rather than a pair of doublets as observed for the *N*-methyl protons of **5-BF$_4$**. The N−H of **7**, which does not split the *N*-methyl signal, appears as a broad peak at δ 8.47 ppm. The ^{31}P{^{1}H} NMR spectrum of **7** shows a singlet at δ 149.7 ppm, indicating that the two phosphorus atoms are equivalent. Several attempts to obtain single crystals of **7** for X-ray structural determination have not been successful; in fact, this complex, and other phosphite complexes reported in this work, are sticky solids: they all resist single-crystal formation.

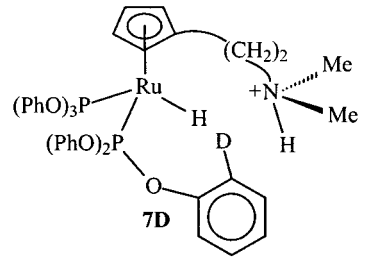
The sharpness of the hydride signal of **7** indicates that the H···H interaction between the hydride ligand and N−H on the pendant amine arm is very weak, if it exists at all. On the contrary, complex **1**, the dppm analogue of **7**, which shows a broad hydride signal, exhibits a strong Ru−H···H−N dihydrogen-bonding interaction, and the two hydrogen atoms undergo rapid exchange via the intermediacy of a η^2-dihydrogen species (Scheme 1).[3] Broadening of the hydride signal of WH(CO)$_2$(NO)-(PMe$_3$)$_2$ was observed in the presence of acidic alcohol, due to the formation of an intermolecular M−H···H−OR dihydrogen bond.[13] Significant broadening of the hydride signals of both *cis* and *trans* isomers of RuH$_2$-(dppm)$_2$ were also observed upon addition of excess phenol.[1f] Lack of Ru−H···H−N dihydrogen-bonding interaction in **7** was also supported by the fact that practically no NOE was detected between Ru−H and N−H. Variable-temperature T_1 measurements for the hydride ligand of **7** yielded a T_1(min) of 890 ms (at 400 MHz and 290 K); this value is very similar to that of the hydride ligand of **8** (T_1(min) = 900 ms at 400 MHz and 248 K). The similarity of the T_1(min) values of the hydride ligands of **7** and **8** lends further support to the notion that intramolecular dihydrogen-bonding interaction in the former is minimal. It is obviously true that the less donating triphenyl phosphite ligands lower the basicity of the metal center in **7**, which in turn decreases the hydridicity of the hydride ligand to such an extent that the Ru−H···H−N dihydrogen bond is no longer stable. The M−H···H−X dihydrogen bond is a hydride−proton interaction, and its bond strength can be modulated by tuning the nucleophilicity of M−H and/or the electrophilicity of H−X.[1b,14] Epstein, Berke, and coworkers have reported that the strengths of the dihydrogen bonds in the tungsten hydride−alcohol complexes W(CO)$_2$(NO)(L)$_2$H···HOR increase with the donor abilities of the ligand L (PPh$_3$ < P(O^{i}Pr)$_3$ < PEt$_3$ < PMe$_3$).[13]

Unlike the dppm analogue **1**, **7** is stable toward H_2 loss even after refluxing in THF or heating at 90 °C in chlorobenzene for 2 days. This is not unexpected since lack of Ru−H···H−N dihydrogen bonding in **7** precludes the possibility of eliminating H_2 via the intermediacy of a η^2-H_2 species.

To learn more about the reaction of **5-BF$_4$** with H_2, we reacted [(η^5-$C_5H_4(CH_2)_2NMe_2D^+$)Ru(P(OPh)$_3$)(η^2-P(OPh)$_2$OC$_6$H$_4$)]BF_4^- (**5D-BF$_4$**), the deuterated form of **5-BF$_4$** in which the amine sidearm was deuterated, with H_2 and studied the distribution of deuterium in the product. A combination of ^{1}H and ^{2}H NMR spectroscopic studies clearly indicated that all the deuterium atoms had been transferred to the triphenyl phosphite ligand, and the Ru−H and N−H groups were deuterium-free (eq 3).



5D-BF$_4$



7D (3)

The result of the labeling experiment is in consonance with the proposed reaction mechanism depicted in Scheme 2. It is noteworthy that the crucial step of the hydrogenolysis of **5-BF$_4$** with H_2 seems to be the protonation of the ortho-carbon in Ru−C by the relatively weak alkylammonium acid sidearm; this step might be triggered or induced by the incoming H_2. It is

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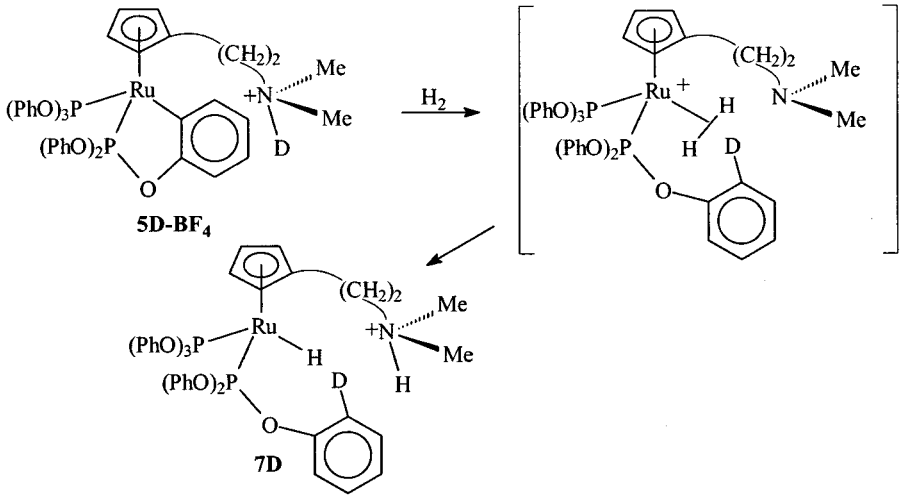
Scheme 2



therefore not surprising to find that **6**, which is devoid of an ammonium proton, is unreactive toward H_2. Protonation of the ortho-carbon of the orthometalated complex by weak acid had been demonstrated by the reaction of the iridium complex IrH(C≡CPh)(PPh^{t}Bu$_2$)-(η^2-C$_6$H$_4$P^{t}Bu$_2$) with the weak carbon acid PhC≡CH to form IrH(C≡CPh)$_2$(PPh^{t}Bu$_2$)$_2$; the protonation mechanism, which was established with the aid of a deuterium isotope study, does not, however, involve direct delivery of the acidic acetylenenic hydrogen to the ortho-carbon. It involves the incoming acetylene triggering the reductive elimination of the preexisting Ir−C and Ir−H bonds.[10]

As expected, the ^{1}H NMR spectrum of **8** shows a relatively upfield singlet signal for its nonprotonated amine group (δ 2.29 ppm), and no N−H signal is observable in the downfield region. The two equivalent phosphite ligands of **8** appear as a singlet at δ 143.7 ppm in the ^{31}P{^{1}H} NMR spectrum.

Since complex **1**, the dppm analogue of **7**, is believed to play a crucial role in catalytic reduction of CO_2 to formic acid, we are thus interested in studying the catalytic activity of **7** (or its precursor **5-BF$_4$**) in CO_2 hydrogenation. No catalytic activity was, however, found. Lack of activity in **7** is attributable to low hydridicity of the hydride ligand. In **7**, although the protonated amine sidearm, like that of **1**, can H-bond with one of the oxygen atoms of an incoming CO_2 molecule, thus enhancing the electrophilicity at the carbon, the hydride ligand is unfortunately not hydridic enough to allow its abstraction by the electrophilic carbon center.

Summary

Our previous work has demonstrated that the aminocyclopentadienyl-chelated complex [(η:$^5\eta^1$-C$_5$H$_4$(CH$_2$)$_n$-NMe$_2$)Ru(dppm)]$^+$ (**3**) reacts with pressurized H_2 to give (η^5-C$_5$H$_4$(CH$_2$)$_n$NMe$_2$H$^+$)Ru(dppm)H (**1**), in which the Ru−H forms a Ru−H···H−N dihydrogen bond with the ammonium proton of the sidearm; the latter loses H_2 slowly at room temperature and reverts to the former.[3] In the case of (η^5-C$_5$H$_4$(CH$_2$)$_2$NMe$_2$H$^+$)Ru(PPh$_3$)$_2$H, whereas no Ru−H···H−N dihydrogen bond is present in the solid state, it is likely that in solution several fluxional pathways are present, one of which leads to a thermodynamically more stable species that contains a dihydrogen bond between the hydride and the ammonium proton. However, the complex does not lose H_2 in solution at room temperature.[4] We have here demonstrated that in (η^5-C$_5$H$_4$(CH$_2$)$_2$NMe$_2$H$^+$)Ru(P(OPh)$_3$)$_2$H (**7**), which contains the less donating phosphite ligands, the stable conformation of the complex in solution is one in which no Ru−H···H−N dihydrogen-bonding interaction is present between the hydride and the ammonium proton. We attribute the lack of interaction to reduced hydridicity of the hydride ligand in **7**. In summary, this work, together with our previous one and that of Sabo-Etienne, Chaudret, and co-workers, provides a fairly complete picture of intramolecular M−H···H−N dihydrogen-bonding interactions in aminocyclopentadienyl ruthenium hydride complexes.

Experimental Section

All reactions were performed under an atmosphere of dry nitrogen using standard Schlenk techniques. All chemicals were obtained from Aldrich except dicyclopentadiene and deuterated NMR solvents, which were purchased from BDH and Armar, respectively. The ligands C$_5$H$_5$(CH$_2$)$_2$NMe$_2$[15] and the complexes RuCl$_2$(PPh$_3$)$_3$[16] and (η^5-C$_5$H$_4$(CH$_2$)$_2$NMe$_2$)Ru-(PPh$_3$)$_2$Cl[3] were prepared according to published procedures. Solvents were distilled under a dry nitrogen atmosphere with appropriate drying agents (solvent/drying agent): ethanol/Mg−I$_2$, tetrahydrofuran/Na-benzophenone, toluene/Na-benzophenone, hexane/Na, diethyl ether/CaH$_2$, chlorobenzene/P$_2$O$_5$. High-purity hydrogen gas was supplied by Hong Kong Oxygen.

Proton NMR spectra were obtained from a Bruker DPX 400 spectrometer. Chemical shifts were reported relative to residual protons of the deuterated solvents. ^{31}P and ^{13}C NMR spectra were recorded on a Bruker DPX 400 spectrometer at 161.7 and 100.6 MHz, respectively; ^{31}P chemical shifts were externally referenced to 85% H$_3$PO$_4$ in D$_2$O, while ^{13}C chemical shifts were internally referenced to the residual peaks of deuterated solvents. Relaxation time T_1 measurements were carried out at 400 MHz by the inversion−recovery method using the standard 180°−τ−90° pulse sequence. High-pressure

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studies were carried out in a commercial 5 mm Wilmad pressure-valved NMR tube. Elemental analyses were performed by M-H-W Laboratories, Phenix, AZ.

(η^5-$C_5H_4(CH_2)_2NMe_2$)Ru(P(OPh)$_3$)$_2$Cl (4). A solution containing (η^5-$C_5H_4(CH_2)_2NMe_2$)Ru(PPh_3)$_2$Cl (1.00 g, 1.12 mol) and triphenyl phosphite (1.02 mL, 3.92 mmol) in toluene (50 mL) was refluxed for 48 h. Upon removal of the solvent under vacuum, 20 mL of diethyl ether was added to the residual paste with vigorous stirring to produce a yellow powder. The solid was then washed with hexane (2 × 20 mL) and dried in vacuo. Yield: 0.97 g (86%). Anal. Calcd for $C_{45}H_{44}NO_6P_2ClRu$: C, 60.50; H, 4.96; N, 1.58. Found: C, 59.96; H, 5.01; N, 1.63. ^{1}H NMR ($CDCl_3$, 400 MHz, 20 °C): δ 1.82 (br s, 2 H, CH_2N), 2.21 (m, 2 H, $C_5H_4CH_2$), 2.28 (s, 6 H, NCH_3), 3.54 (br s, 2 H of Cp ring), 3.93 (br s, 2 H of Cp ring), 6.81−7.33 (m, 30 H of P(OPh)$_3$). ^{31}P{^{1}H}NMR ($CDCl_3$, 161.7 MHz, 20 °C): δ 138.3 (s).

(η^5-$C_5H_4(CH_2)_2NMe_2$)Ru(P(OPh)$_3$(P(OPh)$_2$OC$_6$H$_4$) (6). A sample of **4** (0.25 g, 0.28 mmol) was added to excess $AgSO_3CF_3$ in THF (20 mL), and the resulting solution was stirred at room temperature for 2 days. The solution was filtered to remove the silver chloride, and the solvent of the filtrate was removed by vacuum to yield a brown oily liquid. Elution of this oily compound through a neutral alumina column (1 cm × 10 cm) with toluene followed by ethanol gave, after evaporation of the solvents, the pure complex as a tacky yellow solid. Yield: 0.12 g (50%). Anal. Calcd for $C_{45}H_{43}NO_6P_2Ru$: C, 63.08; H, 5.06; N, 1.63. Found: C, 62.86; H, 5.34; N, 1.67. ^{1}H NMR (acetone-d_6, 400 MHz, 20 °C): δ 1.86 (m, 2 H, CH_2N), 2.03 (s, 6 H, NCH_3), 2.06 (m, 2 H, $C_5H_4CH_2$), 4.08 (br s, 1H of Cp ring), 4.09 (br s, 1 H of Cp ring), 4.37 (br s, 1 H of Cp ring), 4,86 (br s, 1 H of Cp ring), 6.89−7.52 (m, 29 H of phosphites). ^{31}P{^{1}H} NMR (acetone-d_6, 161.7 MHz, 20 °C): 144.3 (d, ^2J(PP) = 99.9 Hz, P(OPh)$_3$), 170.9 (d, ^2J(PP) = 99.9 Hz, P(OPh)$_2$(OC$_6$H$_4$). ^{13}C-{^{1}H} NMR (acetone-d_6, 100.6 MHz, 20 °C): 111.1 (d, ^2J(PC) = 16.0 Hz, Ru-*C*).

The complex can be prepared by an alternative method: A sample of **4** (0.12 g, 0.13 mmol) was added to a solution of sodium methoxide (0.13 g, 2.31 mmol) in methanol (30 mL), and the solution was allowed to reflux for 24 h. The resulting solution was filtered, and the solvent of the filtrate was removed by vacuum to yield a yellow oil. Elution of the oily product through a neutral alumina column (1 cm × 10 cm) with toluene followed by ethanol gave, upon removal of the solvents, the pure product. Yield: 0.08 g (33%).

[(η^5-$C_5H_4(CH_2)_2NMe_2H^+$)Ru(P(OPh)$_3$(P(OPh)$_2$OC$_6$H$_4$)]-BF$_4$ (5-BF$_4$). To a sample of **6** (0.10 g, 0.12 mmol) in 15 mL of tetrahydrofuran was added 1.2 equiv of tetrafluoroboric acid in etheral solution (HBF_4 Et_2O, 54%) (19 μL, 0.14 mmol), and the resulting solution was stirred for 1 h. It was then concentrated to 1−2 mL, and 20 mL of hexane was added to precipitate the product. It was collected by filtration, washed with diethyl ether (2 × 15 mL), and dried in vacuo to yield a sticky yellowish brown solid. Yield: 0.08 g (73%). Anal. Calcd for $C_{45}H_{44}BNO_6F_4Ru$: C, 57.22; H, 4.69; N, 1.48. Found: C, 57.54; H. 4.59; N, 1.57. ^{1}H NMR ($CDCl_3$, 400 MHz, 20 °C): δ 2.39 (m, 2 H, CH_2N), 2.60 (d, 3 H, J(HH) = 4.36 Hz, NCH_3), 2.70 (d, 3 H, J(HH) = 4.30 Hz, NCH_3), 2.87 (m, 2 H, $C_5H_4CH_2$), 5.04 (br s, 1 H of Cp ring), 5.20 (br s, 1 H of Cp ring), 5.45 (br s, 1 H of Cp ring), 5.66 (br s, 1 H of Cp ring), 6.95−7.38 (m, 29 H of phosphites), 8.20 (br s, 1 H, N*H*). ^{31}P{^{1}H} NMR ($CDCl_3$, 161.7 MHz, 20 °C): δ 144.2 (d, ^2J(PP) = 89 Hz, P(OPh)$_3$), 172.9 (d, ^2J(PP) = 89 Hz, P(OPh)$_2$(OC$_6$H$_4$)). ^{13}C{^{1}H} NMR ($CDCl_3$, 100.6 MHz, 20 °C): δ 111.2 (d, ^2J(PC) = 16.1 Hz, Ru-*C*).

[(η^5-$C_5H_4(CH_2)_2NMe_2H^+$)Ru(P(OPh)$_3$)$_2$H]BF$_4$ (7). A solution of **5** (0.20 g, 0.21 mmol) in chlorobenzene (15 mL) was stirred at room temperature under 25 atm of H_2 in a stainless steel autoclave for 16 h. The reaction was carefully vented, and the solvent of the resulting solution was removed by vacuum. The product was washed with 3 × 20 mL portions of hexane and 20 mL of diethyl ether to yield a sticky pale brown solid. Yield: 0.15 g (75%). Anal. Calcd for $C_{45}H_{46}BNO_6F_4P_2Ru$: C, 57.09; H, 4.90; N, 1.48. Found: C, 57.64; H, 5.04; N, 1.53. ^{1}H NMR (benzene-d_6, 400 MHz, 20 °C): δ −11.83 (t, 1H, ^2J(HP) = 26.0 Hz, Ru-*H*), 2.33 (br s, 2H, CH_2N), 2.61 (s, 6H, NCH_3), 2.88 (br s, 2 H $C_5H_4CH_2$), 4.48 (s, 2 H of Cp ring), 5.49 (s, 2 H of Cp ring), 7.23−7.60 (m, 30 H of P(OPh)$_3$), 8.47 (br s, 1 H N*H*). ^{31}P{^{1}H} NMR (benzene-d_6, 161.7 MHz, 20 °C): δ 149.7 (s).

(η^5-$C_5H_4(CH_2)_2NMe_2$)Ru(P(OPh)$_3$)$_2$H (8). A sample of **7** (0.15 g, 0.16 mmol) was added to a suspension of excess powdered potassium hydroxide in ethanol (20 mL). The mixture was stirred overnight at room temperature. It was filtered to remove the unreacted KOH, and the solvent of the filtrate was removed by vacuum to yield a black oily substance, which was then extracted with 4 × 20 mL portions of hexane. The solvent of the extract was removed, and a very sticky brown solid was obtained. Yield: 0.09 g (65%). Anal. Calcd for $C_{45}H_{45}NO_6P_2Ru$: C, 62.93; H, 5.28; N, 1.63. Found: C, 62.81; H, 5.20; N, 1.48. ^{1}H NMR (benzene-d_6, 400 MHz, 20 °C): δ −11.53 (t, ^2J(HP) = 36.0 Hz, 1H, Ru*H*)), 2.21 (br s, 2 H, CH_2N). 2.29 (br s, 8 H, $C_5H_4CH_2$ and NCH_3), 4.44 (s, 2 H of Cp ring), 4.50 (s, 2 H of Cp ring), 7.10−7.63 (m, 30 H of P(OPh)$_3$). ^{31}P{^{1}H} NMR (benzene-d_6, 161.7 MHz, 20 °C): δ 143.7 (s).

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