Rapid, reversible ortho metalation in chlorohydridotris(triphenylphosphine)ruthenium(III) and its role in the catalytic hydrogenation of alkynes

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d (Scheme II). The methyl group 16 of the chiral center is relatively close to the azomethine proton 14 (spectrum B), however, not in a completely eclipsed position but somewhat above the Rh plane on the side of cod proton 5. Besides the 14/16 interaction, spectrum B also shows a weak increase of the proton signals 23 and 24 of the ethyl group, but no increase of the ortho protons 18, in agreement with conformation d. Spectrum C demonstrates spacial proximity of the phenyl protons to cod protons 6 and especially 5. There is also a slight increase of the signals of methyls 16 and 24, but not of imine proton 14.

In spectra D and E the olefinic protons 6 and 5 were irradiated. In the case of 6, the signal increases for one of the diastereotopic protons 23, 24, and for the phenyl protons 18. In the case of 5, only the phenyl protons are enhanced in good agreement with conformation d. In addition, spectrum D indicates that there is still a very slow exchange of **3** with $[(cod)RhCl]_2$ (signals 31).

Saturation of methyl protons 16 increases 14 and 18 and very weakly 5 and 24 (spectrum F). The orientation of methyl group 25 of the ethyl substituent follows from spectrum G. Irradiation of 25 increases 23 and 24, as expected, and in addition 16, 6, and 14. Thus, in conformation d (Scheme II) methyl 25 must be located below the Rh plane close to the imine N2 on the side of cod proton 6, almost equidistant to the methyl protons 16, the imine proton 14, and the olefin proton 6. Irradiation of 9, 1, 2 (not shown in Figure 5) establishes the neighborhood of pyrrole protons 9 and 10 and cod protons 1 and 2.

Conclusion

The conformations of complexes **1–3** in the solid state and in solution have been determined by X-ray structure analyses and NOE difference spectroscopy. The rotation of the chiral substituent with respect to the Rh coordination plane is the only intramolecular motion open to compounds **1–3** able to change the shape of the molecules. In the crystal and in solution the phenyl ring of a C*HMePh or a C*MeEtPh substituent prefers not to eclipse bonds in the rhodium coordination plane and adopts a more or less perpendicular arrangement to that plane, sometimes being a littler close to the imine part in the chelate ring and sometimes to the adjacent cod double bond. A hydrogen substituent at the asymmetric center tends to orient toward the cod double bond in solution as well as in the solid state; it may deviate from that position by up to 60°. The methyl group of the asymmetric center usually is close to the imine system of the chelate ligand also in complex **3**, where the hydrogen is replaced by an ethyl substituent. In complex **1** there are only minor differences between solid-state conformation a and solution conformation c (Scheme II).

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Supplementary Material Available: A table of atomic coordinates and thermal parameters for complex **2** including the hydrogen atoms and tables of the determination of absolute configuration, least-squares planes and atomic deviations, and structure factors for complex **2** (14 pages). Ordering information is given on any current masthead page.

Rapid, Reversible Ortho Metalation in $RuHCl[P(C_6H_5)_3]_3$ and Its Role in the Catalytic Hydrogenation of Alkynes

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Reaction of $RuHCl[P(C_6H_5)_3]_3$, **1**, and alkynes produces the ortho-metalated complex $RuCl[P(C_6H_4)(C_6H_5)_2][P(C_6H_5)_3]_2$, **3**, which is present during catalytic alkyne hydrogenation reactions. **3** is converted to **1** by reaction with H_2. The $^2H\{^1H\}$ NMR spectrum of **1**-d_2 produced by reaction of D_2 and **3** establishes rapid, reversible, intramolecular hydrogen isotope exchange between hydride and ortho-aryl phosphine sites, with deuterium preferred in the latter sites. The exchange and position of equilibrium result in an apparently slow rate of intermolecular exchange between D_2 and the hydride site. Examination of hydrogen isotope exchange during alkyne hydrogenation establishes that **3** is not an intermediate in the hydrogenation reaction.

Introduction

Intramolecular C–H activation in transition-metal phosphine and phosphite complexes has been of interest for a considerable time period.[3] The impression one garners from the existing literature is that intramolecular C–H activation is relatively slow.[4,5] As a consequence, it generally has not been regarded as a potential fundamental step in the mechanisms of reactions catalyzed by these

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complexes. In the course of an investigation of the basis for selective hydrogenation of alkynes by $RuHCl[P(C_6H_5)_3]_3$,[6] **1**, we obtained results establishing rapid intramolecular C–H activation in this complex. These results permit clarification of the exchange of D_2 with **1** and of the mechanism of alkyne hydrogenation catalyzed by **1**.

Experimental Section

Reagents and Solvents. All manipulations were carried out under an argon atmosphere in a Vacuum Atmospheres dry box or under a nitrogen atmosphere with use of Schlenk techniques. Benzene, toluene, toluene-d_8, pentane, and diethyl ether solvents were distilled from sodium benzophenone ketyl. Ethanol, methanol, and dichloromethane and chloroform-*d* (Aldrich) were degassed prior to use. Triethylamine was purified by distillation. Hexynes (Albany International) and hexenes (Wiley) were purified by treatment with activated alumina, tested for peroxides, and degassed. Distillation from calcium hydride proved necessary to remove all traces of peroxides from 1-hexene. Triphenylphosphine and diphenylacetylene were purified by recrystallization. Hydrogen and deuterium gases were used as received (Matheson).

$RuHCl[P(C_6H_5)_3]_3$ was prepared from $RuCl_2[P(C_6H_5)_3]_3$[7] by the H_2/triethylamine reduction procedure.[8] Reduction by sodium borohydride[8] invariably yielded impure product, as judged by ^{31}P NMR spectroscopy. $RuDCl[P(2,6\text{-}D_2C_6H_3)_3]_3$ was prepared by repeated equilibration at 75 °C of $RuHCl[P(C_6H_5)_3]_3$ in toluene with fresh portions of D_2 gas.[4]

Spectroscopic and Analytical Methods. Proton NMR spectra were recorded in $CDCl_3$ solution at 180, 201.9, or 250 MHz on instruments using Oxford Superconducting magnets and Nicolet 1180 computers. Phosphorus-31 NMR spectra were recorded in $CDCl_3$ or toluene-d_8 solution at 72.9 MHz on the 180-MHz spectrometer equipped with a 10-mm bore probe. Deuterium NMR spectra were recorded in CH_2Cl_2 solution at 31 Mz on the 201.9-MHz spectrometer equipped with a 10-mm bore probe. Spin saturation transfer data were collected and processed employing Nicolet Technology Corp. software. Chemical shifts are reported relative to $(CH_3)_4Si$ for ^1H and ^2H NMR spectra and relative to external 85% H_3PO_4 for ^{31}P NMR spectra.

Microanalyses were performed by Mr. Vazken H. Tashinian in the U.C. Berkeley Microanalytical Laboratory.

Preparation of $\overline{RuCl[P(C_6H_4)(C_6H_5)_2][P(C_6H_5)_3]_2}\cdot X(CH_2Cl_2)$, 3. A stirred solution of 400 mg (0.43 mM) of $RuHCl[P(C_6H_5)_3]_3$ in 2.5 mL of CH_2Cl_2 was reacted with either 200 μL (~4 equiv) of 2- or 3-hexyne or 400 mg (~10 equiv) of diphenylacetylene for 90 min. The red-violet initial solution turned extremely dark brown. An equal volume of pentane was added, and the solution was stored at −40 °C. After 36 h, a microcrystalline brown solid was collected and was washed with pentane. Product yields were typically 35% (150 mg). The solid decomposed within an hour when redissolved: ^1H NMR, see Figure 1; $^{31}P\{^1H\}$ NMR ($CDCl_3$) δ 38.8 (d), 1.1 (t), J_{P-P} = 20.6 Hz. Anal. Calcd for $C_{54}H_{44}ClP_3Ru\cdot CH_2Cl_2$ (X = 1): C, 65.53; H, 4.60; P, 9.22; Cl, 10.56. Found: C, 65.00; H, 4.56; P, 8.90; Cl, 10.88. The ^1H NMR spectrum of the sample with this analysis contained roughly 1 equiv of CH_2Cl_2, as judged by integration.[9]

Hydrogen Isotope Exchange during Alkyne Hydrogenation. Two reaction tubes equipped with Kontes Teflon vacuum valves were filled with 30 mL each of a 2.5×10^{-4} M solution of perprotio- or peredeuterio-1 in toluene. Both were degassed on a vacuum line and then frozen. 2-Hexyne (500 μL) was trap-to-trap distilled into one of the tubes, and both tubes were pressurized to 650 mm with D_2 or H_2 gas, respectively. The tubes were thawed and permitted to react (stirred) for 30 min, a period of time corresponding to approximately 20 turnovers for alkyne hydrogenation. Both tubes were frozen to halt reaction, and all volatiles were removed by trap-to-trap distillation on the vacuum line. Toluene (1 mL) was distilled into the tube that had contained hexyne, and the contents were exposed briefly to D_2 or H_2 gas, respectively, to convert any **3** remaining to **1**. The toluene was then removed. The resulting residues were each dissolved in 0.5 mL of $CDCl_3$ and placed in 5-mm NMR tubes.

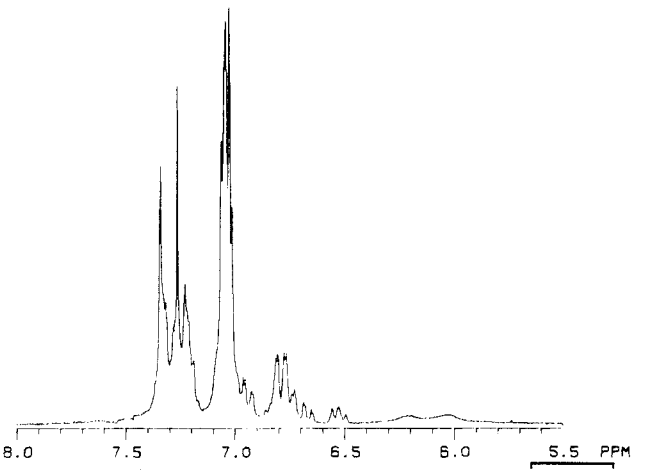

Figure 1. ^1H NMR spectrum (200 MHz) of $RuCl[P(C_6H_4)(C_6H_5)_2][P(C_6H_5)_3]_2$.

Results and Discussion

In the presence of four or more equivalents of 3-hexyne, $RuHCl[P(C_6H_5)_3]_3$, **1**, is rapidly converted to two new ^{31}P NMR detectable species, **2**[10] and **3**. These are the only complexes observed during alkyne hydrogenation catalyzed by **1**.[11] (In contrast, only **1** is detected during alkene hydrogenation.) Solids obtained from reaction of **1** with 2-hexyne, 3-hexyne, and diphenylacetylene all had ^{31}P NMR spectra which were identical with that of **3**. The ^1H NMR spectra of the three solids (Figure 1) were identical, excepting variation[9] in the amount of CH_2Cl_2 of crystallization, and established that **3** does not contain a hydride ligand or any alkyne-derived hydrocarbon fragment. Analytical data were consistent with identification of **3** as the orthometalated complex $\overline{RuCl[P(C_6H_4)(C_6H_5)_2][P(C_6H_5)_3]_2}\cdot X(CH_2Cl_2)$, where X was typically about 1.[9] Reaction with H_2 resulted in immediate, quantitative conversion of **3** to **1**.

We attempted to confirm the ortho-metalated nature of **3** by examining the product of the reaction with **3** with D_2 gas. Cleavage of the ruthenium–ortho-carbon bond by D_2 is expected to result in deuterium incorporation in one ortho-aryl site and in the hydride site.[12,13] The peaks due to these sites, which are located at 7.25 and −18.05 ppm, respectively, in the spectrum of an authentic sample of $RuDCl[P(2,6\text{-}D_2C_6H_3)_3]_3$,[4] should have a 1:1 ratio in the $^2H\{^1H\}$ NMR spectrum of the product. Examination of the spectrum of the product within minutes of a brief exposure to D_2 revealed only the peak at 7.25 ppm. The peak at −18.05 ppm was detected after acquisition time sufficiently long to improve the signal/noise ratio. Integration established that 97.5% of the deuterium was present in the phosphine ortho C–H site and only 2.5% as RuD.

These observations *are* consistent with formation of the expected product if a rapid intramolecular equilibration

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(9) Considerable variability was seen in the amount of CH_2Cl_2 of solvation found in isolated **3**, as judged by ^1H NMR spectroscopy and analytical data. Variation has a marked effect upon the calculated analysis.
(10) **2**: $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 70.9 (d), 34.1 (d), J_{P-P} = 32.8 Hz.
(11) An amount of uncoordinated triphenylphosphine equivalent to **2** was also detected in these reactions.
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of deuterium and hydrogen between the ortho-aryl and hydride sites (eq 1) is postulated. In our specific case, the equilibrium is represented by eq 2. The position of

$$RuDCl[P(C_6H_5)_3]_3 \rightleftharpoons \overline{RuHDCl[P(C_6H_4)(C_6H_5)_2][P(C_6H_5)_3]_2} \rightleftharpoons RuHCl[P(C_6H_4D)(C_6H_5)_2][P(C_6H_5)_3]_2 \quad (1)$$

$$\underset{B}{RuDCl\{[P(C_6H_5)_3]_3\text{-}d_1\}} \rightleftharpoons \underset{A}{RuHCl\{[P(C_6H_5)_3]_3\text{-}d_2\}} \quad (2)$$

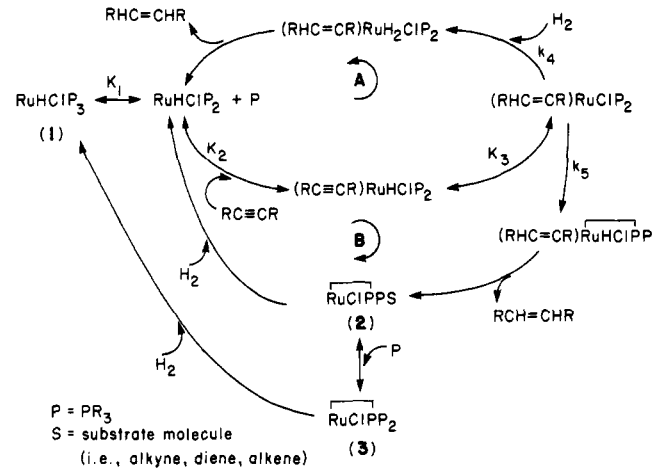
equilibrium between B and A depends upon the difference in the zero-point vibration energies of these species and upon statistical factors. A total of 19 sites is accessible to deuterium, one on the metal and 18 on the phenyl rings ortho to the phosphorus substituent. There are 153 possible isomers of A and 18 of B. Thus $A/B = K_{EQ} = 153/18 \exp[-\Delta E/kT]$ where ΔE is the zero-point energy difference. Assuming that A and B are identical except for contributions made by the vibrations involving the sites in question and limiting contributions to those involving stretching of these bonds, it can be demonstrated that $K_{EQ} = 8.5 \exp[hc(\nu_{RuD} + \nu_{CH} - \nu_{RuH} - \nu_{CD})/2kT]$ where ν is in cm^{-1}. K_{EQ} is calculated to be 15.5 at 25 °C, using known vibrational frequencies.[8] This corresponds to a phosphine C–D to Ru–D integration ratio of 97:3, in excellent agreement with the observed values.

Precedent for equilibration of deuterium between sites is found in the reaction of ortho-metalated $\overline{Co[P(OC_6H_4)(OC_6H_5)_2][P(OC_6H_5)_3]_4}$ with deuterium gas.[14] More than six atoms of deuterium were incorporated per molecule, yet the vast majority of the product was present as a cobalt hydride. The equilibrium preference of deuterium for ortho-aryl C–H sites and the existence of a relatively rapid exchange between Co–H and ortho-aryl C–H sites were not specifically recognized in this case.

Complex 1 has long been known to undergo ortho metalation reactions. Prior to our investigation, however, it was not appreciated that ortho metalation reactions of 1 occur in a rapid, reversible, and intramolecular fashion. Both the stoichiometric hydrogenation of maleic acid by 1, which forms the dimeric ortho-metalated product $\{\overline{RuCl[P(C_6H_4)(C_6H_5)_2][P(C_6H_5)_2][P(C_6H_5)_3]}\}_2$,[5] and the catalytic ortho deuteration of triphenylphosphine[4] are slow reactions. The later reaction has been suggested to occur by concerted elimination of H_2 from 1,[15] but this is clearly inconsistent with appearance of hydrogen in the hydride site of 1 after reaction of 3 with D_2. Our observations demonstrate that the intramolecular oxidative addition of the ortho-aryl C–H bond to Ru and the complementary reductive elimination are fast relative to the above reactions. They also clarify some confusing aspects of the interaction of 1 with D_2 and are suggestive of possible alternate mechanisms for alkyne hydrogenation reactions.

Previous investigators have commented upon the inertness of the hydride ligand of 1 toward exchange with D_2.[8,16] Deuterium incorporation into the hydride position of 1 is not detected after exposure to D_2 gas (one atmosphere) for 24 h. Slight incorporation of deuterium in the phosphine ligands is noted during the same time period.[4,8] Solutions of 1 have been reported to catalyze extremely rapid formation of HD from gaseous mixtures of H_2 and D_2.[16] These observations appear to require that the original hydride ligand population remains unique during hydrogen exchange. Reversible hydrogen-induced formation of HCl and $H_2Ru[P(C_6H_5)_3]_3$ from 1, with all original hydride contained in the HCl, was postulated.[16] Reversible formation of $H_4Ru[P(C_6H_5)_3]_3$ from H_2 and the dihydride has been demonstrated[17] and would provide a pathway for hydrogen exchange. The rapid equilibration of hydride and ortho-aryl sites and preferential incorporation of deuterium in the latter explains the apparent inertness of the hydride site toward deuterium exchange. Exchange appears to be slow because significant incorporation of deuterium in the hydride site cannot occur until the phosphines are extensively ortho deuterated. Given the difficulty of detecting small levels of phosphine deuteration by infrared or by ^1H NMR spectroscopy, it is not surprising that the rate of exchange was presumed to be slow[8,16] and that the original hydride population was presumed to remain unique during hydrogen exchange.[5]

Scheme I



$RuHCl[P(C_6H_5)_3]_3$ hydrogenates alkynes[18-20] to *cis*-alkenes[19] at a rate roughly 0.1 times as fast as it hydrogenates alkenes.[6] Nonetheless, alkynes are selectively hydrogenated in competition experiments. Such behavior is typical of many catalysts which selectively hydrogenate alkynes.[21-23] The change in color of the solution from the red-violet characteristic of 1 to brown[6,18] and ^{31}P NMR observations during alkyne hydrogenation[6] minimally suggest that different Ru complexes are present than during alkene hydrogenations. Furthermore, the identification of 3 as an ortho-metalated complex resulting from stoichiometric alkyne hydrogenation and the reaction of 3 with H_2 to regenerate 1 formally establish a mechanism for alkyne hydrogenation, pathway B of Scheme I,[24] that is distinct from the mechanism proposed for alkene hydrogenation, pathway A.[25-29] The demonstrated rapidity

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(24) 2 has been identified in the scheme as an ortho-metalated complex with one less phosphine than 3. The available evidence does not eliminate other formulations for this complex, however.
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of the intramolecular oxidative addition of the ortho-aryl C–H bond to Ru invalidates the previous objection to this type of mechanism,[5] its presumed insufficient rate. The existence of distinct reaction mechanisms could provide a basis for the selective catalytic hydrogenation of alkynes. The observations above *do not* necessitate, however, that the bulk of alkyne hydrogenation occur by the mechanism of pathway B or that either of the majority species during alkyne hydrogenation, **2** and **3**, is actually an intermediate in the catalytic process. These points can be resolved experimentally.

Hydrogenation of alkynes by the mechanism of pathway B *requires* incorporation of a hydrogen atom from a phosphine ortho-aryl site in the alkene product. The replacement for this hydrogen atom comes from H_2 gas. If pathway B prevails, hydrogenation of alkyne by **1** requires isotopic exchange between phosphine ortho-aryl sites and H_2 gas occur at a rate equal to the rate of alkene formation. Examination of the ^1H NMR spectrum of **1** recovered from alkyne hydrogenation reactions after a time sufficient for 20 turnovers under D_2 revealed only slightly more deuterium had been incorporated than during exposure to D_2 alone for an identical period of time. Near complete exchange would have been expected if pathway B prevailed, barring substantial kinetic isotope effects or rapid loss of deuterium label into the large substrate pool. To preclude this possibility, the reincorporation of hydrogen in predeuterated **1** was examined after alkyne hydrogenation. Once again, only slightly more label exchange occurred during hydrogenation than during exposure to H_2 alone. When this reaction was monitored in situ by $^2H\{^1H\}$ NMR, rapid loss of the deuteride peak was observed. Concurrently, the phosphine peak lost integrated intensity and a new peak appeared at a shift appropriate for olefinic deuterons at rates comparable to the rate of appearance of **2** and **3**. The ratio of the phosphine peak to olefinic peak was 17:2, as expected for a stoichiometric hydrogenation. Further loss of deuterium from the phosphine peak was exceedingly slow. Identical changes were observed in the absence of H_2. Thus, all evidence is consistent with little or no hydrogenation dependent exchange.

The formation and persistence of **3** during alkyne hydrogenation, given its rapid rate of reaction with H_2, suggest that the availability of H_2 is limited under reaction conditions typically used in the present work ($\leq$1 atm of H_2, moderate magnetic stirring). Many investigators have not taken special precautions to optimize H_2 transport during hydrogenation reactions. The reported slower rates of alkyne hydrogenation relative to alkene hydrogenations for many selective homogeneous catalysts could reflect a transport-limited availability of H_2 during the former reactions rather than the true limiting rates.

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Registry No. **1**, 55102-19-7; **2** (5 = 3-hexyne), 97731-68-5; **3**, 82008-46-6; $RuDCl[P(2,6\text{-}D_2C_6H_3)]_3$, 97749-31-0; 2-hexyne, 764-35-2; 3-hexyne, 928-49-4; diphenylacetylene, 501-65-5.

(27) Although the ^{31}P NMR spectrum of **1** establishes that phosphine dissociation is thermodynamically unfavorable,[28] spin saturation transfer[29] experiments conducted by saturating preirradiation of added triphenylphosphine provide evidence for exchange of free and bound phosphine. Rate constants measured over the phosphine concentration range 7.5×10^{-3} to 1.0×10^{-1} M (0.5–6.7 equiv/1) were independent of phosphine concentration within experimental error and had a value of 0.6 s^{-1} at 25 °C. The independence of rate is indicative of a dissociative mechanism of phosphine exchange.

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