Inorg. Chem. **2006**, *45*, 5976–5979

Dynamic Behavior of the Diphosphine Ligand in $H_4Ru_4(CO)_{10}$(dppe) Revisited: Kinetic Data Supporting a Nondissociative Isomerization of the Dppe Ligand

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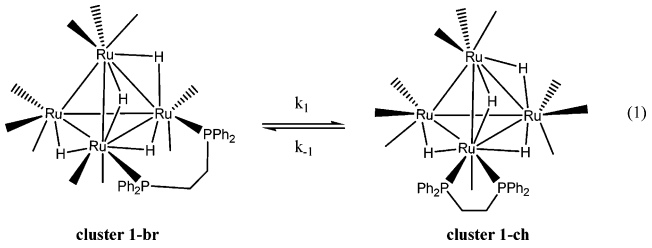
Received March 18, 2006

The kinetics for the bridge-to-chelate isomerization of the dppe ligand in $H_4Ru_4(CO)_{10}$(dppe) have been investigated by UV–vis and NMR spectroscopies over the temperature range of 308–328 K. The isomerization of the ligand-bridged cluster 1,2-$H_4Ru_4(CO)_{10}$(dppe) (**1-br**) was found to be reversible by ^{31}P NMR spectroscopy, affording a K_{eq} = 15.7 at 323 K in favor of the chelating dppe isomer **1-ch**. The forward (k_1) and reverse (k_{-1}) first-order rate constants for the reaction have been measured in different solvents and in the presence of ligand-trapping agents (CO and PPh_3). On the basis of the activation parameters and reaction rates that are unaffected by added CO and PPh_3, a sequence involving the nondissociative migration of a phosphine moiety and two CO groups between basal ruthenium centers is proposed and discussed.

Introduction

The bridge-to-chelate isomerization of the dppe ligand in $H_4Ru_4(CO)_{10}$(dppe) was reported in this journal several years ago by Shapley and Churchill, and their findings served as the first unequivocal paradigm for the coordinative flexibility of a diphosphine ligand in a metal cluster compound.[1,2] The conversion of the kinetically formed bridging isomer to the thermodynamically more stable chelating isomer, which is depicted in eq 1, was found to proceed rapidly in refluxing



cluster 1-br cluster 1-ch (1)

$CHCl_3$ and cyclohexane solvents. A subsequent study on the related clusters $H_4Ru_4(CO)_{10}[PhP_2(CH_2)_nPPh_2]$ confirmed that this isomerization behavior was restricted to dppe, with the ligands $Ph_2P(CH_2)_nPPh_2$ (where n = 1, 3, 4) exhibiting only bridging coordination to the tetraruthenium polyhedron.[3] Clearly, the length of the carbon backbone associated with the diphosphine ligand serves as a variable in the isomerization reaction. The composition of the carbon chain that tethers the two phosphine centers in these ligands and its effect on the P−P isomerization was also demonstrated by the synthesis and examination of $H_4Ru_4(CO)_{10}$(prophos). While the replacement of a hydrogen atom on the ethane bridge in dppe by a methyl group yields the structurally similar prophos ligand,[4] the corresponding 1,2-$H_4Ru_4(CO)_{10}$(prophos) cluster shows no evidence for diphosphine ligand isomerization to the chelated cluster 1,1-$H_4Ru_4(CO)_{10}$(prophos). This observation is of interest, as it indicates that steric effects within the carbon backbone of the diphosphine ligand also influence this particular transformation. Since then, several other reports outlining analogous isomerization behavior in a variety of metal clusters have appeared in the literature.[5–9]

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10.1021/ic060463r CCC: $33.50
Published on Web 06/23/2006

Herein we present our kinetic data for the isomerization of the dppe ligand in $H_4Ru_4(CO)_{10}$(dppe), which support a nondissociative diphosphine ligand pathway that involves the participation of an intermediate that possesses μ_2-dppe and μ_2-CO ligands. These data are contrasted with the related clusters 1,1-$H_4Ru_4(CO)_{10}$[(Z)-$Ph_2PCH{=}CHPPh_2$] and 1,1-$H_4Ru_4(CO)_{10}$[1,2-$(PPh_2)C_6H_4$] that exhibit only a chelating diphosphine ligand. The nature of the ancillary P−P ligand in controlling the coordination mode adopted by the diphosphine ligand and its influence on the dynamics of the isomerization are discussed.

Experimental Section

General. The starting cluster $H_4Ru_4(CO)_{12}$ was prepared from $Ru_3(CO)_{12}$,[10] and the title clusters 1,2- and 1,1-$H_4Ru_4(CO)_{10}$(dppe) were synthesized according to the procedures reported by Shapley and Churchill.[1] The chemicals dppe, PPh_3, and *p*-dimethoxybenzene used in our studies were purchased from Aldrich Chemical Co. and were used as received. All reaction and NMR solvents were distilled from an appropriate drying agent using Schlenk techniques and stored under argon in storage vessels equipped with a high-vacuum Teflon stopcock.[11]

The IR spectral data were recorded on a Nicolet 20 SXB FT-IR spectrometer in sealed 0.1 mm NaCl cells, while the ^{1}H and ^{31}P NMR spectra were recorded at 200 and 121 MHz, respectively, on a Varian Gemini-200 and Varian 300-VXR spectrometers. The reported ^{31}P chemical shift data, which were recorded in the proton-decoupled mode, are referenced to external H_3PO_4 (85%), taken to have $\delta = 0$.

Kinetic Studies. The UV−vis studies were carried out using a cluster concentration of ca. 10^{-4} M using 1.0 cm quartz UV−visible cells that were equipped with a high-vacuum Teflon stopcock to facilitate handling on the vacuum line. Fresh solutions of 1,2-$H_4Ru_4(CO)_{10}$(dppe) were prepared either under argon or CO and used immediately before each kinetic measurement. The Hewlett-Packard 8452A diode array spectrometer employed in our studies was configured with a variable-temperature cell holder and was connected to a VWR constant-temperature circulator, allowing for the quoted temperatures to be maintained within ±0.5 K. The ^{1}H and ^{31}P NMR kinetic and equilibration studies were conducted in 5 mm NMR tubes that possessed a J-Young valve for the easy admission of trapping ligand (PPh_3 or CO gas). All NMR studies employed CD_2Cl_2 as a solvent with a cluster concentration of ca. 10^{-2} M. The NMR samples were heated in the same VWR temperature bath and quenched in an external ice bath immediately before NMR analysis.

The UV−vis kinetics were monitored by following the decrease of the 300 nm absorbance band as a function of time typically for 4−6 half-lifes. The rate constants for the approach to equilibrium (k_e) were determined by nonlinear regression analysis using the single-exponential function:[12]

$$A(t) = A\infty + \Delta A\, e^{(-k_e t)}$$

The reversible nature of the bridge-to-chelate isomerization in $H_4Ru_4(CO)_{10}$(dppe) was established at 323 K by ^{31}P NMR. The integrated intensities of the ^{31}P signals for the bridging and chelating clusters exhibited clean exponential decays and growths, respectively, and afforded values for k_e that were found to be in excellent agreement with those data obtained from the UV−vis experiments. The K_{eq} value reported here for the bridge−chelate equilibrium in $H_4Ru_4(CO)_{10}$(dppe) was determined after the isomerization reactions had reached 10 half-lifes.[13] The ^{1}H NMR kinetic experiment was conducted in the presence the of *p*-dimethoxybenzene, which was added as an internal standard. Here the rate of consumption of cluster **1-br** was measured as a function of time for slightly over 4 half-lifes. The quoted activation parameters were calculated from plots of $\ln(k/T)$ versus T^{-1},[14] with the error limits representing deviation of the data points about the least-squares line of the Eyring plot.

Results and Discussion

The kinetics for the reaction depicted in eq 1 were initially probed by ^{1}H and ^{31}P NMR spectroscopy using toluene-d_8 and $CDCl_3$ as solvents; however, the low solubility of the isomeric clusters in these solvents led to sensitivity problems that were remedied by a change to CD_2Cl_2. The higher solubility of both clusters in CD_2Cl_2 greatly facilitated the rate measurements. Heating a CD_2Cl_2 solution of freshly prepared **1-br** (ca. 10^{-2} M) under argon at 323 K revealed a smooth decrease in the ^{31}P bridging resonance at δ 35 and the formation of a new signal at δ 66. The peak positions of these ^{31}P resonances are in excellent agreement with the weighted-average chemical shift data calculated from the reported slow-exchange spectral data of the bridging and chelating isomers.[1] The isomerization was clean and afforded a 94:6 equilibrium mixture in favor of **1-ch** after 30 h at 323 K (ca. 10 half-lives). The fact that no mention of an equilibrium involving clusters **1-br** and **1-ch** was made in the original report is attributed to the aforementioned solubility problems that could easily complicate the observation of the small amount of the dppe-bridged cluster **1-br** at equilibrium. Nonlinear regression analysis of the ^{31}P NMR data afforded the first-order rate constants (k_e) for the consumption and formation of **1-br** and **1-ch**, respectively. These computed rate constants to equilibrium were found to be identical within experimental error, with the average of these rates reported in Table 1, as well as the values for the forward (k_1) and reverse (k_{-1}) rate contributions.[15]

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(13) The ^{31}P spin−lattice (T_1) relaxation times for the isomeric clusters were determined by using the standard inversion−recovery pulse sequence. The T_1 values found for the clusters **1-br** (3.4 s) and **1-ch** (2.1 s) were used in the determination of an appropriate acquisition delay for the accurate collection of our kinetic and thermodynamic data free from saturation effects. Here the use of a 41.5° flip angle and an acquisition delay of 20 s ensured complete relaxation (>99.6%) of all ^{31}P nuclei in solution.
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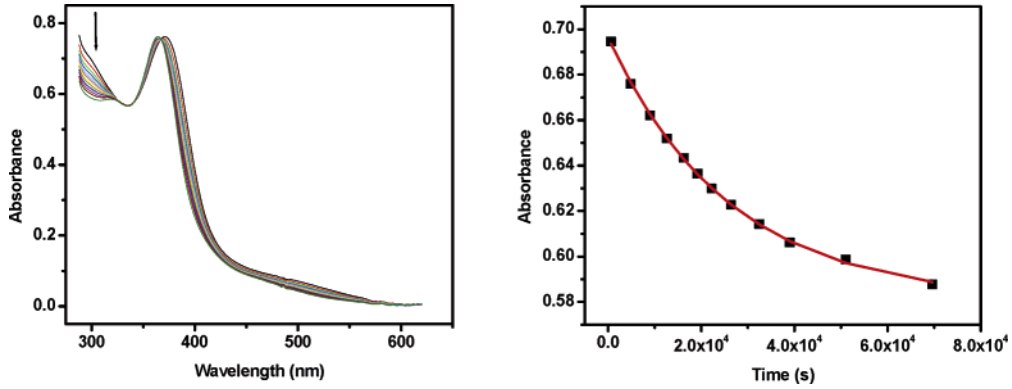


Figure 1. UV−vis spectral changes for the isomerization of **1-br** ⇄ **1-ch** in toluene at 323 K (left) and the absorbance versus time curves for the experimental data (■) and the least-squares fit of k_e (right).

Table 1. Kinetic Data for Diphosphine Isomerization in $H_4Ru_4(CO)_{10}(dppe)$[a]

temp (K)	solvent	10^5k_e (s^{-1})[b]	10^5k_1 (s^{-1})	10^5k_{-1} (s^{-1})	method
308.0	toluene	1.78 ± 0.0	1.67 ± 0.04	0.11 ± 0.04	UV−vis
313.0	toluene	2.57 ± 0.09	2.42 ± 0.09	0.15 ± 0.09	UV−vis
313.0	toluene[c]	2.35 ± 0.04	2.21 ± 0.04	0.14 ± 0.04	UV−vis
313.0	CH_2Cl_2	1.95 ± 0.05	1.83 ± 0.05	0.12 ± 0.05	UV−vis
318.0	toluene	3.84 ± 0.03	3.61 ± 0.03	0.23 ± 0.03	UV−vis
323.0	toluene	4.95 ± 0.10	4.65 ± 0.10	0.30 ± 0.10	UV−vis
323.0	toluene[c]	4.30 ± 0.04	4.04 ± 0.04	0.26 ± 0.04	UV−vis
323.0	CH_2Cl_2	5.75 ± 0.11	5.41 ± 0.11	0.34 ± 0.11	UV−vis
323.0	THF	3.81 ± 0.07	3.58 ± 0.07	0.23 ± 0.07	UV−vis
323.0	CD_2Cl_2	5.88 ± 0.09	5.53 ± 0.09	0.35 ± 0.09	^{31}P NMR
323.0	CD_2Cl_2[d]	7.40 ± 0.47	6.96 ± 0.47	0.44 ± 0.47	^{1}H NMR
328.0	toluene	7.37 ± 0.07	6.93 ± 0.07	0.44 ± 0.07	UV−vis

[a] All kinetic data were collected under argon unless otherwise noted. [b] The quoted rate constants (k_e) represent the rate toward equilibrium, as determined by following the decrease in the 300 nm band (UV−vis), changes in the ^{31}P resonances for the bridging and chelating isomers (^{31}P NMR), or the decrease in the hydride resonance for the bridging isomer (^{1}H NMR). [c] Experiments conducted under 1 atm of CO. [d] Experiment conducted in the presence of 10 equiv of PPh_3.

The effect of added PPh_3 on the reaction was also studied by ^{1}H NMR spectroscopy in CD_2Cl_2 at 323 K by monitoring the rate of consumption of **1-br**. The progress of the reaction was determined through the use of the hydride resonance at δ −17.15 belonging to the four rapidly exchanging hydride groups.[1] The conversion from **1-br** to **1-ch** takes place cleanly and without the incorporation of PPh_3 into either **1-br** or **1-ch**. Good first-order kinetics were found for over 4 half-lives from the plot of ln[**1-br**] versus time, and the computed value of k_e [7.40(0.47) × 10^{-5} s^{-1}] agrees nicely with the rate obtained from the ^{31}P NMR experiment. The similarity in the k_e values and the absence of PPh_3 incorporation into the isomeric clusters **1-br** and **1-ch** support a nondissociative, unimolecular isomerization of the dppe ligand.

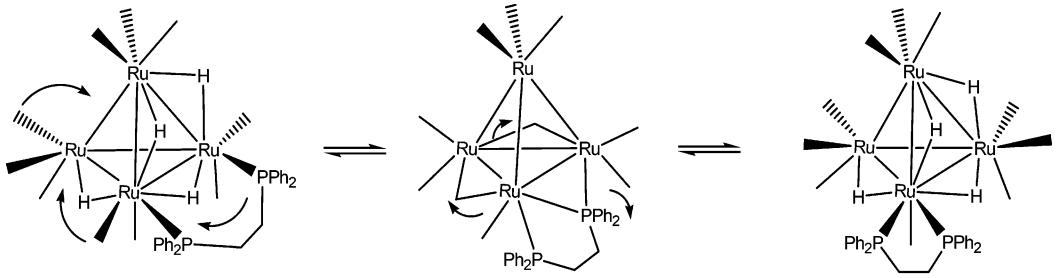
The equilibrium between **1-br** and **1-ch** was more fully investigated by UV−vis spectroscopy over the temperature range of 308−328 K using toluene as the reaction solvent. Here the rate to equilibrium was measured by following the decrease in the 300 nm band belonging to **1-br**. Figure 1 shows the spectral changes that accompany the isomerization. Isosbestic points at 368 and 334 nm confirm that the isomerization is free from kinetic complications. As in the case of the NMR reaction carried out with added PPh_3, the presence of added CO (1 atm) afforded rates indistinguishable to those reactions conducted under argon (entries 2 and 3; entries 6 and 7), while reactions run in CH_2Cl_2 and THF (entries 4, 8, and 9) showed no substantial solvent effect on the isomerization.[16] This latter observation argues against the formation of a highly polarized intermediate or transition state. The Eyring activation parameters for the forward and reverse directions of the isomerization were calculated as $\Delta H^{\ddagger}$ = 13.2(9) kcal/mol and $\Delta S^{\ddagger}$ = −38(3) eu and $\Delta H^{\ddagger}$ = 13.0(8) kcal/mol and $\Delta S^{\ddagger}$ = −44(3) eu, respectively.

Our kinetic data support a nondissociative, intramolecular process that involves the migration of the dppe ligand across a ruthenium−ruthenium bond from **1-br** to **1-ch**. A rate-limiting process involving the dissociative loss of CO, H_2, or release of one end of the dppe ligand from the Ru_4 cluster may be eliminated from consideration on the basis of the invariant rates in the presence of added CO and PPh_3, coupled with the large negative entropies of activation. The computed values for $\Delta S^{\ddagger}$ are consistent with a structural reorganization whereby one of the terminally bound η^1-PPh_2 moieties transforms into a μ-PPh_2 moiety as it transits across a Ru−Ru bond.[17,18] Implicit in such a scenario is the simultaneous migration of CO ligands and an "opening up" of the bridging hydride groups. Scheme 1 illustrates a plausible scenario for the isomerization of the dppe ligand in $H_4Ru_4(CO)_{10}(dppe)$. Given the documented edge−terminal−edge hydride mobility in both clusters **1-br** and **1-ch**, a merry-go-round migration involving two equatorially bound CO groups and one end of the dppe ligand would allow the permutation of these three ligands between the three ruthenium centers. Not shown in our isomerization scheme is the terminal hydride group at each ruthenium center in the intermediate cluster containing the bridging dppe and CO ligands.[19] The transient existence of terminal hydride groups facilitates the overall merry-go-round migration of the phosphine and CO ligands by eliminating the two basally

(15) The values of k_1 and k_{-1} for a reversible first-order isomerization were computed with the aid of the following equations: $k_e = k_1 + k_{-1}$ and $K_{eq} = k_1/k_{-1}$. Here the magnitude of K_{eq} is assumed to be constant over the temperature range over our studies. See: Espenson, J. H. *Chemical Kinetics and Reaction Mechanisms*, 2nd ed.; McGraw-Hill: New York, 1995.

(16) The UV−vis data have also been treated in terms of a reversible equilibrium, as were those data obtained from the ^{31}P NMR experiment.

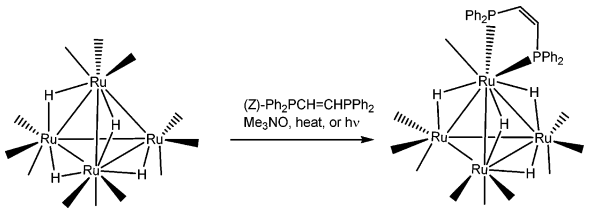
Scheme 1



cluster **1-br** cluster **1-ch**

confined edge-bridged hydrides that would otherwise retard the proposed migratory path of the nonhydride ligands.

The lack of observable bridge-to-chelate isomerization for the prophos ligand in 1,2-$H_4Ru_4(CO)_{10}$(prophos) suggests that the presence of a single methyl group on the two-carbon ethane chain is sufficient condition to negate the isomerization reaction ($\Delta G^{\ddagger}_{\text{prophos}} > \Delta G^{\ddagger}_{\text{dppe}}$). This is understandable and expected if the atoms associated with the ethane backbone must adopt an eclipsed conformation during the transit of the diphosphine ligand across the ruthenium−ruthenium bond. Indirect proof for the importance of such subtle steric effects in the diphosphine isomerization reaction derives from the related clusters $H_4Ru_4(CO)_{10}$[(*Z*)-$Ph_2PCH{=}CHPPh_2$][20] and $H_4Ru_4(CO)_{10}$[1,2-$(Ph_2P)_2C_6H_4$][21] recently prepared by us. These two clusters exhibit only chelating diphosphine ligands irrespective of the methods used to activate the parent cluster, as shown in eq 2 for the former cluster. It is believed that the unsaturated C=C backbone that links the two phosphine centers promotes the bridge-to-chelate isomerization in the case of the unsaturated ligands (*Z*)-$Ph_2PCH{=}CHPPh_2$ and 1,2-$(Ph_2P)_2C_6H_4$ through the elimination of the aforementioned eclipsing interactions in the saturated carbon bridges of dppe, prophos, and longer-chain diphosphine homologues.



(2)

Acknowledgment. We thank Prof. John Shapley for helpful comments concerning this work. Financial support from the Robert A. Welch Foundation (Grant No. B-1093) is appreciated.

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