Ruthenium Dihydride Complexes: NMR Studies of Intramolecular Isomerization and Fluxionality Including the Detection of Minor Isomers by Parahydrogen-Induced Polarization

Daniele Schott, Christopher J. Sleigh, John P. Lowe, Simon B. Duckett,* and Roger J. Mawby

Department of Chemistry, University of York, Heslington, York YO10 5DD, U.K.

Martin G. Partridge

Synetix PCEO, P.O. Box 1, Billingham, Cleveland TS23 1LB, U.K.

NMR studies reveal that complexes $Ru(CO)_2(H)_2L_2$ (L = PMe_3, PMe_2Ph, and $AsMe_2Ph$) can have three geometries, *ccc, cct*-L, and *cct*-CO, with equilibrium ratios that are highly dependent on the electronic properties of L; the *cct*-L form is favored, because the σ-only hydride donor is located trans to CO rather than L. When L = PMe_3, the *ccc* form is only visible when p-H_2 is used to amplify its spectral features. In contrast, when L = $AsMe_2Ph$, the *ccc* and *cct*-L forms are present in similar quantities and, hence, must have similar free energies; for this complex, however, the *cct*-CO isomer is also detectable. These complexes undergo a number of dynamic processes. For L_2 = dppe, an interchange of the hydride positions within the *ccc* form is shown to be accompanied by synchronized CO exchange and interchange of the two phosphorus atoms. This process is believed to involve the formation of a trigonal bipyramidal transition state containing an η^2-H_2 ligand; in view of the fact that k_{HH}/k_{DD} is 1.04 and the synchronized rotation when L_2 = dppe, this transition state must contain little H–H bonding character. Pathways leading to isomer interconversion are suggested to involve related structures containing η^2-H_2 ligands. The inverse kinetic isotope effect, $k_{HH}/k_{DD} = 0.5$, observed for the reductive elimination of dihydrogen from $Ru(CO)_2(H)_2$dppe suggests that substantial H–H bond formation occurs before the H_2 is actually released from the complex. Evidence for a substantial steric influence on the entropy of activation explains why $Ru(CO)_2(H)_2$dppe undergoes the most rapid hydride exchange. Our studies also indicate that the species $[Ru(CO)_2L_2]$, involved in the addition of H_2 to form $Ru(CO)_2(H)_2L_2$, must have singlet electron configurations.

Introduction

Over the past forty years there have been many reports of the ability of ruthenium complexes to catalyze reactions. An early example of ruthenium-based catalysis was the use of $Ru(CO)_3(PPh_3)_2$, originally synthesized by Collman and Roper,[1] to catalyze the conversion of alkenes to aldehydes under high pressures of H_2 and CO. In this case, Wilkinson and co-workers found that $Ru(CO)_3(PPh_3)_2$ was converted to $Ru(CO)_2(H)_2(PPh_3)_2$ before hydroformylation commenced[2]
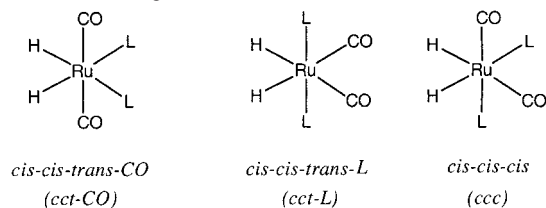
and also that the addition of PPh_3 decreased the rate of hydroformylation. This could imply that the dissociation of PPh_3 is required at some point in the catalytic cycle, perhaps to provide a vacant site for alkene coordination. However, it is possible that PPh_3 could compete for a site made available by the dissociation of CO, and in complexes containing mutually trans hydride and carbonyl ligands, the trans labilizing influence of the hydride ligand could well lead to CO loss.[3] Eisenberg and co-workers have also examined the role of $Ru(CO)_3(PPh_3)_2$ in hydroformylation, and have reported that the catalysis can be initiated and accelerated photochemically.[4] Related ruthenium complexes

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* Author to whom correspondence should be addressed. E-mail: sb3@york.ac.uk.

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Ruthenium Dihydride Complexes

Scheme 1. Labeling Scheme for Ru(H)$_2$(CO)$_2$L$_2$

cis-cis-trans-CO   cis-cis-trans-L   cis-cis-cis
(cct-CO)   (cct-L)   (ccc)

such as Ru(CO)(H$_2$)(PPh$_3$)$_3$ have found use in catalytic C–C bond-forming reactions involving aromatic ketones and suitable alkenes that yield ortho-alkylated adducts.[5] Ruthenium complexes also feature as successful asymmetric hydrogenation catalysts[6] and have found an ever-widening role as olefin metathesis catalysts.[7]

One of the principal problems associated with the examination of reaction mechanisms relates to the need to characterize reaction intermediates and probe their dynamic behavior. This problem is further exacerbated by the fact that each intermediate can exist in several distinct structural forms with different activities. Halpern and Brown most elegantly illustrated the importance of detecting minor species during studies involving the hydrogenation of prochiral enamides by cationic rhodium complexes. Careful NMR work revealed that, contrary to initial suggestions, the less-stable enamide isomer reacted substantially faster with H$_2$ and was responsible for the observed enantiomeric selectivity in the hydrogenation product.[8] In this paper we report on the characterization and the reactivity of a series of ruthenium complexes with the general formula Ru(CO)$_2$(H)$_2$L$_2$. Previously, complexes of this type containing two monodentate ligands L had been shown to adopt a preferred geometry in which the ligands L are mutually trans and the other two ligand pairs are mutually cis.[9] This structure, unambiguously labeled *cct-P,* is illustrated in Scheme 1. For Ru(CO)$_2$(H)$_2$-(AsMe$_2$Ph)$_2$, a second isomer in which all the ligand pairs are mutually cis (*ccc*) is readily observed.[10]

Detailed studies of the reactions of Ru(CO)$_2$(H)$_2$(PMe$_2$Ph)$_2$ with alkynes and alkenes have been reported.[11,12] This dihydrido complex converts alkynes RC≡CH (where R = Ph or CMe$_3$) to alkenes in a reaction sequence which also involves the formation of alkynyl complexes Ru(CO)$_2$(C≡CR)H(PMe$_2$Ph)$_2$. A sequence consistent with these observations would involve initial CO loss to generate a site for

alkyne binding, combination of alkyne and hydride ligands to form a vinyl ligand, and reoccupation of the now vacant site by CO. Elimination of alkene, leaving the 16-electron species Ru(CO)$_2$(PMe$_2$Ph)$_2$, could be followed by the oxidative addition of the alkyne, and this is consistent with deuterium labeling studies which indicate that the hydride ligand in the product Ru(CO)$_2$(C≡CR)H(PMe$_2$Ph)$_2$ is derived from the alkyne.[11] An analogue of Ru(CO)$_2$(PMe$_2$Ph)$_2$, the complex Ru(CO)$_2$(PBu$^t_2$Me)$_2$, has been isolated and shown to possess a singlet ground state and a C_{2v} structure.[13] Interestingly, the singlet state of the related model complex Ru(PH$_3$)$_4$ has been calculated to lie 48.9 kJ mol^{-1} below the triplet state, while calculations for Fe(PH$_3$)$_4$ indicate that the triplet state is the more stable by 33.4 kJ mol^{-1}.[14] The complexes described in this paper are Ru(CO)$_2$(H)$_2$(dppe), **1** (dppe = PPh$_2$CH$_2$CH$_2$PPh$_2$); Ru(CO)$_2$(H)$_2$(PMe$_2$Ph)$_2$, **2**; Ru(CO)$_2$(H)$_2$(PMe$_3$)$_2$, **3**; Ru(CO)$_2$(H)$_2$(AsMe$_2$Ph)$_2$, **4**; and Ru-(CO)$_2$(H)$_2$(PMe$_3$)(PMe$_2$Ph), **5**. We characterize the fluxional behavior of the complexes and describe a study of their reactions with parahydrogen (*p*-H$_2$). We pay particular attention to the detection and characterization of minor isomers of these dihydrides and discuss the shape and electronic configuration of the associated intermediates. On the basis of these data, steric and electronic effects are separated and linked to isomer stability. In addition, structural interconversion is linked to the formation of an intermediate containing an η^2-H$_2$ ligand. Some of this work has already been published as a preliminary communication.[15]

Experimental Section

The synthesis of the dichloro complexes of ruthenium Ru-(CO)$_2$Cl$_2$L$_2$ (where L = PMe$_3$, PMe$_2$Ph, and AsMe$_2$Ph) was achieved according to literature methods.[16,17] These complexes were then converted to dihydrido analogues Ru(CO)$_2$(H)$_2$L$_2$ via NaBH$_4$ reduction in methanol.[9] Ru(CO)$_2$Cl$_2$(PMe$_3$)(PMe$_2$Ph) was prepared according to literature methods by adding the appropriate quantity of PMe$_3$ to an ethanolic solution of [Ru(CO)$_2$Cl$_2$(PMe$_2$Ph)]$_2$ and stirring the solution for 1 h. White crystals of Ru(CO)$_2$Cl$_2$(PMe$_3$)-(PMe$_2$Ph) were obtained on removal of the solvent, and these were converted to Ru(CO)$_2$(H)$_2$(PMe$_3$)(PMe$_2$Ph) by reaction with NaBH$_4$ in methanol under a hydrogen atmosphere. It should be emphasized that the product Ru(CO)$_2$(H)$_2$(PMe$_3$)(PMe$_2$Ph) is contaminated by both Ru(CO)$_2$(H)$_2$(PMe$_3$)$_2$ (5%) and Ru(CO)$_2$(H)$_2$(PMe$_2$Ph)$_2$ (15%) after this process. The complex Ru(CO)$_2$(H)$_2$(dppe) was obtained by UV irradiation of a toluene solution of Ru(CO)$_3$(dppe)[2] under 3 atm of H$_2$. A ^{31}P-NMR spectrum recorded after 2 h of irradiation showed that the resonance for Ru(CO)$_3$(dppe) had almost vanished, and that new doublets for Ru(CO)$_2$(H)$_2$(dppe) **1** had appeared at δ 71.5 and 64.6. A quantitative conversion to **1** was achieved after the removal of the mixture of CO and H$_2$ by the freeze/pump/thaw

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method, followed by repressurization with H_2, and irradiation for an additional 2 h. The same technique, using D_2 instead of H_2, was employed to obtain $Ru(CO)_2(D)_2(dppe)$ **1-D$_2$**. A similar approach has been used to prepare $Ru(CO)_2(H)_2(dmpe)$.[18]

A sample of ^{13}CO-enriched $Ru(CO)_2(H)_2(PMe_3)_2$ was obtained as follows. First, a sample of $Ru(CO)_x(^{13}CO)_{3-x}(PMe_3)_2$ (where $x = 3, 2, 1,$ or 0) was prepared by photolysis of $Ru(CO)_3(PMe_3)_2$ under ^{13}CO. The solution was then placed under an atmosphere of hydrogen and photolyzed for 15 min. The ^1H-NMR spectrum of the solution now contained a triplet at δ −7.48 for the hydride resonance of the product with fine structure due to the coupling to one or two ^{13}C nuclei.

According to NMR spectroscopy, complexes **1−4** were free from any impurities at the outset of the measurements. In the case of the NMR studies on **5**, where a mixture of species was present originally, and **4**, where slight decomposition was observed at higher temperatures, 2-D monitoring of the dynamic behavior of the system demonstrated that none of the extra species were involved in the reported exchange processes.

Exchange Process Monitoring. To monitor the exchange pathways involving complexes **1−4**, a series of phase-sensitive EXSY spectra were recorded at selected temperatures with different mixing times τ (usually 25, 50, 75, 200, 400, 600, and 800 ms). For processes involving the exchange of nuclei between two sites, exact rate constants can be determined via analysis of the intensity versus the mixing time profile.[19] The addition of a third spin, however, complicates matters. Several methods have been applied to the determination of rate constants in multispin systems: of these methods, a comprehensive matrix method is the most thorough.[19] In this work, we have employed Jeener's simplification of the matrix method for two sites,[19] the comprehensive matrix approach,[20] and direct simulation. For the studies of **3** and **4** involving parahydrogen enhancement, we have used Jeener's approach alone. Here, integration of the diagonal-peak and cross-peak resonance volumes provides the data necessary for the calculation of the rate constant for exchange according to eq 1

$$\ln\left(\frac{\frac{a_A}{a_{AB}} + 1}{\frac{a_A}{a_{AB}} - 1}\right) = k_{ex}t_m \quad (1)$$

where a_A and a_{AB} are respectively the integrals of diagonal-peak and cross-peak volume, k_{ex} is the exchange rate constant, and t_m is the mixing time. This process is straightforward for the exchange of hydrides within the *ccc* isomer of complexes $Ru(CO)_2(H)_2L_2$. Since the *intra−ccc* interchange process occurs independently of the *ccc−cct* interconversion process, rate constants for the former process were calculated using an "effective diagonal" made up of the sum of volume elements due to the *ccc* isomer. It should also be noted that the equilibrium concentrations of the *cct* and *ccc* isomers of **2** and **3** revealed that $k_{cct\rightarrow ccc} \ll k_{ccc\rightarrow cct}$. To check the validity of this approximation, we analyzed the data for **4** using the simplified approach and then demonstrated that the matrix method yielded the same solution.

For the least-mean-squares method, the integrals of the diagonal peaks and corresponding exchange cross-peaks were first normal-

ized to 100%. A kinetic model was then constructed that allowed the peak intensities to be explicitly calculated as a function of the exchange rate constant and reaction time. The calculated peak intensities were compared to the experimental values, noting the squares of the differences.[21] The rate constants were varied until the sum of the squares of the differences between measured and simulated points was minimized. This was carried out using Microsoft Excel 97. Rate constants obtained in this way were multiplied by a factor of 2 to take into account the analysis method.[22]

Results

Characterization and Dynamic Behavior of Ru(CO)$_2$-(H)$_2$(dppe) 1. NMR spectra of **1** were recorded in a d_8-toluene solution at 296 K. As described in the previous section, the ^{31}P-NMR spectrum of **1** contained a pair of doublet resonances at δ 71.5 and 64.5. In the ^1H-NMR spectrum of **1**, the resonances for the two hydride ligands appeared as doublets of doublets of doublets centered at δ −7.55 and −6.32, and the H−H coupling constant, $^2J_{HH}$, was −4.5 Hz. For the resonance at δ −7.55, the magnitudes of the coupling constants to phosphorus, $|^2J_{PH}|$, 21.3 and 26.4 Hz, revealed that the hydride ligand concerned was cis to both phosphorus atoms (and, therefore, trans to CO). For the resonance at δ −6.32, the values of $|^2J_{PH}|$ were 21.7 and 73.8 Hz, indicating that this hydride ligand was cis to one phosphorus atom and trans to the other. Selective irradiation at the frequency corresponding to δ 71.5 in the ^{31}P spectrum removed the smaller of the two doublet splittings for the resonance at δ −6.32 and one of the two doublet splittings for the resonance at δ −7.55, while irradiation at the frequency corresponding to δ 64.5 removed the larger of the two doublet splittings for the resonance at δ −6.32 and, again, one doublet splitting for the other resonance. This established that the ^{31}P nucleus giving the resonance at δ 71.5 was cis to both hydride ligands, whereas that responsible for the resonance at δ 64.5 was trans to one hydride and cis to the other. In the $^{13}C\{^1H\}$-NMR spectrum, the resonances for the carbonyl ligands were a triplet ($|^2J_{PC}| = 4.7$ Hz) at δ 201.3 and a doublet of doublets ($|^2J_{PC}| = 7.1$ and 79.5 Hz) at δ 203.8, placing one carbonyl ligand cis to both phosphorus atoms and the other cis to one phosphorus atom and trans to the other. Clearly $Ru(CO)_2(H)_2(dppe)$ **1** possesses the *ccc* structure shown in Figure 1.

Assignments of resonances for individual carbon and hydrogen atoms within the dppe ligand were made on the basis of $^{13}C\{^1H, ^{31}P\}$, COSY, HMQC, and nOe spectra.[23] These studies were performed at 295 K, a temperature at

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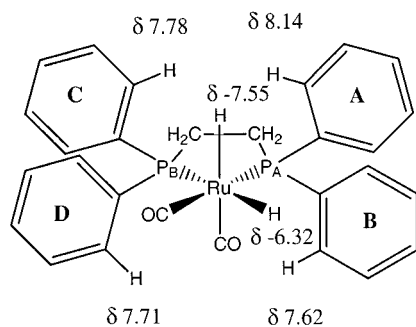
Figure 1. Schematic view of the structure of **1**. The phenyl rings are indicated by the labels A−D, and the chemical shifts of the ortho protons and hydride ligands are indicated.

which it was clear that rotation about all the phosphorus−phenyl bonds was rapid on the NMR time scale. The data obtained from these spectra are listed in Table 1a. It should be noted that separate sets of proton and carbon signals were detected for each of the four phenyl rings (labels A−D in Figure 1). In the nOe spectrum (measured in phase-sensitive mode) the signal at δ −6.32, due to the hydride ligand trans to phosphorus, connected strongly to the phenyl ortho proton resonances at δ 8.14 and 7.62, thereby identifying these resonances as belonging to the rings (A and B) attached to the right-hand phosphorus atom P_A in Figure 1. Since the resonance at δ −7.55 connected strongly with ortho protons at δ 8.14 and 7.78, it was clear that the δ 8.14 resonance must belong to ring A and δ 7.78 to ring C. Data from selectively ^{31}P-decoupled $^{13}C\{^1H\}$ spectra confirmed that rings A and B were attached to the right-hand phosphorus atom (P_A resonance at δ 71.5) and C and D to the left-hand phosphorus atom (P_B resonance at δ 64.5).

The nOe spectra (normally ^{31}P-decoupled) also contained *positive* cross-peaks connecting the two hydride resonances. This observation indicated that the hydride ligands interchanged positions, and analysis according to the methods outlined in the Experimental Section yielded the rate constants and activation parameters listed in Table 2 (observations between 295 and 328 K). Interestingly, positive cross-peaks also connected specific *ortho*-phenyl protons in different phenyl rings, as illustrated by Figure 2. It was evident, for example, that phenyl ring A must exchange with ring C (responsible for the resonances at δ 8.14 and 7.78, respectively). Similarly, it could be seen that ring B must exchange positions with ring D. At 306.5 K, the rate constant for hydride interchange was determined to be 1.20 s^{-1}, while that for *ortho*-phenyl proton exchange was 1.28 s^{-1}. Figure 3 illustrates the match between the experimental data and the simulated data at 317 K.

To examine the fluxional process in more detail, a high-resolution 2-D EXSY measurement was performed in which couplings between hydride ligands and ^{31}P nuclei were retained (Figure 4). This spectrum revealed that the four components of the hydride resonance at δ −6.32, which correspond to the four different combinations of phosphorus spin states, connected to specific components within the δ −7.55 resonance. Mann and co-workers have previously used this approach to study the hydride ligand interchange
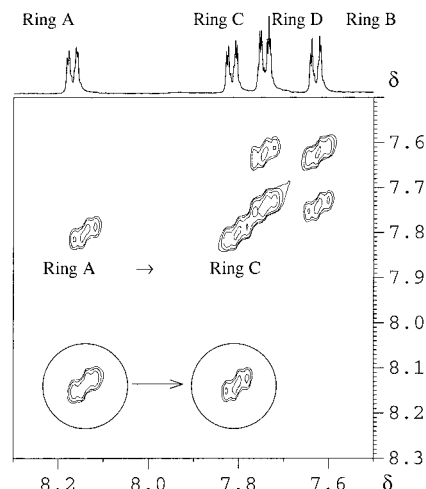

Figure 2. Two-dimensional $^1H-^1H$-nOe spectrum (positive contours) of complex **1**, showing resonance connections in the ortho proton region that arise due to phenyl ring interchange in **1** at 296 K. The spectrum was recorded with a mixing time of 1 s. Transfer of magnetization from the ortho proton resonance of ring A into the corresponding resonance of ring C (see Figure 1 for ring labels) is specifically highlighted.
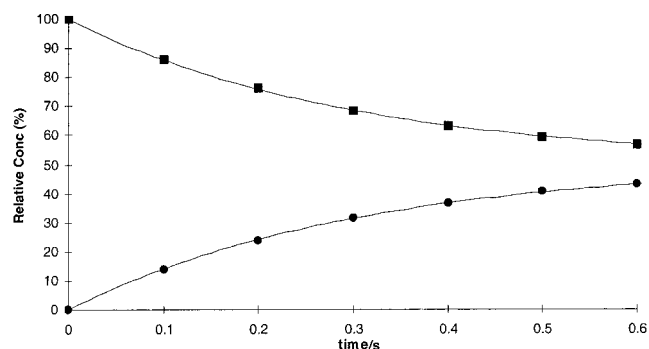

Figure 3. Simulation/experimental trace showing data mapping the exchange of ring A (■) into ring C (●) of **1** in toluene-d_8 at 317 K. The defined points represent experimental data, and the solid line indicates the simulated values obtained when k_{ex} is 3.28 s^{-1}.
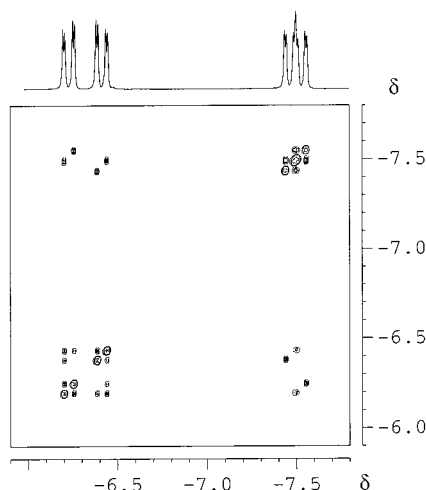

Figure 4. $^1H\{^{31}P\}$-EXSY spectrum (positive contours) of a sample containing **1** in $C_6D_5CD_3$ at 305 K with a mixing time of 0.5 s. Exchange peaks connect the hydride resonances of *ccc*-**1**.

pathway of Ru(CO)(H)$_2$(PPh$_3$)$_3$.[24] The observed connections matched those required for an *intra*-molecular process

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Table 1

a. NMR Data for Complex **1** in Toluene-d_8 at 296 K

nucleus	Ru(CO)$_2$-(H)$_2$(dppe) **1**	δ (multiplicity)	assignment	coupling constant (Hz) assignment
^{1}H	hydride	−7.55 (ddd)	Ru-H	−4.5 $^2J_{HH}$, 21.3 $|^2J_{PH}|$, 26.4 $|^2J_{PH}|$
		−6.32 (ddd)	Ru-H	−4.5 $^2J_{HH}$, 21.7 $|^2J_{P(A)H}|$, 73.8 $|^2J_{P(B)H}|$
	dppe, ortho	8.14 (m^a)	ring A	8.4 $|^3J_{P(B)H}|$
		7.62 (m^a)	ring B	8.3 $|^3J_{P(B)H}|$
		7.78 (m^a)	ring C	8.3 $|^3J_{P(A)H}|$
		7.71 (m^a)	ring D	8.4 $|^3J_{P(A)H}|$
	dppe, meta	7.14 (m^a)	ring A	
		7.09 (m^a)	ring B	
		7.12 (m^a)	ring C	
		7.15 (m^a)	ring D	
	dppe, para	7.10 (m^a)	ring A	
		7.04 (m^a)	ring B	
		7.07 (m^a)	ring C	
		7.10 (m^a)	ring D	
	dppe, ethane bridge	2.09 (m)	close to ^{31}P$_{(B)}$	
		2.24 (m)	close to ^{31}P$_{(B)}$	
		1.97 (m)	close to ^{31}P$_{(A)}$	
		2.26 (m)	close to ^{31}P$_{(A)}$	
^{31}P		71.5 (d)	dppe, ^{31}P$_{(A)}$	12.7 $|^2J_{PP}|$
		64.5 (d)	dppe, ^{31}P$_{(B)}$	12.7 $|^2J_{PP}|$

nucleus	Ru(CO)$_2$-(H)$_2$(dppe) **1**	δ (multiplicity)	assignment	coupling constant (Hz) assignment
^{13}C	dppe, C^1	136.3 (d)	ring A	15.0 $|^1J_{P(A)C}|$
		137.2 (d)	ring B	14.8 $|^1J_{P(A)C}|$
		137.6 (d)	ring C	14.2 $|^1J_{P(B)C}|$
		137.6 (d)	ring D	14.6 $|^1J_{P(B)C}|$
	dppe, C^2 and C^6	133.7 (d)	ring A	12.5 $|^2J_{P(A)C}|$
		132.2 (d)	ring B	13.1 $|^2J_{P(A)C}|$
		132.3 (d)	ring C	12.6 $|^2J_{P(B)C}|$
		131.7 (d)	ring D	11.4 $|^2J_{P(B)C}|$
	dppe, C^3 and C^5	127.8 (d)	ring A	9.1 $|^3J_{P(A)C}|$
		128.2 (d)	ring B	10.2 $|^3J_{P(A)C}|$
		128.1 (d)	ring C	10.8 $|^3J_{P(B)C}|$
		128.3 (d)	ring D	10.0 $|^3J_{P(B)C}|$
	dppe, C^4	129.8 (s)	ring A	
		129.3 (s)	ring B	
		129.4 (s)	ring C	
		129.5 (s)	ring D	
	dppe, ethane bridge	30.5 (dd)	close to ^{31}P$_{(B)}$	16.0 $|^2J_{CP}|$, 27.0 $|^1J_{CP}|$
		29.5 (dd)	close to ^{31}P$_{(A)}$	20.8 $|^2J_{CP}|$, 28.3 $|^1J_{CP}|$
	CO	203.8 (dd)	trans to ^{31}P$_{(A)}$	7.1 $|^2J_{P(B)C}|$, 79.5 $|^2J_{P(A)C}|$
		201.3 (t)	CO cis to both ^{31}P	4.7 $|^2J_{PC}|$

b. NMR Data for Complexes **2**−**6** in Toluene-d_8

complex, temp	nucleus	δ (multiplicity)	assignment	coupling constant (Hz) assignment
Ru(CO)$_2$(H)$_2$-(PMe$_2$Ph)$_2$	^{1}H-NMR	7.64 (m)	C$_6$H$_5$ (o-H)	
cct-**2**		1.60 (t)	CH_3	6.5 $|^2J_{PH} + {}^4J_{PH}|$
296 K		−7.13 (t)	Ru-H	26.0 $|^2J_{PH}|$
	^{31}P-NMR	12.0 (s)	PMe$_2$Ph	
ccc-**2**	^{1}H-NMR	−7.08 (ddd)	Ru-H	27 $|^2J_{PH}|$, 21 $|^2J_{PH}|$, −5.9 $^2J_{HH}$
333 K		−7.66 (ddd)	Ru-H	73 $|^2J_{PH}|$, 32 $|^2J_{PH}|$, −5.9 $^2J_{HH}$
	^{31}P-NMR	9.1 (d)	PMe$_2$Ph	28 $|^2J_{PP}|$
		0.2 (d)	PMe$_2$Ph	28 $|^2J_{PP}|$
Ru(CO)$_2$(H)$_2$-(PMe$_3$)$_2$	^{1}H-NMR	1.24 (t)	CH_3	7.0 $|^2J_{PH} + {}^4J_{PH}|$
cct-**3**		−7.48 (t)	Ru-H	26 $|^2J_{PH}|$
296 K	^{31}P-NMR	−2.2 (s)	PMe$_3$	
	^{13}C-NMR	202.4 (t)	CO	9.3 $|^2J_{CP}|$
		24.8 (t)	CH_3	16.4 $|^2J_{CP} + {}^4J_{CP}|$
ccc-**3**	^{1}H-NMR	−7.51 (ddd)	Ru-H	30 $|^2J_{PH}|$, 22 $|^2J_{PH}|$, −6.0 $^2J_{HH}$
333 K		−7.77 (ddd)	Ru-H	73 $|^2J_{PH}|$, 33 $|^2J_{PH}|$, −6.0 $^2J_{HH}$
	^{31}P-NMR	−6.8 (d)	PMe$_3$	20 $|^2J_{PP}|$
		−16.4 (d)	PMe$_3$	20 $|^2J_{PP}|$
cct-**4**	^{1}H-NMR	1.46 (s)	CH_3	
298 K		−7.42 (s)	Ru-H	
Ru(CO)$_2$(H)$_2$-(AsMe$_2$Ph)$_2$	^{1}H-NMR	1.20 (s)	CH_3	
ccc-**4**		1.17 (s)	CH_3	
298 K		1.16 (s)	CH_3	
		1.13 (s)	CH_3	
		−6.86 (d)	Ru-H	−5.8 $^2J_{HH}$
		−8.70 (d)	Ru-H	−5.8 $^2J_{HH}$

complex, temp	nucleus	δ (multiplicity)	assignment	coupling constant (Hz) assignment
Ru(CO)$_2$(H)$_2$-(PMe$_3$)(PMe$_2$Ph)	^{1}H-NMR	7.66 (m)	C$_6$H$_5$ (o-H)	
cct-**5**		1.58 (dd)	P(CH_3)$_2$Ph	8.5 $|^2J_{PH}|$, 2.0 $|^4J_{PH}|$
298 K		1.22 (dd)	P(CH_3)$_3$	9.3 $|^2J_{PH}|$, 2.0 $|^4J_{PH}|$
		−7.35 (t)	Ru-H	27 $|^2J_{PH}|$
	^{31}P-NMR	11.3 (d)	PMe$_2$Ph	222 $|^2J_{PP}|$
		−1.5 (d)	PMe$_3$	222 $|^2J_{PP}|$
ccc-**5** isomer **1**	^{1}H-NMR	−7.33 (ddd)	Ru-H	−5.7 $^2J_{HH}$
		−7.87 (ddd)	Ru-H	74.3 $|^2J_{PH}|$, 32.5 $|^2J_{PH}|$, −5.7 $^2J_{HH}$
333 K	^{31}P-NMR	1.4 (d)	PMe$_2$Ph	22 $|^2J_{PP}|$
		−5.6 (d)	PMe$_3$	22 $|^2J_{PP}|$
ccc-**5** isomer **2**	^{1}H-NMR	−7.41 (ddd)	Ru-H	−6.5 $^2J_{HH}$
		−7.78 (ddd)	Ru-H	71.8 $|^2J_{PH}|$, 33.9 $|^2J_{PH}|$, −6.5 $^2J_{HH}$
333 K	^{31}P-NMR	9.9 (d)	PMe$_2$Ph	28 $|^2J_{PP}|$
		−15.4 (d)	PMe$_3$	28 $|^2J_{PP}|$
Ru(CO)(H)$_2$-(PMe$_3$)$_3$ **6**	^{1}H-NMR	1.27 (m)	[P(CH_3)$_3$]$_2$	
		1.34 (m)	P(CH_3)$_3$	
333 K		−7.77 (qdd)	Ru-H	29.1 $|^2J_{PH}|$, −7.3 $^2J_{HH}$, 20.0 $|^2J_{CH}|$
		−8.44 (dtd)	Ru-H	79.5 $|^2J_{PH}|$, 30.1 $|^2J_{PH}|$, −7.3 $^2J_{HH}$
	^{31}P-NMR	0.3 (d)	PMe$_3$	
		−10.8 (t)	PMe$_3$	

^{a} Resonance belongs to X[AE]$_2$M spin system.

involving simultaneous interchange of hydride and phosphine positions. Phosphine interchange has also been monitored directly via heteronuclear 1-D ^{31}P-EXSY spectra,[25] and at 306.5 K the rate of this process was determined to be 1.34 s^{-1}. Similarly, ^{13}C{^{1}H}-EXSY spectra demonstrated that the two carbonyl ligands interchanged positions at a rate of 1.28 s^{-1} at 306.5 K. Therefore, it was clear that the processes of hydride, carbonyl, and phosphine interchange had essentially

(25) Stott, K.; Stonehouse, J.; Keeler, J.; Hwang, T. L.; Shaka, A. J. *J. Am. Chem. Soc.* **1995**, *117*, 4199.

Table 2. Rate Constants and Activation Parameters (error) for Mutual Hydride Exchange in *ccc*-**1**−**4**

complex	ligand	process	temp, K	rate, s^{-1}	$\Delta G_{350}^{\ddagger}$, kJ mol^{-1}	$\Delta H^{\ddagger}$, kJ mol^{-1}	$\Delta S^{\ddagger}$, J K^{-1} mol^{-1}
1	dppe	H ↔ H	327.7	8.74	73.7 (0.7)	85.5 (2)	34 (7)
		H ↔ H	306.4	1.20			
		Ph(A) ↔ Ph(C)	306.4	1.28			
		$^{31}P_a$ ↔ $^{31}P_b$	306.4	1.34			
		$^{13}CO_a$ ↔ $^{13}CO_b$	306.4	1.28			
2	PMe$_2$Ph	H ↔ H	350.3	0.77	86.8 (1)	76 (10)	−30 (28)
3	PMe$_3$	H ↔ H	350.2	0.96	86.7 (1)	68 (6)	−80 (16)
4	AsMe$_2$Ph	H ↔ H	351.1	1.42	85.8 (0.5)	90 (5)	11 (11)

the same rate constants and were connected by a common pathway. The exact details associated with this type of analysis can be found in the Supporting Information.

To determine the kinetic isotope effect for this process, the interchanges of rings A and C and of the two phosphorus atoms were monitored for both Ru(CO)$_2$(D)$_2$(dppe), **1-D$_2$**, and Ru(CO)$_2$H$_2$(dppe) at 310 K. Rate constants of 1.78 (A → C, which is equivalent to C → A) and 1.72 s^{-1} (P → P) were obtained for Ru(CO)$_2$(D)$_2$(dppe), while Ru(CO)$_2$-(H)$_2$(dppe) yielded values of 1.84 (A → C) and 1.80 s^{-1} (P → P). Using the average of the two rate constants for Ru(CO)$_2$(D)$_2$(dppe) and the two rate constants for Ru(CO)$_2$-(H)$_2$(dppe), the ratio k_{HH}/k_{DD} was determined to be 1.04.

Reaction of Ru(CO)$_2$(H)$_2$(dppe), 1, with *p*-H$_2$: Evidence for H$_2$ Reductive Elimination. When a d_6-benzene solution of **1** was treated at 323 K with parahydrogen (3 atm pressure), PHIP-enhanced hydride resonances at δ −6.33 and −7.55 were observed in the ^{1}H-NMR spectrum. The enhancement decayed over a period of 10 min as the *p*-H$_2$ enrichment was depleted, with the reappearance of the regular nonenhanced signals of **1**. This suggested that **1** underwent reductive elimination of H$_2$ at a significant rate at 323 K. Furthermore, the fact that *p*-H$_2$-enhanced signals were observed required H$_2$ addition to proceed in a spin-correlated process via a diamagnetic intermediate. No enhancement would be expected if the intermediate had a triplet electronic spin state, since rapid quenching of the spin coherence would result due to strong interaction with the magnetic anisotropy associated with the presence of unpaired electrons. The validity of this deduction was tested by irradiating C$_6$D$_6$ solutions of Ru(CO)$_3$dppe and ^{13}CO-labeled Fe(CO)$_5$ under *p*-H$_2$ directly in the NMR probe while recording the ^{1}H-NMR spectra. The sample containing Ru(CO)$_3$dppe yielded *p*-H$_2$-enhanced signals for the hydride resonances of **1**, while the signal for Fe(^{13}CO)$_4$(H)$_2$ showed no enhancement.

Reductive elimination of H$_2$ from **1** was monitored over the temperature range 343−373 K via the mapping of hydride/dihydrogen connections using the 1-D nOe sequence of Keeler.[25] Subsequent analysis provided values of $\Delta H^{\ddagger} = 97 \pm 10$ kJ mol^{-1} and $\Delta S^{\ddagger} = 2 \pm 2$ J K^{-1} mol^{-1} for this reaction. At 369 K the rate of reductive elimination of H$_2$ from **1** was 0.253 s^{-1}, while the corresponding rate of elimination of D$_2$ from **1-D$_2$** was 0.56 s^{-1}. The ratio k_{HH}/k_{DD} for reductive elimination of hydrogen from **1** is, therefore, approximately 0.5.

NMR Examination of Ru(CO)$_2$(H)$_2$(PMe$_2$Ph)$_2$, 2. When the ^{1}H-NMR spectrum of **2** in d_8-toluene was recorded at 296 K under an atmosphere of normal hydrogen, only one
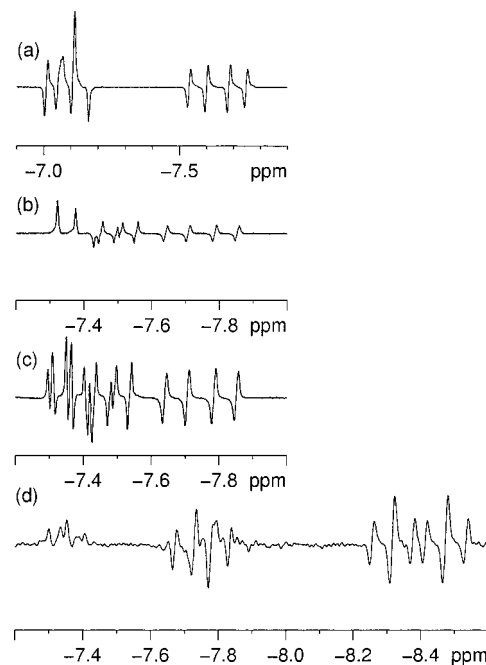

Figure 5. ^{1}H-NMR spectra obtained with *p*-H$_2$ in C$_6$D$_5$CD$_3$ showing the hydride region only. The antiphase components arise in transitions involving protons that originate from *p*-H$_2$: (a) spectrum of **2** at 333 K; (b) spectrum of **3** at 333 K; (c) spectrum of ^{13}CO-labeled **3** at 333 K; (d) spectrum of Ru(CO)(H)$_2$(PMe$_3$)$_3$ observed via the warming of **3** with PMe$_3$ in the presence of *p*-H$_2$ at 333 K.

hydride resonance (δ −7.13, $|^2J_{PH}| = 26$ Hz) was initially visible. The associated ^{31}P-NMR signal appeared at δ 12.0. As expected, these signals matched those previously reported for the *cct*-P isomer of **2**.[9] When the data accumulation was continued for a period of several hours, however, an additional pair of hydride resonances was detected at δ −7.16 and −7.77. These signals were assigned to the *ccc* isomer of **2**. Integration of the hydride resonances gave a value of 24 for the equilibrium constant $K = [cct$-P$]/[ccc]$. When a d_8-toluene solution of **2** was exposed to *p*-H$_2$ (3 atm) at 333 K, the two hydride resonances for the *ccc* isomer, now at δ −7.08 and −7.66, were detected as enhanced signals (Figure 5a). A ^{1}H−^{1}H-COSY experiment confirmed their connectivity. The resonance at δ −7.08 showed splitting by two inequivalent ^{31}P nuclei of 27 and 21 Hz, values characteristic of a hydride ligand cis to both ^{31}P nuclei. In contrast, the hydride resonance at δ −7.66 showed splittings of 73 and 32 Hz, indicating that the hydride ligand associated with this resonance was trans to one ^{31}P nucleus and cis to the other. The spectral characteristics of **2** are summarized in Table 1b. Comparison of the spectral characteristics of **1** and **2** reveals fairly similar chemical shifts (δ −7.55 and −7.16,

Table 3. Rate Constants and Activation Parameters (error) for Isomer Interchange in **2**−**4** and Reductive Elimination of H_2 for **1**

complex	ligand	process	temp, K	rate, s^{-1}	$\Delta G_{350}^{\ddagger}$, kJ mol^{-1}	$\Delta H^{\ddagger}$, kJ mol^{-1}	$\Delta S^{\ddagger}$, J K^{-1} mol^{-1}
2	PMe_2Ph	*ccc* → *cct*-P	350.3	0.70	87.4 (1)	112 (10)	70 (25)
3	PMe_3	*ccc* → *cct*-P	350.2	0.32	89.4 (1)	107 (6)	50 (18)
4	$AsMe_2Ph$	*ccc* → *cct*-As	351.1	0.39	86.8 (1)	92 (4)	15 (10)
4	$AsMe_2Ph$	*cct*-As → *ccc*	351.1	0.39	85.8 (1)	88 (5)	−3 (13)
1	dppe	reductive elimination	350	0.022	97.7 (1)	97 (10)	2 (2)

respectively) for the hydride ligand trans to CO but a bigger gap (δ −6.32 and −7.77) between the values for the hydride ligand trans to phosphorus.

NMR Examination of $Ru(CO)_2(H)_2(PMe_3)_2$, 3. The ^1H-NMR spectrum of **3** in a d_6-benzene solution at 296 K indicated the presence of only one isomer which was characterized by a triplet resonance at δ −7.48 ($|^2J_{PH}| = 26$ Hz) for the hydride ligands and a virtual triplet[26] at δ 1.24 for the PMe_3 ligand. The ^{31}P-NMR spectrum of **3** consisted of a singlet at δ −2.2, and the $^{13}C\{^1H\}$-NMR spectrum contained only one resonance in the region characteristic of carbonyl ligands, a triplet ($|^2J_{CP}| = 9.3$ Hz) at δ 202.4.[27] Even after overnight accumulation of the ^1H-NMR spectra, no signal attributable to another isomer of **3** could be detected. However, when the p-H_2 experiment described above was repeated for **3** (again at 333 K), two new hydride signals, with splitting patterns similar to those for the hydride resonances of *ccc*-**2**, were seen at δ −7.51 and −7.77 (Figure 5b) and were assigned to the *ccc* isomer of **3**. The spectral characteristics of *ccc*-**3** are listed in Table 1b. Since the two hydride signals of this isomer of $Ru(CO)_2(H)_2(PMe_3)_2$ were only detected at and above 333 K, we concluded that reductive elimination of H_2 from $Ru(CO)_2(H)_2(PMe_3)_2$ was relatively slow at lower temperatures. In the p-H_2 experiment, it was also noticed that the hydride resonance for the *cct*-P isomer was distorted, with both emission and absorption features clearly visible in the ^{31}P-decoupled ^1H spectrum, despite the fact that the two hydride ligands in this isomer are equivalent.[28] An elegant explanation of this effect has been reported by Aime et al.,[29] who studied the addition of p-H_2 to the cluster $Os_3(CO)_{10}(NCCH_3)_2$. Enhanced hydride signals were observed for $Os_3(CO)_{10}(H)_2$, a species which, like *cct*-P-**3**, contains magnetically equivalent hydrides and, therefore, should not show enhancement. This reaction, however, proceeds by way of the unsymmetrical Os_3-$(CO)_{10}H(\mu$-H)(NCCH_3$), and the enhancement is passed on from the intermediate to the product. Similarly, the enhancement of the hydride signal for *cct*-P-**3** is partially due to the fact that it can be formed via *ccc*-**3**. A similar parahydrogen experiment with ^{13}CO-enriched $Ru(CO)_2(H)_2(PMe_3)_2$ showed a more substantial enhancement of the hydride resonances for the *cct*-P isomer, as shown in Figure 5c. The additional enhancement is due to the formation of a second-order spin system containing the hydride ligands.

Exchange Studies Facilitated by Parahydrogen. Thanks to the signal enhancement provided by the use of parahy-

drogen, it was possible to obtain EXSY spectra of the *ccc* isomers of **2** and **3**. For each complex, the two hydride resonances for the *ccc* isomer showed cross-peaks to one another and to the hydride resonances for the *cct*-P isomers. However, since the *ccc* isomer in these complexes could only be detected by virtue of the parahydrogen enhancement, the signals for the *cct*-P isomer failed in each case to yield cross-peaks to hydrides of the *ccc* isomer, and consequently, the spectra were not symmetrical about the diagonal. Rate constants for the interchange of hydride ligands in the *ccc* isomers of **2** and **3** and for the conversion of the *ccc* isomers to the corresponding *cct*-P isomers are given in Table 2. The associated enthalpies and entropies of activation, determined from 16 rate constants for **2** and 25 values for **3** between 350 and 366 K, are listed in Table 3. Interchange of hydride ligands in *ccc*-**3** was also monitored by means of ^{31}P-coupled ^1H−^1H-EXSY spectra (as described above for complex **1**, Figure 4 shows a typical spectrum obtained for **1**). The pattern of connections again matched that required for an *intra*-molecular process in which exchanges of the two hydride ligands and of the two phosphorus ligands occurred concurrently. The exact details of the analysis of the spectra can be found in the Supporting Information.

To determine whether ligand exchange within the *ccc* isomer involved CO dissociation, a sample of **3** was dissolved in CO-saturated d_8-toluene before being treated with p-H_2 in the normal way. The ratios of the exchange-peak to diagonal-peak volumes in the associated EXSY spectrum (recorded at 358.6 K) were not altered by the presence of the CO. This ruled out CO loss at any stage up to, and including, the rate-limiting step. When the process was repeated with PMe_3 instead of CO, the aim of the experiment was defeated by the appearance of two new and enhanced hydride resonances at δ −7.77 and −8.44 (Figure 4d). The former was a quartet of antiphase doublets ($|^2J_{PH}| = 29.1$ Hz, $^2J_{HH} = -7.3$ Hz), and the latter was a doublet of triplets of antiphase doublets ($|^2J_{PH}| = 79.5$ Hz, $|^2J_{PH}| = 30.1$ Hz, and $^2J_{HH} = -7.3$ Hz). Evidently the two hydride ligands were in the same complex, the former trans to CO and the latter trans to PMe_3. When the corresponding ^{13}CO-labeled complex was examined, the resonance at δ −7.77 exhibited an additional 20.0 Hz doublet splitting, confirming that it represented the hydride ligand trans to CO. The complex was identified as *mer-cis* $Ru(CO)(H)_2(PMe_3)_3$, **6**.[30]

Unambiguous confirmation of the retention of the phosphine ligands within the metal's coordination sphere during hydride interchange came from the ^1H−^1H-EXSY observation of a mixture of $Ru(CO)_2(H)_2(PMe_3)(PMe_2Ph)$ **5**, $Ru(CO)_2(H)_2(PMe_3)_2$ **3**, and $Ru(CO)_2(H)_2(PMe_2Ph)_2$ **2**. No

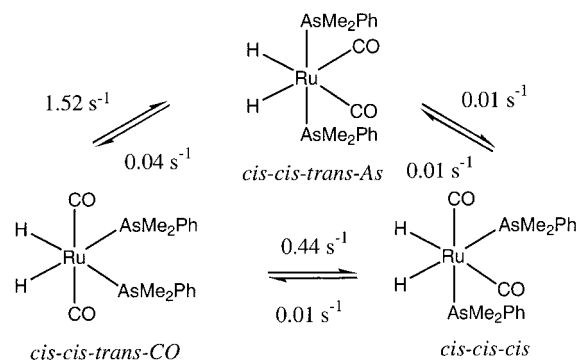(26) Jenkins, J. M.; Shaw, B. L. *Proc. Chem. Soc., London* **1963**, 279.
(27) Gill, D. F.; Mann, B. E.; Shaw, B. L. *J. Chem. Soc., Dalton Trans.* **1973**, 311.
(28) We note that similar, weaker, distortions were visible in the corresponding resonances of **2**.
(29) Aime, S.; Gobetto, R.; Canet, D. *J. Am. Chem. Soc.* **1998**, *120*, 6770.

(30) Kohlmann, W.; Werner, H. *Z. Naturfosch., B: Chem. Sci.* **1993**, *48*, 1499.
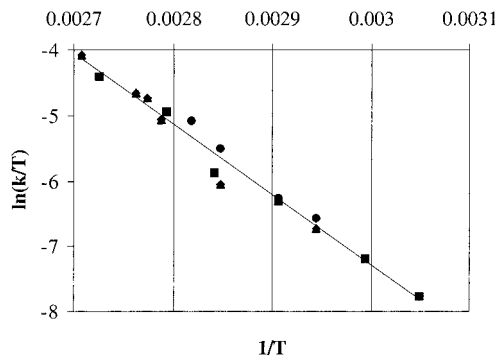
Scheme 2

Figure 6. Eyring plot for *ccc* interchange within **4**. Experimental points indicated with ■ correspond to measurements using normal H_2 and the least-mean squares simulation, ▲ correspond to points determined using *p*-H_2, and ● correspond to points determined using normal H_2 and the full matrix analysis.

cross-peaks connecting the different complexes were observed, whereas the expected connections for hydride exchange within the *ccc* isomers and for the interconversion of *ccc* and *cct*-P isomers of the individual complexes were visible. For *cct*-P-**5**, the hydride resonance was a triplet ($|^2J_{PcisH}| = 26.5$ Hz) at δ −7.35, a chemical shift between those for *cct*-P-**3** and *cct*-P-**2**. The $^{31}P\{^1H\}$-NMR spectrum of *cct*-P-**5** consisted of doublet resonances at δ 11.3 and −1.5, both with $|^2J_{PP}| = 222$ Hz which is indicative of mutually trans phosphine ligands.

Characterization and Dynamic Behavior of Ru(CO)$_2$-(H)$_2$(AsMe$_2$Ph)$_2$, 4. When a ^{1}H-NMR spectrum of Ru(CO)$_2$-(H)$_2$(AsMe$_2$Ph)$_2$, **4**, was recorded in d_8-toluene at 296 K, three hydride resonances were detected at δ −7.60, −6.86, and −8.70. These have been shown to arise from the *cct*-As and *ccc* isomers of **4**; both have been previously characterized.[9] It has also been reported previously that these two isomers exist in equilibrium in solution, and that the *cct*-As isomer reacts preferentially with the alkyne MeO$_2$CC≡CCO$_2$-Me; subsequent reequilibration of the *ccc* and *cct*-As isomers takes around 15 min at room temperature.[11] We examined this system by both 1- and 2-D EXSY methods in conjunction with the use of both normal and *p*-H_2. No NMR evidence was obtained for isomer interconversion at room temperature, confirming the slowness of the reequilibration at this temperature. However, a new hydride resonance was detected at δ −9.35 in the ^{1}H-NMR spectrum, and exchange peaks were observed between this resonance and the *cct*-As isomer of **4** at 318 K. The species responsible for the additional hydride resonance is believed to be the *cct*-CO isomer of **4**. Analysis of the exchange-peak intensity as a function of mixing time yielded values for the rate constants for *cct*-As-**4** → *cct*-CO-**4** and the reverse process of 0.02 and 1.31 s^{-1}, respectively. At this temperature the solution was found to contain the *cct*-As and *ccc* and *cct*-CO isomers in a 53.9: 45.2:0.9 ratio. At 327 K, EXSY analysis indicated that all three isomers of **4** were interconverting. The rate constants for the interconversion between isomers at 327 K are given in Scheme 2 (estimated error ±1 in last significant figure).

Detailed study of the isomerization process was hampered by the fact that at temperatures above 327 K, **4** begins to slowly decompose. Nonetheless, it was possible to obtain values of $\Delta H^{\varnothing}$ and $\Delta S^{\varnothing}$ for the conversion of *cct*-As into *ccc* as 1.6 ± 0.7 kJ mol^{-1} and 4.1 ± 2.0 J K^{-1} mol^{-1}, respectively. When **4** was treated with *p*-H_2 at temperatures

above 323 K, the hydride resonances for *ccc*-**4** at δ −6.86 and −8.70 showed emission-absorption characteristics indicating that the hydride ligands were exchanging with free *p*-H_2. At 343 K, the enhanced antiphase character indicated a 1035-fold increase in signal strength for the *ccc*-**4** hydride resonances over those observed in the absence of *p*-H_2. Rate constants for the hydride exchange within the *ccc* isomer and interconversion of *ccc* and *cct*-As isomers were determined at temperatures between 323 and 369 K using both normal and *p*-H_2 according to the methods outlined in the Experimental Section. The values of $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ for these processes were calculated and are summarized in Tables 2 and 3. Figure 6 illustrates the Eyring plot for the exchange of hydride ligands within *ccc*-**4**, showing the excellent agreement between data obtained by the different methods.

Discussion

Our studies of the three complexes of Ru(CO)$_2$(H)$_2$L$_2$ (**3**, L = PMe$_3$; **2**, L = PMe$_2$Ph; **4**, L = AsMe$_2$Ph) have revealed a strong dependence of the relative stabilities of the *cct*-L and *ccc* isomers on the nature of the ligand. For L = PMe$_3$, the *cct*-L isomer is the more stable of the two by such a wide margin that the *ccc* isomer cannot be detected without the use of *p*-H_2. The gap narrows for L = PMe$_2$Ph, where both isomers can be detected without resorting to *p*-H_2. At 295 K the [*cct*-L]:[*ccc*] ratio is 24, corresponding to a free energy difference of 7.8 kJ mol^{-1} in favor of the *cct*-L form. This difference is further reduced to only 0.7 kJ mol^{-1} for AsMe$_2$Ph, but here matters are complicated by the presence of the third (*cct*-CO) isomer. All three isomers can be detected at 295 K in a *cct*-L:*ccc*:*cct*-CO ratio of 56.4:42.7: 0.9. Evidently, the change of donor atom in L has a major effect on the isomer equilibrium. This can be readily rationalized since the donor ability of the phosphines described here can be ranked as PMe$_3$ > PMe$_2$Ph > dppe on the basis of Tolman's study.[31] The greater the σ-donor ability of the phosphine, the greater the preference of the hydride (which can only make a σ-bond with a metal) for a position trans to the π-acceptor CO rather than trans to phosphine. Thanks to this electronic effect, the *cct*-L isomer,

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(31) Tolman, C. A. *Chem. Rev.* **1977**, *77*, 313.

in which both hydrides are trans to CO, is increasingly favored. Steric effects can be deduced to play a less significant role in controlling the equilibrium position, since increasing the size of either the donor atom or the substituents would be expected to favor the *cct*-L isomer. This is the opposite of what is observed experimentally.

The *ccc* isomers of **2**–**4** and *ccc*-Ru(CO)$_2$(H)$_2$(dppe), **1**, all undergo intramolecular exchange of their two hydride ligands, with **1** having the fastest rate; Table 2 contains the corresponding values of $\Delta G^{\ddagger}_{350}$, $\Delta H^{\ddagger}$, and $\Delta S^{\ddagger}$. The values of $\Delta H^{\ddagger}$ fall across the series AsMe$_2$Ph > dppe > PMe$_2$Ph > PMe$_3$ from 90 to 85.5 to 76 to 68 kJ mol^{-1}. This decrease signifies that the activation enthalpy is reduced by an increase in the electron density at the metal in accordance with the electron donating ability of L (see later). The corresponding values of $\Delta S^{\ddagger}$ at 11 (11), 34 (7), -30 (28), and -80 (16) J K^{-1} mol^{-1}, respectively, reveal that the enhanced rate of exchange in the dppe system arises from a favorable entropy change on moving to the transition state. This difference might, therefore, signify that the ethane bridge connecting the phosphorus centers in **1** modifies the ground-state geometry in a way which reduces the activation barrier to exchange. This theory receives support from the fact that the couplings between the hydride ligand that is trans to L and the ^{31}P nucleus that is cis to it vary from 21.7 Hz in **1** to 32 and 33 Hz in **2** and **3**, respectively. A narrowing of the P–Ru–P bond angle to 84.7°, as a consequence of the ethane bridge connecting the two phosphorus centers of the dppe ligand in the related complex Ru(dppe)(CO)$_2$(OSO$_2$-CF$_3$)$_2$, has been reported.[32] In contrast, the corresponding P–Ru–P bond angles in *mer*-Ru(CO)(H)$_2$(PMe$_2$Ph)$_3$ are 100.8° and 98.5°.[33] These data, therefore, support conclusively that dppe complex **1** undergoes the most rapid exchange as a direct consequence of the steric influence of the bulky chelating phosphine. However, despite the fairly wide variation, none of these values of $\Delta S^{\ddagger}$ are sufficiently positive to suggest a dissociative mechanism for the exchange process.

In addition to the $\Delta S^{\ddagger}$ changes, evidence was presented earlier which demonstrated that the exchange does not involve the loss of CO or ligand L. Various pathways have been suggested for intramolecular exchange of hydride ligands. Rearrangement by a tunneling mechanism,[34–36] originally described by Muetterties for complexes Fe(H)$_2$L$_4$ and Ru(H)$_2$L$_4$ (where L is a phosphorus ligand), and the related trigonal twist mechanism described by Mann[24] were both candidates; however, both can be ruled out because the exchanges of all three pairs of ligands (hydrides, carbonyls, and the ligands L) occur simultaneously and have the same rate constant. Another potential route would involve the

formation of an intermediate formyl complex by combination of carbonyl and hydride ligands; however, this appears to be uncommon for ruthenium,[37–39] and we saw no evidence in our *p*-H$_2$ studies for the formation of a species containing a formyl ligand. We believe that the most likely pathway involves the reversible formation of a transition state featuring significant shortening of the H–H distance or a thermally accessible η^2-H$_2$ intermediate with a trigonal bipyramidal shape. Species containing η^2-bonded H$_2$ ligands have featured extensively in the literature as intermediates in the reverse process of H$_2$ addition to transition metal centers to give dihydride complexes.[40] For the dihydride Re-(CO)(H)$_2$(PR$_3$)$_2$(NO), an intramolecular exchange mechanism involving a trigonal bipyramidal η^2-H$_2$ complex has been proposed.[41] The observation that the activation enthalpies decrease with increased electron donating ability of L, requires special comment, therefore, because such a trend would be expected to parallel an increase in the stability of the dihydride form over its η^2 counterpart. Such a constraint can, however, be readily rationalized as a ground-state effect where the inherent instability of the *ccc* form or the associated lengthening of the Ru–H distance due to the trans influence of the phosphine ligands controls the overall activation enthalpy. The process of hydride exchange is, however, further complicated by the fact that in **1** it is accompanied by simultaneous exchange of the L and CO pairs. Therefore, rotation about the resultant H–H bond must be restricted. A barrier to rotation about the M–H$_2$ axis can arise from electronic interactions between the η^2-bonded H$_2$ and the transition metal center and nonbonded interactions between the hydrogen atoms and the ancillary ligands. Barriers to rotation for octahedral d^6 complexes, such as W(CO)$_3$(PR$_3$)$_2$(η^2-H$_2$), are generally low because the d$_\pi$–σ^* interaction does not change significantly with rotation. However, higher barriers have been observed for complexes such as OsX{NH=C(Ph)C$_6$H$_4$}(H)$_2$(PiPr$_3$)$_2$ (X = Cl, Br, and I), where the formation of an elongated dihydrogen ligand has been proposed to account for the barrier.[42] The direct correlation between increased rotational barriers and longer H–H distance has been discussed for [Os(H$_2$)Cl(H$_2$PCH$_2$-CH$_2$PH$_2$)$_2$]$^+$, where an elongated H–H bond has been predicted.[43] Our observation that the ratio k_{HH}/k_{DD} was 1.04 for the dppe complex could be interpreted to indicate that the exchange in **1** proceeds with limited H–H bonding in reaching the transition state (see later). If this situation corresponds to an elongated H–H bond, the degree of bond making and breaking during the approach from the ground state must be about equal.

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Scheme 3
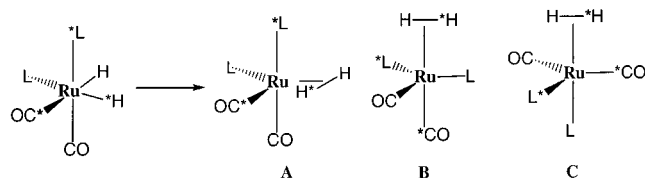
Furthermore, there is evidence that, since H_2 is a single-face π-acceptor, its rotation couples with the movement of other single-face π-acceptor ligands during the isomerization process. The complexes $RuH_2(H_2)_2(PH_3)_2$ and $[Os(NH_3)_4\text{-}(H_2)(CH_2)]^+$ provide examples of such coupled rotations.[44] Such a linking has also been observed for the more closely related iron(0) system $Fe(CO)_4(alkene)$, where NMR observations require synchronous Berry pseudorotation (exchanging the carbonyl ligands) and alkene rotation.[45] The similarity in bonding between the single-face π-acceptor ligand H_2 and an alkene is, therefore, especially relevant in this regard.

Albright et al. have modeled the hydride exchange pathway in the complexes $Ru(H)_2(PMe_3)_4$ and $Fe(H)_2(CO)_4$.[46] In their scheme, structures containing $\eta^2\text{-}H_2$ ligands with both square pyramidal and trigonal bipyramidal ligand arrangements are considered as possible transition states for the interchange process. Therefore, it would seem sensible to suggest that the three structures containing $\eta^2\text{-}H_2$ ligands shown in Scheme 3 might be featured as either the transition state for hydride exchange in $Ru(CO)_2(H)_2L_2$ or intermediates involved in the pathway. Their studies reveal that structure A in Scheme 3 is likely to be higher in energy than either B or C when the four additional ligands are strong σ-donors, but that this difference is reduced by the addition of π-acceptor carbonyls so that in $Fe(CO)_4(H)_2$ form A yields the most stable transition state.

If it is assumed that the $\eta^2\text{-}H_2$ ligand occupies one of the equatorial sites, as shown in structure A, a Berry pseudorotation achieves the required interchange of both the pair of carbonyl ligands and the pair of ligands L for the *cis-cis-cis* isomer (Scheme 4). Since the exchanges of hydride ligands, carbonyl ligands, phosphorus atoms, and the pairs of phenyl rings within the dppe ligand all occur at the same rate for **1**, the Berry pseudorotation must be linked to the rotation of the dihydrogen ligand. Such a situation is well-known for $Fe(CO)_4(alkene)$ and has been predicted for $Fe(CO)_4(H)_2$.[45,46]

Interestingly, the direction of the rotation of the H_2 ligand must also be controlled, because only one direction (that shown in Scheme 4) achieves interchange of the identities of the hydride ligands. A random choice of direction would result in a hydride ligand exchange rate only half that of the carbonyl ligands and phosphorus centers. It seems likely that the interactions between the H_2 ligand with the substituents on the L ligands determine the preferred direction of rotation.

Interconversion of the *ccc* and the *cct-L* isomers of complexes **2**−**4** was also observed, but on a slower time scale than ligand interchange within the *ccc* isomers. This is consistent with the higher $\Delta H^{\ddagger}$ values for this process: **2**, 112 (10) kJ mol^{-1}; **3**, 107 (6) kJ mol^{-1}; and **4**, 92 (4) kJ mol^{-1}. Unfortunately, the large errors for the $\Delta S^{\ddagger}$ values make them unreliable as an indicator of the molecularity of the *inter*-isomer rearrangement process, but there is other evidence to rule out the loss of a carbonyl ligand or a phosphine ligand. Structure B in Scheme 3 would allow the *ccc* isomer to equilibrate with the *cct-L* isomer if the $\eta^2\text{-}H_2$ ligand completed an anticlockwise rotation to place the H−H bond along the Ru−CO bond before reestablishing the two Ru−H bonds. Neither structure A nor B, however, allows access to a form with trans CO's. Significantly, access to structure C would enable interconversion of the *ccc* isomer into both the *cct-CO* and *cct-L* without hydride interchange within the *ccc* form. The rates and activation parameters measured for these processes indicate that these three exchange pathways have substantially different barriers. We also note that structure B would serve as an intermediate (or transition state) that, via clockwise rotation of the $\eta^2\text{-}H_2$ ligand and reestablishment of the two Ru−H bonds, would lead to interchange of the hydrides, carbonyls, and phosphines within the *ccc* isomer. We suggest for $Ru(CO)_2(H)_2L_2$, containing 2 π-acceptor ligands, that the trigonal bipyramidal form, corresponding to situation A where the $\eta^2\text{-}H_2$ ligand is located in the equatorial plane, accounts for the lower-energy pathway, while access to the higher-energy form B accounts for the slower *ccc−cct* isomer interconversion.

Values of $\Delta H^{\ddagger} = 97 \pm 10$ kJ mol^{-1} and $\Delta S^{\ddagger} = 2 \pm 2$ J K^{-1} mol^{-1} obtained for the reductive elimination of H_2 from **1** indicated that there is a substantially higher barrier to reductive elimination. The observed kinetic isotope effect, k_{HH}/k_{DD}, for this process of 0.5 requires a substantial amount of dihydrogen bond formation in the associated transition state; this contrasts with the evidence that the amount of H−H bond formation in the transition state for a simple hydride ligand exchange is relatively small. The value of 0.5 also contrasts with the kinetic isotope effects for the reductive elimination of hydrogen from the eight-coordinate $W(H)_2(I)_2(PMe_3)_4$, which has been estimated to be 2 at 333,[47] and from $Ir(H_2)(H)_2Cl(PBu^t_2Me)_2$, which is 1.8 at 293 K.[48] However, H_2 elimination from the classical dihydride $(fulvalene)Cr_2(CO)_6(H)_2$ has been found to be 1.1 times slower than the corresponding elimination of D_2.[49] Given the enhanced stability of the $\eta^2\text{-}D_2$ form over the corresponding $\eta^2\text{-}H_2$ isotopomer reported for $W(CO)_3(PCy_3)_2(\eta^2\text{-}H_2)$, the observation of an inverse kinetic isotope effect for reductive elimination from **1** suggests that access to the more stable $\eta^2\text{-}D_2$ state surpasses the increased stability associated with M−D versus M−H bonds in the initial dihydride complexes.

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Scheme 4
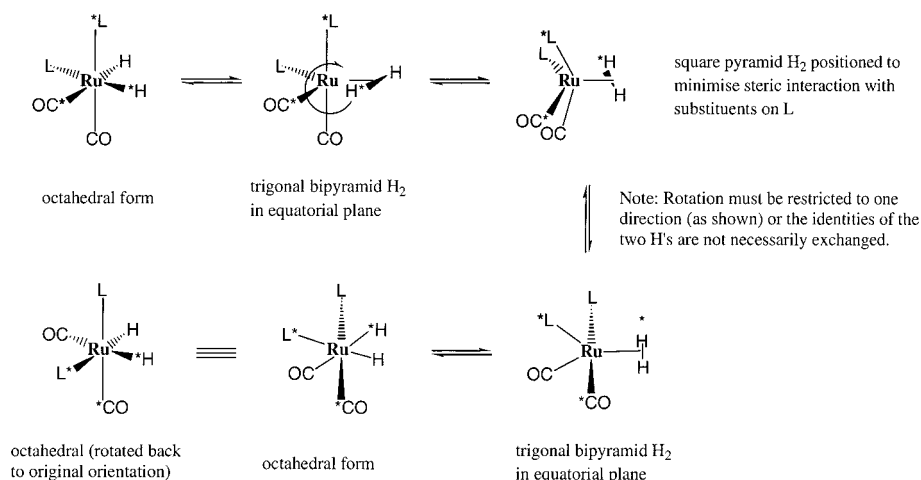
These studies also reveal information about the spin states of the associated 16-electron intermediates Ru(CO)$_2$L$_2$. In view of the observation that we can monitor the exchange process in **1**−**4** by NMR and that the formation of **1** from Ru(CO)$_2$(dppe) proceeds with the observation of p-H$_2$-enhanced NMR signals for **1**, we can state unequivocally that Ru(CO)$_2$(dppe) is diamagnetic in nature. Theoretical and experimental studies of the reaction of H$_2$ with Fe(CO)$_4$ suggest that the latter has a triplet ground state in agreement with the failure to obtain p-H$_2$-enhanced signals for Fe-(^{13}CO)$_4$(H)$_2$ at 296 K.[50,51] Singlet ground states have, however, been suggested for Ru(CO)$_4$,[52] Ru(CO)$_2$L$_2$[53] (L = PBu^t$_2$Me), and Ru(PH$_3$)$_4$,[14] in agreement with our observation of p-H$_2$-enhanced ccc-Ru(CO)$_2$(H)$_2$L$_2$. Studies with p-H$_2$, therefore, provide a ready means of studying spin state effects in reaction mechanisms.

Conclusions

Our NMR studies of complexes Ru(CO)$_2$(H)$_2$L$_2$ (L = PMe$_3$, PMe$_2$Ph, and AsMe$_2$Ph) enable us to conclude that they can have three possible geometries, ccc, cct-L, and cct-CO. The equilibrium ratio of these three isomers is dramatically influenced by the electronic properties of L, with better donors favoring the cct-L form. Consequently the ccc form for L = PMe$_3$ is only visible when p-H$_2$ is used to amplify its spectral features. In contrast, when L = AsMe$_2$Ph, the ccc and cct-L forms have similar free energies, and a new cct-CO species becomes visible as a minor isomer.

These complexes, and also Ru(CO)$_2$(H)$_2$(dppe), have been shown to undergo a number of dynamic processes which involve rearrangements of the ligand sphere. Interchange of the hydride positions within **1**, which exists solely as the ccc isomer, has been shown to be accompanied by synchronized exchange of the two carbonyl ligands and the dppe phosphorus atoms. We suggest that this process involves the accessing of a five-coordinate complex containing an η^2-H$_2$ ligand which, in view of the small normal kinetic isotope effect and restricted rotation, must have only a weak H−H interaction. The associated transition state is most likely to place the η^2-H$_2$ ligand equatorial as shown in structure A in Scheme 3. Access to this intermediate is facilitated by an increase in the electron density available to the metal center in accordance with a ground-state effect where placing the hydride trans to a good σ-donor is less favored.

In contrast to the dihydride exchange pathway, the kinetic isotope effect, k_{HH}/k_{DD}, of 0.5 observed for the reductive elimination of dihydrogen from Ru(CO)$_2$(H)$_2$dppe suggests that substantial H−H bond formation occurs before the dihydrogen is released. Our studies also indicate that the key intermediates Ru(CO)$_2$L$_2$ involved in the elimination and addition of hydrogen must have singlet electron configurations, in agreement with previous studies.[11,42,43]

Supporting Information Available: Analysis of hydride interchange in Ru(CO)$_2$(H)$_2$(dppe) **1** and ccc-Ru(CO)$_2$(H)$_2$(PMe$_3$)$_2$ **3**. This material is available free of charge via the Internet at http://pubs.acs.org.

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