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Kinetic Generation of *cis*-$C_5H_5(CO)_2ReH_2$ from the Reaction of $C_5H_5(CO)_2Re(\mu\text{-}H)Pt(H)(PPh_3)_2$ with Diphenylacetylene

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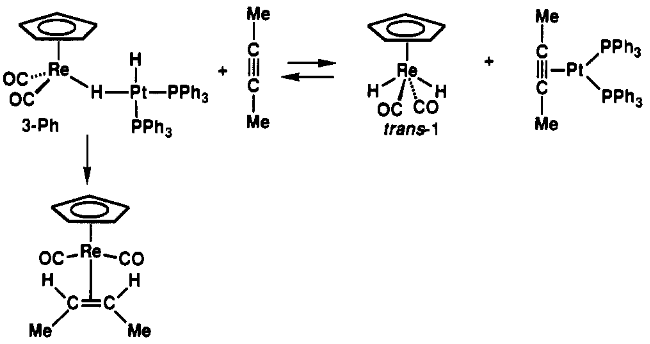
Protonation of $K[C_5H_5(CO)_2ReH]$ with CF_3CO_2H at −78 °C produced a 65:35 mixture of *cis*-$C_5H_5(CO)_2ReH_2$ (***cis*-1**) and *trans*-$C_5H_5(CO)_2ReH_2$ (***trans*-1**). At 24 °C, this mixture equilibrated to a 2:98 ***cis*-1**:***trans*-1** mixture. Reaction of $C_5H_5(CO)_2Re(\mu\text{-}H)Pt(H)(PPh_3)_2$ (**3-Ph**) with diphenylacetylene at −9 °C initially produced an 84:16 ***cis*-1**:***trans*-1** mixture. Photolysis of ***trans*-1** in a methylcyclohexane glass at 10 K gave a 40:60 ***cis*-1**:***trans*-1** photostationary state. *cis*-$C_5H_5(CO)_2ReHD$ (***cis*-1-HD**) has an unusual intermediate magnitude of J_{HD} = 6.5 Hz, which suggested the possibility that ***cis*-1** might be in equilibrium with $C_5H_5(CO)_2Re(\eta^2\text{-}HD)$ (***cis*-1-η^2-HD**). However, it was not possible to detect measurable amounts of $C_5H_5(CO)_2Re(\eta^2\text{-}H_2)$ (***cis*-1-η^2-H_2**) by IR spectroscopy.

Introduction

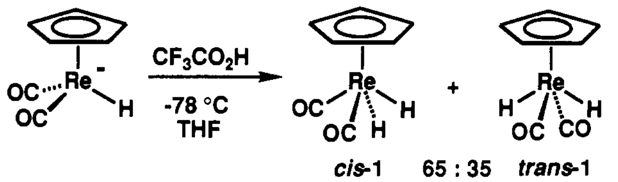
We recently reported that the heterobimetallic dihydride $C_5H_5(CO)_2Re(\mu\text{-}H)Pt(H)(PPh_3)_2$ (**3-Ph**)[1] reacted with alkynes to give (alkene)rhenium complexes.[2] In order to help understand how these two metals act cooperatively to reduce alkynes, we have investigated the mechanism of this reaction in detail.[3] When $C_5H_5(CO)_2Re(\mu\text{-}H)Pt(H)(PPh_3)_2$ (**3-Ph**) and 2-butyne are mixed, an initial equilibrium with *trans*-$C_5H_5(CO)_2ReH_2$ (***trans*-1**) and $(Ph_3P)_2Pt(CH_3C{\equiv}CCH_3)$ is established on the same time scale as the hydrogenation proceeds. Since the carbonyl ligands are cis in the crystal structure of **3-Ph**, we thought that *cis*-$C_5H_5(CO)_2ReH_2$ (***cis*-1**) might be formed initially and we set out to prepare ***cis*-1** independently.



Here we report the preparation of *cis*-$C_5H_5(CO)_2ReH_2$ (***cis*-1**), its equilibration with the ***trans*-1**, its direct observation in the low-temperature reaction of $C_5H_5(CO)_2Re(\mu\text{-}H)Pt(H)(PPh_3)_2$ (**3-Ph**) with diphenylacetylene, and its generation from photolysis of ***trans*-1** in a methylcyclohexane glass. In addition, we report that ***cis*-1** has an unusual intermediate J_{HD} = 6.5 Hz, which suggests that *cis*-$C_5H_5(CO)_2ReHD$ (***cis*-1**) might be in equilibrium with $C_5H_5(CO)_2Re(\eta^2\text{-}HD)$ (***cis*-1-η^2-HD**). However, we were unable to obtain IR spectral evidence for measurable quantities of $C_5H_5(CO)_2Re(\eta^2\text{-}H_2)$ (***cis*-1-η^2-H_2**).

Results

Generation of *cis*-$C_5H_5(CO)_2ReH_2$ (*cis*-1) by Protonation of $K[C_5H_5(CO)_2ReH]$. Because of our interest in the possible intermediate formation of *cis*-$C_5H_5(CO)_2ReH_2$ (***cis*-1**) in the reaction of $C_5H_5(CO)_2Re(\mu\text{-}H)Pt(H)(PPh_3)_2$ (**3-Ph**) with alkynes, we set out to independently prepare and spectrally characterize ***cis*-1**. When the reaction of $K[C_5H_5(CO)_2ReH]$[4] with CF_3CO_2H in THF-d_8 at −78 °C was monitored by ^1H NMR, a 35:65 mixture of the known *trans*-$C_5H_5Re(CO)_2H_2$ (***trans*-1**) (δ 5.40, −9.90) and a new compound with a 5:2 ratio of resonances at δ 5.57 and −9.27 was observed. This new compound was assigned the structure *cis*-$C_5H_5Re(CO)_2H_2$ (***cis*-1**). The initial ***cis*-1**:***trans*-1** ratio formed by protonation was 65:35 either when CF_3CO_2H was added to a THF-d_8 solution of $K[C_5H_5(CO)_2ReH]$ or when a solution of $K[C_5H_5(CO)_2ReH]$ was added to a solution of acid.



The initially formed 65:35 ***cis*-1**:***trans*-1** mixture was converted to a 2:98 equilibrium mixture at 24 °C. The rate of isomerization of ***cis*-1** could not be quantitatively reproduced, and the half-life for equilibration varied from 10 to 40 min. The problems with the reproducibility of the cis to trans isomerization rate will be discussed subsequently.

The IR spectrum of ***trans*-1** was subtracted from the spectrum of the mixture to obtain the IR spectrum of ***cis*-1**. In THF at −78 °C, ***cis*-1** has absorptions at 1997 (m, relative integrated absorbance 0.82) and 1920 cm^{-1} (s, relative integrated absorbance 1.0). For comparison, ***trans*-1** has CO absorptions at 2011 (m, relative integrated absorbance 0.59) and 1936 cm^{-1} (s, relative integrated absorbance 1.0). We hoped to definitively assign the cis and trans isomers by using the relative integrated absorbances of the CO bands to calculate the bond angle (2θ) between the CO's in ***cis*-1** and ***trans*-1**.[5] Using the formula $\cot^2\theta = I_{sym}/I_{asym}$, the angles between the carbonyl groups were calculated to be 96° for ***cis*-1** and 113° for ***trans*-1**.

Earlier Pasman and Snel[6] protonated $Li[\eta^5\text{-}(C_5H_4SiPh_3)(CO)_2ReH]$ with CF_3CO_2H and obtained a 10:1 mixture of isomeric dihydrides. At room temperature, the major kinetic product isomerized to the minor initial isomer. The kinetic isomer was assigned a cis configuration, since its IR spectrum showed CO

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absorptions of "near equal intensity", while the thermodynamic isomer was assigned a trans configuration, since it had a more intense lower energy CO band in the IR spectrum.

The difference between the OC–Re–CO bond angles calculated from the IR spectra of *cis*-$C_5H_5(CO)_2ReBr_2$ (78°) and *trans*-$C_5H_5(CO)_2ReBr_2$ (120°) is relatively large.[7] It initially seemed odd that there was a smaller difference between the bond angles calculated for **cis-1** and **trans-1** (96 and 113°, respectively). However, X-ray crystal structures of four-legged piano stool Re complexes containing hydride ligands also have relatively small trans OC–Re–CO angles. For example, in *trans*-$C_5H_5(CO)_2Re(H)GeCl_3$, OC–Re–CO is 104° [8] and in *trans*-$(C_5H_4Me)Re(CO)_2(TeH)H$, OC–Re–CO is 101°.[9] The angle calculated for **cis-1** is larger than that observed in *cis*-$C_5H_5(CO)_2Re(H)SiPh_3$ (OC–Re–CO = 84°)[10] and $(C_5H_4CH_3)Mo(CO)_3H$ (cis OC–Mo–CO = 83.1 and 85.7°, trans OC–Mo–CO = 101.7°).[11]

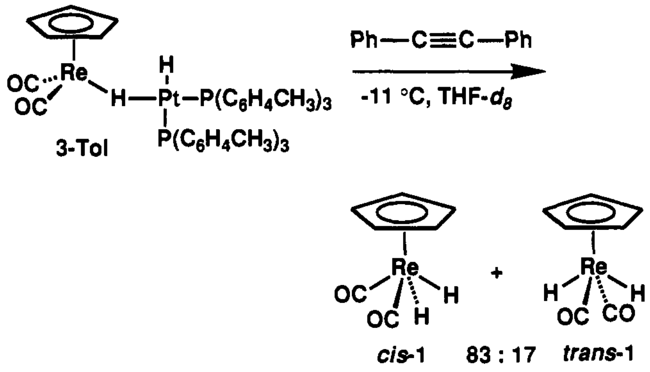
In the proton-coupled ^{13}C NMR spectrum of **trans-1** at 24 °C in toluene-d_8, a triplet at δ 195.1 (J_{CH} = 12.6 Hz) was observed for CO coupled to two equivalent hydrides. For **cis-1**, a broad peak at δ 200.9 with a width at half-height of 12 Hz was observed. Because the hydrides of **cis-1** are strongly coupled (J_{HD} = 6.5 Hz corresponds to J_{HH} = 45.5 Hz for **cis-1**) and have the same chemical shift, the same spectrum would be obtained for the magnetically inequivalent hydrides of a static cis dihydride and for cis hydride ligands undergoing rapid interchange. The width of the ^{13}CO resonance of **cis-1** is consistent with $J_{CH} + J_{CH'} \approx 12$ Hz.

Generation of *cis*-$C_5Me_5(CO)_2ReH_2$ (*cis*-2) by Protonation of K[$C_5Me_5(CO)_2ReH$]. A mixture of *cis*-$C_5Me_5(CO)_2ReH_2$ (**cis-2**) and *trans*-$C_5Me_5(CO)_2ReH_2$ (**trans-2**) was generated by addition of CF_3CO_2H to a THF-d_8 solution of K[$C_5Me_5(CO)_2ReH$][12] at −78 °C. The ^1H NMR spectrum showed hydride resonances at δ −8.72 and −9.65 for **cis-2** and **trans-2** in a ratio of 67:33. The initially formed 67:33 **cis-2**:**trans-2** mixture was converted to a 3:97 equilibrium mixture at 24 °C at a rate similar to that observed for **cis-1**. Graham has observed **cis-2** in the direct photolysis of **trans-2** in aromatic solvents.[13]

The IR spectrum of **cis-2** was obtained by subtraction of the IR spectrum of **trans-2** from the spectrum of the mixture of isomers. In THF at −78 °C, **cis-2** has absorptions at 1987 (relative integrated absorbance 1.0) and 1900 cm^{-1} (relative integrated absorbance 0.93). For comparison, **trans-2** has CO absorptions at 1996 (relative integrated absorbance 1.0) and 1920 cm^{-1} (relative integrated absorbance 0.66). The relative integrated absorbances of the CO bands were used to calculate OC–Re–CO bond angles of 92° for **cis-2** and 102° for **trans-2**. These angles are comparable to those estimated for **cis-1** (96°) and **trans-1** (113°).

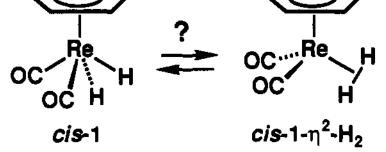
Generation of *cis*-$C_5H_5(CO)_2ReH_2$ (*cis*-1) from $C_5H_5(CO)_2Re(\mu\text{-}H)Pt(H)(PPh_3)_2$ (3-Ph). *cis*-$C_5H_5(CO)_2ReH_2$ (**cis-1**) was also generated by reaction of $C_5H_5(CO)_2Re(\mu\text{-}H)Pt(H)(PPh_3)_2$ (**3-Ph**) (3 mg, 2 μmol) with diphenylacetylene (5.8 mg, 32 μmol) in toluene-d_8 at −10 °C. An initial rapid reaction occurred in the first 90 min to give 61% **cis-1** and 10% **trans-1**, along with 29% remaining **3-Ph**. The high 87:13 **cis-1**:**trans-1** ratio observed in the ^1H NMR spectrum demonstrates that the cis isomer is the major initial product. Over the next 8 h, the amount of **trans-1** slowly increased to 20% while the amounts of **cis-1** (56%) and of **3-Ph** (24%) slowly decreased. This is consistent with the relatively rapid formation of a near-equilibrium mixture of **3-Ph** and **cis-1** that is gradually drained off to a more stable mixture of **3-Ph** and **trans-1**.

The kinetics of the reaction of the more soluble tolylphosphine complex $C_5H_5(CO)_2Re(\mu\text{-}H)Pt(H)[P(C_6H_4\text{-}p\text{-}CH_3)_3]_2$ (**3-Tol**) with diphenylacetylene in THF-d_8 were studied at −11 ± 2 °C by ^1H NMR spectroscopy. The rate of conversion of $C_5H_5(CO)_2Re(\mu\text{-}H)Pt(H)[P(C_6H_4\text{-}p\text{-}CH_3)_3]_2$ (**3-Tol**) to **cis-1** did not depend on the initial concentration of diphenylacetylene. The first-order rate constants for the disappearance of **3-Tol** were (8.38 ± 0.25) × 10^{-5} s^{-1} (0.092 M PhC≡CPh, −12 ± 1 °C) and (10.8 ± 0.4) × 10^{-5} s^{-1} (0.196 M, PhC≡CPh, −10 ± 1 °C). Considering the small difference in temperature in these two runs due to difficulty in setting the temperature of the NMR probe, these rate constants are not significantly different.



In the reaction of **3-Tol** with 0.092 M PhC≡CPh, the **cis-1**:**trans-1** ratio was initially 83:17 and the maximum amount of **cis-1** was about 20% of all Re species. In the reaction of **3-Tol** with 0.196 M PhC≡CPh, the **cis-1**:**trans-1** ratio was initially only 50:50 and the maximum amount of **cis-1** was only about 8% of all Re species. Again, this discrepancy can be ascribed to variations in the rate of conversion of **cis-1** to **trans-1**. The rates of isomerization of **cis-1** to **trans-1** were substantially faster than observed when **cis-1** was generated by protonation of $C_5H_5(CO)_2ReH^-$. Rate constants were obtained by fitting the kinetic data using the GEAR program;[14] they were calculated to be (3.23 ± 0.20) × 10^{-4} s^{-1} in the 0.092 M PhC≡CPh reaction at −12 ± 1 °C and (10.7 ± 0.5) × 10^{-4} s^{-1} in the 0.196 M PhC≡CPh reaction at −10 ± 1 °C. These large variations in the rate of **cis-1** to **trans-1** isomerization will be discussed subsequently.

Unusual J_{HD} NMR Coupling Constants for *cis*-1 and *cis*-2. Because of the structural similarity of cis metal dihydrides and dihydrogen (η^2-H_2) metal complexes, we set out to distinguish between these structural types on the basis of measurements of the ^1H NMR J_{HD} coupling constants of the monodeuteride complexes. Metal dihydride complexes normally have small J_{HD} values of <2 Hz,[15] while dihydrogen complexes generally have large J_{HD} values of 12–34 Hz.[16]



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(7) Sutton has compared IR-calculated bond angles and bond angles determined by X-ray structure analysis for *cis*-$C_5Me_5Re(CO)_2I_2$ [80° (IR); 78° (X-ray)] and *trans*-$C_5Me_5Re(CO)_2Br_2$ [115° (IR); 104° (X-ray)]: Einstein, F. W. B.; Klahn-Oliva, A. H.; Sutton, D.; Tyers, K. G. *Organometallics* **1986**, *5*, 53.

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CF_3CO_2D (~1.3 equiv) was added to a slurry of $K[C_5H_5(CO)_2ReH]$ in THF-d_8 at −78 °C, and the solution was monitored by NMR at low temperature. In the initial 500-MHz ^1H NMR spectrum at −34 °C, a 1:1:1 triplet (J_{HD} = 5.3 Hz) at δ −9.296 was seen for ***cis*-1-HD** well separated from the resonance of ***cis*-1** at δ −9.240 [$\Delta(\delta_{HD}-\delta_{HH}) = \Delta\delta$ = 52 ppb]. The signals due to ***trans*-1** and ***trans*-1-HD** were not completely resolved and appeared as an overlapping singlet for ***trans*-1** at δ −9.956 superimposed on a triplet for ***trans*-1-HD** at δ −9.959 (J_{HD} = 2.0 Hz, $\Delta\delta$ = 3 ppb; only the two high-field lines of the triplet were observable). The small magnitude of J_{HD} = 2.0 Hz for ***trans*-1-HD** is expected for a metal dihydride. The unusual intermediate value of J_{HD} = 5.3 Hz for ***cis*-1-HD** is larger than that reported for any metal dihydride complex and smaller than that reported for any dihydrogen complex. This suggested the possibility that ***cis*-1** might be in equilibrium with a molecular hydrogen complex ***cis*-1-η^2-H_2**. The large difference of $\Delta\delta$ = 52 ppb between the hydride chemical shifts of ***cis*-1** and ***cis*-1-HD** might also be explained in terms of an isotope effect on the equilibrium constant between two species.

The pentamethylcyclopentadienyl complex ***cis*-2** also exhibited unusually large J_{HD} and $\Delta\delta$ values. CF_3CO_2D (~1.3 equiv) was added to a slurry of $K[C_5Me_5(CO)_2ReH]$ in toluene-d_8 at −78 °C, and the species generated were monitored by NMR at low temperature. In the initial 360-MHz ^1H NMR spectrum at −34 °C, a 1:1:1 triplet (J_{HD} = 4.7 Hz) at δ −8.627 was seen for ***cis*-2-HD** well separated from the resonance of ***cis*-2** at δ −8.572 ($\Delta\delta$ = 55 ppb). The signals due to ***trans*-2** and ***trans*-2-HD** were not resolved and appeared at δ −9.473 ($\omega_{1/2} \approx 4$ Hz, indicating that both J_{HD} and $\Delta\delta$ were less than 2 Hz). The unusual intermediate value of J_{HD} = 4.7 Hz for ***cis*-2-HD** together with the large difference between the hydride chemical shifts of ***cis*-2** and ***cis*-2-HD** again suggested the possibility of an equilibrium between a metal dihydride and a molecular hydrogen complex.

The ^1H NMR spectrum of ***cis*-1** was taken at −103 °C in toluene-d_8 in an unsuccessful attempt to sufficiently slow equilibration so that ***cis*-1** and ***cis*-1-η^2-H_2** might be directly observed.

Another means of distinguishing between metal dihydrides and metal dihydrogen complexes involves measurement of the ^1H NMR relaxation times (T_1), which are unusually short for metal dihydrogen complexes.[17] T_1 values were measured for ***cis*-1** (175 ms) and ***trans*-1** (720 ms) in THF-d_8 at −74 °C and 500 MHz using the inversion–recovery technique. Although T_1 is much shorter for ***cis*-1** than for ***trans*-1**, both relaxation times are in the range normally observed for classical metal dihydrides. Since T_1 values for equilibrating species are an average value, the somewhat shorter value of T_1 for ***cis*-1** compared with ***trans*-1** is consistent with a small amount of ***cis*-1-η^2-H_2** in equilibrium with ***cis*-1**, but it certainly does not require it.

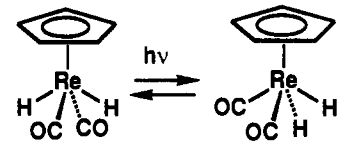
In a third attempt to determine whether ***cis*-1-η^2-H_2** might be in equilibrium with ***cis*-1**, we measured J_{HD} of ***cis*-1-HD** and the difference in hydride chemical shifts ($\Delta\delta$) between ***cis*-1** and ***cis*-1-HD** over a 60 °C temperature range in toluene-d_8 (Table I). Since equilibrium constants vary with temperature, these parameters would be expected to show an abnormally large temperature dependence if ***cis*-1-η^2-H_2** were in equilibrium with ***cis*-1**.

An increase in J_{HD} from 5.8 to 6.5 Hz was seen in going from −35 to +28 °C (Table I). While the absolute magnitude of this change is not large, it is unusual for coupling constants to vary with temperature in the absence of conformational equilibria. While this increase in J_{HD} with temperature is consistent with an increase in the amount of a minor species with a larger J_{HD} such as ***cis*-1-η^2-HD**, it certainly does not provide definitive evidence for such an equilibrium.[18] The large isotopic shifts ($\Delta\delta$) on the hydride resonances of ***cis*-1-HD** and ***cis*-2-HD** were also temperature dependent and increased slightly at lower temperatures (Table I). This is consistent with a temperature dependence of the isotope effect on the equilibrium constant between metal dihydride and dihydrogen complexes. The isotopic shift is not temperature dependent in other known dihydrogen and polyhydride complexes.[19] Again, these observations are consistent with, but do not require, an equilibrium with a dihydrogen complex.

Table I. Temperature Dependence of J_{HD} and the Isotope Effect on the Chemical Shifts of $C_5H_5(CO)_2ReHD$ and $C_5Me_5(CO)_2ReHD$ in Toluene-d_8

complex	T, °C	J_{HD}, Hz	$\Delta(\delta_{HD}-\delta_{HH})$, ppb	$\Delta(\delta_{cis}-\delta_{trans})$, ppb
trans-$C_5H_5(CO)_2ReHD$	−35	<2	<6	
cis-$C_5H_5(CO)_2ReHD$	−35	5.8	52	738
	−3	6.1	49	741
	28	6.5	46	743
trans-$C_5Me_5(CO)_2ReHD$	−35	<2	<6	
cis-$C_5Me_5(CO)_2ReHD$	−35	4.7	56	900
	−3	4.8	53	906
	28	5.0	51	912

Generation of *cis*-$C_5H_5(CO)_2ReH_2$ (*cis*-1) by Photolysis of *trans*-$C_5H_5(CO)_2ReH_2$ (*trans*-1). We were unable to directly observe ***cis*-1-η^2-H_2** by ^1H NMR, possibly because of the slow time scale of NMR. Since the time scale for infrared detection is much shorter, we set out to generate ***cis*-1** in the absence of other reagents and coproducts to see if we could detect a small equilibrium amount of ***cis*-1-η^2-H_2** by IR spectroscopy.



trans-1 *cis*-1

Photolysis of ***trans*-1** in a methylcyclohexane (MCH) glass at 10 K for 10 min led to the formation of a ~40:60 ***cis*-1**:***trans*-1** photostationary state.[20] The glass was warmed to −73 °C, and the IR spectrum of the fluid solution showed major new absorptions at 2006 and 1933 cm^{-1} assigned to ***cis*-1**, in addition to peaks at 2021 and 1950 cm^{-1} for ***trans*-1**. Upon warming to 27 °C, ***cis*-1** isomerized slowly to ***trans*-1**. The kinetics of the isomerization were unusual (Figure 1). The initial rate of isomerization was somewhat slower than that seen in the isomerization of ***cis*-1** generated by protonation of $K[C_5H_5(CO)_2ReH]$; the ***cis*-1**:***trans*-1** ratio decreased from 40:60 to 24:76 over 40 min. At later times, the rate of isomerization became much slower; the ***cis*-1**:***trans*-1** ratio dropped from 23:77 to 19:81 over 120 min.

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(18) The magnitude of J_{HD} also showed a solvent dependence; larger coupling constants were observed in the nonpolar solvent toluene-d_8 (J_{HD} = 6.1 Hz for ***cis*-1** and J_{HD} = 4.8 Hz for ***cis*-2** at −3 °C) than in the more polar solvent THF-d_8 (J_{HD} = 5.4 Hz for ***cis*-1** and J_{HD} = 4.5 Hz for ***cis*-2** at −3 °C). A similar solvent dependence was observed previously for $[Os(H)(\eta^2\text{-}HD)(depe)_2][BF_4]$ (depe = $Et_2PCH_2CH_2PEt_2$), and equilibrium with an η^2-HD complex was proposed: Earl, K. A.; Jia, G.; Maltby, P. A.; Morris, R. H. *J. Am. Chem. Soc.* **1991**, *113*, 3027.

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(20) When the photolysis of ***trans*-1** in MCH solution was carried out at −40 °C, the ***cis*-1**:***trans*-1** ratio was only 5:95.

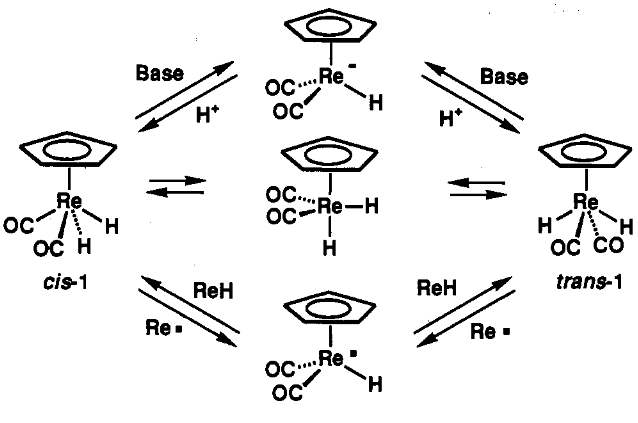
In searching for bands assignable to ***cis*-1-η^2-H_2**, we looked for two nearly equal intensity IR carbonyl bands shifted to lower energy from those of ***cis*-1** that disappeared concurrently with those of ***cis*-1**. In addition to the major bands for ***cis*-1** and ***trans*-1**, ν_{sym} of the minor impurity $C_5H_5Re(CO)_3$ was observed at 2044 cm^{-1} and increased slightly with time (the ν_{asym} band was obscured by the 1950-cm^{-1} band of ***trans*-1**); the ν_{asym} band of *trans*-$C_5H_5(CO)(^{13}CO)ReH_2$ was observed at 1922 cm^{-1} and increased as ***cis*-1** was converted to ***trans*-1** (the ν_{sym} band of *trans*-$C_5H_5(CO)(^{13}CO)ReH_2$ was obscured by the 2006-cm^{-1} band of ***cis*-1**). Two bands at 1991 and 1905 cm^{-1} of similar intensity (~2–4% of the intensity of the bands of ***cis*-1**) decreased at about the same rate as those of ***cis*-1** and were assigned to *cis*-$C_5H_5(CO)(^{13}CO)ReH_2$. In summary, we could find no direct IR evidence for the presence of measurable amounts (>1%) of ***cis*-1-η^2-H_2**.

Kinetics of the Isomerization of *cis*-1 to *trans*-1. As indicated earlier, the rate of isomerization of ***cis*-1** to ***trans*-1** depended on the mode of generation of ***cis*-1**. Even when ***cis*-1** was generated under ostensibly similar conditions, the rate of isomerization varied by a factor of 4 (Table II). The isomerization of ***cis*-1** generated by protonation of $K[C_5H_5(CO)_2ReH]$ followed linear first-order kinetics, but the half-life for isomerization varied from 11 to 40 min at 24 °C (entries 1–3) and varied from 5 to 19 h at −11 °C (entries 4–6).

Initially, we considered two mechanisms for isomerization: (1) an intramolecular rearrangement of the four-legged piano stool via a trigonal bipyramidal transition state and (2) a deprotonation–reprotonation pathway via $C_5H_5(CO)_2ReH^-$.

In agreement with the deprotonation mechanism, the isomerization of ***cis*-1** occurred somewhat more rapidly in the presence of 0.005 M excess $K[C_5H_5(CO)_2ReH]$ (entry 7); the half-life for isomerization at −9 °C was only 138 min.

The deprotonation mechanism suggests that the isomerization of ***cis*-1** should be accompanied by deuterium exchange with added CF_3CO_2D. A large excess (15 equiv) of CF_3CO_2D was added to a 66:34 ***cis*-1**:***trans*-1** mixture generated by addition of 1 equiv of CF_3CO_2H to 1 equiv of $K[C_5H_5(CO)_2ReH]$ in THF-d_8 at low temperature. After 6.5 h at 0 °C, ^1H NMR analysis indicated that isomerization to a 3:97 ***cis*-1**:***trans*-1** mixture had occurred. Integration of the Cp and hydride signals of ***trans*-1** indicated incorporation of only 0.125 D per ***trans*-1**. This experiment indicates that the major pathway for isomerization of ***cis*-1** to ***trans*-1** does not involve exchange with CF_3CO_2D.



A third possible mechanism for isomerization of ***cis*-1** is a radical chain mechanism involving intermediate $C_5H_5(CO)_2ReH^•$, radicals which would not exchange with CF_3CO_2D. The observed erratic rates might be due to variable amounts of radical initiators and quenchers present in solution. In an attempt to generate $C_5H_5(CO)_2ReH^•$ radicals, the isomerization of ***cis*-1** was studied in the presence of the added oxidant $(C_5H_5)_2Fe^+PF_6^-$, (0.004 M). There was an initial burst of isomerization and a rapid continuing rate of isomerization. The rate observed at −11 °C was more than 6 times faster than any previously observed rate (41-min half-life, entry 8).

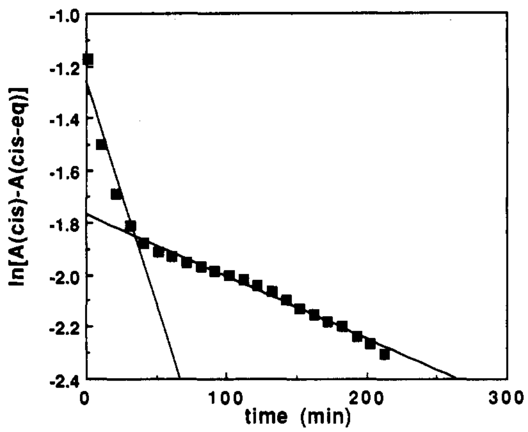


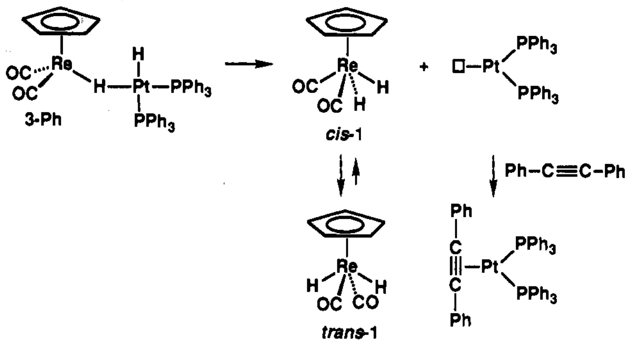
Figure 1. Kinetics of the isomerization of ***cis*-1** in methylcyclohexane at 27 °C.

The observed rates of isomerization of ***cis*-1** generated from the reaction of $C_5H_5(CO)_2Re(\mu$-$H)Pt(H)(PPh_3)_2$ (**3-Ph**) with diphenylacetylene (half-lives of 36 and 11 min at −11 ± 2 °C) were 25–100 times faster than the rates seen for material generated by protonation of $K[C_5H_5(CO)_2ReH]$ (entries 9 and 10).

The observed rate of isomerization of ***cis*-1** generated by photolysis of ***trans*-1** in methylcyclohexane were much slower than the rates observed from other methods of generation.

Discussion

Mechanism of Elimination of $C_5H_5(CO)_2ReH_2$ from $C_5H_5(CO)_2Re(\mu$-$H)Pt(H)(PPh_3)_2$. The results obtained here indicate that *cis*-$C_5H_5(CO)_2ReH_2$ (***cis*-1**) is the major kinetic product of the reaction of diphenylacetylene with $C_5H_5(CO)_2Re(\mu$-$H)Pt(H)(PPh_3)_2$ (**3-Ph**). The first-order kinetics of the reaction require that **3-Ph** dissociate by an intramolecular pathway not accelerated by diphenylacetylene. The kinetic formation of ***cis*-1** is consistent with a least motion pathway for dissociation from **3-Ph**. Since the rate of ***cis*-1** to ***trans*-1** isomerization is fast relative to the rate of diphenylacetylene hydrogenation, the equilibration of ***cis*-1** and ***trans*-1** has little effect on the overall kinetics of the hydrogenation of diphenylacetylene by **3-Ph**.



Mechanism of Equilibration of *cis*-1 and *trans*-1. The rate of isomerization of ***cis*-1** to ***trans*-1** depended strongly on the mode of generation of ***cis*-1** and on the presence of added bases and oxidants. In addition, rate variations of at least 4-fold were seen under ostensibly identical conditions. All of this evidence points to multiple pathways for isomerization of ***cis*-1** to ***trans*-1**.

The rate of an uncatalyzed intramolecular isomerization possibly via a trigonal bipyramidal transition state can be no faster than the slowest observed rate, which was seen late in the isomerization of photochemically generated ***cis*-1** in methylcyclohexane. The half-life for this process was ~350 min at 27 °C.

Table II. Rate of Isomerization of *cis*-$C_5H_5(CO)_2ReH_2$ in THF-d_8

entry	precursor	additive	*T*, °C	*k*, 10^5 s^{-1}	$t_{1/2}$, min
	$[Cp(CO)_2ReH^-]$				
1	0.13 M		24	136 ± 3	11
2	0.056 M		24	50 ± 2	23
3	0.055 M		24	29 ± 2	40
4	0.032		−11	1.01 ± 0.03	1150
5	0.072 M		−11	4.0 ± 0.2	290
6	0.092 M		−12	1.3 ± 0.1	870
7	0.058 M	0.005 M $Cp(CO)_2ReH^-$	−9	8.5 ± 0.1	138
8	0.032 M	0.004 M $Cp_2Fe^+PF_6^-$	−11	28 ± 2	41
	$RePtH_2$ (3-Tol)				
9	0.01 M	0.092 M PhC≡CPh	−12	32 ± 2	36
10	0.01 M	0.196 M PhC≡CPh	−10	107 ± 5	11

A second pathway for isomerization involves deprotonation–reprotonation of ***cis*-1**. Since protonation of $C_5H_5(CO)_2ReH^-$ produced a mixture of ***cis*-1** and ***trans*-1**, it is clear that generation of $C_5H_5(CO)_2ReH^-$ provides a viable mechanism for isomerization. The observations that somewhat faster isomerization rates were seen in the presence of added $C_5H_5(CO)_2ReH^-$ and that some incorporation of deuterium from added CF_3CO_2D into ***trans*-1** was observed during the isomerization of ***cis*-1** provided evidence that some isomerization occurred by this deprotonation–reprotonation mechanism.

The fact that the isomerization of ***cis*-1** in the presence of added CF_3CO_2D produced mainly undeuterated ***trans*-1** strongly suggested the existence of a major isomerization pathway in addition to the deprotonation–reprotonation mechanism. The variability of reaction rates is often cited as a signature of chain reaction mechanisms. The acceleration of the isomerization of ***cis*-1** by added $(C_5H_5)_2Fe^+PF_6^-$ suggested the possibility of a radical mechanism proceeding by hydrogen atom transfer between ***cis*-1** and a $C_5H_5(CO)_2ReH^\bullet$ radical. Brown has provided evidence for substitution reactions of $(CO)_5ReH$ proceeding by a radical chain mechanism involving $(CO)_5Re^\bullet$ intermediates.[21] Another possible mechanism would involve electron transfer to generate radical cations such as $C_5H_5(CO)_2ReH_2^{\bullet+}$ followed by intramolecular isomerization of the radical cation.

A fourth pathway for isomerization was seen in the establishment of a photostationary state between ***cis*-1** and ***trans*-1**. Since the kinetics of the isomerization of ***cis*-1** were all measured in the dark in an NMR probe, photoisomerization is not considered to be important in our kinetic studies.

Is the Molecular Dihydrogen Complex *cis*-1-η^2-H_2 in Equilibrium with *cis*-1? The unusual intermediate value of J_{HD} = 5.3 Hz for ***cis*-1** and the large isotope effect on the chemical shift difference between ***cis*-1** and ***cis*-1-HD** ($\Delta\delta$ = 52 ppb), together with the minor anticipated structural changes involved, suggested that ***cis*-1** might be in equilibrium with ***cis*-1-η^2-H_2**. J_{HD} for η^2-H_2 complexes normally falls in the range from 20 to 35 Hz, while J_{HD} for metal dihydride complexes normally falls in the range from 0 to 2 Hz.

Several examples of well documented equilibria between metal dihydride complexes and metal dihydrogen complexes have been reported. Kubas[22] demonstrated that $W(CO)_3(PPr^i_3)_2(\eta^2\text{-}H_2)$ was in equilibrium with 15–30% of the seven-coordinate $W(CO)_3(PPr^i_3)_2(H)_2$ by solution IR spectroscopy and by variable-temperature NMR. Heinekey[23] reported the equilibrium between $C_5H_5(dmpe)Ru(\eta^2\text{-}H_2)$ and the trans dihydride $C_5H_5(dmpe)Ru(H)_2$ and measured their rate of interconversion by spin saturation transfer NMR experiments. Morris[18] suggested the possibility of an equilibrium between $[Os(H)_3(depe)_2][BF_4]$ and $[Os(H)(\eta^2\text{-}H_2)(depe)_2][BF_4]$ to explain an unusual J_{HD} of 10.5 Hz and to account for solid-state IR data. Bercaw[24] proposed but did not attempt to demonstrate that the unusual intermediate J_{HD} value of 4.8 Hz observed for $C_5Me_5(PMe_3)FeH_3$ was due to an equilibrium between a dihydride and a molecular dihydrogen complex.

In our careful IR studies of ***cis*-1** generated by photolysis of ***trans*-1** in methylcyclohexane, the bands for the ^{13}C isotopomer of ***cis*-1** were readily observed but no additional bands that disappeared along with the bands of ***cis*-1** were seen. This leads us to conclude that the amount of ***cis*-1-η^2-H_2** in equilibrium with ***cis*-1** must be <1%. The unusual intermediate value of J_{HD} = 5.3 Hz and the unusually large upfield isotope effect of $\Delta\delta$ = 52 ppb observed for ***cis*-1** may be due to larger electronic interactions between cis ligands in four-legged piano stool geometries. In Faller's four-legged piano stool compounds *cis*- and *trans*-$CpMo(CO)_2(PPh_3)H$, J_{cisPH} = 64 Hz is substantially larger than $J_{transPH}$ = 21 Hz.[25] In Gladysz' $CpRe(NO)(PPh_3)H_2^+$ complexes, the coupling between cis P and H ligands is substantially larger than the coupling between trans P and H ligands.[26] Heinekey has observed large upfield isotope effects of up to 75 ppb per D on the chemical shifts of $[CpIr(PPh_3)H_3][BF_4]$.[19b] Observations of J_{HD} and $\Delta\delta$ values should be used with great caution as evidence to decide between metal dihydrides and metal dihydrogen complexes, particularly for four-legged piano stool geometries.

Experimental Section

All manipulations were performed under a N_2 atmosphere using standard Schlenk and glovebox techniques. NMR spectra were obtained on a Bruker AM500, AM360, or WP270 spectrometer. ^{31}P chemical shifts are referenced to 85% external H_3PO_4. The reported temperature of the NMR probe is given by $\Delta\delta$ of methanol peaks with 0.03% HCl.[27] IR spectra were recorded on a Mattson Polaris (FT) or Nicolet 740 FTIR spectrometer. Elemental analysis was performed by Galbraith Laboratories, Inc. (Knoxville, TN).

THF, THF-d_8, and toluene-d_8 were distilled from sodium and benzophenone. $K[C_5H_5(CO)_2ReH]$[4] and $K[C_5Me_5(CO)_2ReH]$[12] were prepared as previously described. $C_5H_5(CO)ReH_2$ was prepared as described by Bergman and Yang.[4]

$Pt(CH_2CH_2)[P(C_6H_4\text{-}p\text{-}CH_3)_3]_2$.[28,29] Ethylene was bubbled through a solution of *cis*-$PtCl_2[P(C_6H_4\text{-}p\text{-}CH_3)_3]_2$ (600 mg, 0.69 mmol) in a 1:1 CH_2Cl_2:ethanol mixture (12 mL) at 0 °C for 15 min, and solid $NaBH_4$ (130 mg) was added at 0 °C. Ethylene was bubbled through the mixture for 30 min at room temperature. The mixture was then filtered, and the precipitate was washed with water (20 mL), ethanol (20 mL), and pentane (40 mL) to give a white solid (390 mg, 68% yield), which was stored under N_2. ^1H NMR (500 MHz, C_6D_6): δ 7.6 (broad, ortho H), 6.84 (d, J = 7.6 Hz, meta H), 2.71 (s, C_2H_4, J_{PtH} = 60.2 Hz), 1.99 (s, CH_3).

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^{31}P NMR (202 MHz, C_6D_6): δ 32.8 (J_{PtP} = 3725 Hz). ^{13}C NMR (125 MHz, C_6D_6): δ 138.7 (para C); 135.8 (ipso C, J_{PC} = 22 Hz); 134.3, 128.7 (ortho and meta C); 38.9 (t, J_{PC} = 12 Hz, J_{PtC} = 209 Hz, $CH_2{=}CH_2$).

$C_5H_5(CO)_2Re(\mu\text{-}H)Pt(H)[P(C_6H_4\text{-}p\text{-}CH_3)_3]_2$ (3-Tol). A solution of $C_5H_5(CO)_2ReH_2$ (56 mg, 0.18 mmol) and $Pt(H_2CCH_2)[P(C_6H_4\text{-}p\text{-}CH_3)_3]_2$ (150 mg, 0.18 mmol) in 15 mL of benzene was stirred for 1 h at ambient temperature. The solution was concentrated to 5 mL under vacuum, and 15 mL of hexane was added to afford a bright yellow precipitate, which was filtered off, washed with hexane, and dried under high vacuum to give **3-Tol** (130 mg, 0.12 mmol, 66% yield). ^1H NMR (500 MHz, toluene-d_8): δ 7.54 (dd, J_{PH} = 10 Hz, J = 8 Hz, ortho H), 6.82 (d, J = 7 Hz, meta H), 4.89 (s, C_5H_5), 2.02 (s, CH_3), −7.02 (virtual triplet, $J_{PH+P'H}$ = 108 Hz, J_{PtH} = 603 Hz). $^{13}C\{^1H\}$ NMR (125 MHz, toluene-d_8): δ 205.0 (s, CO), 139.5 (s, para C), 135.0–134.4 (br, ortho and meta C), 132.9 (d, J_{PC} = 47 Hz, ipso C), 80.8 (s, C_5H_5), 21.1 (s, CH_3). $^{31}P\{^1H\}$ NMR (202 MHz, toluene-d_8): δ 27.72 (s, J_{PtP} = 3247 Hz). IR (CH_2Cl_2) 1901, 1830 cm^{-1}. Although the material was homogeneous and >98% pure by ^1H NMR in THF-d_8, elemental analyses for C were consistently low.

Generation of *cis*-$CpRe(CO)_2H_2$ (*cis*-1) by Protonation of $K[C_5H_5(CO)_2ReH]$. An NMR tube was charged with $K[C_5H_5(CO)_2ReH]$ (8 mg, 23 μmol) in a glovebox, and THF-d_8 (0.39 mL) and CF_3CO_2H (~23 μmol) were condensed into the tube on a high-vacuum line at −196 °C. The NMR tube was sealed under vacuum, shaken at −78 °C, and inserted into a precooled NMR probe. The kinetics of the isomerization of ***cis*-1** were followed by ^1H NMR using hexamethylbenzene or triphenylmethane as an internal standard. Spectra were collected at regular intervals using an automated program, and the hydride resonances of ***cis*-1** and ***trans*-1** were carefully integrated. The observed rate was calculated by plotting ln $\{[\textit{cis}\text{-}\mathbf{1}]_t - [\textit{cis}\text{-}\mathbf{1}]_{eq}\}$ versus time.

Generation of *cis*-$CpRe(CO)_2H_2$ (*cis*-1) from $C_5H_5(CO)_2Re(\mu\text{-}H)Pt(H)(PPh_3)_2$. An NMR tube was charged with $C_5H_5(CO)_2Re(\mu\text{-}H)Pt(H)(PPh_3)_2$ (3 mg, 2.3 μmol), phenylacetylene (5.8 mg, 32 μmol), and C_6Me_6 (1.6 mg, 10 μmol) in a glovebox, and toluene-d_8 was condensed into the tube on a high-vacuum line. The tube was sealed, shaken for 1 min at ~0 °C, and placed in a precooled NMR probe at −9 °C.

Generation of *cis*-$C_5Me_5Re(CO)_2H_2$ (*cis*-2) by Protonation of $K[C_5Me_5(CO)_2ReH]$. An NMR tube was charged with $K[C_5Me_5(CO)_2ReH]$ (11 mg, 27 μmol) in a glovebox, and THF-d_8 (0.35 mL) and CF_3CO_2H (~27 μmol) were condensed into the tube on a high-vacuum line at −196 °C. The NMR tube was sealed under vacuum, shaken at −78 °C, and inserted into a precooled NMR probe. For ***cis*-2**: ^1H NMR (THF-d_8, 500 MHz) δ 2.26 (s, Cp*), −8.72 (s, ReH); $^{13}C\{^1H\}$ NMR (THF-d_8, 126 MHz) δ 205.8 (CO), 100.7 (C_5Me_5), 11.5 (Me). For ***trans*-2**: ^1H NMR (THF-d_8, 500 MHz) δ 2.18 (s, Cp*), −9.65 (s, ReH); $^{13}C\{^1H\}$ NMR (THF-d_8, 126 MHz) δ 199.8 (CO), 99.1 (C_5Me_5), 11.8 (Me).

Isomerization of *cis*-1 in the Presence of CF_3CO_2D. A resealable NMR tube was charged with $K[C_5H_5(CO)_2ReH]$ (6 mg) and hexamethylbenzene in a drybox, and THF and 1.1 equiv of CF_3CO_2H were condensed into the tube. The tube was shaken at low temperature and placed in an NMR probe precooled to −9 °C. The ^1H NMR spectrum showed a 66:34 ***cis*-1**:***trans*-1** mixture. The tube was then cooled to −78 °C, and CF_3CO_2D (15 equiv) was added. After 6.5 h (~4 half-lives) at 0 °C, the ^1H NMR spectrum (−9 °C) showed a 3:97 ***cis*-1**:***trans*-1** mixture. Integration of the resolvable hydride resonances of ***cis*-1** and ***cis*-1-HD** showed a 1:2 HD:HH mixture. Since the hydride resonances of ***trans*-1** are not resolvable, an estimate of 1:9:90 DD:HD:HH was made from the Cp:hydride ratio of resonances.

Generation of *cis*-$CpRe(CO)_2H_2$ (*cis*-1) by Photolysis of *trans*-1. A 0.013 M solution of ***trans*-1** in methylcyclohexane was placed in a variable-temperature CaF_2 IR cell. The cell was cooled to 10 K and irradiated for 10 min with a 300-W xenon arc lamp with a WG 320 filter (>300 nm).[30] The cell was warmed to −73 °C, and the IR spectrum was obtained on a Nicolet 740 FTIR spectrometer. The ***cis*-1**:***trans*-1** ratio of the high-energy bands was 40:60. Peaks were observed for ***trans*-1** at 2021 (ν_{sym}) and 1950 cm^{-1} (ν_{asym}), for the ^{13}C isotopomer of ***trans*-1** at 1921 cm^{-1} (ν_{asym}; ν_{sym} was obscured by 1940 peak of ***cis*-1**), for ***cis*-1** at 2008 (ν_{sym}) and 1950 cm^{-1} (ν_{asym}), and for the ^{13}C isotopomer of ***cis*-1** at 1991 (ν_{sym}) and 1905 cm^{-1} (ν_{asym}). The solution was warmed to 300 K, and the spectra were taken at regular intervals. Rates of isomerization were obtained by monitoring the change in intensity of the ***cis*-1** band at 2008 cm^{-1}.

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