Conclusion

The present study has elucidated several structure–reactivity relationships in the [3+2] cycloaddition reaction between transition metal–propargyl complexes and TSI. Accordingly, the bimolecular rate constant is sensitive to the nature of the metal together with its ancillary ligands (η^5-$C_5H_5Cr(NO)_2$ > η^5-$C_5H_5Fe(CO)_2$ > η^5-$C_5H_5Mo(CO)_3$ > η^5-$C_5H_5W(CO)_3$ > $Mn(CO)_5$) and particularly sensitive to replacement of CO with stronger bases (i.e., L = $P(C_6H_5)_3$ > $P(OC_6H_5)_3$ > CO). Methylpropargyl complexes react considerably faster than the corresponding phenylpropargyl complexes. Interestingly and perhaps fortuitously, analogous, structurally related iron–propargyl and $-\eta^1$-allyl complexes cycloadd at comparable rates. The cycloaddition reaction shows a small solvent effect and exhibits a large negative ΔS^*. It was not possible unequivocally to distinguish between a two-step dipolar mechanism and a concerted one from these data alone.

Acknowledgment. We are grateful to the National Science Foundation for support of this research through Grants CHE-7602413 and CHE-7911882.

Registry No. I (M = η^5-$C_5H_5Fe(CO)_2$), 76514-46-0; I (M = η^5-$C_5H_5Mo(CO)_3$), 76498-72-1; I (M = η^5-$C_5H_5Cr(NO)_2$), 76498-73-2; II (M = η^5-$C_5H_5Fe(CO)_2$, R = CH_3), 40695-14-5; II (M = η^5-$C_5H_5Mo(CO)_3$, R = CH_3), 76498-74-3; II (M = $Mn(CO)_4[P(C_6H_5)_3]$, R = CH_3), 76498-75-4; II (M = η^5-$C_5H_5Fe(CO)_2$, R = C_6H_5), 76498-76-5; II (M = η^5-$C_5H_5Mo(CO)_3$, R = C_6H_5), 76498-77-6; II (M = η^5-$C_5H_5Mo(CO)_2[P(C_6H_5)_3]$, R = C_6H_5), 76498-78-7; II (M = η^5-$C_5H_5Mo(CO)_2[P(OC_6H_5)_3]$, R = C_6H_5) (cis isomer), 76498-79-8; II (M = η^5-$C_5H_5Mo(CO)_2[P(OC_6H_5)_3]$, R = C_6H_5) (trans isomer), 76549-10-5; II (M = η^5-$C_5H_5W(CO)_3$, R = C_6H_5), 76498-80-1; II (M = $Mn(CO)_5$, R = C_6H_5), 76498-81-2; II (M = $Mn(CO)_4[P(C_6H_5)_3]$, R = C_6H_5), 76498-82-3; II (M = η^5-$C_5H_5Cr(NO)_2$, R = C_6H_5), 76498-83-4; III (M = η^5-$C_5H_5Fe(CO)_2$, R = R′ = H, R″ = CH_3) (trans isomer), 76514-47-1; III (M = η^5-$C_5H_5Fe(CO)_2$, R = R′ = H, R″ = CH_3) (cis isomer), 76581-97-0; η^5-$C_5H_5Cr(NO)_2CH_2C{\equiv}CC_6H_5$, 76498-84-5; $Cl_2FCC(O)CClF_2$, 79-52-7; TSI, 4083-64-1; η^5-$C_5H_5Fe(CO)_2CH_2C{\equiv}CCH_3$, 34822-36-1; η^5-$C_5H_5Fe(CO)_2CH_2C{\equiv}CC_6H_5$, 33114-75-9; η^5-$C_5H_5Mo(CO)_3CH_2C{\equiv}CCH_3$, 32877-61-5; η^5-$C_5H_5Mo(CO)_3CH_2C{\equiv}CC_6H_5$, 32877-62-6; η^5-$C_5H_5Mo(CO)_2[P(C_6H_5)_3]CH_2C{\equiv}CC_6H_5$, 54775-72-3; η^5-$C_5H_5Mo(CO)_2[P(OC_6H_5)_3]CH_2C{\equiv}CC_6H_5$, 69372-50-5; η^5-$C_5H_5W(CO)_3CH_2C{\equiv}CC_6H_5$, 32993-03-6; $Mn(CO)_5CH_2C{\equiv}CC_6H_5$, 23626-46-2; $Mn(CO)_4[P(C_6H_5)_3]CH_2C{\equiv}CCH_3$, 64070-51-5; $Mn(CO)_4[P(C_6H_5)_3]CH_2C{\equiv}CC_6H_5$, 64070-52-6; η^5-$C_5H_5Fe(CO)_2CH_2CH{=}CH_2$, 38960-10-0; η^5-$C_5H_5Fe(CO)_2CH_2CH{=}CHCH_3$ (*E* isomer), 56389-74-3; η^5-$C_5H_5Fe(CO)_2CH_2CH{=}CHC_6H_5$, 31798-46-6; η^5-$C_5H_5Fe(CO)_2CH_2CH{=}C(CH_3)_2$, 38905-70-3; η^5-$C_5H_5Cr(NO)_2Cl$, 12071-51-1; η^5-$C_5H_5Fe(CO)_2CH_2CH{=}CHCH_3$ (*Z* isomer), 56389-75-4.

Contribution from the Department of Chemistry, California State University, Northridge, California 91330, and the Istituto di Chimica Generale ed Inorganica dell'Università di Torino, 10125 Torino, Italy

Reactions of Protic Acids with a Hydridoorganometal Cluster: $HRu_3(CO)_9(C_2C(CH_3)_3)$

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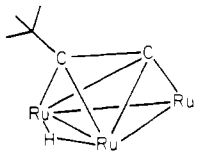
The titrations of $HRu_3(CO)_9C_6H_9$ (I), $HRu_3(CO)_8(C_6H_9)PR_3$ (R = C_6H_5, OCH_3) (II), and $HRu_3(CO)_7(C_6H_9)(PR_3)_2$ (R = C_6H_5, OCH_3) (III) with CF_3SO_3H in CD_2Cl_2 have been followed by variable-temperature ^1H NMR. Initial protonation takes place at the metal core, but significant differences in the relative basicities and the rates of *inter-* and *intra*molecular hydride exchange are observed. In neat sulfuric acid a second protonation of I takes place at the organic ligand to yield a dicationic dihydrido complex $H_2Ru_3(CO)_9(HC{=}CC(CH_3)_3)^{2+}$. In the case of II two isomeric dications are obtained as kinetic products with subsequent rearrangement to the more thermodynamically stable isomer. In D_2SO_4 II gives only the more thermodynamically stable product while deuterated II in H_2SO_4 gives a different isomer ratio than II in H_2SO_4. A mechanism explaining this unusual deuterium isotope effect is presented and discussed.

Introduction

Dynamic NMR studies of the reactions of protic acids with low oxidation state mononuclear organometallic complexes have yielded much useful information about the basicity of different types of organo transition metal compounds.[1] Direct protonation of the metal atom has been demonstrated for many complexes by using NMR techniques. The transition metal "hydride" bond may be long-lived as in the case for π-arene complexes[2] or may be a short-lived intermediate as has been invoked in acid cleavage of metal σ-alkyls[3] and in the protonation of η^4-diene complexes to form η^3-allyl cations.[1] There are also cases where protonation leading to carbon–metal cleavage can be shown to take place directly on the organic ligand (i.e., σ-allyl to π-olefin).[4] There have been few detailed studies on the reactions of low oxidation state polynuclear organometallic complexes with protic acids.[5] The lower reactivity of the polynuclear organometallics holds out the possibility of observing intermediates in multistep protonation processes. Local differences in cluster atom environments and overall electrophilic reactivity of the ligand can be estimated from protonation studies followed by NMR.

Clusters of structural type $(H)Ru_3(CO)_9(C_2R)$ (I) are obtainable in good yields by reaction of $Ru_3(CO)_{12}$ with terminal acetylenes.[6] The dissolution of $Ru_3(CO)_{12}$ in 98% H_2SO_4 has



I

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(1) J. C. Kotz and D. G. Pedrotty, *Organomet. Chem. Rev., Sect. A*, **4**, 470 (1969); L. M. Jackman and F. A. Cotton, Eds., "Dynamic NMR Spectroscopy", Academic Press, New York, 1975.
(2) T. C. Flood, E. Rosenberg, and A. Sarhangi, *J. Am. Chem. Soc.*, **99**, 4334 (1977), and references therein.
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Table I. ^1H NMR Data[a]

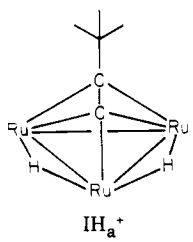
no.	compd	medium	δ(hydride)	δ(*t*-BuCH$_3$)	δ(CH)	δ(PR$_3$)
I	$HRu_3(CO)_9(C_6H_9)$	CD_2Cl_2	−21.0 s (1)	1.4 s (9)		
IH$^+$	$H_2Ru_3(CO)_9(C_6H_9)^+$	CF_3COOH	−20.5 s (2)	1.5 s (9)		
I2H^{2+}	$H_2Ru_3(CO)_9(C_6H_{10})^{2+}$	H_2SO_4	−14.3 s (1) −15.1 s (1)	1.1 s (9)	9.2 s (1)	
II	$HRu_3(CO)_8(C_6H_9)PR_3$					
	R = C_6H_5	CD_2Cl_2	−21.2 d (1) [^2J(PH) = 2.4]	1.3 s (9)		7.2–7.5 m (15)
	R = OCH_3	CD_2Cl_2	−21.2 d (1) [^2J(PH) = 2.4]	1.3 s (9)		3.5 d (9) [^2J(PH) = 13]
IIH$^+$	$H_2Ru_3(CO)_8(C_6H_9)PR_3$					
	R = C_6H_5	CD_2Cl_2 + 1.1 equiv of CF_3SO_3H	−18.3 br (2) [$W_{1/2}$ = 32 (at 25 °C)] −17.1 dd (1) [^2J(HH) = 3, ^3J(PH) = 6] −19.6 dd (1) [^2J(PH) = 14 (at −50 °C)]	1.5 s (9)		7.3–7.6 m (15)
	R = OCH_3	CD_2Cl_2 + 1.1 of CF_3SO_3H	−17.9 br (2) [$W_{1/2}$ = 36 (at 25 °C)] −15.9 dd (1) [^2J(HH) = 3.0, ^2J(PH) = 10.5] 19.9 dd (1) [^3J(PH) = 5.0 (at −60 °C)]			3.5 d (9) [^2J(PH) = 13]
III	$HRu_3(CO)_7(C_6H_9)(P(OCH_3)_3)_2$	CD_2Cl_2	−21.5 m (1)	1.3 (s) (9)		3.7 d (18)
IIIH$^+$	$H_2Ru_3(CO)_7(C_6H_9)(P(OCH_3)_3)_2^+$	CD_2Cl_2 + 1.1 equiv of CF_3SO_3H	−18.4 m (1) [^2J(HH) = 3, ^2J(P$_1$H) = 8, ^2J(P$_2$H) = 10] −21.5 m (1) [^2J(PH) = 8, ^3J(PH) = 2.4]	1.5 s (9)		3.85 d (9) [^2J(PH) = 14] 3.90 d (9) [^2J(PH) = 14]
II2H^{2+}	$H_2Ru_3(CO)_8(C_6H_{10})P(C_6H_5)_3^{2+}$					
	isomer a	H_2SO_4	−14.5 d (1) [^2J(PH) = 14] −15.4 d (1) [^2J(PH) = 14]	1.6 s (9)	9.4 s (1)	7.3 m (15)
	isomer b	H_2SO_4	−19.9 s (1) −20.3 d (1) [^2J(PH) = 9]	1.3 s (9)	9.7 s (1)	7.3 m (15)

[a] *J* values in hertz.

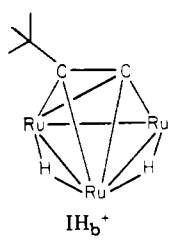
already been shown to give an isolable μ-hydrido monocation ($HRu_3(CO)_{12}^+$).[7] We recently found that I (R = *t*-Bu) forms a stable di-μ-hydrido dication ($H_2Ru_3(CO)_9(HC{=}C\text{-}t\text{-}Bu)$)$^{2+}$.[8] We report here the results of a more detailed study of the protonation of I and of its mono- and bis(phosphine) derivatives.

Results and Discussion

When I is dissolved in CF_3COOH at 25 °C, the ^1H NMR of the resulting pale yellow solution shows no change in the hydrocarbon region aside from a small downfield shift of the *tert*-butyl methyl resonance. In the hydride region however, a new, sharp resonance appears at δ −20.5, which integrates in a ratio of 2:9 with the *tert*-butyl methyl resonance (Table I). I is therefore completely monoprotonated at the metal core in CF_3COOH, and intermolecular proton exchange with the acid is slow on the NMR time scale. IH$^+$ can have either structure IH_a^+ or IH_b^+, where intramolecular hydride migration must be rapid on the NMR time scale in the latter to be consistent with the observed spectrum.

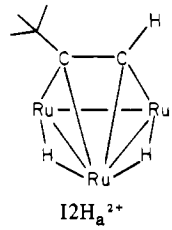


IH_a^+

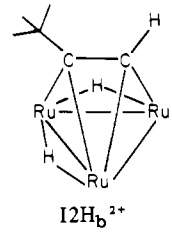


IH_b^+

I dissolves slowly (~3 h) in 95% H_2SO_4 to give pale yellow, air-stable solutions. The ^1H NMR spectrum of these solutions shows two new hydride resonances at δ −14.3 and −15.1 as well as a new peak in the hydrocarbon region at δ 9.2. Each of these new resonances integrates in a 1:9 ratio with the *tert*-butyl methyl resonance (Table I). These results are essentially identical with those obtained in HSO_3Cl, for which structure $I2H_b^{2+}$ has been proposed.[8] This structural assignment was



$I2H_a^{2+}$



$I2H_b^{2+}$

based on ^{13}C NMR evidence[8] and on the low-field ^1H NMR shift of the singlet at δ 9.2, which has been shown to be diagnostic for a CH group σ and π bonded to two metal atoms.[9] The small difference in the observed chemical shifts of the hydride resonances in $I2H^{2+}$ (0.8 ppm) supports $I2H_a^{2+}$ over $I2H_b^{2+}$ since isostructural 48e clusters show 4 ppm differences in the shifts of the hydrides. In general, 48e trinuclear complexes of alkenes and alkynes show markedly shorter (0.25 Å) metal–carbon distances for the formerly 1e σ bonds than for the 2e π bonds with the organic ligand.[9] For the 46e cluster we must consider a structure $I2H_c^{2+}$, which is based on the isoelectronic $Fe_3(CO)_9C_2R_2$.[12] The metal–carbon bonds of the μ_3-π^4 bonding scheme are of similar length in this type of complex, and the C–C axis of the ligand is perpendicular to

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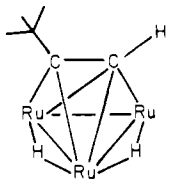
(10) C. Jangala, E. Rosenberg, D. Skinner, S. Aime, L. Milone, and E. Sappa, *Inorg. Chem.*, **19**, 1571 (1980).
(11) Estimated with a coalescence temperature of +20 °C for IIIH$^+$, by using $\Delta G^* = 4.77T_c[9.97 + \log(T_c/\delta\nu)]$: D. Kost, E. H. Coulson, and M. Raban, *J. Chem. Soc. D*, 656 (1971).
(12) J. F. Blount, L. F. Dahl, C. Hoogzand, and W. Hübel, *J. Am. Chem. Soc.*, **88**, 292 (1966).

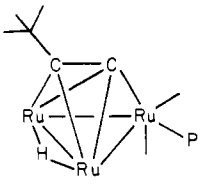
one metal–metal bond and makes an angle of 30° with the other two. In $I2H_a^{2+}$ the C–C axis is parallel to one metal–metal bond and is at 30° to the other two. Structure $I2H_c^{2+}$ is supported by the recent theoretical work of Schilling and Hoffmann.[13]



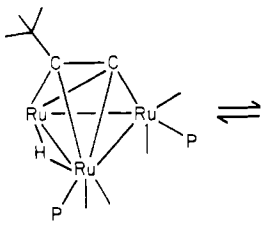
$I2H_c^{2+}$

When I is dissolved in D_2SO_4, no new resonance appears at δ 9.2 even after prolonged periods (3 weeks), and the same hydride resonances appear as in $I2H^{2+}$ but integrate in a total ratio of 1:9 with the *tert*-butyl methyl resonance (Table I). This experiment clearly demonstrates that I undergoes a two-step protonation process in which the second proton directly attacks the organic ligand. Furthermore, although intramolecular proton exchange is slow on the NMR time scale in $I2H^{2+}$, it is rapid enough to randomize the hydride sites during dissolution. This could take place before or after the second protonation step depending on their relative rates.

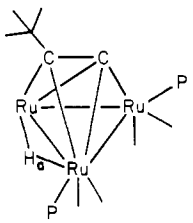
We then undertook an investigation of the reactions of the less symmetrical phosphine-substituted derivatives of I–III, where the possibility of isomer formation could add to our knowledge of the protonation mechanisms. The solution structures of II and III have been evaluated from a detailed analysis of their variable-temperature ^1H (Table I) and ^{13}C NMR.[10] II has the phosphine substituted on the metal atom with the metal–carbon σ bond. Only the equatorial conformer is populated, but exchange between the two equatorial sites is moderately rapid on the NMR time scale ($\Delta G^{\ddagger}$ = 12 kcal/mol) at 25 °C. III exists as an equilibrium mixture of III_a and III_b, which are also exchanging on the NMR time scale at 25 °C.



II



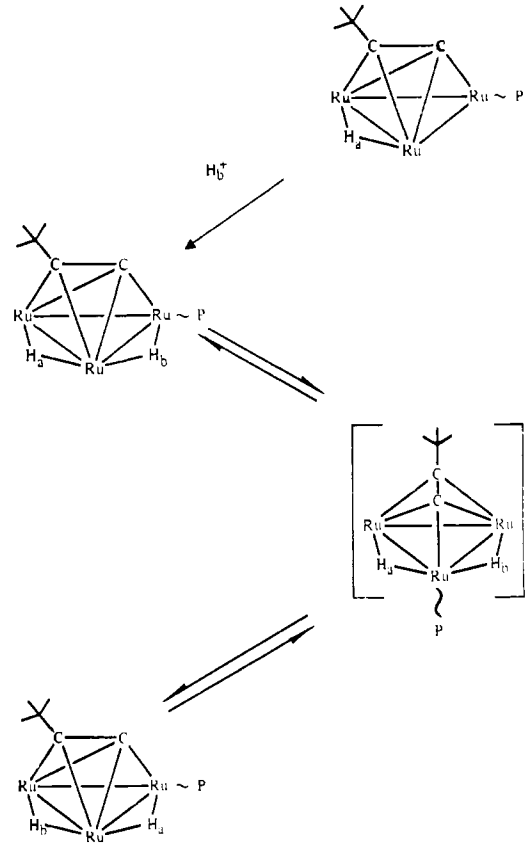
III_a



III_b

In order to examine the variable-temperature, ^1H NMR after the first protonation, we decided to titrate the phosphine derivatives with CF_3SO_3H in CD_2Cl_2 since this would not be possible in CF_3COOH. When 0.064 mmol of $HRu_3(CO)_9(C_6H_9)PR_3$ (R = C_6H_5) in 0.5 mL of CD_2Cl_2 is treated with 3.0 μL of CF_3SO_3H (0.03 mmol), a new sharp *tert*-butyl methyl resonance appears at δ 1.5 equal in intensity to the resonance at δ 1.3. A new broad resonance appears at δ −18.3, which integrates in a ratio of 2:9 with a new *tert*-butyl methyl resonance and is twice the intensity of the remaining hydride doublet for II, which remains sharp and unshifted (Table I). When the temperature of this solution is lowered to −50 °C, the broad hydride resonance at δ −18.3 splits into two nicely resolved doublets of doublets, in a 1:1 ratio at δ −17.1 and −19.6. The rest of the spectrum remains unchanged. These results can be interpreted in terms of quantitative protonation of the cluster to form IIH^+, in which intermolecular proton exchange with unprotonated II is slow on the NMR time scale at room temperature. Intramolecular hydride exchange, on the other hand, is moderately rapid at room temperature but slow at −50 °C. The structure of IIH^+ is deduced from the relative size of the phosphorus–hydrogen couplings (Table I) and is based on analogy with similar coupling in the neutral phosphine-substituted derivatives of II (see Scheme I).[10] An identical experiment done with II (R = OCH_3) gives very similar results. The data along with a spectrum of the hydride region are shown in Figure 1 (Table I). Addition of more CF_3SO_3H to these solutions results in complete protonation when 1.1 equiv of acid has been added.

Scheme I. Pathway for Hydride Site Exchange in IIH^+



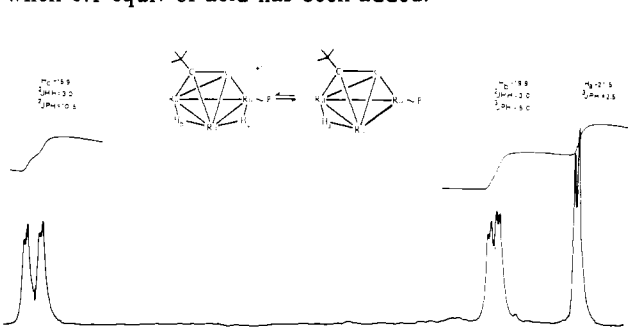


Figure 1. ^1H NMR of the hydride region of $HRu_3(CO)_8(P(OCH_3)_3)(C_6H_9)$ + 0.5 equiv of CF_3SO_3H in CD_2Cl_2 at −60 °C.

(13) B. E. R. Schilling and R. Hoffmann, *J. Am. Chem. Soc.*, **101**, 3456 (1979).

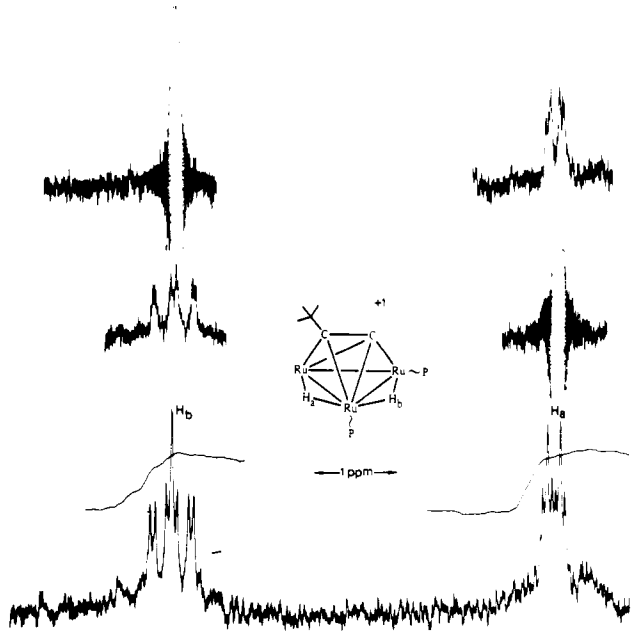
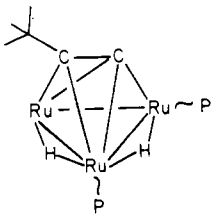


Figure 2. ^1H NMR of the hydride region of $HRu_3(CO)_9C_6H_9(P(C_6H_5)_3)_2$ + 1.1 equiv of CF_3SO_3H in CD_2Cl_2 at room temperature. The ^1H-decoupled spectrum shows above each trace.

Protonation of $HRu_3(CO)_7(PR_3)_2(C_6H_9)$ (III) (R = OCH_3) in CD_2Cl_2 with CF_3SO_3H was carried out under conditions similar to those for II. The ^1H NMR data for III are given in Table I. III protonates essentially quantitatively, and the ^1H NMR spectra of $IIIH^+$ at room temperature show two doublets for the phosphite methyls, a singlet for the *tert*-butyl methyl resonance (Table I), and two sharp multiplet resonances at δ −18.4 (relative intensity 1) and −21.5 (relative intensity 1). These multiplets arise from coupling of the hydrides to each other and to each of the phosphorus centers (Table I). These assignments were deduced from ^1H spin-decoupling experiments on the hydride resonances (see Figure 2) and by comparison of the J(PH) values with the monophosphite species IIH^+. The structure of $IIIH^+$ is



$IIIH^+$

and apparently exists as only one isomer in solution. In the case of IIH^+ and $IIIH^+$ we cannot define the stereochemistry of phosphine substitution on the ruthenium atom.

In CF_3COOH complete monoprotonation of II and III results, and the monoprotonated species give ^1H NMR spectra identical with those of the protonated species described above. Thus phosphine substitution on I does not change the site of protonation or degree of protonation of I under similar conditions (CF_3COOH). However, the experiments outlined above allowed us to differentiate clearly between structures of types IH_a^+ and IH_b^+ for IIH^+ and $IIIH^+$. When I is titrated with CF_3SO_3H in CD_2Cl_2, only one slightly shifted hydride resonance is observed at room temperature, suggesting that intermolecular H^+ exchange is rapid on the NMR time scale under these conditions. At −60 °C with a sixfold excess of CF_3SO_3H two sets of hydride and *tert*-butyl methyl resonances are observed, one of which is identical with those of I. The other set of resonances, which are about 0.2 in relative intensity

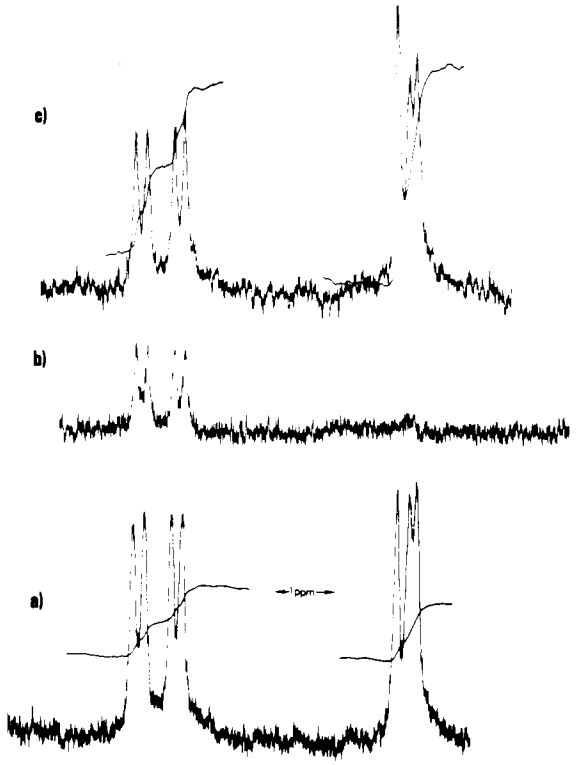
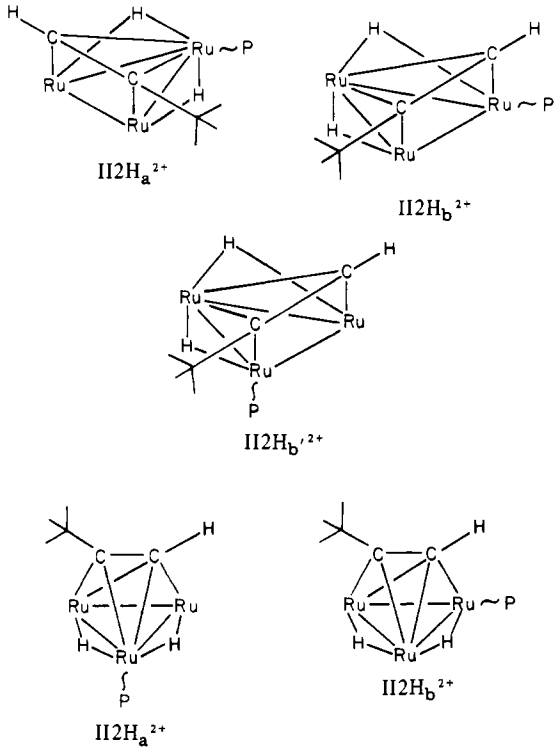


Figure 3. (a) ^1H NMR of the hydride region of II (R = C_6H_5) in H_2SO_4 directly after dissolving. (b) ^1H NMR of the hydride region of II in D_2SO_4 directly after dissolving. (c) ^1H NMR of the hydride region of 65%-deuterated II in H_2SO_4 directly after dissolving.

to those for I, can be assigned to IH_a^+ or IH_b^+ (vide infra). Thus II and III are intrinsically more basic than I since they protonate almost quantitatively with CF_3SO_3H in CD_2Cl_2. Furthermore, intermolecular proton exchange is much slower for II and III than for I when 0.5 equiv of CF_3SO_3H is present, showing that proton transfer in IIH^+ or $IIIH^+$ is slow compared with that in IH^+. We have also estimated the ΔG^* for intramolecular hydride exchange in IIH^+ to be 13.0 kcal/mol at 20 °C ($k \approx 10^3$ s^{-1}) from our variable-temperature ^1H NMR data.[11] This value is very close to the ΔG^* for axial–radial CO exchange at the unique ruthenium atoms in I and II[10] and suggests that hydride migration and axial–radial CO exchange may be mechanistically connected in these complexes.

Having now established that II protonates in a manner analogous to I in CF_3COOH, we then turned our attention to its reaction with H_2SO_4. The ^1H NMR of a solution of II (PR_3 = $P(C_6H_5)_3$) in H_2SO_4 shows two broad singlets at δ 9.4 and 9.7 in ratio of 1.5:1 (combined relative intensity 1), a multiplet at δ 7.3 (relative intensity 15), and two singlets at δ 1.6 and 1.3 in a ratio of 1.5:1 (combined relative intensity 9). In the hydride region two sets of hydride resonances are observed: (1) two doublets in a 1:1 ratio at δ −14.5 and −15.4 (J(PH) = 14 Hz for both) and (2) a broad singlet at δ −19.9, which partially overlaps with a doublet at δ −20.3 (J(PH) = 9 Hz). The overall ratio of the lower field set to the higher field set is 1.5:1 (see Figure 3a). We interpret this spectrum in terms of two sets of isomeric dications analogous to $I2H^{2+}$. (See first set of structures $II2H_a^{2+}$ and $II2H_b^{2+}$.) Here again we cannot exclude the alternative structures for the two isomers of $II2H^{2+}$, in which the organic ligand is π^4-μ_3-bound to the cluster (see $II2H_a^{2+}$ and $II2H_b^{2+}$, second set). The exact equivalence of the J(PH) values in isomer a suggests that the phosphine is in the axial position in $II2H_a^{2+}$.



Over a period of 6 days the a:b isomer ratio gradually changes to >16 as evidenced by the decrease in intensities of the hydride resonances at δ −19.9 and −20.3, the singlet resonance at δ 1.6, and the singlet at δ 9.7. The resonances associated with isomer a increase. The overall change in isomer ratio with time is documented in Table II. Isomer b is thus a kinetic product, which gradually rearranges to the more thermodynamically stable isomer a.

Isomer a can be isolated as its hexafluorophosphate salt by addition of the concentrated sulfuric acid solution to saturated aqueous ammonium hexafluorophosphate. The yellow powder is soluble in methylene chloride, and its NMR spectrum in CD_2Cl_2 is identical with that of $II2H_a^{2+}$ in sulfuric acid. In CD_3CN the hydride region gradually changes with time. The two doublets associated with $II2H_a^{2+}$ gradually diminish in intensity, and a new broad doublet appears in the same region. These changes are interpreted as resulting from deprotonation of $II2H_a^{2+}$ by the more basic solvent, acetonitrile. The methyne resonance at δ 9.28 remains unchanged. Thus, rearrangement of the organic ligand from a 5e donor to a 4e donor increases the basicity of the organic ligand relative to the cluster. The deprotonation of $II2H_a^{2+}$ in acetonitrile is followed by slow decomposition of the cluster, under the experimental conditions, and we were unable to isolate the deprotonated species as $[II2H_a^{2+}][PF_6^-]_2$. We were also unable to isolate $I2H_a^{2+}$ as its hexafluorophosphate salt by the above procedure. $I2H^{2+}$ would be expected to deprotonate more readily than $II2H^{2+}$.

When a sample of II is dissolved in D_2SO_4, only resonances associated with isomer a are observed in the hydride region (see Figure 3b) and only one *tert*-butyl methyl resonance is observed. A trace amount of the hydride resonances of isomer b is seen just above the noise and gradually disappears. The spectrum of this sample remains unchanged for at least 3 weeks. The rate of formation of isomer b is therefore slowed by use of D_2SO_4, and the thermodynamically more stable isomer a is formed in almost its equilibrium concentration.

We then synthesized a deuterated sample of II by neutralization of $[(C_6H_5)_4As]^+[Ru_3(CO)_9(C_6H_9)]^-$[14] with CF_3COOD and then reaction with triphenylphosphine. The ^1H NMR of 65%-deuterated II ($PR_3 = P(C_6H_5)_3$) in H_2SO_4 shows the *tert*-butyl methyl and hydride resonances associated with isomer set b present in greater abundance, with the ratio of a:b as 0.76:1 (Figure 3c). Furthermore, the rate of rearrangement of b to a is shown to be the same for the 65%-deuterated sample (Table II) as for undeuterated $II2H^{2+}$. These experiments constitute evidence for a deuterium isotope effect in the formation of $II2H^{2+}$. We present a mechanism which we feel explains these novel observations.

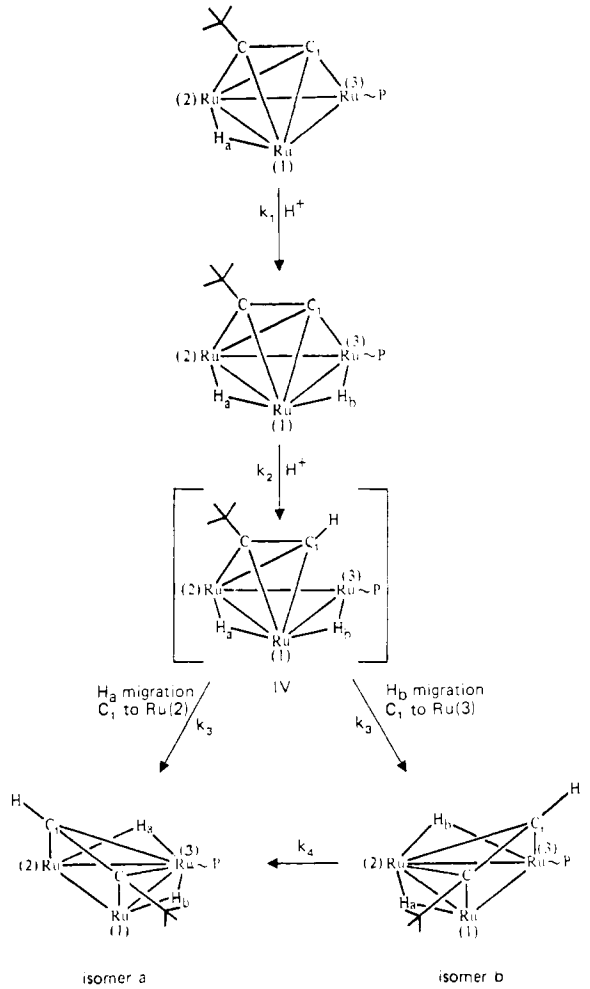
Initial protonation of II occurs on the metal core in H_2SO_4 as well as in acid solutions of CD_2Cl_2 and in neat CF_3COOH (Scheme II). If the second protonation takes place at the carbon atom and is faster than hydride migration, intermediate IV is produced. We propose that rearrangement of organic ligand from a 5e to a 4e ligand requires a twisting motion of the ligand and migration of either H_a or H_b to give isomers

Table II. Ratio of $II2H_a^{2+}$:$II2H_b^{2+}$ with Time

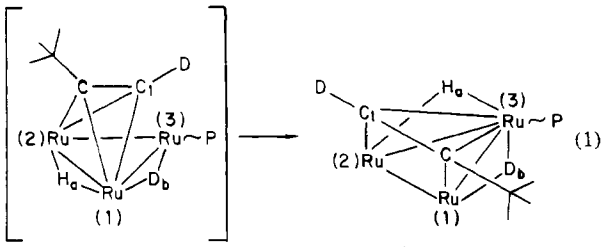
solution	a:b ratio	time[a]
(a) $HRu_3(CO)_8P(C_6H_5)_3(C_6H_9)$ + H_2SO_4	1.5	3 h
	6.0	3 days
	9.0	4 days
	>16.0[b]	6 days
(b) 65% $DRu_3(CO)_8P(C_6H_5)_3(C_6H_9)$ + H_2SO_4	0.76	3 h
	4.6 (9.2)[c]	4 days
	12.0 (24)[c]	7 days

[a] About 3 h was required to dissolve 0.5 mmol of II in 0.6 mL of H_2SO_4 at room temperature. [b] Signal to noise was about 16:1 (see Figure 2). [c] Number in parentheses is corrected for the difference in initial a:b ratio.

Scheme II. Mechanism of Protonation of II

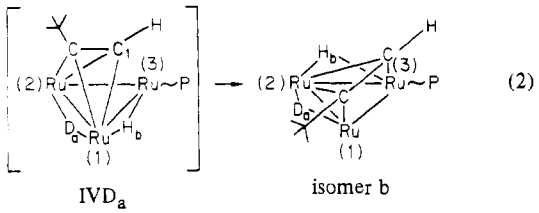


a or b. In D_2SO_4 intermediate IVD_b is formed, from which H_a migration and σ-bond formation to Ru(1) and Ru(2) are favored (eq 1). σ-Bond formation with Ru(2) and Ru(3) with



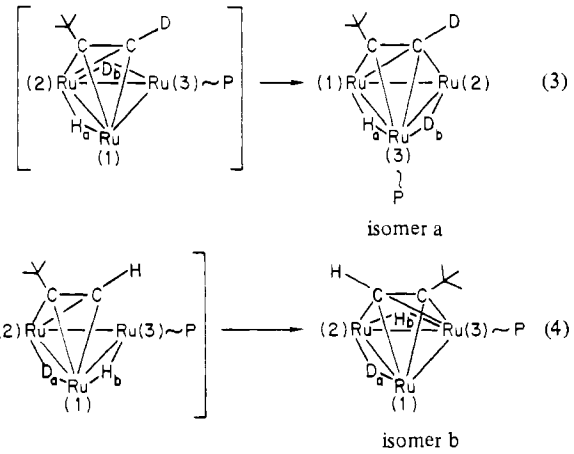
IVD_b isomer a (1)

no H_a or D migration is ruled out since this would yield some isomer b as a kinetic product and this is not observed. The use of 65%-deuterated II gives IVD_a, from which H_b migration and σ-bond formation to Ru(1) and Ru(3) are favored (eq 2).



IVD_a isomer b (2)

These results can also be interpreted in terms of the alternative π^4-μ_3 structures mentioned previously. Here, a twisting motion of the organic ligand must accompany hydride migration to give isomers a and b (eq 3 and 4). Although we



isomer a (3)

isomer b (4)

cannot choose between the two bonding schemes for $II2H^{2+}$, interpretation of the observed deuterium isotope effect requires only that isomers a and b differ in their disposition of the hydride ligand with respect to the phosphine ligand, as they clearly do. An accompanying twisting motion of the organic ligand is also required to give a structure to isomer a which is symmetrical with respect to the phosphine ligand and unsymmetrical with respect to the organic ligand. We cannot rigorously exclude the possibility of intramolecular phosphine ligand migration, but there is no precedent for this process in the literature, while there is precedent for migrations of organic ligands associated with hydride migrations on trimetallic clusters, of the general type proposed here.[9]

It is not possible to extract a number for the deuterium isotope effect from these experiments since we do not know absolute rates of formation of isomer a or isomer b. The observed rate of the rearrangement of isomer b to isomer a does not show a deuterium isotope effect after correction for the initial differences in isomer ratio (see Table II). This is reasonable in that intramolecular hydride exchange does randomize deuterium on the metal core in the formation of isomer a when D_2SO_4 is reacted with II. The deuterium isotope effect is only observed for the more rapid hydride–organic ligand migration. Since we have calculated the rate constant for hydride migration to be 10^3 s^{-1}, the second protonation step must have a rate constant larger than this value. We feel this is not unreasonable in the strong-acid medium H_2SO_4.

These observations point to the existence of deuterium isotope effects in μ-hydrido migrations in general. We are currently investigating simpler nonreactive systems where we can evaluate the μ-hydride deuterium isotope effects more quantitatively. We are also studying the chemistry of isolated $II2H_a^{2+}$.

Experimental Section

Materials. $Ru_3(CO)_{12}$ was synthesized by known literature procedures. Compounds I–III were synthesized by procedures published elsewhere.[10] Solvents and acids were all reagent grade and were dried over molecular sieves before use. Trifluoromethanesulfonic acid was vacuum distilled before use.

Spectra. Proton NMR were run on Varian EM-360 and XL-100 spectrometers. Shifts are reported ±0.05 ppm with respect to CD_2Cl_2 (δ 5.32), sulfuric acid (δ 11.3), or trifluoroacetic acid (δ 11.5) as internal standard. Samples were calibrated for temperature to ±1 °C by using a microthermometer in an NMR tube.

Synthesis of $DRu_3(CO)_8(C_6H_9)P(C_6H_5)_3$. A solution of 636 mg (1 mmol) of I in 40 mL of THF was treated with 14 mL of 0.077 M KOH in absolute ethanol under carbon monoxide atmosphere. A 418-mg (1-mmol) sample of $(C_6H_5)_4AsCl\cdot 2H_2O$ in 2 mL of absolute ethanol was then added, and the solution was filtered and evaporated to dryness. The residue was taken up in absolute ethanol, and 800 mg (80%) of $[As(C_6H_5)_4]^+[Ru_3(CO)_9(C_6H_9)]^-$ crystallized as pale orange crystals at −20 °C. This compound has been fully characterized, and the data are reported in a separate publication.[14] A 2.0-mL amount of CF_3COOD (99% D) was added to 1 g of $[As(C_6H_5)_4]^+[Ru_3(CO)_9(C_6H_9)]^-$. The CF_3COOD was then evaporated and the residue extracted with hot heptane and filtered. The heptane solution yielded 0.8 g of 95% deuterated I by crystallization at −20 °C as determined by ^1H NMR. Deuterated I was then treated with 326 mg of $P(C_6H_5)_3$ in refluxing toluene for 2 h under N_2 atmosphere. The reaction mixture was evaporated to dryness and deuterated II was isolated (silica gel TLC using 8% ether–hexane as eluant) in 55% yield and recrystallized from heptane (−20 °C). The compound was then analyzed by ^1H NMR and found to be 65% (±5%) deuterated. Repeated attempts to improve the percent deuteration by using D_2O-treated silica failed. We suspect that it is during TLC elution that H for D exchange occurs.

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Registry No. I, 57673-31-1; I deuterated, 66973-03-3; IH^+, 76861-93-3; $I2H^{2+}$, 76721-83-0; II (R = C_6H_5), 72582-02-6; II deuterated (R = C_6H_5), 76741-79-2; II (R = OCH_3), 72582-03-7; IIH^+ (R = C_6H_5), 76721-82-9; IIH^+ (R = OCH_3), 76721-81-8; $II2H^{2+}$ isomer a (R = C_6H_5), 76741-78-1; $II2H^{2+}$ isomer b (R = C_6H_5), 76741-77-0; III (R = OCH_3), 72599-26-9; $IIIH^+$ (R = OCH_3), 76741-76-9; $[As(C_6H_5)_4]^+[Ru_3(CO)_9(C_6H_9)]^-$, 76741-75-8; CF_3COOD, 599-00-8; CF_3SO_3H, 1493-13-6; H_2SO_4, 7664-93-9; deuterium, 7782-39-0.

(14) C. Barner-Thorsen, J. Siegel, and E. Rosenberg, to be submitted for publication.