Photoreactivity of ReH$_5$(Cyttp) with CO, CO$_2$ and PMe$_3$

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Photoreactivity of ReH$_5$(Cyttp) (Cyttp=PhP(CH$_2$CH$_2$CH$_2$PCy$_2$)$_2$) with CO, CO$_2$ and PMe$_3$

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The photoreactions of ReH$_5$(Cyttp) (1) (Cyttp=PhP(CH$_2$CH$_2$CH$_2$PCy$_2$)$_2$) with CO, CO$_2$ and PMe$_3$ has been investigated to find the differences in reactivities from those of trismonophosphine analog. Irradiation of 1 under CO, CO$_2$ and excess PMe$_3$ in benzene results in the formation of the complexes, ReH(CO)$_2$(Cyttp) (2), ReH$_2$(η^2-HCO$_2$)(Cyttp) (3) and ReH$_3$(PMe$_3$)(Cyttp) (4), respectively. The resulting products suggest that photoreactions of ReH$_5$(Cyttp) proceed by photoextrusion of H$_2$ giving a phototransient species "ReH$_3$(Cyttp)" which can be trapped by CO, CO$_2$ and PMe$_3$. The structures of 2, 3 and 4 are inferred based on ^{1}H, ^{31}P NMR and I. R. spectroscopy.

Introduction

The irradiation of metal polyhydrides usually results in photoinduced loss of H$_2$ from the complex.[1,2] The resulting unsaturated species can react with various substrates[1a,3-5] and may be active as catalysts in such processes as alkene isomerization and hydrogenation.[5,6] Although the extrusion of H$_2$ from metal polyhydrides is generally the primary photochemical process, irradiation of [ReH$_5$L$_3$] (L=PMe$_2$Ph, PMePh$_2$, PPh$_3$) results in loss of the phosphine instead of H$_2$.[7-10] Thus, photolysis of [ReH$_5$(PMe$_2$Ph)$_3$] yields a new polyhydride dimer, [Re$_2$H$_6$(PMe$_2$Ph)$_5$], by losing coordinated phosphines.[3] In this context, we were interested in comparing the photochemical reactivity of [ReH$_5$L$_3$] with that of rhenium pentahydride complex containing chelating triphosphine ligand, ReH$_5$(Cyttp). Herein we report our results on the photoreactions of 1 with CO, CO$_2$ and excess PMe$_3$ and the characterization for the resulting complexes by spectroscopic method.

Experimental

General Procedures. All reactions and sample manipulations were carried out under an argon atmosphere using either Schlenk techniques or a Vacuum Atmospheres HE43 drybox equipped with Mo-40 catalyst system.[11] Reagent grade solvents were distilled over argon from appropriate drying agents immediately before use.[12] Solutions were transferred by the use of an argon flushed syringe, or stainless steel cannulae. Irradiations were conducted by using a 450-W Ha-

novia medium-pressure Hg lamp through a quartz photolysis vessel (method A) or through a pyrex Schlenk flask with *ca.* 20 cm distance from a light source (method B) under argon or appropriate reagent gas. The irradiation time for each experiment was determined to give an optimum yield of the described product by monitoring the ^{31}P resonances of crude mixtures.

Proton T$_1$ values were measured by the inversion/recovery method at 250 MHz with a 180°-τ-90° pulse sequence and calculated *via* a program provided by the manufacturer. Deuterated solvents were degassed *via* the freeze-thaw method.

Materials. The preparation of compound 1 has been described previously.[13] The tridentatephosphine ligand Cyttp was prepared by use of slightly modified literature procedures.[14] The other chemicals were purchased from commercial sources.

Instrumentation. Infrared spectra were recorded on a Perkin-Elmer Model 283B grating spectrophotometer as Nujol mulls between KBr plates and were calibrated with polystyrene film. NMR specra were collected on solutions in CD$_2$Cl$_2$ or C$_6$D$_6$ with a Bruker AM-250. Residual proton resonances in deuterated solvents were used as internal standards for the ^{1}H-NMR spectra. Phosphorus chemical shifts were referenced to external 85% H$_3$PO$_4$. Elemental analyses were performed by M-H-W Laboratories, Phoenix, AZ. in U. S. A.

Photoreaction of 1 with CO. Irradiation (by method A) of deoxygenated benzene solution (150 m*l*) of 1 (0.30 g, 0.39 mmol) was conducted under a slow, continuous CO purge for 12 h. The reaction mixture was then transferred

to a 250 ml Schlenk flask under argon. Removal of the solvent yielded a white solid which contained ReH(CO)$_2$(Cyttp) and small amounts of uncharacterized product (by ^{31}P-NMR spectroscopy: 1.33(d), −7.24(t) ppm (J_{pp}=32.6 Hz)). The crude material can be easily purified by washing with Et$_2$O to give analytically pure ReH(CO)$_2$(Cyttp). Yield of *cis-mer*-ReH(CO)$_2$(Cyttp) (2) 0.24 g, 75%. Anal. Calcd for C$_{38}$H$_{62}$O$_2$P$_3$ Re: C, 54.99; H, 7.53. Found: C, 54.38; H, 7.67.

Photoreaction of 1 with CO$_2$. Irradiation (by method A) of 150 ml deoxygenated benzene solution of **1** (0.30 g, 0.39 mmol) under a slow, continuous CO$_2$ purge for 3 h gave a color change from colorless to orange. The reaction mixture was transferred to a 250 ml Schlenk flask under argon. Removal of the solvent yielded an orange solid which contains ReH$_2$(HCOO)(Cyttp) and several other uncharacterized products (by ^{31}P{^{1}H} NMR spectroscopy: −19.8(d), −27.9(t) ppm (J_{pp}=16.3 Hz); 15.7(br), −17.5(s) ppm). The crude material can be purified by washing with Et$_2$O to give analytically pure ReH$_2$(HCOO)$_2$(Cyttp). Yield of ReH$_2$(HCOO)(Cyttp) (3) 0.14g, 44%. Anal. Calcd for C$_{37}$H$_{64}$O$_2$P$_3$Re: C, 54.19; H, 7.87. Found: C, 53.89; H, 7.74.

Photoreaction of 1 with PMe$_3$. A solution **1** (0.20 g, 0.26 mmol) and excess PMe$_3$ (0.10 ml, 0.98 mmol) in 150 ml of benzene was irradiated by method A for 10 h to give a yellow solution. The reaction mixture was transferred to a 250 ml Schlenk flask under argon. The volatiles were completely removed under vacuum, and 20 ml of Et$_2$O was added to give a yellow solid. The solid was collected on a filter frit, washed with a small amount of Et$_2$O, and dried under vacuum. The solid is fairly air sensitive. Upon storage (even under argon) for 2-3 days, the impurity was observed (the ^{31}P-NMR spectrum showed many singlets. Thus, the impurity may be due to the oxidation of the chelating ligand) The impurity is easily removed by washing the solid with acetone under argon. Yield of ReH$_3$(PMe$_3$)(Cyttp) (4) 0.18 g, 82%.

Protonation of 4 with HBF$_4$. To a solution of ReH$_3$(PMe$_3$)(Cyttp) (0.10 g, 0.12 mmol) in 25 ml of benzene, exess HBF$_4$·OEt$_2$ (0.010 ml, 0.51 mmol) was added, and the resulting mixture was stirred for 30 min. The solvent was reduced to *ca.* 2 ml, and 30 ml of Et$_2$O was added to give a white
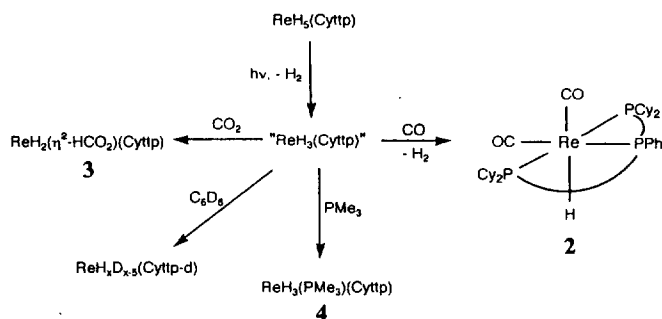
Scheme 1. The photoreactions of ReH$_5$(Cyttp) with CO, CO$_2$, PMe$_3$ and C$_6$D$_6$.

powder. The powder was collected on a filter frit, washed with a small amount of Et$_2$O, and dried under vacuum overnight. Yield of [ReH$_4$(PMe$_3$)(Cyttp)]BF$_4$ (5) 0.090 g, 82%.

Photoreaction of 1 with C$_6$D$_6$. A solution of ReH$_5$ (Cyttp) (0.10 g, 0.13 mmol) in 5 ml of deuterated benzene was irradiated by method B for 1 h to give a light brown solution. The deuterated solvent was completely removed and recovered in a trap in a liquid N$_2$ bath. The solid was collected on a filter frit and dried under vacuum. Yield of ReD$_5$(Cyttp-*d*) (1-*d*) 0.090 g.

Result and Discussion

Although ReH$_5$(Cyttp) (**1**) shows no tendency to lose H$_2$ under thermal conditions (no loss of hydrogen in benzene solution even after 24 h of refluxing), it does tend to lose H$_2$ under photolytic conditions. Thus, irradiation of ReH$_5$(Cyttp) in benzene in the presence of CO, CO$_2$ and excess PMe$_3$ gives the products ReH(CO)$_2$(Cyttp), **2**, ReH$_2$(η^2-HCO$_2$)(Cyttp), **3**, and ReH$_3$(PMe$_3$)(Cyttp), **4**, respectively. The reactions seem to involve the photogenerated reactive 16 e$^−$ "ReH$_3$(Cyttp)". These reactions are summarized in Scheme 1. Selected ^{1}H, ^{31}P{^{1}H} and IR data of compounds **2-4** are listed in Table 1.

The irradiation of ReH$_5$(Cyttp) under CO gives a mixture

Table 1. Selected ^{1}H, ^{31}P-NMR and IR Data for compounds **2-5**

Compound	^{1}H-NMR			^{31}P-NMR			IR(Nujol)
	δ_{ReH}[a]	$J(HP_c)$[b]	$J(HP_w)$	δ_{Pc}[c]	δ_{Pw}	$J(P_cP_w)$	v(ReH)
ReH(CO)$_2$(Cyttp), **e**[e]	−6.08(dt)	33.5	22.9	−20.48(t)	3.42(d)	31.5	1750(m), v(CO)[d]=1840, 1900
ReH$_2$(η^2-HCO$_2$)(Cyttp), **3**[f]	−10.26(dt), δ_{HCO2}=8.66(s)	30.1	13.36	10.44(t)	4.27(d)	17.1	2000(w), 2060(w) v$_{asym}$(HCOO)=1570
ReH$_3$(PMe$_3$)(Cyttp), **4**[e]	−8.13(br), δ_{PMe3}=1.69(d)	— $^2J_{HP}$=6.83	—	δ_P= $\delta_{P'}$=	9.69(s)[g] −52.34(v br)[g]	— —	1815(w, sh), 1840(s), 1855(s), 1870(w, sh)
[ReH$_4$(PMe$_3$)(Cyttp)]BF$_4$, **5**[e]	−5.78(m), −6.57(q) δ_{CH3}=1.85(d)	$^2J_{HP}$=28.9 $^2J_{HPMe3}$=9.0		−4.05(dt) δ_{PMe3}= −43.72(dt)	13.70(t)	16.7 $^2J_{PcPMe3}$=42.1 $^2J_{PwPMe3}$=14.3	1935(w), 1985(w) v(BF$_4$)=1010-1130

[a] ^{1}H chemical shifts are in ppm with respect to Me$_4$Si (δ 0.0). Abbreviations used are : s=singlet or strong, d=doublet, t=triplet, q=quartet, dt=doublet of triplets, br=broad, sh=shoulder, w=weak, m=medium or multiplet in ^{1}H-NMR. [b] Coupling constants are in Hz. P_o, P_w are the central and wing phosphorus atoms in Cyttp ligand. [c] ^{31}P chemical shifts are in ppm with respect to external 85% H$_3$PO$_4$ (δ 0.0). [d] In CH$_2$Cl$_2$. [e] In CD$_2$Cl$_2$. [f] In C$_6$D$_6$. [g] See text.

of products. The major product, **2**, can be obtained in analytically pure form by washing with Et₂O. The ¹H-NMR spectrum of **2** shows a hydride resonance at -6.08 ppm as a doublet of triplets with $^2J_{HPc}=33.5$ and $^2J_{HPw}=22.9$ Hz corresponding to one hydride. These relatively small coupling constants indicate that the hydride is cis to both the central and the wing phosphorus atoms (*e.g.*, $^2J_{HP}=90$-160 Hz for trans couplings found in octahedral complexes[15]). The IR spectrum of **2** exhibits a medium intensity absorption at 1750 cm⁻¹ assignable to Re-H stretching. Strong absorptions at 1840 and 1900 cm⁻¹ in CH₂Cl₂ are observed, indicating the incorporation of CO molecules. The presence of CO ligands and the structure of **2** are confirmed by the ¹³C{¹H} NMR spectrum. The ¹³C{¹H} NMR spectrum reveals two carbon resonances of CO ligands at 201.00 ppm as a doublet of triplets ($^2J_{CPc}=45.02$, $^2J_{CPw}=9.81$ Hz) and 207.22 ppm as a multiplet. The two resonances are assigned to the CO ligand trans and *cis* to the central phosphorus atom, respectively. This is suggested by the observed relatively large carbon-phosphorus coupling and the lower chemical shifts of a doublet of triplets at 201.00 ppm. It is well established that the chemical shift of CO trans to P is at a lower field than that of CO cis to P in an octahedral complex[16]. In the aliphatic region, virtual triplets for the *ipso* carbon atoms of the cyclohexyl groups of the Cyttp ligand are observed at 37.84 and 40.52 ppm with $J_{CP}=14.9$ and 12.1 Hz, respectively. It is known that in the case of chelating triphosphine ligands such as Cyttp and ttp (PhP(CH₂CH₂CH₂PPh₂)₂) the most common configuration is the meridional configuration in octahedral complex.[17] Additionally, the *ipso* carbon of the cyclohexyl group appears as a triplet when Cyttp has a meridional geometry, whereas it gives a doublet of doublets when Cyttp has a facial geometry. Similar trend has been found in other systems.[18] This observation resembles the virtual coupling of methyl resonances of PMePh₂ and PMe₂Ph in the ¹H-NMR spectra in a trans octahedral complex.[15] This suggests that Cyttp is meridional around rhenium. Thus, the structure of **2** is *cis-mer*-ReH(CO)₂(Cyttp) as shown in Scheme 1.

Irradiation of a solution of ReH₅(Cyttp) under CO₂ leads to the formation of an orange solid which corresponds to the formula ReH₂(η²-HCO₂)(Cyttp), **3**, and other uncharacterized products. The CO₂ insertion product **3** can be obtained in pure form by washing the solid with Et₂O. Prolonged reaction times (*e.g.*, 24 h) result in the formation of uncoordinated Cyttp (by ³¹P{¹H} NMR) with low yields of **3**. Since the complex **3** is unstable in CH₂Cl₂, the ¹H and ³¹P{¹H} NMR data were obtained in C₆D₆. The ¹H-NMR spectrum of **3** exhibits a hydride resonance at -10.26 ppm as a doublet of triplets with a relative intensity of two hydrides. The formate proton resonance is observed at 8.66 ppm as a singlet. This value is comparable to those of previously reported formate complexes. For example, the chemical shifts of formate proton in *trans, trans*-W(η¹-HCO₂)(CO)₂(NO)(PPh₃)₂,[19] *trans*-PtH(η¹-HCO₂)(PPh₃)₂,[20] MoH(η¹-HCO₂)(η²-CO₂)(dppe)₂[21] and RuH(η²-HCO₂)(Cyttp)[22] have been observed at 7.08, 9.09, 8.71 and 8.57 ppm, respectively. The formulation of the formate ligand as η²-bound is suggested by an examination of the IR spectrum of complex **3**. Two weak absorptions at 2000 and 2060 cm⁻¹ are assigned to Re-H stretching modes. One strong absorption at 1570 cm⁻¹ is assigned to $v_{asym}(HCO_2)$. The v_{asym}
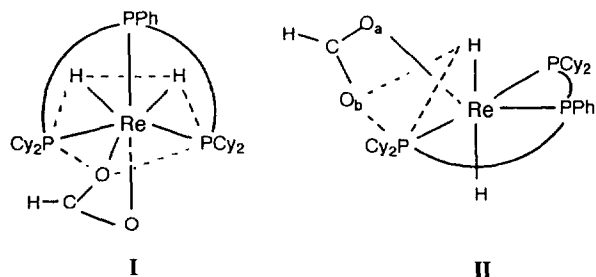

Scheme 2. Possible structures of **3**, based on pentagonal bipyramidal (**I**) and capped octahedral (**II**) structure.

frequency is similar to those reported for known bidentate formate complexes, and would be low for a monodentate complex. For comparison, the complexes Re(η²-HCO₂)(dppe)₂, RuH(η²-HCO₂)(PPh₃)₂[23] and RuH(η²-HCO₂)(Cyttp) exhibit v_{asym} bands at 1554, 1553 and 1575 cm⁻¹, respectively. For the monodentate structures *trans, trans*-W(η¹-HCO₂)(CO)₂, (NO) (PPh₃)₂, *trans*-PtH(η¹-HCO₂)(PPh₃)₂ and MoH(η¹-HCO₂)(η²-CO₂) (dppe)₂, absorptions are seen at 1612, 1620 and 1614 cm⁻¹, respectively. This is also expected from the established effects of coordination mode on the IR spectra of carboxylate complexes.[24] The ³¹P{¹H} NMR spectrum of **3** shows a doublet at 4.27 ppm for the wing phosphorus atoms and a triplet at 10.44 ppm for the central phosphorus atom. This reversed chemical shifts pattern suggests that an oxygen atom is trans to the central phosphorus atom.

Two possible structures based on a pentagonal bipyramdal (**I**) and capped octahedral (**II**) arrangement of ligands can be inferred from I. R., ¹H and ³¹P{¹H} NMR data and are shown in Scheme 2. The equivalence of two hydrides in the rigid solution structure of **3** is also demonstrated by the ¹H-NMR spectrum at 243 K which still contains only hydride resonance with an intensity of two hydrides. Although structure **II** does not seem to have two equivalent hydrides, a fluxional process by which oxygen atom (O_a) moves between positions above and below the equatorial plane would give two equivalent hydrides. Thus, structure **II** cannot be completely ruled out.

Irradiation of a benzene solution of **1** in the presence of excess PMe₃ gives an air-sensitive yellow solid formulated as ReH₃(PMe₃)(Cyttp), **4**. The ¹H-NMR spectrum of **4** at room temperature shows a very broad resonance at -8.13 ppm in the metal-hydride region. The methyl protons of the PMe₃ ligand are also observed at 1.69 ppm as a doublet with $^2J_{HP}=6.8$ Hz. The presence of hydride ligands is also confirmed by IR spectrum which exhibits medium or strong absorption in the range of 1815-1870 cm⁻¹ assignable to $v(ReH)$. The ³¹P{¹H} NMR spectrum of **4** at room temperature contains one singlet at 9.69 ppm and one broad resonance at -52.34 ppm. Since the complex is fluxional, variable-temperature ¹H and ³¹P{¹H} NMR experiments were performed to elucidate the nature of the fluxional process. Results of these experiments suggest that complex **4** exists as an equilibrium mixture of structures **I** and **II** as shown in Scheme 3.

At 283 K the broad hydride resonance in the ¹H-NMR spectrum (Figure 1) begins to decoalesce to give two broad resonances at *ca.* -7.9 and -9.8 ppm. At 263 K, the ¹H-NMR spectrum contains three hydride resonances at *ca.* -7.0, -7.9 and -10.0 ppm. At 223 K, a broad resonance
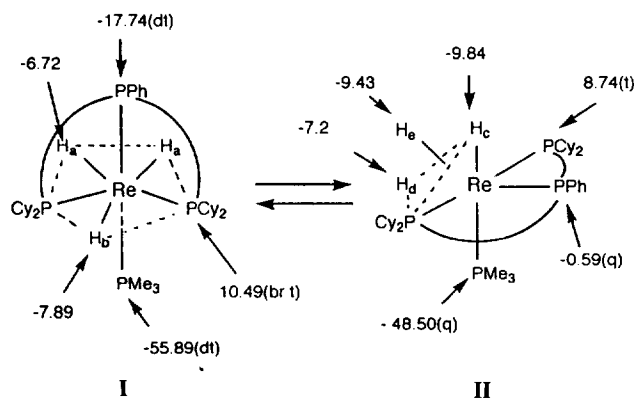
Scheme 3. Possible equilibrium mixtures of **4**. The numbers are chemical shifts of proton and phosphorus atoms in ^{1}H and ^{31}P-NMR.
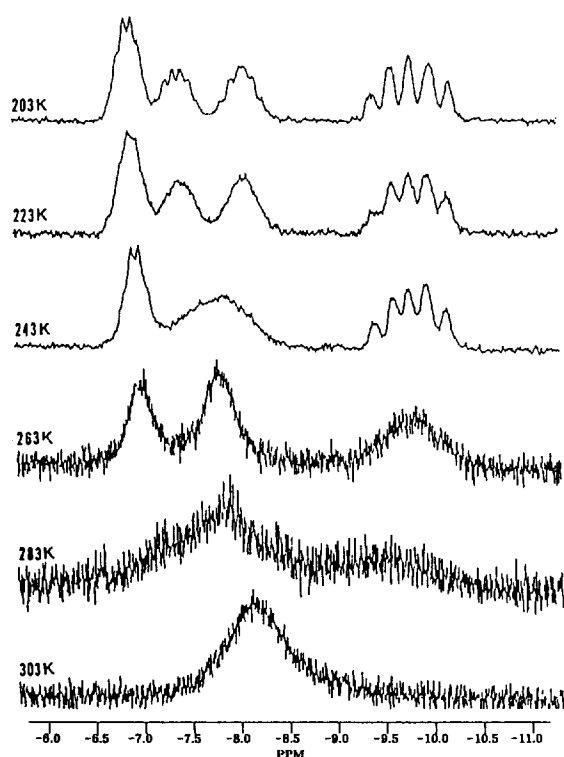

Figure 1. Variable-temperature ^{1}H-NMR spectra of ReH$_3$(PMe$_3$) (Cyttp) in the metal-hydride region in CD$_2$Cl$_2$.

Figure 2. Variable-temperature ^{31}P\{^{1}H\} NMR spectra of ReH$_3$ (PMe$_3$)(Cyttp) in CD$_2$Cl$_2$.

further splits into two hydride resonances. Finally, at 203 K the ^{1}H-NMR reveals four hydride resonance, three multiplets at -6.77, -7.31, -7.86 ppm and a quintet at -9.66 ppm with relative intensities of 2 : 1 : 1 : 2, respectively. Additionally, two different methyl resonance of the PMe$_3$ ligands (for structure **I** and **II**) are observed at 1.73 and 1.85 ppm as doublets with $^2J_{HP}=6.8$ and 4.7 Hz, respectively. This suggests that the spectrum arises from two related trihydride complexes. Similarly, variable temperature ^{31}P-NMR spectra (Figure 2) show two sets of phosphorus resonances. At 283 K, several new resonances begin to appear. At 263 K, six phosphorus resonances are observed. The low temperature limiting spectrum at 203 K can be grouped into two sets: the resonances at 10.49, -17.74 and -55.89 ppm as broad
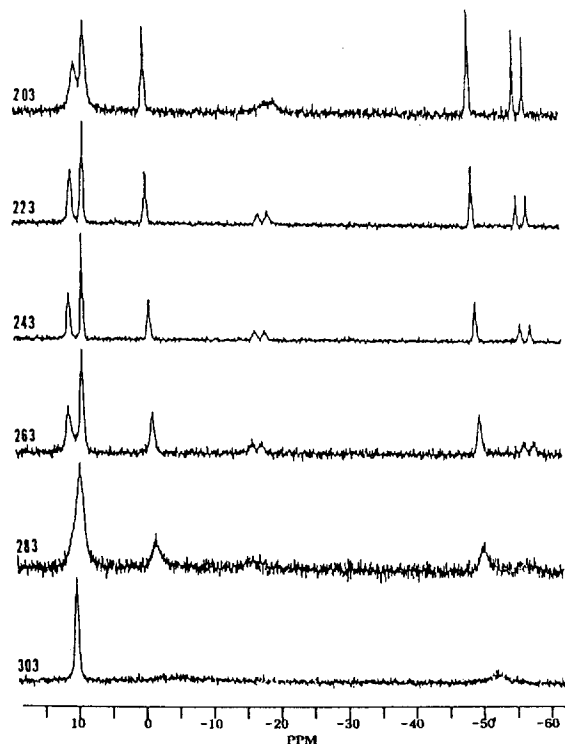
features, a doublet of multiplets (presumably doublet of triplets), and a doublet of triplets, respectively, for structure **I** and the resonances at 8.74, -0.59, -48.50 ppm as a triplet, a quartet and a quartet, respectively, for structure **II**. The resonances at -55.89 and -48.50 ppm are assigned to the phosphorus atoms of the PMe$_3$ ligands in structure **I** and **II**, respectively. The labelling scheme and the chemical shifts of hydride and phosphorus ligands in the ^{1}H and ^{31}P\{^{1}H\} NMR spectra at 203 K are shown in Scheme 3. This is based on a selective ^{31}P decoupling experiment. The selective decoupling of the phosphorus resonance at -55.89 ppm (PMe$_3$ in structure **I**) results in changing the resonance for methyl protons at 1.73 ppm from a doublet to a singlet in the ^{1}H-NMR spectrum. The hydrides resonances are not changed much, as expected from the fact that three hydrides are *cis* to the PMe$_3$ ligand in structure **I**. The resonance at -17.74 ppm is assigned to the central phosphorus atom in structure **I**, since it shows large phosphorus-phosphorus coupling ($^2J_{PcPMe3}=135.4$ Hz), comparable to that of the resonance at -55.89 ppm ($^2J_{PcPMe3}=151.3$ Hz). Thus, two phosphorus atoms occupy axial positions in a pentagonal bipyramidal structure as shown in structure **I**. The broad phosphorus resonance at 10.49 ppm (P_W) is assigned to the two wing phosphorus atoms in structure **I**. This is evidenced by other selective ^{31}P decoupling experiments described below. The selective decoupling of the phosphorus resonance at 8.74 ppm ($P_{W'}$: prime represents structure **II**) results in dramatic changes of the hydride resonances at -7.31 and -9.66 ppm. These two resonances become a doublet and a singlet and a doublet of doublets. Other hydride resonances at -6.77 and -7.86 ppm are also slightly changed. This is caused by an experimental difficulty, since the resonance at 8.74

ppm is very close to that at 10.49 ppm. Thus, the resonance at -9.66 ppm reveals two inequivalent hydrides. The doublet at -9.84 ppm (H_c) is assigned to the hydride trans to the PMe₃ ligand in structure **II**, since selective decoupling of the phosphorus resonance at -0.59 ppm (P_c) changes the resonance at -9.84 ppm (H_c) from a doublet of doublets ($^2J_{HPMe3}=61.0$, $^2J_{HPc}=34.7$ Hz) to a doublet with a large coupling constant ($^2J_{HPMe3}=59.0$ Hz). Alternatively, the doublet at *ca.* -7.2 ppm (H_d) is assigned to the hydride trans to the central phosphorus atom in structure **II**, since this resonance is associated with a relatively large coupling $^2J_{HP}=34.3$ Hz. The remaining singlet at -9.43 ppm (H_e) is assigned to the capping hydride in structure **II**. The hydride resonances at -6.72 and -7.89 ppm are assigned to two equivalent equatoral hydrides (H_a) and one remaining hydride (H_b), respectively. Structure **I** for compound **4** is analogous to the structure of ReH₃(PMePh₂)₄[25] in which hydride ligands were located by X-ray crystallography. The structure also resembles that of ReH₃(dppe)₂[4] in which hydride ligands were not located but it was indicated that the geometry might be that of a pentagonal bipyramid. Interestingly, compound **4** exists as an equilibrium mixture which has never been observed before in rhenium trihydride complexes with phosphine ligands.

This result contrasts with that found in the irradiation of ReH₅(PMe₂Ph)₃ with **6** equivalent of PEt₂Ph which gave all possible species of the form ReH₅(PMe₂Ph)₃₋ₙ(PEt₂Ph)ₙ along with free PMe₂Ph due to the photodissociation of a phosphine ligand.[8] The classical hydride formulation of compound **3** is also confirmed by T_1 measurements of hydride resonances in ¹H-NMR. The T_1 minimum value of 99 ms at *ca.* -6.8 ppm at 238 K would be too high for it to be considered as containing a molecular hydrogen ligand. Compound **4** is easily protonated by HBF₄·OEt₂ to give compound **5**, [ReH₄(PMe₃)(Cyttp)]BF₄. The ¹H-NMR spectrum of **5** exhibits hydride resonances at -5.78 (multiplet) and -6.57 ppm (quartet) with relative intensities of 4 hydrides, respectively. The methyl protons of the PMe₃ ligands in **5** appear as doublets at 1.85 ppm with $^2J_{HP}=9.0$ Hz. The ³¹P{¹H} NMR spectrum of **5** exhibits the phosphorus resonance of PMe₃ at -43.72 ppm as a doublet of triplets with $^2J_{PcPMe3}=42.1$ and $^2J_{PwPMe3}=14.3$ Hz. The P_c and P_w atoms appear as a triplet and a doublet of triplets with $^2J_{PcPw}=16.7$ Hz, respectively. Thus, complexes **5** also adopt a triangulated dodecahedral structure in which the phosphine ligand occupies a position trans to the central phosphorus atom.

The photoreaction of **1** in C₆D₆ results in H/D exchange of the hydrides and phenyl protons of the Cyttp ligand. After 2h of irradiation, *ca.* 87.2, 94.6 and 38.1% deuteration of hydride ligands and ortho and meta hydrogens in Cyttp are observed (by ¹H and ²H-NMR). After 10 h of irradiation, nearly all hydride ligands and phenyl protons in Cyttp are deuterated. The observation implies that H/D exchange occurs by both inter- and intramolecular (orthometallation) pathways.

In summary, although it has been established that photoreactions of the trismonophosphine complex ReH₅(PMe₂Ph)₃ involve dissociation of a phosphine, those of ReH₅(Cyttp) at least formally proceed by photoextrusion of H₂ giving a phototransient species "ReH₃(Cyttp)" which can be trapped

by CO, CO₂ and PMe₃.

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The magnitude of $\rho_X(\rho_{nuc})$ versus the extent of bond formation in S_N2 Reactions

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The secondary deuterium kinetic isotope effects (SDKIE) involving deuterated aniline nucleophiles are reported for the reactions of benzyl bromides and chlorides and benzoyl chlorides in acetonitrile. The benzyl systems behave normally as to the trend of changes in SDKIE with the magnitude of $\rho_X(\rho_{nuc})$, whereas benzoyl system shows an anomaly; $|\rho_X|$ decreases with increase in the extent of bond making estimated by the SDKIE. This has been ascribed to the negative charge accumulation at the reaction center carbon in the transition state. The magnitude of ρ_{XY} is found to decrease by *ca.* 0.03 with ten degree rise in the reaction temperature.

Introduction

Applicability of the magnitude of $\rho_X(\rho_{nuc})$ as a measure of the extent of bond making in the transition state (TS) has an open question.[1] For example, ρ_X can change sign[2] at certain σ_Y, $\hat{\sigma}_Y$ at which $\rho_X = 0$, as both σ_X and σ_Y are varied in an S_N2 type reactions, Scheme 1. It is absurd to interpret this sign change of ρ_X at $\hat{\sigma}_Y$ as a possibility of the negative degree of bond formation; in reality only the charge reversal takes place, as we often encounter with ρ_Y for S_N2 reactions at a benzylic carbon.

The magnitude of $\rho_X(\rho_{nuc})$ in S_N2 reactions is, however, often loosely related to the extent of bond formation in the TS within a series of reactions.[3] For example the magnitude of ρ_X increases in parallel with that of ρ_{XY}, Eq. (1), the cross-interaction constant[4] between

$$\log(k_{XY}/k_{HH}) = \rho_X\sigma_X + \rho_Y\sigma_Y + \rho_{XY}\sigma_X\sigma_Y \qquad (1)$$

substituents (*X*) in the nucleophile and those (*Y*) in the substrate, as the substituent *Y* is varied to a more electron-withdrawing one for reactions of para-Y- substituted 1-[5] and 2-phenylethyl[6] and Y-benzyl[7] arenesulfonates with anilines,
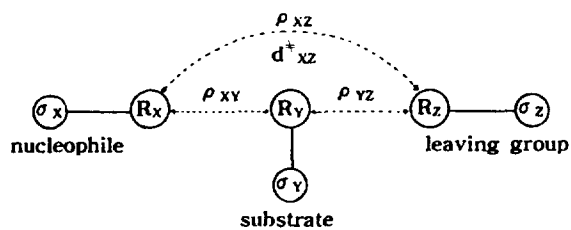
Scheme 1.

$XC_6H_4NH_2$. The magnitude of ρ_{XY} is known to increase with increasing degree of bond formation.[4] The parallel changes in $|\rho_X|$ and $|\rho_{XY}|$ in fact correctly reflect that a greater $|\rho_X|$ corresponds to a tighter TS for a more electron-withdrawing *Y* substituent within the series of reactions.

In this paper, we show that for associative S_N2 reaction series, in which negative charge developes at C_α, in the TS with $\rho_Y > 0$, an inverse proportionality between $|\rho_X|$ and the extent of bond making is obtained, in contrast to a proportionality between $|\rho_X|$ and the extent of bond making in the TS for a dissociative S_N2 reaction series, in which positive charge develops at the reaction center, C_α, in the TS with $\rho_Y < 0$. Hence care should be exercised in the interpretation of the magnitude of ρ_X as a measure of bond formation within a series of S_N2 reactions.

The secondary α-deuterium kinetic isotope effect (SDKIE) involving deuterated aniline nucleophile, $XC_6H_4NH_2(D_2)$, k_H/k_D, has been shown to be useful in determining the relative extent of bond making in the S_N2 TS.[8] As a nucleophile, $XC_6H_4NH_2(D_2)$, attacks the reaction center, C_α, the two N-H (D) vibrations, both bending and stretching modes,[9] are sterically hindered and force constants(and hence vibrational frequencies) increase in the TS.[10] This results in an inverse type of SDKIE, $k_H/k_D < 1/0.$[10] in all normal S_N2-type reactions, and the size of the inverse SDKIE values reflect the degree of steric hindrance and hence the degree of bond formation; the smaller the SDIKE value, the greater is the extent of bond formation.

We have determined the SDKIE values for the reactions of benzyl chlorides and bromides and benzoyl chlorides in acetonitrile at one temperature. In addition, the rates are measured also at other (1-2) temperatures and the temperature effect of various ρ values are discussed.