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Oxidation and Substitution Kinetics of $\text{Re}_2(\text{CO})_8\{\text{P}(\text{C}_6\text{H}_{11})_3\}_2$

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The kinetics of reactions of $ax,ax\text{-Re}_2(\text{CO})_8(\text{PCy}_3)_2$ ($\text{Cy} = \text{C}_6\text{H}_{11}$) with $\text{C}_{16}\text{H}_{33}\text{I}$, $\text{P}(\text{OPh})_3$, and $\text{P}(\text{OEt})_3$ in decalin have been studied. Reaction with $\text{C}_{16}\text{H}_{33}\text{I}$ leads to $cis\text{-Re}(\text{CO})_4(\text{PCy}_3)\text{I}$ by three paths. The major one accounts for ca. 93% of the total reaction rate, and the data are consistent with rate-determining dissociation of PCy_3 . Rate-determining CO dissociation can account for another 5%, but there seems to be an additional, but very minor, path accounting for ca. 2% of the reaction. The values of ΔH^\ddagger and ΔS^\ddagger corresponding to PCy_3 dissociation are close to 30 kcal mol⁻¹ and -3 cal K⁻¹ mol⁻¹, respectively. It is suggested that, as the PCy_3 ligand leaves, the remaining $\text{Re}_2(\text{CO})_8(\text{PCy}_3)$ moiety adjusts its bonding so as to maintain 18-electron configurations for both Re atoms and that this accounts for the low values of both activation parameters. In spite of the bulk of the PCy_3 substituents, a rather high lower limit, $\Delta H^\ddagger \geq 41$ kcal mol⁻¹, is estimated for homolysis of the Re-Re bond.

Introduction

Kinetic evidence and crossover experiments suggest very strongly that the metal-metal-bonded complexes $ax,ax\text{-Mn}_2(\text{CO})_8\text{L}_2$ ($\text{L} = \text{P-}n\text{-Bu}_3$, PPh_3 , $\text{P}(\text{C}_6\text{H}_{11})_3$, etc.) can undergo rate-determining homolysis in substitution and oxidation reactions.¹ For $\text{L} = \text{PPh}_3$, at least, the homolysis process can be induced by some of the oxidizing or substituting reagents as well as occur spontaneously. There is a pronounced decrease in the values of ΔH^\ddagger with increasing Tolman cone angles² of the substituents, and this appears to be due to release of steric strain on formation of transition states that must have considerably lengthened Mn-Mn bonds.^{1,3} On the other hand, neither $\text{Mn}_2(\text{CO})_{10}$ nor $\text{Re}_2(\text{CO})_{10}$ reacts via rate-determining spontaneous homolysis,⁴ and their reaction mechanisms are still under investigation. Even $ax,ax\text{-Re}_2(\text{CO})_8(\text{PPh}_3)_2$, with its relatively large substituents, does not appear to undergo homolysis.^{4b} We have studied some reactions of $ax,ax\text{-Re}_2(\text{CO})_8(\text{PCy}_3)_2$ ($\text{Cy} = \text{C}_6\text{H}_{11}$) in order to see whether the much larger cone angle of PCy_3 is sufficient to bring about rate-determining homolysis, but the results reported below suggest that ligand dissociative mechanisms predominate.

Experimental Section

The ligands PCy_3 (Strem Chemicals, Inc.) and $\text{P}(\text{OPh})_3$ (BDH) were used as received, and $\text{P}(\text{OEt})_3$ (Eastman Kodak) was distilled over sodium. 1-Iodoheptadecane (RI, ICN Pharmaceuticals) was distilled at reduced pressure. Decalin (Aldrich) was dried over molecular sieves and stored under argon. It was shown to be free of detectable tetralin by UV-vis spectroscopic measurements.⁵ $\text{Re}_2(\text{CO})_{10}$ (Strem Chemicals, Inc.) was used as received. Argon was obtained from Canox Ltd., CO from Union Carbide, and analyzed CO-N₂ mixtures from Matheson of Canada, Ltd. Infrared spectra were measured with a Perkin-Elmer 298 spectrophotometer, and UV-vis spectra were measured with a Cary 210 spectrophotometer.

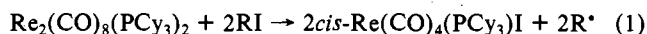
The known complex⁶ $ax,ax\text{-Re}_2(\text{CO})_8(\text{PCy}_3)_2$ was prepared in high yield as follows. $\text{Re}_2(\text{CO})_{10}$ (400 mg, 0.61 mmol) and PCy_3 (1.3 g, 5 mmol) were dissolved in decalin (20 mL), and the solution was degassed by several freeze-pump-thaw cycles in a Schlenk tube sealed with a rubber septum cap. The solution was heated to 185 °C under partial vacuum for 40 min, and a white precipitate was deposited on cooling. This was separated by filtration, washed several times with dry cyclohexane, recrystallized from a dichloromethane-methanol mixture, and dried under vacuum. The product was characterized spectroscopically. It showed a maximum at 299 nm in decalin ($\epsilon 1.84 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$) and CO-stretching bands in decalin at 1976 (sh) cm^{-1} ($\epsilon 3.11 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$) as compared with bands at 295 nm and 1997 w and 1951 s cm^{-1} in acetonitrile.⁶ No CO-stretching bands at higher fre-

quencies, assignable to $\text{Re}_2(\text{CO})_9(\text{PCy}_3)$, were evident.

Kinetic Measurements. Amounts of complex sufficient to provide concentrations generally of ca. $2 \times 10^{-4} \text{ M}$ were dissolved in decalin (10 mL) in Schlenk tubes. After the tubes were sealed with rubber septum caps, the solutions were degassed by several freeze-pump-thaw cycles and the atmosphere above the solutions was established by introduction of the appropriate gas. The reaction tubes were placed in an oil bath and the reacting solutions maintained at a constant temperature (± 0.2 °C) that was measured with an iron-constantan thermocouple connected to a digital multimeter. The other reactants were introduced, either as the pure species or in solution as convenient, by means of syringes fitted with stainless steel needles and the solutions thoroughly shaken. Reacting solutions were well-shielded from laboratory light. Samples were withdrawn by syringe at noted times, cooled in small phials in ice, and stored in the dark and their IR spectra measured when convenient. Slight positive pressures of the gas above the reacting solutions were maintained at all times. Reactions were monitored for ca. 3 half-lives by following the decreasing absorbance of the band at 1952 cm^{-1} , and values of A_∞ were measured after 7-8 half-lives. Excellent linear plots of $\ln(A_t - A_\infty)$ were obtained.

Results and Discussion

Reaction Products. Reaction of the bisaxial complex $\text{Re}_2(\text{CO})_8(\text{PCy}_3)_2$ with 1-iodohexadecane (RI) proceeds smoothly at elevated temperatures to form a product that shows IR bands at 2087 m, 2004 m, 1992 vs, and 1937 s cm^{-1} . The same product is obtained from the very fast reaction of the complex with I_2 . Very similar spectra are also shown by the products of reactions of $\text{Mn}_2(\text{CO})_8(\text{PCy}_3)_2$ with I_2 ⁷ and of $\text{Mn}_2(\text{CO})_8\text{L}_2$ ($\text{L} = \text{PPh}_3$, $\text{P-}n\text{-Bu}_3$, PCy_3) with 1,1,2,2-tetrachloroethane.⁸ These reactions have all been concluded to form $cis\text{-Mn}(\text{CO})_4(\text{L})\text{X}$, and it seems that this type of product is generally formed by reactions of $\text{M}_2(\text{CO})_8\text{L}_2$ with halogens or halocarbons. The initial reaction of $\text{Re}_2(\text{CO})_8\text{L}_2$ with RI can therefore be described stoichiometrically as in eq 1. The alkyl radicals presumably react further



to form $\text{C}_{16}\text{H}_{32}$ and $\text{C}_{16}\text{H}_{34}$. $cis\text{-Re}(\text{CO})_4(\text{PCy}_3)\text{I}$ appears to undergo a further slow reaction to form $(\mu\text{-I})_2\text{Re}_2(\text{CO})_6(\text{PCy}_3)_2$ as evidenced by the appearance of bands at 2016 s, 1925 s, and 1909 m cm^{-1} .

Reaction with $\text{P}(\text{OPh})_3$ proceeds cleanly to form a product with a strong band at 1976 cm^{-1} . This is intermediate between, and well-separated from, the bands at 1952 and 1984 cm^{-1} shown⁶ respectively by $\text{Re}_2(\text{CO})_8(\text{PCy}_3)_2$ and $\text{Re}_2(\text{CO})_8\{\text{P}(\text{OPh})_3\}_2$. It therefore seems reasonable to assign it to the mixed-ligand complex $ax,ax\text{-Re}_2(\text{CO})_8(\text{PCy}_3)\{\text{P}(\text{OPh})_3\}$. Similar intermediate bands have been ascribed to the mixed-ligand complexes $\text{Mn}_2(\text{CO})_8\text{-}(\text{P-}n\text{-Bu}_3)(\text{PPh}_3)$ and $\text{Mn}_2(\text{CO})_8(\text{PPh}_3)(\text{PCy}_3)$, which are formed during crossover experiments with unmixed complexes.^{1,9} Mixed

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Table I. Rate Constants for the Reaction of $\text{Re}_2(\text{CO})_8(\text{PCy}_3)_2^a$ in the Absence of Added PCy_3 in Decalin

$T, ^\circ\text{C}$	$10^4 k_{\text{obsd}}, \text{s}^{-1}$
160.0	15.9, 15.6, 15.5, 16.5
150.0	5.97, 6.25, 6.24, 6.10, 6.06, 5.60
140.2	2.86, 2.36, 2.65
129.8	1.02, 1.01, 1.04
119.3	0.381, 0.398, 0.385
150.0	5.83, ^b 5.77, ^b 5.90, ^c 5.74 ^c

$$\Delta H^\ddagger = 29.9 \pm 0.4 \text{ kcal mol}^{-1}; \Delta S^\ddagger = -3.2 \pm 0.9 \text{ cal K}^{-1} \text{ mol}^{-1}$$

$$\sigma(k_{\text{obsd}})^d = \pm 6.2\%$$

^aUnless indicated otherwise, reaction is with RI where [RI] varies over the range $(5-600) \times 10^{-5}$ M. The initial concentration of the complex is ca. 2×10^{-4} M. ^bReaction with 0.01 M $\text{P}(\text{OEt})_3$. ^cReaction with 0.1 M $\text{P}(\text{OPh})_3$. ^dProbable error for an individual measurements of k_{obsd} .

Table II. Dependence of k_{obsd} on $[\text{PCy}_3]$ and $[\text{RI}]$ for the Reaction of $\text{Re}_2(\text{CO})_8(\text{PCy}_3)_2$ with RI at 150 °C in Decalin

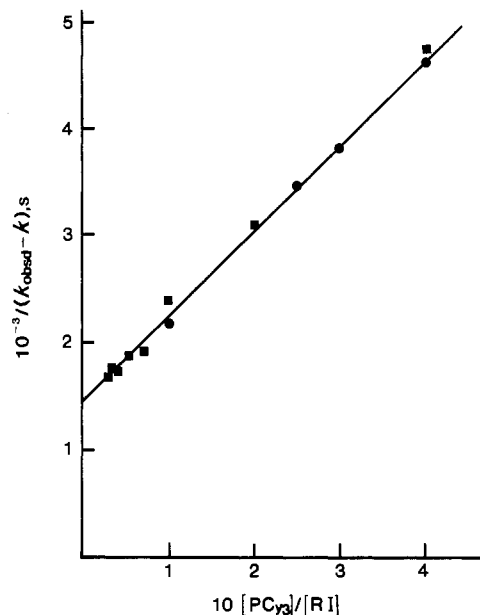
$10^2[\text{RI}], \text{M}$	$10^2[\text{PCy}_3], \text{M}$	$[\text{PCy}_3]/[\text{RI}]$	$10^5 k_{\text{obsd}}, \text{s}^{-1}$	$10^5 k_{\text{calcd}}^a, \text{s}^{-1}$	$100\Delta, \%$
1.00	0.10	0.10	50.4	48.7	3.4
1.00	0.25	0.25	33.3	33.5	-0.7
1.00	0.30	0.30	30.7	30.5	0.5
1.00	0.40	0.40	26.2 ^c	26.1	0.4
1.00	1.00	1.00	15.4	15.7	-1.5
1.00	2.00	2.00	12.5	10.3	21.5
1.00	5.00	5.00	7.78	6.94	12.1
1.00	10.00	10.00	5.19	5.74	-9.6
1.00	20.00	20.00	4.90	5.13	-4.4
1.00	20.00	20.00	4.76	5.13	-7.2
1.00	20.00	20.00	2.02 ^d		
1.00	20.00	20.00	1.97 ^e		
5.00	2.00	0.40	25.5	26.1	-2.3
10.00	2.00	0.20	36.7	37.3	-1.6
20.00	2.00	0.10	46.1	48.7	-5.3
30.00	2.00	0.067	56.3	54.6	+3.2
40.00	2.00	0.050	57.2	58.1	-1.5
50.00	2.00	0.040	61.4	60.5	1.6
60.00	2.00	0.033	61.3	62.2	-1.4
70.00	2.00	0.029	63.9	63.4	0.7

^aValues calculated according to $1/(k_{\text{calcd}} - 4.5 \times 10^{-5}) = 1471 + 7900[\text{PCy}_3]/[\text{RI}]$, where 1471 and 7900 s are the gradient and intercept, respectively, found from the linear least-squares analysis of the data in Figure 1. ^b $\Delta = (k_{\text{obsd}} - k_{\text{calcd}})/k_{\text{calcd}}$. ^cThe average of the following values of $10^5 k_{\text{obsd}} (\text{s}^{-1})$: 26.9 (71.0), 26.0 (40), 25.6 (32.9), 26.4 (26.8), 26.4 (20.0), 26.5 (18.0), 26.9 (12.3), 25.6 (9.51), 24.1 (7.0), 27.1 (5.0). Values in parentheses are $10^2[\text{Re}_2(\text{CO})_8(\text{PCy}_3)_2]$ at the beginning of reaction. ^dUnder 41.5% CO in a CO-N₂ mixture. ^eUnder 100% CO.

complexes are also produced by reaction of $\text{Re}_2(\text{CO})_8(\text{PPh}_3)_2$ with $\text{P}(\text{OPh})_3$ ¹⁰ and $\text{P}(\text{OCH}_2)_3\text{CET}$.^{10,11} Reaction of $\text{Re}_2(\text{CO})_8(\text{PCy}_3)_2$ with $\text{P}(\text{OEt})_3$ leads cleanly to a product with a strong band at 1966 cm^{-1} , and it seems likely that this too corresponds to a mixed-ligand product.

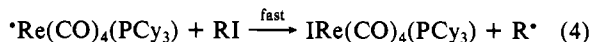
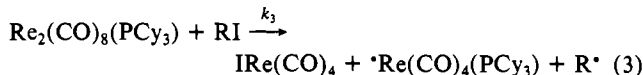
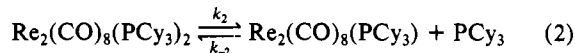
Kinetics. Rate constants for the reactions are given in Tables I and II. In the absence of added PCy_3 , the rate constants for reaction with RI are independent of [RI] over the range $(5-600) \times 10^{-5}$ M. Activation parameters were derived by a least-squares analysis of the dependence of $\ln(k_{\text{obsd}}/T)$ on $1/T$. The uncertainties quoted in Table I are standard deviations, and each measurement of k_{obsd} was assumed¹² to have the same percent probable error.

In the presence of constant $[\text{PCy}_3]$ the values of k_{obsd} increase to a limiting value with increasing [RI]. For constant [RI], k_{obsd} decreases with increasing $[\text{PCy}_3]$ but appears to approach a lower limit of ca. $5 \times 10^{-5} \text{ s}^{-1}$. This lower limit is further reduced to

**Figure 1.** Dependence of $1/(k_{\text{obsd}} - k)$ on $[\text{PCy}_3]/[\text{RI}]$ when $k = 4.5 \times 10^{-5} \text{ s}^{-1}$: (●) $10^2[\text{RI}] = 1 \text{ M}$, $10^3[\text{PCy}_3] = 1-4 \text{ M}$; (■) $10^2[\text{PCy}_3] = 2 \text{ M}$, $10^2[\text{RI}] = 5-70 \text{ M}$.

ca. $2 \times 10^{-5} \text{ s}^{-1}$ for reactions carried out either under pure CO or under 41.5% CO in a CO-N₂ mixture. When $[\text{PCy}_3]/[\text{RI}] = 0.4$, the values of k_{obsd} are less than half the maximum value and are independent of $[\text{Re}_2(\text{CO})_8(\text{PCy}_3)_2]$ over the range $(5-70) \times 10^{-5} \text{ M}$ (see footnote c in Table II).

Mechanisms. The results are consistent with the major path for reaction with RI being the dissociative one shown in eq 2-5.



Although the final fate of the R^* radicals is not known, there is no evidence that they interfere with the kinetics at all, any more than similarly formed alkyl radicals affect the kinetics of photochemically¹³ or thermally^{1,8,9} induced reactions of related complexes. The lack of dependence of k_{obsd} on $[\text{Re}_2(\text{CO})_8(\text{PCy}_3)_2]$ (Table I) supports the dissociative mechanism and rules out initial rate-determining homolysis of the Re-Re bond.¹

This dissociative mechanism cannot account for all the results, however. In particular, a plot of $1/k_{\text{obsd}}$ against $[\text{PCy}_3]/[\text{RI}]$ for reactions at constant [RI] and variable $[\text{PCy}_3]$ should be linear whereas it is not. It is quite curved in a way that shows that there is a contribution to the rate from a path or paths not retarded by free PCy_3 ; i.e., the rates at high $[\text{PCy}_3]$ are faster than expected for the PCy_3 dissociative reaction. If this additional rate corresponds to a rate constant k , then a linear dependence of $1/(k_{\text{obsd}} - k)$ on $[\text{PCy}_3]/[\text{RI}]$ should be obtained as required by eq 6. A

$$k_{\text{obsd}} - k = k_2 k_3 [\text{RI}] / (k_{-2} [\text{PCy}_3] + k_3 [\text{RI}]) \quad (6)$$

value of $k = 4.5 \times 10^{-5} \text{ s}^{-1}$ is needed to provide the best linear plot of $1/(k_{\text{obsd}} - k)$ against $[\text{PCy}_3]/[\text{RI}]$. This was determined by adjusting k until $\sum \Delta^2$ was minimized. ($\Delta = (k_{\text{obsd}} - k_{\text{calcd}})/k_{\text{calcd}}$, and values of k_{calcd} were obtained from a weighted

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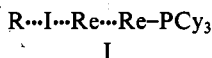
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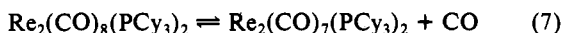
linear least-squares analysis of $1/(k_{\text{obsd}} - k)$ vs. $[\text{PCy}_3]/[\text{RI}]$. Only values of k_{obsd} corresponding to $[\text{PCy}_3]/[\text{RI}] \leq 1$ were used so that $k < 0.3k_{\text{obsd}}$. A plot of $1/(k_{\text{obsd}} - 4.5 \times 10^{-5})$ against $[\text{PCy}_3]/[\text{RI}]$ is shown in Figure 1. Data for higher values of $[\text{PCy}_3]/[\text{RI}]$ (≤ 20) also lie on the straight line, and a value of $\sigma(k_{\text{obsd}}) = 100\{\sum \Delta^2/(N - 3)\}^{1/2} = 6.3\%$ was obtained from all 27 values of k_{obsd} , $\sigma(k_{\text{obsd}})$ being a measure of the probable error for an individual determination of k_{obsd} . Its value is closely compatible with that found from the temperature dependence studies (Table I). If one point with $\Delta = 0.215$ is omitted, the probable error drops to 4.6% and the data are therefore in very good accord with rate equation 6.

The ratio k_3/k_{-2} at 150 °C can be estimated to be 0.19 ± 0.01 from the slope and intercept of the plot in Figure 1 and shows that Re₂(CO)₈(PCy₃) is only a little less susceptible to attack by RI than by PCy₃. Reaction 3 probably does not proceed via a transition state such as I (in which equatorial CO ligands have



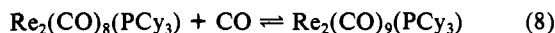
been omitted for clarity). Formation of I would involve concerted breaking of the R-I and Re-Re bonds and formation only of an I-Re bond, and this would be a very high energy process. A more likely alternative is for the reaction to occur via one-electron oxidation. Such processes have been invoked previously,¹⁴ and ligand dissociation often appears to precede attack by halocarbon. One-electron oxidation of saturated 18-electron carbonyls is also known but evidently does not occur here with Re₂(CO)₈(PCy₃)₂.

The rate constant obtained when $[\text{PCy}_3]/[\text{RI}] = 20$ is reduced from 5×10^{-5} to $2 \times 10^{-5} \text{ s}^{-1}$ when reactions are carried out under atmospheres containing $\geq 40\%$ CO. This reduction is presumably caused by the existence of a reversible CO dissociative path, eq 7, that occurs in addition to PCy₃ dissociation. Re₂(CO)₇(PCy₃)₂



is scavenged by a one-electron-oxidation reaction with RI.

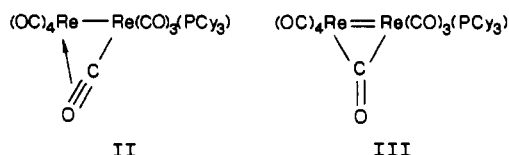
The CO dissociative path can be shown to account for a little over 5% of the total rate of reaction, and there is almost certainly a third but minor path that accounts for slightly less than 2% of the total reaction. Thus, the decrease in the rate constant caused by the presence of CO is $(5-2) \times 10^{-5} \text{ s}^{-1} = (3 \pm 0.3) \times 10^{-5} \text{ s}^{-1}$ (if the probable error of each rate constant is 6%). It amounts to 5% of the maximum rate constant observed ($60 \times 10^{-5} \text{ s}^{-1}$, Table I), but it must, in principle, represent a lower limit for the contribution of the CO dissociative path. This is because the CO could compete (eq 8) with PCy₃ for the Re₂(CO)₈(PCy₃) formed



by PCy₃ dissociation (eq 2). The CO would, therefore, actually cause an *increase* in the observed rate if there were no CO dissociative path, and this effect would partially offset the decrease caused by the reverse of reaction 7. Thus, even when $[\text{PCy}_3]/[\text{RI}]$ is large, some of the rate observed under CO must be due to the PCy₃ dissociative path. However, the effect must be quite small. Since $k_3/k_{-2} = 0.19$, the rate constant for the PCy₃ dissociative path can be estimated to be ca. $0.5 \times 10^{-5} \text{ s}^{-1}$ when $[\text{PCy}_3]/[\text{RI}] = 20$ and this is significantly less than the value of $2 \times 10^{-5} \text{ s}^{-1}$ actually found. The difference of $1.5 \times 10^{-5} \text{ s}^{-1}$ cannot simply be ascribed to the scavenging of Re₂(CO)₈(PCy₃) by CO, as in eq 8, because this would imply that 75% of the product of reaction under CO with $[\text{PCy}_3]/[\text{RI}] = 20$ would be Re₂(CO)₉(PCy₃). In fact, none of this complex was detected, so only a rather small part of the $1.5 \times 10^{-5} \text{ s}^{-1}$ difference can be ascribed to reaction 8 and the proportion of the total reaction occurring via CO dissociation can only be very slightly greater than 5%. It follows

that the $1.5 \times 10^{-5} \text{ s}^{-1}$ difference must mainly correspond to a third, if minor, path that accounts for only a little less than ca. 2% of the total reaction. It is also of interest that the rate constant for reaction via the minor paths when $[\text{PCy}_3]/[\text{RI}] = 20$ is $4.5 \times 10^{-5} \text{ s}^{-1}$, which is exactly the value required in eq 6 to resolve all the data for the PCy₃ dissociative path as in Figure 1. The third path obviously cannot involve CO or PCy₃ dissociation as rate-determining steps, but what is involved is not revealed by the data.

The two minor paths account only for ca. 7% of the maximum value of k_{obsd} at 150 °C so that the activation parameters quoted in Table I must be very close to ΔH_2^\ddagger and ΔS_2^\ddagger . The low value of ΔS^\ddagger is unusual for a simple dissociative mechanism, but negative values have been found when there are good reasons to suppose that the residual complex moiety, generated during ligand dissociation, can synchronously arrange itself as the transition state is approached so as to avoid becoming coordinatively unsaturated.¹⁵ Possible ways for Re₂(CO)₈(PCy₃) to do this are shown in II and III. Either II or III could be subject to quite rapid outer-sphere



electron-transfer reaction with RI. On the other hand, reaction of the P-donor ligands PCy₃, P(OPh)₃, and P(OEt)₃ with II and III would be slower than with a form of Re₂(CO)₈(PCy₃) that contains a vacant coordination site and this could also contribute to the relatively high value of k_3/k_{-2} discussed above. A structure analogous to II has been shown to obtain for Mn₂(CO)₉¹⁶ and has been inferred for Mn₂(CO)₇L₂ (L = various P-donor ligands) from rates of CO addition.¹⁷ Interestingly, the rates of CO addition are quite dependent on the size of L.

The activation parameters ΔH_2^\ddagger and ΔS_2^\ddagger are very different from those for displacement of PPh₃ from Re₂(CO)₈(PPh₃)₂ by CO ($\Delta H^\ddagger = 38.8 \pm 0.5 \text{ kcal mol}^{-1}$; $\Delta S^\ddagger = 21.5 \pm 1.2 \text{ cal K}^{-1} \text{ mol}^{-1}$).¹⁰ These parameters were originally assigned to Re-Re homolysis, but a PPh₃ dissociative mechanism seems more likely.^{4b} The differences can be ascribed to simple nonformation of intermediates analogous to II or III from Re₂(CO)₈(PPh₃)₂. If dissociation of PCy₃ from Re₂(CO)₈(PCy₃)₂ to form unbridged Re₂(CO)₈(PCy₃) has $\Delta S^\ddagger = \text{ca. } +20 \text{ cal K}^{-1} \text{ mol}^{-1}$ (a typical value for such a reaction) then ΔH^\ddagger for that process would have to be $\geq 41 \text{ kcal mol}^{-1}$ for the process not to occur in competition with formation of the bridged intermediate. This implies that the bridging CO stabilizes the intermediate to the extent of $\Delta H^\circ \geq 11 \text{ kcal mol}^{-1}$, which is comparable with the value of $\geq 8 \text{ kcal mol}^{-1}$ inferred in a similar way for an unsaturated Os₃ cluster¹⁸ and does not seem an unreasonable value. In view of the values of ΔS^\ddagger for formation of bridged and unbridged intermediates the enthalpy stabilization due to CO bridging would have to decrease to $\leq 7 \text{ kcal mol}^{-1}$ in the Re₂ carbonyls for the unbridged form to have a lower free energy and so be formed preferentially. The structure of Re₂(CO)₉ is unbridged,¹⁹ as is, we infer, that of Re₂(CO)₈(PPh₃). Steric effects may stabilize the bridging form in Re₂(CO)₈(PCy₃) as they seem to do in Mn₂(CO)₇L₂.¹⁷

The rate constants for reactions with the phosphites would be expected to correspond only to that for the PCy₃ dissociative path since CO dissociation would not lead to the observed products. The rate constants at 150 °C are, indeed, a little less than the

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maximum value for reaction with RI²⁰ although the precision of the difference is rather small.

Finally, the absence of a major path involving rate-determining homolysis shows that any strain due to the very large PCy₃ substituents is not sufficient to induce this process to any extent, although the very minor path might correspond to homolysis.

- (20) The fact that the rate constants for reaction with P donors and with RI are so close shows that reaction with the latter cannot be due to reaction with HI or I₂ formed by decomposition of RI. No decomposition of RI to I₂ is evident at the temperatures used, and such decomposition is known to be very slow.²¹
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Since the homolysis would probably involve a value of ca. +20 kcal K⁻¹ mol⁻¹ for ΔS[‡],^{1,3,8} the value of ΔH[‡] for homolysis must be ≥41 kcal mol⁻¹, which is comparable to the lower limit for Re₂(CO)₁₀.²²

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Metal Ion Promoted Synthesis of a Monothiocarbamate and Kinetics and Mechanism for Its Oxygen- to Sulfur-Bonded Rearrangement

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The residual nucleophilicity of coordinated OH⁻ in (NH₃)₅CoOH²⁺ has been utilized in the synthesis of the oxygen-bonded monothiocarbamate complex (NH₃)₅CoOC(NHCH₃)S²⁺, from its reaction with methyl isothiocyanate in trimethyl phosphate solution. In water the O-bonded linkage isomer isomerizes intramolecularly and completely to the inherently more stable S-bonded form, which has been crystallized and characterized. This O to S isomerization reaction occurs by both spontaneous and base-catalyzed pathways; $k_1(\text{obsd}) = k_{1S} + k_{1OH}[\text{OH}^-]$, where $k_{1S} = (8.8 \pm 0.10) \times 10^{-5} \text{ s}^{-1}$ and $k_{1OH} = (3.7 \pm 0.3) \times 10^{-2} \text{ s}^{-1}$ ($\mu = 0.1 \text{ M}$, NaClO₄; 25 °C). Parallel hydrolysis (30 ± 7%) is observed only for the OH⁻-catalyzed route, and the mechanistic significance of this observation is discussed. A major conclusion is that the spontaneous isomerization process has significant associative character, not generally recognized as characteristic of cobalt(III) substitution processes. The kinetics and course of reaction have also been studied for the slower subsequent reactions of the (NH₃)₅CoS(NHCH₃)O²⁺ isomer. The usual base hydrolysis rate law is observed, $k_2(\text{obsd}) = k_{2S} + k_{2OH}[\text{OH}^-]$, although here k_{2S} is negligible (<10⁻⁷ s⁻¹); $k_{2OH} = (1.12 \pm 0.03) \times 10^{-2} \text{ M}^{-1} \text{ s}^{-1}$; $\mu = 0.1 \text{ M}$, NaClO₄; 25 °C). Only starting material, colloidal (and ultimately precipitated) cobaltic sulfide, and some Co^{II}(aq) are observed at any stage of this reaction. It is argued that either (i) the expected (NH₃)₅CoOH²⁺ coproduct is decomposed rapidly by liberated CH₃NHC(O)S⁻ or, alternatively, (ii) OH⁻ directly attacks the coordinated S-C(O)R group of the (NH₃)₅CoS(NHCH₃)O²⁺ complex, with elimination of (NH₃)₅CoSH²⁺ and CH₃NHCO₂⁻ as the immediate products, and cobaltic sulfide then results from the reaction of the latter complex in OH⁻ solution. Evidence is presented to support the second alternative.

Introduction

The oxygen- and nitrogen-bonded nitrite complexes (NH₃)₅CoONO²⁺ and (NH₃)₅CoNO₂²⁺ remain the classic pair of linkage isomeric complexes in inorganic chemistry.¹ Since their discovery in the late nineteenth century,^{2,3} additional examples have been slow to emerge. In the past decade we have set about synthesizing new pairs of linkage isomers in an attempt to understand the detailed mechanism of rearrangement between the isomers. The reader is referred to the most recent review¹ and to a selection of subsequent publications⁴⁻¹³ for the present status of intramolecular rearrangements of this kind. This article is the

first of several further studies from our laboratories dealing with new examples of rearrangement between (NH₃)₅CoABⁿ⁺ and (NH₃)₅CoBAⁿ⁺ linkage isomers, where the ambidentate ligand AB includes amides NH₂C(O)R, ureas NH₂C(O)NR₂, urethane NH₂C(O)OCH₂CH₃, sulfonamides NH₂S(O)R, sulfamide NH₂S(O)₂NH₂, sulfonamides NH₂S(O)₂R, methanesulfinate CH₃SO₂⁻, chlorosulfate ClSO₃⁻, and the monothiocarbamate CH₃NHC(O)S⁻. Herein we report the synthesis of a pair of *N*-methylmonothiocarbamate complexes with the (NH₃)₅Co^{III} moiety, where the ligand is bound through sulfur or oxygen. The kinetics and product distribution for the spontaneous and base-catalyzed oxygen to sulfur rearrangement are described. We also report on the subsequent and slower base hydrolysis reaction of the S-bonded isomer (NH₃)₅CoSC(NHCH₃)O²⁺.

Discussion

Synthesis. Monothiocarbamates are uncommon (and unstable) species, and the reaction between (NH₃)₅CoOH²⁺ and CH₃NCS in an inert solvent affords a convenient synthesis of a metal ion stabilized derivative, here the *N*-methylmonothiocarbamate ion (the sodium salt of this species, prepared by conventional methods, was known previously¹⁴). The residual nucleophilicity of OH⁻ bound to Co(III) has been demonstrated many times,¹⁵⁻¹⁹ and the

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