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Reactions of Rhenium Cyclopentadienyl and Indenyl Dichloromethane Complexes of the Formula $[(\eta^5\text{-}C_xH_y)Re(NO)(PPh_3)(ClCH_2Cl)]^+BF_4^-$ with Ketones: Substitution Rates and Mechanism

Michael A. Dewey, Yuanlin Zhou, Yumin Liu, and J. A. Gladysz*

Department of Chemistry, University of Utah, Salt Lake City, Utah 84112

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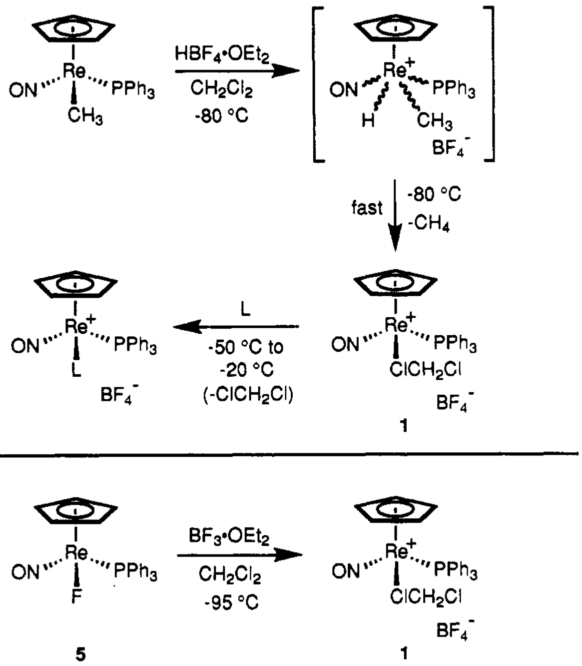
Rates of reaction of the coordinatively saturated cyclopentadienyl and indenyl dichloromethane complexes $[(\eta^5\text{-}C_xH_y)Re(NO)(PPh_3)(ClCH_2Cl)]^+BF_4^-$ (x/y = **1**, 5/5; **2**, 9/7) and cyclohexanone to give $[(\eta^5\text{-}C_xH_y)Re(NO)(PPh_3)(\eta^1\text{-}O{=}\overline{C(CH_2)_4CH_2})]^+BF_4^-$ (x/y = **3**, 5/5; **4**, 9/7) are measured by $^{31}P\{^1H\}$ NMR under pseudo-first-order conditions (CH_2Cl_2, −70 to −30 °C, 10–60-fold excesses of cyclohexanone). These substitutions are first-order in both **1**/**2** and cyclohexanone, even at cyclohexanone concentrations of 1.0–3.4 M. Eyring plots of the second-order rate constants give $\Delta H^\ddagger$ of 15 ± 1 kcal/mol and $\Delta S^\ddagger$ of −5 ± 4–5 eu. There is only a modest kinetic indenyl ligand effect (factor of 6 at −60 to −50 °C). Thus, C_xH_y ring slippage is viewed as unlikely during substitution. Faster reactions of **1** with tropone ($\Delta H^\ddagger$ 12 ± 2 kcal/mol, $\Delta S^\ddagger$ −17 ± 11 eu) and methyl ethyl sulfide give similar rate data. These results and competition experiments with ethyl chloride exclude pathways involving initial dichloromethane dissociation. An associative mechanism that features a square pyramidal intermediate with a bent nitrosyl ligand is considered. Testable aspects of this model and stereochemical implications are discussed.

As introduced in the preceding paper, we have conducted an extensive study of the chemistry of the chiral, coordinatively saturated, substitution-labile dichloromethane complex $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(ClCH_2Cl)]^+BF_4^-$ (**1**).[1,2] Complex **1** is easily generated from the methyl complex $(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(CH_3)$, as shown in the upper portion of Scheme I. Both **1** and the companion chlorobenzene complex[3] react with neutral donor ligands (L) such as nitriles,[2,3] aldehydes,[4] ketones,[5] esters,[6] ethers,[7] alcohols,[8] alkenes,[9] allenes,[10] alkynes,[11] sulfides,[12] sulfoxides,[12] and alkyl halides[13] to give the corresponding Lewis base adducts $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(L)]^+BF_4^-$ in high yields. When **1** is generated from enantiomerically pure methyl complex, these adducts form with high enantiomeric purities and overall retention of configuration at rhenium. Thus, **1** has considerable configurational sta-

Scheme I. Syntheses of the Chiral Rhenium Dichloromethane Complex 1



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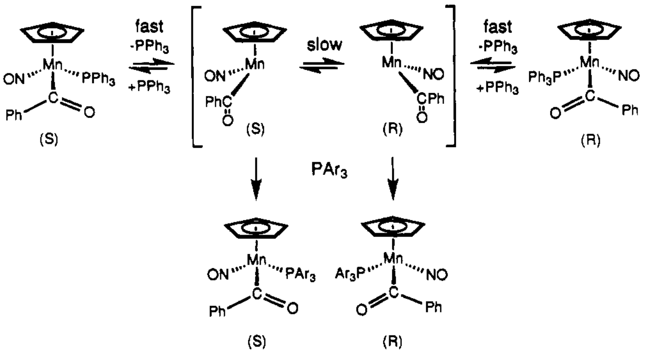
Scheme II. Dissociative Substitution with Retention of Configuration at Manganese



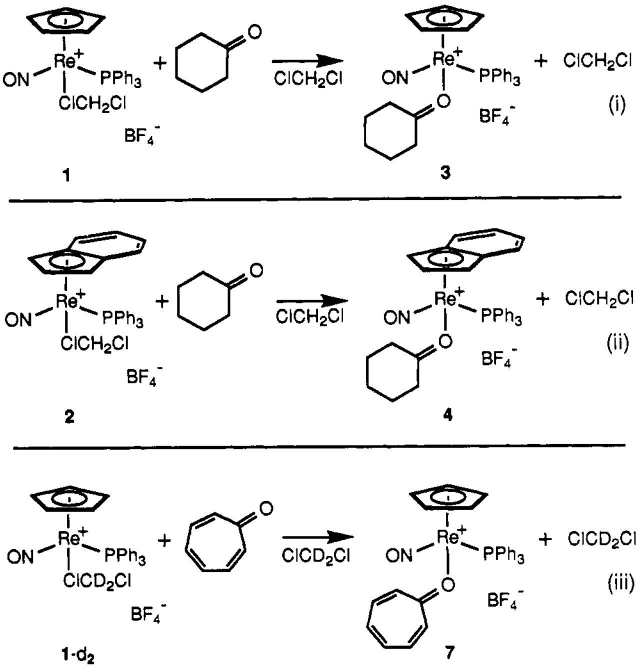
bility and constitutes a functional equivalent of the chiral Lewis acid $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)]^+$ (**I**).

Complex 1 decomposes at a significant rate above −20 °C, and isolation attempts have been unsuccessful to date. The initial decomposition step appears to involve carbon–chlorine bond cleavage, and the cationic bridging chloride complex $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)]_2Cl^+BF_4^-$ ultimately forms.[2] Importantly, enantiomerically pure 1 converts to a bridging chloride complex of high enantiomeric purity.[2] Thus, it is not possible to measure a racemization rate—a situation encountered whenever an enantiomerically pure compound transforms to another enantiomerically pure compound more rapidly than it loses configuration.

All steps in the upper portion of Scheme I engender a number of mechanistic questions. We have initially focused our attention on the substitution of the dichloromethane ligand in 1. In a seminal series of papers, Brunner established that the chiral, coordinatively saturated cyclopentadienyl manganese complexes $(\eta^5\text{-}C_5H_5)Mn(NO)(PPh_3)(COR)$ underwent PPh_3 ligand substitution by dissociative mechanisms involving intermediates of the composition $(\eta^5\text{-}C_5H_5)Mn(NO)(COR)$.[14,15] Further, under appropriate conditions configurations were retained at manganese. These data were interpreted as illustrated in Scheme II. Hückel MO calculations by P. Hofmann showed that d^6 16-valence-electron transition metal fragments of the formula $(\eta^5\text{-}C_5H_5)MLL'$ should have pyramidal, and hence chiral, ground states.[16,17] Thus, we expected the corresponding rhenium species $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)]^+$ (I) to have appreciable configurational stability and originally anticipated that 1 would undergo dissociative substitution.

To our surprise, preliminary rate data acquired with acetonitrile[2] and tropone[18] some time ago suggested that 1 undergoes substitution predominantly by *associative* mechanisms. Thus, in order to further probe the reaction coordinate, analogous indenyl complexes were sought. Substitution reactions of indenyl complexes have been extensively studied and often show greatly enhanced rates, or "kinetic indenyl ligand effects".[19] In these cases, η^5 to η^3 linkage isomerization ("slippage")[20] is implicated prior

Scheme III. Principal Substitution Reactions Selected for Rate Studies



to or during the rate determinating step. With the availability of the indenyl dichloromethane complex $[(\eta^5\text{-}C_9H_7)Re(NO)(PPh_3)(ClCH_2Cl)]^+BF_4^-$ (**2**) and related compounds described in the preceding paper,[1] we undertook a detailed study of the rates of the reactions shown in Scheme III. The results, and selected data for other substitutions, are described in the narrative below.

Results

1. Reactions of 1 and 2 with Cyclohexanone. Reactions of dichloromethane complex 1, and the corresponding deuteriodichloromethane complex 1-d_2, with excess cyclohexanone have been previously monitored by $^{31}P\{^1H\}$ and ^1H NMR between −40 and −15 °C.[5b] The σ-cyclohexanone complex $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(\eta^1\text{-}O{=}\overline{C(CH_2)_4C}H_2)]^+BF_4^-$ (**3**) formed in 93% yield (Scheme III, eq i). Similarly, reaction of the indenyl dichloromethane complex 2 with cyclohexanone gave $[(\eta^5\text{-}C_9H_7)Re(NO)(PPh_3)(\eta^1\text{-}O{=}\overline{C(CH_2)_4C}H_2)]^+BF_4^-$ (**4**) in quantitative yield by $^{31}P\{^1H\}$ NMR, as described in the preceding paper (Scheme III, eq ii).[1]

Complex 1 was first generated by the standard method shown in the top portion of Scheme I. Rates of reaction with cyclohexanone were monitored by $^{31}P\{^1H\}$ NMR under pseudo-first-order conditions involving 10–40-fold excesses of cyclohexanone. Data were acquired at five temperatures between −60.5 and −29.6 °C, as summarized in Table I. In all cases, the disappearance of 1 was followed. Reactions were first-order in 1, as illustrated by the representative plot in Figure 1. Additional details are given in the Experimental Section.

At each temperature, rates were measured at several cyclohexanone concentrations. As shown in Figure 2, the observed rate constants (k_{obs}) were proportional to the cyclohexanone concentrations. Thus, the reactions were also first-order in cyclohexanone, or second-order overall.

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Table I. Summary of Rate Data for the Reaction of $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(ClCH_2Cl)]^+BF_4^-$ (1) and Cyclohexanone (L)

run	T (°C)	[1] (M)	[L] (M)	[L]/[1]	no. of half-lives	10^4k_{obs} (s^{-1})	10^4k_1 ($s^{-1}\cdot M^{-1}$)
1	−29.6	0.0339	0.665	19.6	2.0	24.5	37.6
2	−29.6	0.0336	0.822	24.5	2.6	35.1	43.4
3	−29.6	0.0456	0.911	20.0	2.2	36.0	39.5
4	−29.6	0.0541	1.08	20.0	2.3	46.2	42.8
5	−35.3	0.0337	0.337	10.0	1.0	7.25	23.0
6	−35.3	0.0346	0.519	15.0	1.7	10.7	21.2
7	−35.3	0.0352	0.703	20.0	2.3	14.6	21.3
8	−35.3	0.0439	0.877	20.0	2.0	18.7	22.0
9	−41.4	0.0343	0.346	10.1	3.3	2.66	8.05
10[a]	−41.4	0.0313	0.663	21.2	1.9	4.48	6.88
11	−41.4	0.0395	0.739	18.7	3.2	6.39	8.86
12	−41.4	0.0447	0.894	20.0	3.5	8.04	9.20
13[a]	−41.4	0.0324	1.14	35.2	2.2	8.05	7.14
14	−41.4	0.0599	1.20	20.0	1.3	9.14	7.73
15	−41.4	0.0599	1.24	20.7	2.3	9.95	8.18
16	−41.4	0.0641	1.28	20.0	2.6	9.55	7.62
17	−41.4	0.0758	1.51	20.0	2.5	11.2	7.57
18	−50.0	0.0496	0.993	20.0	1.1	2.13	2.17
19	−50.0	0.0655	1.31	20.0	1.9	3.04	2.36
20	−50.0	0.0813	1.63	20.0	2.9	3.12	1.96
21	−60.5	0.0864	2.41	27.9	1.6	0.953	0.400
22	−60.5	0.0965	2.90	30.0	1.8	1.06	0.370
23	−60.5	0.0850	3.39	39.9	2.0	1.16	0.345

[a] In these experiments, 1 was generated as illustrated in the bottom portion of Scheme I.

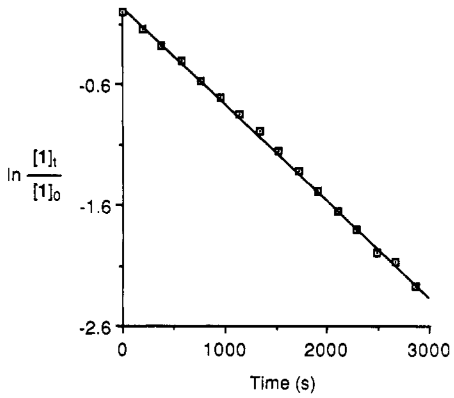

Figure 1. Representative plot of the data for the conversion of 1 to 3 (run 12 of Table I).

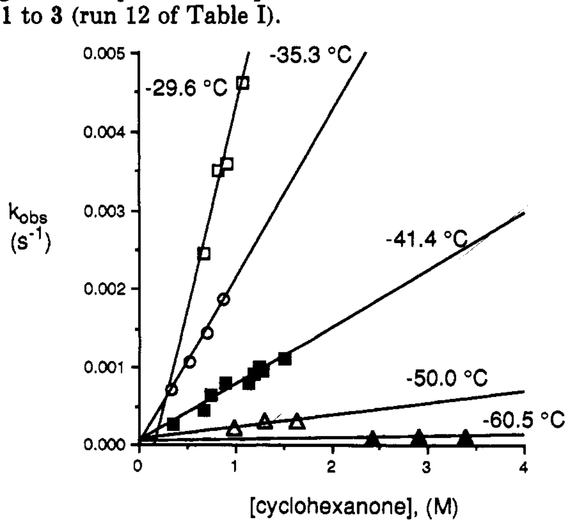

Figure 2. Dependence of k_{obs} on cyclohexanone concentration for the conversion of 1 to 3. Data: Table I.

The second-order rate constants for each run, k_1, were calculated by dividing k_{obs} by the *average* cyclohexanone concentration (start and completion of run).[21] The k_1 values at each temperature were averaged, as summarized in Table II. An Eyring plot of these data (Figure 3) gave the activation parameters listed in Table II.

Table II. Second-Order Rate Constants and Activation Parameters for Substitution Reactions of Dichloromethane Complexes 1 and 2[a]

compd	ligand	T (°C)	10^4k_1 ($s^{-1}\cdot M^{-1}$)	activation param
1	cyclohexanone	−29.6	40.8 ± 1.6	$\Delta H^{\ddagger} = 15 \pm 1$
1	cyclohexanone	−35.3	21.9 ± 0.49	$\Delta S^{\ddagger} = -5 \pm 4$
1	cyclohexanone	−41.4	7.91 ± 0.27	
1	cyclohexanone	−50.0	2.16 ± 0.15	
1	cyclohexanone	−60.5	0.365 ± 0.016	
2	cyclohexanone	−39.6	62.7 ± 7.4	$\Delta H^{\ddagger} = 15 \pm 1$
2	cyclohexanone	−45.1	24.0 ± 1.8	$\Delta S^{\ddagger} = -5 \pm 5$
2	cyclohexanone	−50.2	12.9 ± 0.45	
2	cyclohexanone	−54.8	6.14 ± 0.55	
2	cyclohexanone	−60.1	2.23 ± 0.21	
2	cyclohexanone	−70.1	0.454 ± 0.054	
1-d_2	tropone	−53.8	32.9 ± 3.4	$\Delta H^{\ddagger} = 12 \pm 2$
1-d_2	tropone	−59.2	12.4 ± 0.27	$\Delta S^{\ddagger} = -17 \pm 11$
1-d_2	tropone	−64.5	7.83 ± 0.33	
1-d_2	tropone	−69.9	3.77 ± 0.47	
1-d_2	tropone	−75.2	1.46 ± 0.16	
1	methyl ethyl sulfide	−80.2	3.10 ± 0.15	

[a] Error limits given for k_1 values and activation parameters represent 68% and 95% confidence limits, respectively; see Experimental Section.

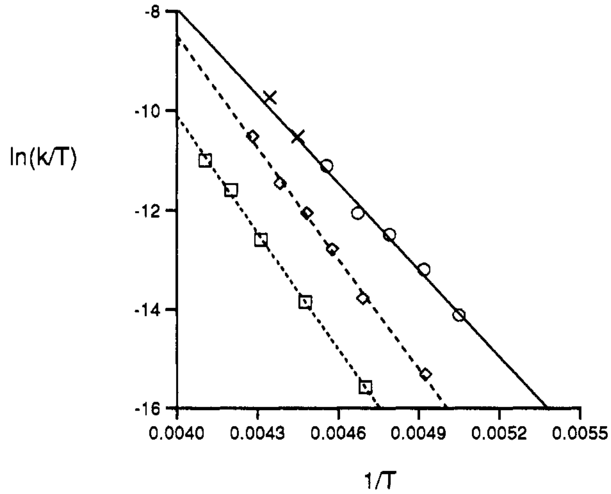

Figure 3. Eyring plots for the conversion of 1 to 3 (□) over the temperature range −29.6 to −60.5 °C, the conversion of 2 to 4 (◇) over the temperature range −39.6 to −70.1 °C, and the conversion of 1-d_2 to 7 (○) over the temperature range −53.8 to −75.2 °C. The additional points (×) were not utilized in calculating the activation parameters in Table II and are explained in footnote 26. Data: Table II.

We sought to test whether the rates of reaction of 1 might be recipe-dependent. Importantly, minor byproducts are evident by NMR when 1 is generated as in the top portion of Scheme I.[2,22] Thus, 1 was also prepared by the reaction of fluoride complex $(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(F)$ (5) and $BF_3\cdot OEt_2$,[23] as illustrated in the bottom portion of Scheme I. This yields 1 that is pure by the most rigorous

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(22) (a) Although the quantities are too small for conclusive identification, a cationic *trans* methyl hydride complex would be one plausible byproduct (see Scheme I; *cis* isomers should eliminate methane at faster rates).[2] Upon additions of Lewis bases, these species also convert to adducts $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(L)]^+BF_4^-$. For this reason, the disappearances of 1 or 2 were monitored as opposed to the appearances of 3 or 4. (b) The concentrations of 1 and 2 in Tables I and III–V assume complete conversion of the precursors $(\eta^5\text{-}C_xH_y)Re(NO)(PPh_3)(CH_3)$. However, any systematic or random errors do not affect the k_1 values.

Table III. Summary of Rate Data for the Reaction of $[(\eta^5\text{-}C_9H_7)Re(NO)(PPh_3)(ClCH_2Cl)]^+BF_4^-$ (2) and Cyclohexanone (L)

run	T (°C)	[2] (M)	[L] (M)	[L]/[2]	no. of half-lives	10^4k_{obs} (s^{-1})	10^4k_1 ($s^{-1}\cdot M^{-1}$)
1	−39.6	0.0314	0.315	10.0	3.0	21.8	72.4
2	−39.6	0.0319	0.417	13.1	2.8	25.4	63.0
3	−39.6	0.0516	0.525	10.2	2.5	26.6	52.8
4	−45.1	0.0333	0.330	9.91	2.9	9.32	29.5
5	−45.1	0.0330	0.550	16.7	2.9	14.9	27.8
6	−45.1	0.0339	0.771	22.7	3.2	18.0	23.8
7	−45.1	0.0333	0.991	29.8	2.9	20.1	20.6
8	−45.1	0.0336	1.21	36.0	2.5	27.3	22.8
9	−45.1	0.0333	1.87	56.2	2.3	35.9	19.3
10	−50.2	0.0333	0.314	9.43	2.0	4.23	14.0
11	−50.2	0.0315	0.524	16.6	2.6	5.48	10.7
12	−50.2	0.0323	0.734	22.7	1.9	9.04	12.5
13	−50.2	0.0318	0.944	29.7	2.3	11.8	12.7
14	−50.2	0.0320	1.15	35.9	2.3	14.7	12.9
15	−50.2	0.0318	1.57	49.4	3.0	21.2	13.6
16	−50.2	0.0312	1.84	59.0	2.7	24.8	13.6
17	−54.8	0.0326	0.754	23.1	1.4	4.06	5.46
18	−54.8	0.0331	0.964	29.1	2.7	5.75	6.05
19	−54.8	0.0332	1.19	35.8	2.0	8.12	6.90
20	−60.1	0.0324	0.530	16.4	1.9	1.31	2.53
21	−60.1	0.0318	0.955	30.0	2.2	1.86	1.97
22	−60.1	0.0327	1.56	47.8	2.1	3.39	2.19
23	−70.1	0.0318	1.60	50.3	1.6	0.593	0.373
24	−70.1	0.0331	1.88	56.7	1.6	0.898	0.480
25	−70.1	0.0328	2.05	62.4	1.9	1.04	0.510

$^{31}P\{^1H\}$ and ^1H NMR criteria. Rates of reaction with cyclohexanone were measured, as summarized in runs 10 and 13 in Table I. The k_1 values obtained were close to those that would be predicted on the basis of the other runs (see second and fifth data points at −41.4 °C in Figure 2).

Analogous rate data were acquired for the reaction of indenyl complex 2 with cyclohexanone between −70.1 and −39.6 °C, as summarized in Table III. The k_{obs} values were again proportional to cyclohexanone concentrations, as shown in Figure 4. The average k_1 values at each temperature are summarized in Table II, and an Eyring plot is given in Figure 3. The resulting activation parameters are listed in Table II. Interestingly, the k_1 values at −50 and −60 °C are only 6.0–6.1 times greater than those for the reaction of 1 and cyclohexanone.[24] Hence, there is only a modest kinetic indenyl ligand effect.

2. Reactions of 1 with Ethyl Chloride. Importantly, the preceding data remain consistent with dissociative mechanisms under certain boundary conditions. As derived below, any intermediate would have to be scavenged more rapidly by the dichloromethane solvent than cyclohexanone. This hypothetical partitioning would be a function of relative (1) concentrations and (2) rate constants or nucleophilicities. Thus, additional substitution reactions were studied that would bear upon this issue.

We were unable to design a direct probe of the relative nucleophilicities of dichloromethane and cyclohexanone. Therefore, ethyl chloride was chosen as a ligand that should give an upper bound for the nucleophilicity of dichloromethane.[25] Thus, 1 was generated from the methyl

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(24) A reviewer has questioned whether the 6-fold increase in k_1 values is consistent with the virtually identical activation parameters for the reactions of 1 and 2 with cyclohexanone (Table II). First, if the $\Delta H^\ddagger$ values are identical, then a $\Delta\Delta S^\ddagger$ of 3.6 eu will give a 6-fold rate difference at −60 °C. Alternatively, if the $\Delta S^\ddagger$ values are identical, then a $\Delta\Delta H^\ddagger$ of 0.76 kcal/mol will give a 6-fold rate difference at −60 °C. In actuality, the $\Delta H^\ddagger$ values for 1 and 2 are 15.4 and 14.7 kcal/mol prior to significant digit roundoff.

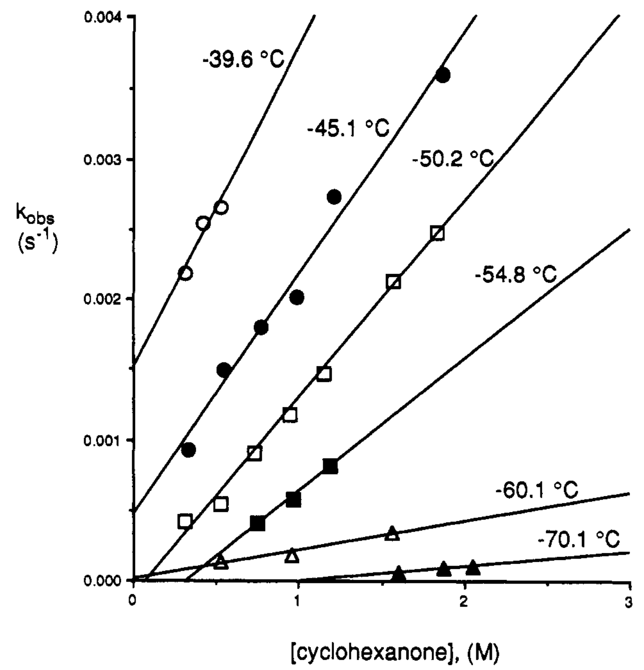


Figure 4. Dependence of k_{obs} on cyclohexanone concentration for the conversion of 2 to 4. Data: Table III.

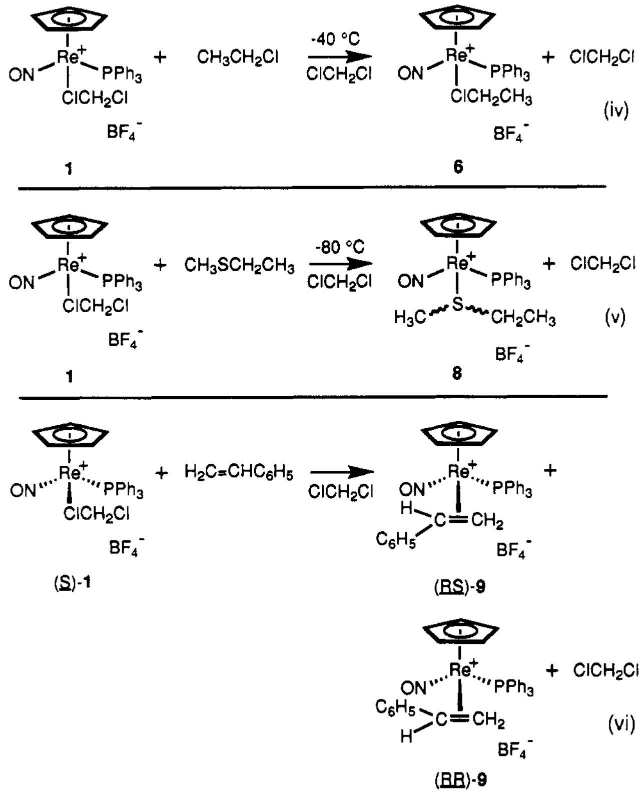
complex $(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(CH_3)$ (0.0183 mmol) in 0.300 mL (4.68 mmol) of dichloromethane at −80 °C. Then ethyl chloride was added (0.331 mL, 4.58 mmol). The sample was warmed to −40 °C. After 15 min, ca. 30% conversion to the previously reported ethyl chloride complex $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(ClCH_2CH_3)]^+BF_4^-$ (6)[13a] had occurred, as assayed by $^{31}P\{^1H\}$ NMR (13.5 ppm). When the sample was warmed to −20 °C, conversion to 6 was complete (Scheme IV, eq iv).

As little as 1% of unreacted 1 would have been detected in the preceding experiment. Since essentially equimolar amounts of dichloromethane and ethyl chloride were present, ethyl chloride must be at least 100 times more basic than dichloromethane toward the rhenium fragment I. Although notable exceptions exist, closely related compounds commonly give parallel nucleophilicity and basicity orders. Hence, this further supports our proposal[25] that ethyl chloride should be a stronger nucleophile than dichloromethane.

Competition experiments involving ethyl chloride and cyclohexanone were conducted next. Complex 1 was generated from $(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(CH_3)$ (0.0183 mmol) in 0.200 mL of dichloromethane at −80 °C. Then a mixture of cyclohexanone (0.019 mL, 0.183 mmol, 10 equiv) and ethyl chloride (0.331 mL, 4.58 mmol, 250 equiv) was added. The sample was warmed to −50 °C, but $^{31}P\{^1H\}$ NMR spectra showed only a very slow reaction. The sample was then kept at −40 °C for 20 min. A $^{31}P\{^1H\}$ NMR spectrum showed a 56:29:15 (or 66:34:18) ratio of ethyl chloride complex 6, cyclohexanone complex 3, and unreacted 1. After an additional 20 min, only 6 and 3 were present (65:35). As the sample was warmed above −30 °C, 6 gradually converted to 3. At −10 °C, only 3 remained (>99% conversion).

(25) (a) Electronically, the second "spectator" chlorine should diminish the nucleophilicity and basicity of dichloromethane relative to that of ethyl chloride. (b) However, dichloromethane contains two reactive sites and is slightly smaller on the basis of atomic van der Waals radii. In some circumstances, it is important to statistically correct for the former. However, the analysis presented in the Discussion relies only upon the magnitude of the phenomenological rate constants, k_{-1} and k_2.

Scheme IV. Other Substitution Reactions Studied



The preceding experiment establishes that the kinetic ratio of substitution products **6** and **3** at −40 °C is (66–65):(34–35). When this is corrected for the ethyl chloride/cyclohexanone mole ratio (250:10), a relative nucleophilicity of 1:13 is obtained. Also, as little as 1% of **6** would have been detected at −10 °C. Therefore, the relative basicities of ethyl chloride and cyclohexanone toward **I** must be 1:≥1000.

3. Reactions of 1 with Other Ligands. In order to strengthen the analyses presented below, rate data for more nucleophilic ligands were desired. Reactions of **1** or **1**-d_2 with tropone have been shown to give the σ complex [(η^5-C_5H_5)Re(NO)(PPh_3)(η^1-O=CCH=CHCH=CH-CH=CH)]$^+BF_4^-$ (**7**) in quantitative spectroscopic yields, as illustrated in Scheme III, eq iii.[5b] Thus, rates of disappearance of **1**-d_2 were measured by ^{1}H NMR between −53.8 and −75.2 °C under pseudo-first-order conditions, as summarized in Table IV.[26] Figure 5 shows that the k_{obs} values were proportional to tropone concentration at each temperature. Table II lists the average values for the second-order rate constants, k_1, at each temperature, and the resulting activation parameters.[26b,c]

The k_1 value at −59.2 °C was 34 times greater than that for the reaction of **1** and cyclohexanone at −60.5 °C. Rate accelerations extrapolated from Eyring plots ranged from 15 (−40.0 °C) to 33 (−59.2 °C). Unfortunately, **2** and

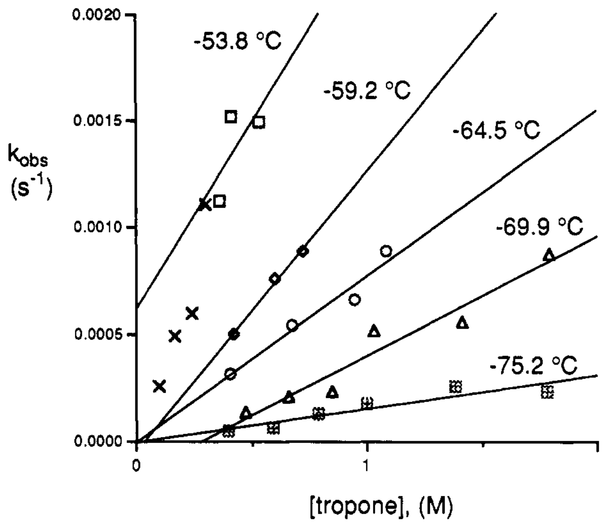


Figure 5. Dependence of k_{obs} on tropone concentration for the conversion of **1**-d_2 to **7**. The additional points (×) were not utilized in calculating the k_1 value at −53.8 °C in Table II and are explained in footnote 26. Data: Table IV.

Table IV. Summary of Rate Data for the Reaction of [(η^5-C_5H_5)Re(NO)(PPh_3)($ClCD_2Cl$)]$^+BF_4^-$ (1-d_2) and Tropone (L)

run	T (°C)	[1-d_2] (M)	[L] (M)	[L]/[1-d_2]	no. of half-lives	10^4k_{obs} (s^{-1})	10^4k_1 ($s^{-1}\cdot M^{-1}$)
1	−53.8	0.0358	0.358	10.0	2.5	11.2	32.6
2	−53.8	0.0348	0.417	12.0	2.8	15.1	37.6
3	−53.8	0.0384	0.537	14.0	2.2	14.9	28.6
4	−59.2	0.0350	0.420	12.0	1.3	4.92	12.0
5	−59.2	0.0376	0.601	16.0	1.4	7.51	12.7
6	−59.2	0.0343	0.721	21.0	1.4	8.82	12.4
7	−64.5	0.0368	0.405	11.0	1.6	3.14	8.00
8	−64.5	0.0356	0.676	19.0	2.3	5.34	8.07
9	−64.5	0.0350	0.946	27.0	2.2	6.54	7.01
10	−64.5	0.0360	1.08	30.0	1.7	8.81	8.25
11	−69.9	0.0336	0.471	14.0	0.9	1.31	2.83
12	−69.9	0.0366	0.658	18.0	1.0	2.03	3.13
13	−69.9	0.0369	0.849	23.0	1.0	2.31	2.75
14	−69.9	0.0355	1.03	29.0	2.2	5.15	5.07
15	−69.9	0.0362	1.41	39.0	2.6	5.53	3.96
16	−69.9	0.0351	1.79	51.0	2.9	8.68	4.89
17	−75.2	0.0360	0.396	11.0	0.48	0.446	1.14
18	−75.2	0.0371	0.593	16.0	0.58	0.607	1.03
19	−75.2	0.0377	0.791	21.0	1.1	1.29	1.65
20	−75.2	0.0370	0.999	27.0	1.1	1.73	1.75
21	−75.2	0.0373	1.38	37.0	1.1	2.56	1.87
22	−75.2	0.0302	1.78	59.0	1.5	2.28	1.29

tropone did not react cleanly, as detailed in the preceding paper.[1] Hence, a kinetic indenyl ligand effect could not be measured.

The reaction of **1** and methyl ethyl sulfide has been shown to give the thioether complex [(η^5-C_5H_5)Re(NO)(PPh_3)(S(Me)Et)]$^+BF_4^-$ (**8**) in quantitative spectroscopic yields, as depicted in Scheme IV, equation v.[12] Thus, the disappearance of **1** was monitored by $^{31}P\{^1H\}$ NMR at −80.2 °C under pseudo-first-order conditions. The k_{obs} values were proportional to methyl ethyl sulfide concentration, as summarized in Table V and Figure 6. The average k_1 value (Table II) was 417 times greater than that for the reaction of **1** and cyclohexanone, and 5 times greater than that for the reaction of **1** and tropone, as extrapolated from Eyring plots (−80.2 °C).

Finally, we sought to conduct additional probes of both the configurational stability of **1** and the stereochemistry of dichloromethane ligand substitution. Thus, **1** was generated from the optically active methyl complex (+)-(*S*)-(η^5-C_5H_5)Re(NO)(PPh_3)(CH_3).[27] The sample was kept

(26) (a) Secondary and solvent kinetic deuterium isotope effects are manifested in the rates of reaction of **1**-d_2. However, we presume these are negligible. (b) Rates of reaction of **1**-d_2 and tropone were also measured in the presence of 2–8-fold excesses of tropone, and at higher temperatures (−48.5, −43.1 °C). Only runs that utilized at least 10-fold excesses of tropone are given in Table IV. However, all data (corrected for the decrease in tropone concentrations during the runs)[21] are provided in the supplementary material. When these points are included in Figure 5, the non-zero intercept for the −53.8 °C plot vanishes. (c) When the preceding data are utilized to generate an Eyring plot, $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ of 12 ± 1 kcal/mol and −14 ± 4 eu are obtained.

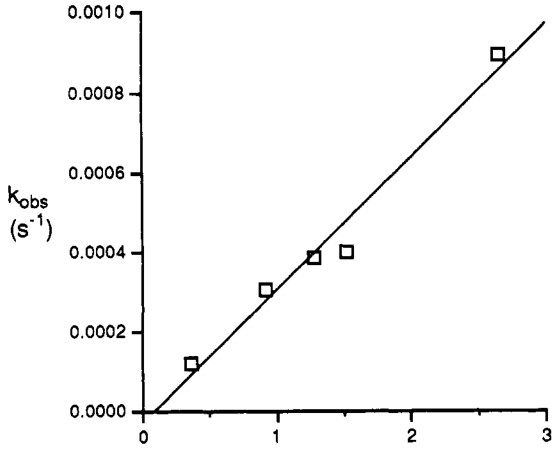


Figure 6. Dependence of k_{obs} on methyl ethyl sulfide concentration for the conversion of 1 to 8. Data: Table V.

Table V. Summary of Rate Data for the Reaction of $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(ClCH_2Cl)]^+BF_4^-$ (1) and Methyl Ethyl Sulfide (L)

run	*T* (°C)	[1] (M)	[L] (M)	[L]/[1]	no. of half-lives	10^4k_{obs} (s^{-1})	10^4k_1 ($s^{-1}\cdot M^{-1}$)
1	−80.2	0.0342	0.365	10.7	1.2	1.16	3.17
2	−80.2	0.0340	0.912	26.8	1.4	3.03	3.32
3	−80.2	0.0346	1.28	37.0	1.3	3.85	3.01
4	−80.2	0.0334	1.52	45.5	1.8	4.00	2.63
5	−80.2	0.0344	2.66	77.3	2.1	8.93	3.36

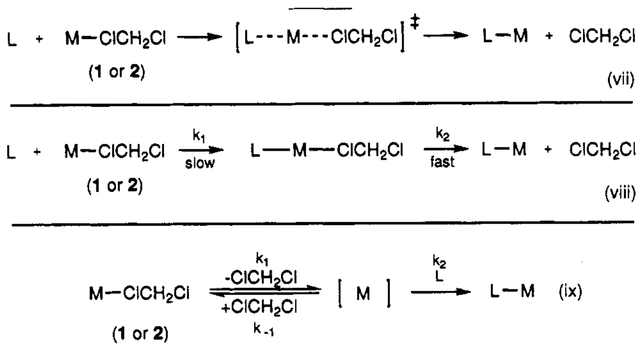
at −40 °C for 3 h. As previously assayed by ^{13}C NMR in CH_2Cl_2/CD_2Cl_2 solvent mixtures, the dichloromethane ligand exchanges with solvent on this time scale.[2] Importantly, any substitution that proceeds with inversion of configuration, and in which the nucleophile and leaving group are identical, must give a racemate.[28]

Styrene was then added to give a (81 ± 2):(19 ± 2) mixture of the previously characterized diastereomeric alkene complexes, (+)-(*RS*)- and (+)-(*RR*)-$[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(H_2C{=}CHC_6H_5)]^+BF_4^-$ (9),[9a,d] as shown in Scheme IV, eq vi. The enantiomeric purity of each diastereomer was assayed by ^1H NMR with the chiral shift reagent (+)-Eu(hfc)$_3$, as described earlier.[9a,d] Within detection limits (1–2%), only one enantiomer of each diastereomer was observed. Hence, the dichloromethane ligand in 1 must exchange with dichloromethane solvent with retention of configuration at rhenium. We therefore presume that the dichloromethane ligand is also replaced by other types of ligands with retention. This in turn strongly suggests that all of the steps in the top portion of Scheme I occur with retention.

Discussion

1. Associative vs Dissociative Mechanisms. The substitution reactions in Scheme III are first-order in dichloromethane complex and first-order in ketone, or second-order overall. Three possible mechanisms are sketched in Scheme V: a single-step associative process (eq vii), a two-step associative process (eq viii), and a dissociative process (eq ix). Equations vii and viii always give second-order rate laws. Also, the first step of eq viii

Scheme V. Some Possible Associative and Dissociative Substitution Mechanisms for Dichloromethane Complexes 1 and 2



will commonly be rate determining when reactions proceed to completion, as the ligand with the lower thermodynamic binding affinity (basicity) should more readily dissociate from the intermediate ($k_2 > k_{-1}$).

It is important to critically examine whether the preceding data can under any circumstances be accommodated by the dissociative mechanism in Scheme V, eq ix. This pathway gives the familiar type of rate expression shown in eq x.

$$d[M\text{-}ClCH_2Cl]/dt = -k_1k_2[M\text{-}ClCH_2Cl][L]/(k_{-1}[ClCH_2Cl] + k_2[L]) \quad (x)$$

Under the conditions used for the reactions in Scheme III, the dichloromethane concentration is essentially constant, and somewhat less than that of the neat solvent, 15.6–17.7 M (calculated from densities of 1.325 and 1.508 g/mL at 20 and −80 °C).[29] In the limit $k_{-1}[ClCH_2Cl] \gg k_2[L]$—which implies that the second step is rate determining—the second-order rate law shown in eq xi is obtained.

$$d[M\text{-}ClCH_2Cl]/dt = -k_1k_2[M\text{-}ClCH_2Cl][L]/k_{-1}[ClCH_2Cl] = -k_{obs}[M\text{-}ClCH_2Cl][L] \quad (xi)$$

In the opposite limit, $k_2[L] \gg k_{-1}[ClCH_2Cl]$—which implies the initial dichloromethane dissociation step is rate determining—the first-order rate law shown in eq xii is obtained. A transition between these two limits is normally evidenced by curvature in plots of the types in Figures 2 and 4–6.

$$d[M\text{-}ClCH_2Cl]/dt = -k_1[M\text{-}ClCH_2Cl] \quad (xii)$$

One test of the viability of the dissociative process in Scheme V, eq ix is as follows. If conditions can be identified under which the limit $k_{-1}[ClCH_2Cl] \gg k_2[L]$ cannot hold and a second-order rate law is still observed, then such mechanisms must be rejected. The rate constants k_{-1} and k_2 represent the statistically uncorrected[25b] nucleophilicities of dichloromethane and ketone toward the hypothetical intermediate.

Consider the runs at −29.6 to −41.4 °C in Figure 2 or −45.1 and −50.2 °C in Figure 4 that involve the highest cyclohexanone concentrations (1.0–1.7 M). No curvature or other sign of deviation from a second-order rate law is evident. The concentration of dichloromethane is ca. 10 times that of cyclohexanone in these experiments. There-

(27) Agbossou, F.; O'Connor, E. J.; Garner, C. M.; Quirós Méndez, N.; Fernández, J. M.; Patton, A. T.; Ramsden, J. A.; Gladysz, J. A. *Inorg. Synth.* **1992**, *29*, 211.

(28) A classical example is the racemization of chiral secondary alkyl iodides, RR'CHI, in the presence of I^-.

(29) *Industrial Solvents Handbook*, 4th ed.; Flick, E. W., Ed.; Noyes Data Corp: Park Ridge, NJ, 1991.

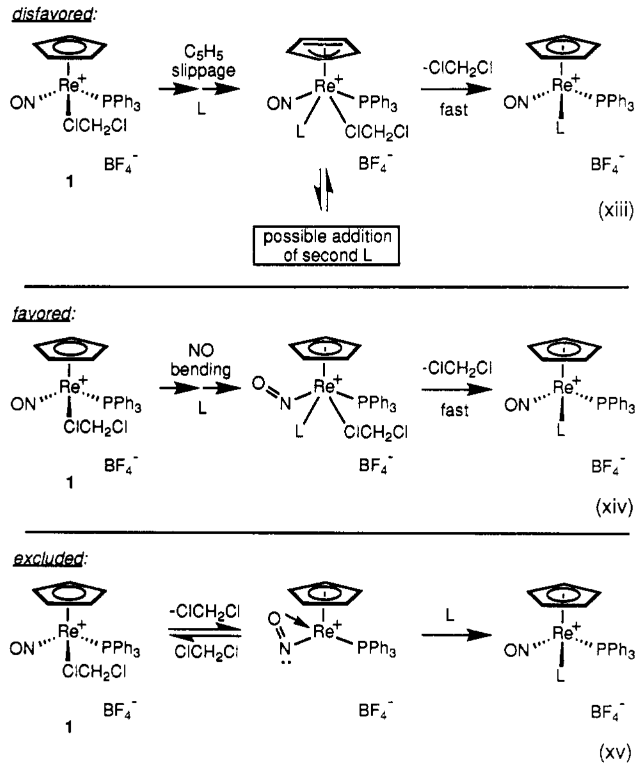
fore, if a dissociative mechanism is operative, $10k_{-1} \gg k_2$. However, the competition experiment described above showed cyclohexanone to be 13 times more nucleophilic than ethyl chloride at −40 °C. Given that ethyl chloride is more nucleophilic than dichloromethane, it must certainly be the case that $k_2 > 13k_{-1}$ or $k_2[L] > k_{-1}[ClCH_2Cl]$—in violation of the boundary condition under which a dissociative mechanism can give a second-order rate law.

With more nucleophilic ligands, it should become even less likely that the limit $k_{-1}[ClCH_2Cl] \gg k_2[L]$ can be maintained. However, the much faster reactions of 1 with tropone (factor of 15 at −40 °C) and methyl ethyl sulfide still exhibit second-order kinetics. Importantly, if a dissociative mechanism were operating with the rate law in eq xi, this acceleration would by necessity be derived from an increase in the k_2 value (the other terms remain constant as the ligand is varied). Thus, for these ligands, $k_2[L]$ must be at least $15k_{-1}[ClCH_2Cl]$ at −40 °C—an even greater violation of the boundary condition. On this basis, we reject all dissociative pathways as significant contributors to the mechanisms of dichloromethane ligand substitution in 1 and 2.[30]

Although the dichloromethane solvent made it more difficult to eliminate the possibility of dissociative mechanisms in Schemes III-IV, we do not wish to give the impression of surprise at the outcome. For example, Casey has studied the thermolyses of numerous coordinatively saturated cyclopentadienylrhenium complexes in detail.[31] Intricate rearrangements have been observed, the mechanisms of which conspicuously avoid possible 16-valence-electron intermediates. Similarly, we have found that the rhenium atoms in styrene complexes (*RS*)- and (*RR*)-**9** (Scheme IV, eq vi) migrate from one ligand π face to the other at 90–100 °C *without* dissociation.[9d]

In general, the rates of formation of coordinatively unsaturated species from third-row transition metal complexes are much slower than for first-row complexes.[32] In one recent example, the 19-valence-electron manganese complex $(\eta^5\text{-}C_5H_4CH_3)Mn(NO)(CO)_2$ was found to undergo CO substitution by a dissociative mechanism, with a $\Delta H^\ddagger$ value of 17.2 ± 1.9 kcal/mol and a $\Delta S^\ddagger$ value of 21.5 ± 3.6 eu.[32b] In contrast, the related rhenium complex $(\eta^5\text{-}C_5H_5)Re(NO)(CO)_2$ was inert under comparable conditions. Rhenium amido and alkoxy complexes of the

Scheme VI. Specific Mechanisms Considered for the Substitution of the Dichloromethane Ligands in 1 and 2



formula $(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(XR_n)$ are capable of PPh_3 ligand dissociation slightly above room temperature.[8b,33] However, these processes are anchimerically assisted by the amido and alkoxy ligand lone pairs.

2. Possible Associative Mechanisms. Many associative substitution reactions of coordinatively saturated transition metal complexes have been documented.[19,34] According to the prevailing viewpoint in recent reviews,[34] few if any of these proceed via a single-step associative mechanism of the type shown in Scheme V, eq vii. This relative of an S_N2 displacement at carbon would entail a 20-valence-electron transition state. Rather, associative substitutions are believed to be limited to cases where "... the metal complex can delocalize a pair of electrons onto one of its ligands and make available a vacant low-energy orbital on the metal ..."[34b] Thus, the associative mechanism shown in Scheme V, eq viii, remains viable, provided that nucleophilic attack is preceded or accompanied by a decrease in hapticity of an ancillary ligand, or an equivalent process.

Hence, associative substitutions of coordinatively saturated cyclopentadienyl complexes are frequently interpreted as proceeding via cyclopentadienyl ligand slippage.[19,20] Accordingly, marked kinetic indenyl ligand effects—as high as 10^8—have been observed for a variety of compounds. However, the indenyl dichloromethane complex **2** reacts with cyclohexanone only 6 times faster than the cyclopentadienyl analog **1** at −50 to −60 °C. A large rate enhancement would have provided unambiguous support for mechanisms involving slippage, such as illustrated in Scheme VI, eq xiii. From this modest effect alone, we do not believe there is a compelling reason to

(30) (a) At first glance, the non-zero intercepts observed for the highest temperature plots in Figures 4 and 5 might be taken as evidence for contributing dissociative mechanisms, or other pathways in which the ketones attack following the rate determining step. Dichloromethane dissociations from 1 or 2 would have positive $\Delta S^\ddagger$ values, in contrast to associative processes which should have negative $\Delta S^\ddagger$ values. Thus, dissociative pathways should be more competitive at higher temperatures. However, we question the statistical significance of the non-zero intercepts. In both Figures 4 and 5, additional points can be added to all lines at the origin without greatly diminishing the individual *R* values. Further, the non-zero intercept for the −53.8 °C plot in Figure 5 vanishes when additional data are included.[26b] Finally, only the intercept for the −39.6 °C plot in Figure 4 gives a first-order rate constant (0.0015 s^{-1}) that is comparable to the product of the second-order rate constant (0.00627 s^{-1} M^{-1}) and typical ketone concentrations (≥0.315 M). (b) Nonetheless, the non-zero intercept for the −39.6 °C plot in Figure 4 may be real. Indenyl complexes can react 575–6000 times faster than cyclopentadienyl complexes in dissociative substitutions, as determined in cases involving first-row and second-row transition metals:[19] White, C.; Mawby, R. J. *Inorg. Chem. Acta* **1970**, *4*, 261. Hart-Davis, A.-J., White, C.; Mawby, R. J. *Ibid.* **1970**, *4*, 441. Jones, D. J.; Mawby, R. J. *Ibid.* **1972**, *6*, 157.

(31) (a) Casey, C. P. *Science* **1993**, *259*, 1552. (b) Casey, C. P.; Vosejpka, P. C.; Underiner, T. L.; Slough, G. A.; Gavney, J. A., Jr. *J. Am. Chem. Soc.*, in press.

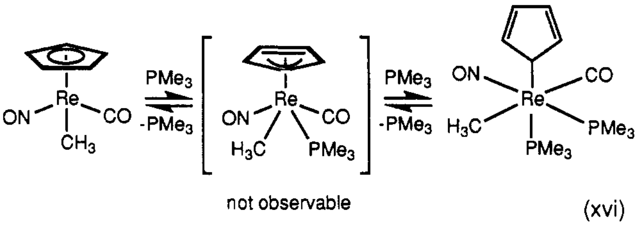
(32) (a) Wieland, S.; van Eldik, R. *Organometallics* **1991**, *10*, 3110. (b) Neto, C. C.; Kim, S.; Meng, Q.; Sweigart, D. A.; Chung, Y. K. *J. Am. Chem. Soc.* **1993**, *115*, 2077.

(33) Dewey, M. A.; Gladysz, J. A. *Organometallics* **1990**, *9*, 1351.

(34) (a) Howell, J. A. S.; Burkinshaw, P. M. *Chem. Rev.* **1983**, *83*, 557. (b) Basolo, F. *Inorg. Chim. Acta* **1985**, *100*, 33.

advocate intermediate η^3-C_xH_y or η^1-C_xH_y species in Scheme III.

It should be emphasized, however, that phosphorus and ketone ligands have been observed to add to the rhenium complexes $[(\eta^5\text{-}C_9H_7)Re(NO)(CO)_2]^+BF_4^-$,[1] $(\eta^5\text{-}C_xH_y)Re(CO)_3$,[35,36] and $(\eta^5\text{-}C_5H_5)Re(NO)(CO)(CH_3)$[37,38] to give the corresponding η^1-C_xH_y complexes. The last reaction is depicted in eq xvi. In no instance has a η^3-C_xH_y species



(xvi)

been detected, suggesting that $\eta^3 \rightarrow \eta^1$ processes are faster than $\eta^5 \rightarrow \eta^3$ processes. Thus, the mechanism in Scheme VI, eq xiii, does have ample precedent. Furthermore, it would not be surprising if reactions of **2** were eventually found that did give η^1-indenyl complexes.

We next consider the mechanistic alternative that **1** and **2** undergo nitrosyl ligand bending prior to or concurrent with nucleophilic attack, as illustrated in Scheme VI, eq xiv. This well-precedented isomerization also reduces the valence-electron count about the metal by 2 and is frequently invoked in associative substitution reactions of nitrosyl complexes.[19,39,40] Additional support comes from a recent theoretical study, which predicts that the substitution of carbon monoxide by PMe_3 in the six-coordinate linear nitrosyl complex *trans*-$W(NO)(CO)_4Cl$ should occur via a seven-coordinate bent nitrosyl complex (∠ W-N-O 135.7°).[40]

However, Casey has carefully studied additions of phosphorus nucleophiles to rhenium and tungsten cyclopentadienyl linear nitrosyl complexes, as exemplified above in eq xvi.[37,38] The possibility of intermediates or products with bent nitrosyl ligands was considered. Significantly, only η^1-cyclopentadienyl species were detected. This suggests that cyclopentadienyl ligand slippage is thermodynamically preferred to nitrosyl ligand bending, at least in this series of equilibria.

We can identify at least one means of accommodating our rate data in the context of Casey's preparative data. Namely, it is still possible that nitrosyl ligand bending is a kinetically faster process than cyclopentadienyl ligand slippage. Accordingly, to our knowledge *no kinetic indenyl ligand effect has been observed in the presence of a nitrosyl ligand* to date. Further, several linear nitrosyl analogs of the cationic square pyramidal intermediate in Scheme VI, eq xiv, have been isolated or characterized spectroscopically.[1,2,41] Hence, we presently favor this mechanism for the dichloromethane ligand substitution reactions in Schemes III–IV.[42]

We now consider the activation parameters for the reactions in Scheme III (Table II). Typically, $\Delta S^\ddagger$ values for associative substitutions of transition metal complexes range from −20 to −40 eu.[34a] Thus, those for the reactions of **1** and **2** with cyclohexanone (−5 ± 4–5 eu) are among the *least* negative measured to date.[43] Importantly, $\Delta S^\ddagger$ data are available for several substitutions that exhibit kinetic indenyl ligand effects. For example, the manganese and rhenium tricarbonyl complexes $(\eta^5\text{-}C_9H_7)M(CO)_3$ react with phosphorus nucleophiles to give dicarbonyl complexes $(\eta^5\text{-}C_9H_7)M(CO)_2(L)$ with $\Delta S^\ddagger$ values of −31 to −37 eu (calculated from three temperatures).[36,44] Similar reactions of rhodium cyclopentadienyl complexes $(\eta^5\text{-}C_5H_4X)Rh(CO)_2$ yield $\Delta S^\ddagger$ values of −15 to −40 eu.[45] We know of no substitution that shows a kinetic indenyl ligand effect and gives a $\Delta S^\ddagger$ value in the range of −5 to −10 eu.

Intuitively, the isomerization of a linear nitrosyl ligand to a bent nitrosyl ligand should provide, due to the increased degrees of freedom, a small *gain* in entropy. Indeed, $\Delta S^\ddagger$ data are available for several associative substitutions of coordinatively saturated linear nitrosyl complexes.[39] Although the values vary, some are in the range of −1 to −7 eu.[39b,d] These seem to be connected with less reactive nucleophiles that would logically give later transition states (less bond forming and greater NO bending). Similarly, the $\Delta S^\ddagger$ value for the reaction of **1** and cyclohexanone is less negative than that for the faster reaction of **1** and tropone (−17 ± 11 eu).[26c]

3. Outstanding Issues and Future Directions. Stereochemistry often provides a diagnostic probe of the mechanism. Unfortunately, none of the substitution pathways analyzed above for **1** account in an intuitively satisfying way for the retention of configuration at rhenium. An example of a mechanism that *would* have been enthusiastically received on this count is shown in Scheme VI, eq xv. Here, the nitrosyl ligand oxygen serves as an internal nucleophile for the backside displacement of dichloromethane. This inverts the rhenium configuration and gives an intermediate with a η^2-nitrosyl ligand. Although we are unaware of any precedent for such a nitrosyl ligand binding mode, many complexes with isoelectronic alkylnitroso (O=NR)[46] and η^2-acyl ligands have been isolated.

Subsequent attack of the new ligand L would displace the η^2-nitrosyl ligand oxygen and again invert the rhenium

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(42) A simplification in the mechanisms shown in Scheme VI, eqs xiii–xiv, deserves emphasis. Consider solvent exchange (L = $ClCH_2Cl$ or $ClCD_2Cl$), which proceeds with retention of configuration at rhenium as established above. If the stereochemistry of either square pyramidal intermediate were fixed, microscopic reversibility would be violated—that is, the solvent would attack the interstice between the nitrosyl and dichloromethane ligands in the forward direction, and the interstice between the PPh_3 and dichloromethane ligands in the reverse direction. Thus, an additional equilibrium that exchanges the L/$ClCH_2Cl$ positions without racemization must be operative, at least when L is dichloromethane.

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configuration, for overall retention. Alternatively, the nitrosyl ligand oxygen could equally well effect the *frontside* displacement of the dichloromethane ligand. Similar roles could be envisioned for the benzoyl ligand in the manganese complexes shown in Scheme II. However, Scheme VI, eq xv—and the frontside variant—constitute *dissociative* mechanisms that would give rate laws identical to Scheme V, eq ix. Therefore, they are excluded by our data.

It is possible to formulate an ad-hoc rationalization of stereochemistry for the mechanism in Scheme VI, eq xiv. For example, the nucleophile attacks the interstice between the smaller nitrosyl and dichloromethane ligands, *anti* to the bulky PPh_3. Further, the nucleophile binds *syn* to the most weakly bound ligand, which it eventually displaces.[42] Inversion would seemingly require attack at the interstice between the nitrosyl and PPh_3 ligands and more structural reorganization to reach a transition state.

However, we wish to emphasize that our data do not point in a clear and unequivocal way to a unique mechanism for the reactions in Schemes III–IV. We view Scheme VI, eq xiv, as a provisional model that offers a number of testable features. For example, study of isoelectronic osmium dichloromethane complexes $[(\eta^5\text{-}C_xH_y)Os(CO)(PPh_3)(ClCH_2Cl)]^+X^-$, which are currently unknown, could establish whether the nitrosyl ligand in **1** and **2** is (1) responsible for the absence of a kinetic indenyl ligand effect and (2) essential for retention of configuration at the metal. It would similarly be of interest to examine the stereochemistry as a function of phosphine size and donor properties. Useful data may also be forthcoming for related reactions of other chiral, nonracemic metal complexes.[47]

In summary, this study has rigorously established associative mechanisms for the substitution reactions in Schemes III–IV. On the basis of presently available data, nitrosyl ligand bending, as opposed to $\eta^5\text{-}C_xH_y$ ligand slippage, has been proposed as a means of avoiding 20-valence-electron intermediates or transition states. Attempts to further define the reaction coordinates are in progress.

Experimental Section

Chemical sources: cyclohexanone (Aldrich), distilled at 1 atm; tropone (Lancaster), vacuum distilled; ethyl chloride, methyl ethyl sulfide, styrene, and $BF_3\cdot OEt_2$ (Aldrich), used as received; $HBF_4\cdot OEt_2$ (Aldrich), standardized as described previously (5.8 M);[2] CH_2Cl_2 and CD_2Cl_2, stirred over CaH_2 and then vacuum distilled; methylrhenium complexes[1,27] and $(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(F)$ (**5**),[23] prepared as reported previously.

Rate Measurements. (A) Cyclohexanone. A 5-mm NMR tube was charged with $(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(CH_3)$ and capped with a septum under a dry N_2 atmosphere. Then CH_2Cl_2 (typically 0.55–0.60 mL; varied to give a ca. 0.6-mL solution after addition of all reagents) was added via syringe, and the sample was cooled to −80 °C. Then $HBF_4\cdot OEt_2$ (1 equiv) was added via syringe, and the tube was shaken to generate $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(ClCH_2Cl)]^+BF_4^-$ (**1**). Cyclohexanone was added via syringe (−80 °C), and the tube was rapidly shaken and transferred to a precooled NMR probe (Varian XL-300). The disappearance of **1** was monitored by $^{31}P\{^1H\}$ NMR (12.2 ppm; run 22, Table I) for 1–3 half-lives, and the clean formation of $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(\eta^1\text{-}O{=}\overline{C(CH_2)_4CH_2})]^+BF_4^-$ (**3**,[5b] 18.6 ppm) was observed. After data acquisition, the liquid level in the tube was marked and the volume assayed gravimetrically (water replacement). These data were used to calculate [L] and [**1**].[22b] Experiments with indenyl analogs **2** and **4** (12.8, 19.8 ppm; run 2, Table III), or in which **1** was generated from **5** and $BF_3\cdot OEt_2$,[23] were conducted analogously.

(B) Tropone. An NMR tube was charged with $(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(CH_3)$ as in procedure A. Then CD_2Cl_2 and $HBF_4\cdot OEt_2$ were similarly added to give **1**-d_2. An aliquot of a solution of tropone in CD_2Cl_2 that had been prepared in a volumetric flask (e.g., 0.557 g in 1.0 mL) was added (−80 °C), such that the total volume of liquids injected became 0.600 mL (ambient temperature). The tube was shaken and transferred to a precooled NMR probe. The disappearance of **1**-d_2 was monitored by ^1H NMR (δ 5.68; Table IV) for 0.5–2.9 half-lives, and the clean formation of $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(\eta^1\text{-}O{=}\overline{CCH{=}CHCH{=}CHCH{=}CH})]^+BF_4^-$ (**7**;[5b] δ 5.60) was observed. The solution volume at the reaction temperature was calculated from a plot of CD_2Cl_2 volume versus temperature (15 points, +20 to −80 °C).[29]

(C) Methyl Ethyl Sulfide. These experiments were conducted analogously to procedure A. The disappearance of **1** was monitored, and the clean formation of $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(S(Me)Et)]^+BF_4^-$ (**8**;[12] 18.9 ppm) was observed.

Data Reduction. Probe temperatures were calibrated with methanol.[48] Corrections were made for decoupler-induced heating in the $^{31}P\{^1H\}$ NMR experiments as described previously.[49] The errors for the k_1 values in Table II are 68% confidence limits calculated by the program Statview[50] using the standard method.[51] The errors for $\Delta H^\ddagger$ and $\Delta S^\ddagger$ values are 95% confidence limits calculated from the standard errors of the slope and intercept of the corresponding Eyring plot by Statview, again using a standard method.[52] Other protocols are described in the text and are evident from Tables I–V and Figures 1–6.

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Supplementary Material Available: A table of rate data for the reaction of **1**-d_2 and tropone and figures depicting the dependence of k_{obs} on [tropone] and the Eyring plot for the conversion of **1**-d_2 to **7** (3 pages).[26b] Ordering information is given on any current masthead page.

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