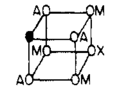
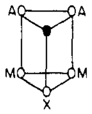
Table I. Silicon-29 Isotropic Chemical Shifts and Spin-Spin Coupling Constants for Singly Substituted Double Three- and Double Four-Membered Germanosilicate Rings[a]

species		δ_i (ppm)[b]	^2J (Hz)	^4J (Hz)
	A	-97.86_7	7.5	0.0
	M	-100.32_5	7.5	0.0
	X	-99.73_6	7.5	0.0
	A	-89.26_3	4.3	1.0
	M	-90.57_8	4.3	1.0
	X	-88.27_1	4.3	1.0

[a] Data from an isotopically enriched, 2:1 (N:Si) tetramethylammonium germanosilicate solution, 1 M in Si and 0.25 M in Ge (Figures 2 and 3), at 25 °C. [b] In parts per million from an external standard of tetramethylsilane.

In this case, computer simulation reveals that four bond couplings cannot be neglected, and a value of ^4J of ~ 1.0 Hz gives the best fit. (We must emphasize that the accuracy of this measurement is low, due to the relatively poor resolution and signal to noise of the experimental spectrum.) The good agreement between the simulated and observed spectra nevertheless provides particularly convincing evidence in support of the existence of the double three-membered ring in solution and confirms the earlier assignment[6] of the peak at $\delta = -90.3$ ppm to this structure. Table I compiles the chemical shifts and coupling constants observed in the spectra of the enriched tetramethylammonium germanosilicate solutions. Additional support for both structures is provided by comparing the coupling constants deduced in this work with those of similar structures reported elsewhere.[9]

Concluding Remarks

The results we have presented above are of interest for two reasons. First, they demonstrate that soluble heteroatom-substituted silicate cages may be prepared, and their ^{29}Si NMR solution spectra may be resolved and assigned. Further substitutions are also possible (e.g., double Ge substitution) and will be discussed elsewhere. Second, these results enable us to more definitely assign the peaks at −100.0 and −90.2 ppm, in solution, to the unsubstituted double four- and double three-membered cage structures. We thus believe that the combined used of ^{29}Si enrichment and heteroatom substitution may be a useful technique with which to assign novel silicate species in solution, which should be of relevance to structural studies of the sol-gel process, zeolite synthesis, and the speciation of silicate anions during various weathering processes.

Acknowledgment. We thank Dr. R. Ramachandran for his help with the 2D NMR experiment.

Mechanism of the Reaction of a Solvated Rhenium Acyl Complex with Neutral Transition-Metal Hydrides. Relative Nucleophilicity of Such Hydrides

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Abstract: The forward rate constant k_1 for $EtRe(CO)_5 \rightleftarrows EtC(O)(CH_3CN)Re(CO)_4$, as determined by the rate of establishment of the equilibrium in CH_3CN, agrees with the observed first-order rate constant for the reaction of $EtRe(CO)_5$ with an excess of any of several transition-metal hydrides. The rate-determining step in the reaction of $EtRe(CO)_5$ with these hydrides is therefore the formation of a rhenium propionyl complex. The formation of EtCHO from $EtC(O)(CH_3CN)Re(CO)_4$ and $HRe(CO)_5$ (which occurs at much lower temperatures than the formation of EtCHO from $EtRe(CO)_5$ and $HRe(CO)_5$) is first order in $EtC(O)(CH_3CN)Re(CO)_4$ and first order in $HRe(CO)_5$. The second-order rate constants for the reaction of a series of transition-metal hydrides with $EtC(O)(CH_3CN)Re(CO)_4$ have been measured; the order of these rate constants is substantially the reverse of the order of kinetic acidities of these hydrides, implying that the hydrides react as nucleophiles with $EtC(O)(CH_3CN)Re(CO)_4$. The rate of dissociation of coordinated acetonitrile from $EtC(O)(CH_3CN)Re(CO)_4$ has been measured; the results suggest a dissociative mechanism for the reaction of $EtC(O)(CH_3CN)Re(CO)_4$ with transition-metal hydrides. $EtC(O)Re(CO)_5$ only reacts with $HRe(CO)_5$ after carbonyl ligand dissociation, implying that the metal and not the acyl carbonyl is the site of nucleophilic attack by transition-metal hydrides on acyl complexes.

Previous investigations of the reactions of alkyl carbonyl complexes with transition-metal hydrides have suffered from the fact that, while intermediate formation of acyl complexes has been implied by solid kinetic evidence,[1-3] these acyl intermediates have not been directly observable.[4] The *formation* of these acyls has always been the rate-determining step, and it has thus been kinetically impossible to investigate their subsequent reaction with transition-metal hydrides. We have recently discovered[5] the re-

Table I. Equilibrium Constants for Reaction 1 at Various Temperatures

K_1[a]	T, °C	K_1[a]	T, °C	K_1[a]	T, °C
4.1	40.6	3.5	46.0	2.7	55.8
4.0	41.4	3.2	51.4	2.4	60.4
3.6	45.8	2.7	55.4	2.0	65.2

[a] Standard deviation is ±0.2.

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(1) In alkane elimination from 2 equiv of $Os(CO)_4(H)R$: (a) Okrasinski, S. J.; Norton, J. R. *J. Am. Chem. Soc.* **1977**, *9*, 295. (b) Norton, J. R. *Acc. Chem. Res.* **1979**, *12*, 139. (c) Carter, W. J.; Okrasinski, S. J.; Norton, J. R. *Organometallics* **1985**, *4*, 1376.

(2) In aldehyde elimination from $CpMo(CO)_3R/CpMo(CO)_3H$: (a) Jones, W. D.; Huggins, J. M.; Bergman, R. G. *J. Am. Chem. Soc.* **1981**, *103*, 4415. (b) Jones, W. D.; Bergman, R. G. *J. Am. Chem. Soc.* **1979**, *101*, 5447.

(3) An aldehyde elimination from $p\text{-}CH_3OC_6H_4CH_2Mn(CO)_5$: (a) Halpern, J. *Acc. Chem. Res.* **1982**, *15*, 332. (b) Nappa, M. J.; Santi, R.; Diefenbach, S. P.; Halpern, J. *J. Am. Chem. Soc.* **1982**, *104*, 619. (c) Nappa, M. J.; Santi, R.; Halpern, J. *Organometallics* **1985**, *4*, 34.

(4) We have shown by competition studies[1b,c] that $H(CH_3)Os(CO)_4$ is three times as reactive as Et_3P toward the acyl we believe to be formed from $H(CH_3)Os(CO)_4$—a result that implies that M-H attack on the acyl is nucleophilic.

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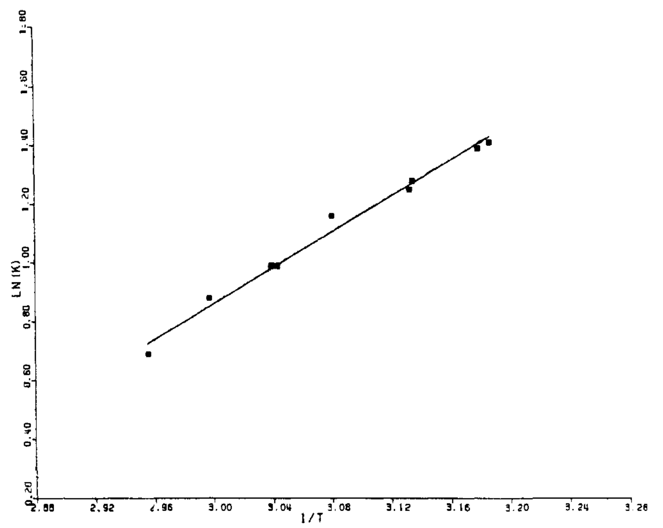


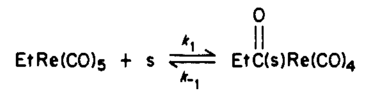
Figure 1. log of the measured equilibrium constant K_1 for reaction 1 (from Table I) vs. $10^3 \times (1/T$ (Kelvin)).

Table II. Determination of k_1 from the Rate of Approach to Equilibrium of Reaction 1

T, °C	$10^2[\mathrm{EtRe(CO)_5}]_0$, M	10^5k(approach to equil)^a	10^5k_1,^{a,b} $\mathrm{s^{-1}}$
65.2	6.4	33 (1)	22 (1)
60.4	6.3	16.2 (2)	11.4 (3)
55.5	6.8	9.6 (2)	7.0 (2)
55.4	6.8	10.3 (4)	7.5 (3)
51.4	7.3	6.9 (2)	5.3 (2)
50.1	6.3	6.6 (1)	5.0 (1)
46.0	6.6	4.9 (2)	3.8 (2)

[a] Numbers in parentheses are estimated standard deviations in the least significant figure. [b] Calculated from $k_1 = [K_1/(K_1 + 1)]k$(approach to equil).

versible formation of a solvated acyl from $\mathrm{EtRe(CO)_5}$ in acetonitrile solution



$$\mathrm{EtRe(CO)_5} + \mathrm{s} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \mathrm{EtC(=O)(s)Re(CO)_4} \quad (1)$$

($\mathrm{s{\cdot}CH_3CN}$ or $\mathrm{CD_3CN}$)

As this acyl is *observable* in significant quantities at equilibrium, we have been able to examine the kinetics and mechanism of its reaction with transition-metal hydrides.

Results

The equilibrium constant K_1 $(=k_1/k_{-1})$ for reaction 1 has been measured from 41 to 66 °C by ^{1}H NMR measurement of the intensities of the separate ethyl resonances of $\mathrm{EtRe(CO)_5}$ and $\mathrm{EtC(O)(s)Re(CO)_4}$. As shown in Table I and Figure 1, K_1 decreases with increasing temperature; $\Delta H°$ for reaction 1 is −5.8 (2) kcal/mol, and $\Delta S°$ is −15.8 (4) eu. The negative value of $\Delta S°$ reflects (and confirms) the presence of coordinated solvent on the right-hand side of equilibrium 1. A somewhat imprecise but very negative $\Delta S°$, −50 ± 10 eu, has been reported[6a] for the equilibrium

$$[\mathrm{CpFe(PPh_3)(CO)CH_3}]^+ + \mathrm{CH_3CN} \rightleftharpoons [\mathrm{CpFe(PPh_3)(CH_3CN)C(O)CH_3}]^+ \quad (2)$$

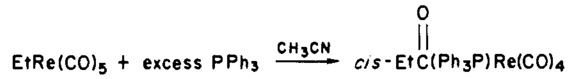
(reaction 2) between the positively charged $[\mathrm{CpFe(PPh_3)(CO)CH_3}]^+$ and its acetyl derivative with coordinated acetonitrile, and negative values of $\Delta S°$ seem to be associated with carbonyl insertion reactions of all sorts.[6]

Table III. Observed Rate Constants for the Disappearance of $\mathrm{EtRe(CO)_5}$ in the Presence of Excess Hydride in Acetonitrile (Reactions 4, 5, and 6)

T, °C	$[\mathrm{EtRe(CO)_5}]_0$, M	hydride	[hydride], M	10^5k_{obsd},^{a} $\mathrm{s^{-1}}$
65.2	6.4×10^{-2}	$\mathrm{HRe(CO)_5}$	0.67	19.9 (4)
60.4	6.3×10^{-2}	$\mathrm{HRe(CO)_5}$	0.75	11.4 (4)
55.5	6.8×10^{-2}	$\mathrm{HRe(CO)_5}$	0.91	7.4 (2)
55.4	6.8×10^{-2}	$\mathrm{HRe(CO)_5}$	0.84	7.2 (3)
55.4	6.8×10^{-2}	$\mathrm{HRe(CO)_5}$	1.32	6.3 (1)
55.4	6.9×10^{-2}	$\mathrm{HMn(CO)_5}$	0.84	6.56 (8)
55.4	6.4×10^{-2}	$\mathrm{HWCp(CO)_3}$	0.81	8.4 (1)
50.1	6.3×10^{-2}	$\mathrm{HRe(CO)_5}$	0.73	4.50 (7)
50.0	6.3×10^{-2}	$\mathrm{HMn(CO)_5}$	0.87	4.64 (8)
50.0	6.3×10^{-2}	$\mathrm{HWCp(CO)_3}$	0.71	5.16 (9)
44.8	6.3×10^{-2}	$\mathrm{HRe(CO)_5}$	0.64	2.45 (4)
40.2	6.4×10^{-2}	$\mathrm{HRe(CO)_5}$	0.75	1.65 (2)

[a] Numbers in parentheses are the estimated standard deviations in the least significant figure.

The approach of reaction 1 to equilibrium is slow enough that its rate can easily be determined (Table II) by monitoring the decrease in intensity of the methyl ^{1}H NMR resonance (δ 1.73) of $\mathrm{EtRe(CO)_5}$. At any given temperature, combination of the measured first-order rate constant for approach to equilibrium $(=k_1 + k_{-1})$ with the measured value of K_1 $(=k_1/k_{-1})$ yields the value given in Table II for k_1, the rate constant for formation of the acetonitrile-solvated propionyl complex from $\mathrm{EtRe(CO)_5}$.[7] The rate constant k_1 is approximately equal to the pseudo-first-order rate constant for the disappearance of $\mathrm{EtRe(CO)_5}$ in reaction 3, although the slightly larger value of the latter (k_{obsd} for reaction 3 is $14.3(2) \times 10^{-5}\ \mathrm{s^{-1}}$ at 60.2 °C) may reflect some degree of nucleophilic assistance by $\mathrm{Ph_3P}$ in acyl formation.[8]



$$\mathrm{EtRe(CO)_5} + \text{excess } \mathrm{PPh_3} \xrightarrow{\mathrm{CH_3CN}} cis\text{-}\mathrm{EtC(=O)(Ph_3P)Re(CO)_4} \quad (3)$$

Knowledge of k_1 has allowed us to investigate whether, as proposed, the formation of the propionyl solvate is rate-determining in the formation of propionaldehyde from $\mathrm{EtRe(CO)_5}$ and various transition-metal hydrides (e.g., reactions 4–6).[5,9,10] Measured

$$\mathrm{EtRe(CO)_5} + \text{excess } \mathrm{HRe(CO)_5} \xrightarrow{\mathrm{s}} \mathrm{EtCHO} + \mathrm{Re_2(CO)_9(s)} \quad (4)$$

$$\mathrm{EtRe(CO)_5} + \text{excess } \mathrm{HMn(CO)_5} \xrightarrow{\mathrm{s}} \mathrm{(s)Re(CO)_4Mn(CO)_5} \quad (5)$$

$$\mathrm{EtRe(CO)_5} + \text{excess } \mathrm{HW(CO)_3Cp} \xrightarrow{\mathrm{s}} [\mathrm{(s)Re(CO)_4W(CO)_3Cp}] \xrightarrow{\mathrm{CO}} \mathrm{Re(CO)_5W(CO)_3Cp} \quad (6)$$

$$-\mathrm{d}[\mathrm{EtRe(CO)_5}]/\mathrm{d}t = k_{\mathrm{obsd}}[\mathrm{EtRe(CO)_5}] \quad (7)$$

values of k_{obsd} for all three reactions are given in Table III. The value of k_{obsd} is clearly independent of both the concentration and nature of the hydride: at 55.4 °C, for example, k_{obsd} for reaction 4 is not significantly affected by $[\mathrm{HRe(CO)_5}]$ and averages $7.0 \times 10^{-5}\ \mathrm{s^{-1}}$, k_{obsd} for reaction 5 is $6.6 \times 10^{-5}\ \mathrm{s^{-1}}$, and k_{obsd} for reaction 6 is $8.4 \times 10^{-5}\ \mathrm{s^{-1}}$. Furthermore, k_{obsd} for reactions 4–6 is equal

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(5) Warner, K. E.; Norton, J. R., *Organometallics* **1985**, in press.

(6) (a) Magnuson, R. H.; Meirowitz, R.; Zulu, S.; Giering, W. P. *J. Am. Chem. Soc.* **1982**, *104*, 5790. (b) Calderazzo, F.; Cotton, F. A. *Inorg. Chem.* **1962**, *1*, 30. (c) Fachinetti, G.; Fochi, G.; Floriani, C. *J. Chem. Soc., Dalton Trans.* **1977**, 1946. (d) Cotton, J. D.; Crisp, G. T.; Latif, L. *Inorg. Chim. Acta* **1981**, *47*, 171.

(7) Similar experiments on i-$\mathrm{BuRe(CO)_5}$ at 53 °C gave K_1 for i-$\mathrm{BuRe(CO)_5} \rightleftharpoons i$-$\mathrm{BuC(O)(CD_3CN)Re(CO)_4}$ as 2.4 (3), k(approach to equil) as 9.8 (3) $\times 10^{-5}\ \mathrm{s^{-1}}$, and k_1 as 6.9 (3) $\times 10^{-5}\ \mathrm{s^{-1}}$.

(8) Bergman and Wax (Wax, M. J.; Bergman, R. G. *J. Am. Chem. Soc.* **1981**, *103*, 7028) have observed a separate second-order term, first order in $\mathrm{CpMo(CO)_3Me}$ and first order in $\mathrm{PMePh_2}$, in the rate law for formation of $\mathrm{CpMo(CO)_2(PMePh_2)Ac}$ from $\mathrm{CpMo(CO)_3Me}$ and $\mathrm{PMePh_2}$ in THF and its derivatives; they have interpreted this term as the result of direct $\mathrm{PMePh_2}$ attack on $\mathrm{CpMo(CO)_3Me}$ without intermediate formation of a solvated acyl. However, the recent demonstration by Webb et al.[38] of catalysis of acyl formation by nucleophiles not ultimately coordinated (e.g., $\mathrm{Ph_3P{=}O}$) has complicated the interpretation of this term.

(9) In reactions 4 and 5 the initially formed acetonitrile solvate has been isolated and characterized,[5] whereas in reaction 6 it has been characterized only by its formation of the known[10] $\mathrm{Re(CO)_5W(CO)_3Cp}$ upon carbonylation.

(10) Wrighton, M. S.; Ginley, D. S. *J. Am. Chem. Soc.* **1975**, *97*, 4246 and references therein.

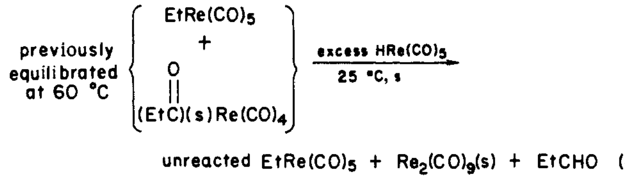
Table IV. Observed Rate Constants for the Disappearance of $EtC(O)(CD_3CN)Re(CO)_4$ in the Presence of $HRe(CO)_5$[a]

T,[b] °C	$[HRe(CO)_5]$, M	10^4k_{obsd},[c] s^{-1}
10.8	0.27	1.22 (3)
10.8	0.71	2.49 (5)
10.7	1.43	4.79 (11)
10.7	2.03	6.42 (21)

[a] In acetonitrile-d_3, with initial concentrations of $EtC(O)(CD_3CN)Re(CO)_4$ from 0.02 to 0.08 M. The $EtC(O)(CD_3CN)Re(CO)_4$ was generated by heating $EtRe(CO)_5$ solutions to 60 °C for 3.5 h and cooling them to −196 °C. [b] These reactions were monitored in the IBM WP-200SY NMR probe, and their temperature was therefore subject to its temperature fluctuations. The temperature was determined before and after each run by use of the methanol thermometer: Van Geet, A. L. *Anal. Chem.* **1970**, *42*, 679. [c] Numbers in parentheses are the estimated standard deviations in the least significant figure.

to k_1 (7.5×10^{-5} s^{-1}) at 55.4 °C, and a comparison of the k_1 data in Table II with the data for reaction 4 in Table III shows that the equality is maintained over a significant temperature range.

The rate-determining step in reactions 4–6 must therefore be the same as the rate-determining step in reaction 1 in the forward direction: either the direct formation of a solvated propionyl complex, or the formation of a coordinatively unsaturated propionyl complex which rapidly becomes saturated. The kinetic competence in reaction 4 of the solvated propionyl complex can be demonstrated by taking advantage of the slowness with which equilibrium 1 is maintained. At 25 °C and below equilibrium 1 is essentially frozen, and the addition of $HRe(CO)_5$ consumes only $EtC(O)(s)Re(CO)_4$ and leaves $EtRe(CO)_5$ unchanged. The pseudo-first-order rate constant for the reaction of $EtC(O)(s)Re(CO)_4$ with excess $HRe(CO)_5$ is thus much faster than k_1 (the rate constant for the generation of $EtC(O)(s)Re(CO)_4$ from $EtRe(CO)_5$) at 25 °C. Other hydrides also react rapidly with $EtC(O)(s)Re(CO)_4$, and approaches like that in reaction 8 permit determination of the rate of reaction of these hydrides with this *observable* acyl solvate.



$$\text{previously equilibrated at 60 °C}\left\{\begin{matrix} EtRe(CO)_5 \\ + \\ \overset{O}{\overset{\|}{(EtC)}}(s)Re(CO)_4 \end{matrix}\right\} \xrightarrow[25\ °C,\ s]{\text{excess } HRe(CO)_5} \text{unreacted } EtRe(CO)_5 + Re_2(CO)_9(s) + EtCHO \quad (8)$$

Kinetics of the Reaction of the Solvated Acyl $EtC(O)(s)Re(CO)_4$ with Hydrides. ^1H NMR monitoring of the methylene resonance of $EtC(O)(CD_3CN)Re(CO)_4$ when the $HRe(CO)_5$ is added to reaction 8 has permitted the determination (Table IV) of the pseudo-first-order rate constants for disappearance of $EtC(O)(s)Re(CO)_4$ in the presence of excess $HRe(CO)_5$. As Figure 2 shows, these pseudo-first-order rate constants vary linearly with the amount of $HRe(CO)_5$ present, at least up to 1.43 M; within this concentration range, the reaction of $EtC(O)(s)Re(CO)_4$ with $HRe(CO)_5$ (eq 9 with HM = $HRe(CO)_5$) therefore obeys the rate law in eq 10. (The kinetic behavior of this reaction with higher concentrations of entering hydride, and the detailed mechanism of reaction 9 will be discussed below.) Measurement of k_9 for

$$EtC(O)(s)Re(CO)_4 + HM \xrightarrow[s]{k_9} EtCHO + MRe(CO)_4(s) \quad (9)$$

$$-d[EtC(O)(s)Re(CO)_4]/dt = k_9[EtC(O)(s)Re(CO)_4][HM] \quad (10)$$

M = $Re(CO)_5$ over a temperature range of −6 to 22 °C (see Table V) has permitted extrapolation to 25 °C, where $k_9 = 2.75(8) \times 10^{-3}$ M^{-1} s^{-1} for $HRe(CO)_5$. In comparison, extrapolation of k_1 from the temperatures in Table III down to 25 °C gives $k_1 = 2.9$ (3) $\times 10^{-6}$ s^{-1}. Thus, at the concentrations of $HRe(CO)_5$ (0.5–1.0 M) employed in reaction 4, the formation of $EtC(O)(s)Re(CO)_4$ is at least two orders of magnitude slower than its disappearance by reaction with $HRe(CO)_5$—in agreement with the conclusion above that the formation of $EtC(O)(s)Re(CO)_4$ from $EtRe(CO)_5$ is the rate-determining step in reaction 4.

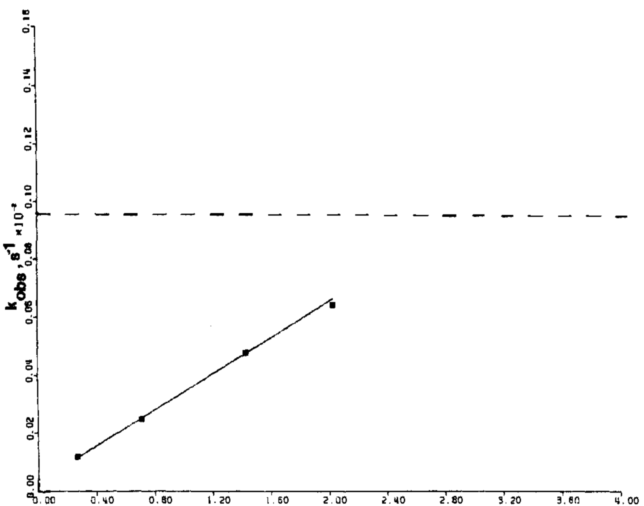


Figure 2. Observed rate constants from Table IV for the disappearance of $EtC(O)(CD_3CN)Re(CO)_4$ at 10.7 °C as a function of concentration of $HRe(CO)_5$. The dashed line represents k_{18}, the rate of dissociation from $EtC(O)(CH_3CN)Re(CO)_4$, extrapolated to 10.7 °C.

Table V. Observed Rate Constants for the Disappearance of $EtC(O)(CD_3CN)Re(CO)_4$[a] in the Presence of an Excess of Various Hydrides

T,[b] °C	HM ([HM], M)	10^4k_{obsd},[c] s^{-1}	10^4k_9,[c,d] M^{-1} s^{-1}
−6.2	$HRe(CO)_5$ (1.16)	1.46 (4)	1.26 (3)
−0.5	$HRe(CO)_5$ (0.84)	2.34 (4)	2.79 (5)
5.9	$HRe(CO)_5$ (0.98)	4.52 (9)	4.61 (9)
5.6	$DRe(CO)_5$ (0.95)	4.13 (8)	4.35 (8)
9.8	$HRe(CO)_5$ (0.55)	3.76 (5)	6.84 (9)
16.3	$HRe(CO)_5$ (0.82)	10.1 (2)	12.3 (2)
22.3	$HRe(CO)_5$ (0.80)	17.2 (5)	21.5 (6)
−6.8	$HMn(CO)_5$ (0.78)	0.93 (1)	1.20 (1)
−1.0	$HMn(CO)_5$ (0.81)	1.30 (2)	1.60 (2)
0.0	$HMn(CO)_5$ (0.82)	1.47 (3)	1.79 (4)
9.6	$HMn(CO)_5$ (1.65)	6.8 (1)	4.1 (1)
16.1	$HMn(CO)_5$ (0.80)	4.9 (1)	6.1 (1)
25.1	$HMn(CO)_5$ (0.53)	10.5 (2)	19.8 (4)
4.6	$H_2Os(CO)_4$ (0.88)	1.12 (2)	1.27 (2)
9.7	$H_2Os(CO)_4$ (1.08)	2.47 (6)	2.29 (6)
16.7	$H_2Os(CO)_4$ (1.32)	5.74 (6)	4.35 (5)
25.3	$H_2Os(CO)_4$ (0.72)	8.3 (1)	11.5 (1)
16.5	$HWCp(CO)_3$ (1.00)	0.68 (1)	0.68 (1)
25.6	$HWCp(CO)_3$ (1.02)	1.74 (2)	1.77 (2)
25.4	$DWCp(CO)_3$ (0.39)	0.50 (1)	1.28 (3)
25.6	$HWCp(CO)_2L$[e] (0.62)	0.77 (1)	1.24 (2)
25.5	$HWCp(CO)_2L$[e] (0.90)	0.93 (2)	1.03 (2)
25.5	$HCrCp(CO)_3$ (0.91)	0.180 (3)	0.198 (3)
−0.1	PEt_3 (0.74)	1.03 (3)	1.39 (4)

[a] In acetonitrile-d_3, with initial concentrations of $EtC(O)(CD_3CN)Re(CO)_4$ from 0.02 to 0.08 M. The $EtC(O)(CD_3CN)Re(CO)_4$ was generated by heating $EtRe(CO)_5$ solutions to 60 °C for 3.5 h and cooling them to −196 °C. [b] These reactions were monitored in the JEOL FX-100 NMR probe, and their temperature was therefore subject to its temperature fluctuations. The temperature was determined before and after each run by use of the methanol thermometer: Van Geet, A. L. *Anal. Chem.* **1970**, *42*, 679. [c] Numbers in parentheses are estimated standard deviations in the least significant figure. [d] $k_9 = k_{obsd}/[HM]$. [e] L = PMe_3; interconversion of the cis and trans isomers is sufficiently rapid to permit treatment of both as a single species in these experiments: Kalck, P.; Pince, R.; Poilbanc, R.; Rousell, J. *J. Organomet. Chem.* **1970**, *24*, 445.

Pseudo-first-order rate constants for the disappearance of $EtC(O)(s)Re(CO)_4$ in the presence of other hydrides HM^5 and the second-order rate constants k_9 derived from them by division by [HM] are given in Table V. The comparative $HRe(CO)_5/DRe(CO)_5$ results indicate a very small kinetic isotope effect (k_H/k_D = 1.1 (1)), as do the comparative $HW(CO)_3Cp/DW(CO)_3Cp$ results (k_H/k_D = 1.4 (2)). The temperature dependence

Table VI. Comparison of the Kinetic Acidities of Neutral Transition-Metal Hydrides with Their Nucleophilicities toward $EtC(O)(CD_3CN)Re(CO)_4$[a]

hydride	pK_a[b]	kinetic acidity k_{11},[c] $M^{-1}\ s^{-1}$	relative kinetic acidity	nucleophilicity[d] 10^4k_9, $M^{-1}\ s^{-1}$	relative nucleophilicity
$HRe(CO)_5$	21.1 (3)	ca. 6.4×10^{-4}	4×10^{-8}	27.5 (8)[e]	139[e]
$HMn(CO)_5$	15.1 (1)	$2.1(2) \times 10^2$	1×10^{-2}	19.8 (2)	100
$H_2Os(CO)_4$	20.8 (1)	ca. 6.5×10^{-3}	4×10^{-7}	11.5 (6)	58
$HWCp(CO)_3$	16.1 (1)	$2.5(2) \times 10^2$	1×10^{-2}	1.77 (2)	9
$HWCp(CO)_2PMe_3$[g]	26.6 (2)	$<10^{-3}$	$<10^{-7}$	1.03 (2)	5
$HCrCp(CO)_3$	13.3 (1)	$1.7(2) \times 10^4$	1[f]	0.198 (3)	1[f]

[a] At 25 °C in CD_3CN, with values in parentheses being the estimated standard deviations in the last decimal place. [b] From ref 13. [c] Second-order rate constants for proton transfer onto $PhNH_2$, from ref 12. [d] Second-order rate constants for the reaction of $EtC(O)(CD_3CN)Re(CO)_4$ with the hydride. [e] Extrapolated to 25 °C from the data in Table V. [f] Defined as unity for this relative scale. [g] Interconversion of the cis and trans isomers is sufficiently rapid to permit treatment of both as a single species in these experiments: Kalck, P.; Pince, R.; Poilbanc, R.; Rousell, J. *J. Organomet. Chem.* **1970**, *24*, 445.

of k_9 for $HRe(CO)_5$ gives $\Delta H^‡ = 15.0\ (2)$ kcal/mol and $\Delta S^‡ = -19.8\ (8)$ eu; for $HMn(CO)_5$ it gives $\Delta H^‡ = 10.9\ (8)$ kcal/mol and $\Delta S^‡ = -35\ (3)$ eu; for $H_2Os(CO)_4$ it gives $\Delta H^‡ = 17.1\ (8)$ kcal/mol and $\Delta S^‡ = -15\ (3)$ eu.

Comparison of the extrapolated 25 °C value of k_9 for $HRe(CO)_5$ with the values of k_9 *measured* at this temperature for the other hydrides (Table VI) yields the *relative* reactivity of these hydrides toward $EtC(O)(s)Re(CO)_4$, with that of the least reactive hydride, $HCr(CO)_3Cp$, taken as unity. It is particularly instructive to compare these relative reactivities with the relative kinetic acidities of the same hydrides (also measured in acetonitrile at 25 °C, and also in Table VI) toward aniline,[12] and with the known[13] pK_a values of these hydrides in acetonitrile. We have argued[12] that the relative kinetic acidities k_{11} of various hydrides HM in the known proton-transfer reaction 11 reflect the relative

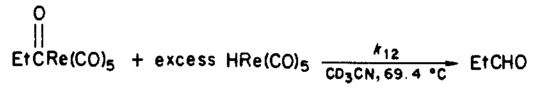
$$PhNH_2 + HM \xrightarrow[s,\ 25\ °C]{k_{11}} PhNH_3^+ + M^- \qquad (11)$$

structural and electronic rearrangements required before proton transfer can occur, and thus that (as the overall barrier to proton transfer to any base should be dominated by the barrier to proton *removal* from HM) the same *relative* kinetic acidities should be diagnostic for a proton-transfer mechanism in *any* reaction of HM.

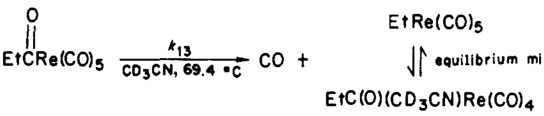
It is clear from Table VI that the relative hydride reactivities k_9 toward $EtC(O)(s)Re(CO)_4$ do not agree at all with their relative kinetic acidities k_{11}. Indeed, the order of increasing reactivity toward $EtC(O)(s)Re(CO)_4$ is largely the *reverse* of the order of increasing reactivity of proton transfer onto aniline. We therefore conclude that the reaction of these hydrides with $EtC(O)(s)Re(CO)_4$ does *not* occur by a proton-transfer mechanism.

In an effort to understand the origins of the reactivity of $EtC(O)(s)Re(CO)_4$ toward transition-metal hydrides, we have also investigated its reactivity toward other reagents. The quantitative formation of CH_3CHO from $MeMn(CO)_5$ and $HGePh_3$[5] implies that acyl solvates such as $EtC(O)(s)Re(CO)_4$ react with $HGePh_3$. $EtC(O)(s)Re(CO)_4$ does not react with 2 atm of hydrogen gas after 20 h at room temperature,[14-18] nor does it react with an excess of the hydride-transfer reagent $NaHB(OMe)_3$ after 3 days at room temperature. It is thus unlikely that the reaction of $EtC(O)(s)Re(CO)_4$ with transition-metal hydrides occurs by hydride transfer. The high reactivity of $EtC(O)(s)Re(CO)_4$ toward PEt_3 (see Table V) suggests, however, that the reaction of the acyl solvate with transition-metal hydrides involves some other form of nucleophilic attack by the latter.

Kinetics of the Reaction of $EtC(O)Re(CO)_5$ with Transition-Metal Hydrides. $EtC(O)(s)Re(CO)_4$ has two conceivable sites for nucleophilic attack: the propionyl carbonyl and the metal. We have examined the reaction of the unsolvated, coordinatively saturated $EtC(O)Re(CO)_5$ with $HRe(CO)_5$ in order to distinguish between these possibilities. The observed rate constant for the disappearance of $EtC(O)Re(CO)_5$ in reaction 12 is 1.38 (4) × $10^{-5}\ s^{-1}$—effectively identical with the rate of its disappearance by decarbonylation, reaction 13: $k_{13} = 1.48\ (4) \times 10^{-5}\ s^{-1}$ at 69.4 °C. (In an NMR tube the decarbonylation equilibrium lies completely to the right.) Thus *only after decarbonylation* can $EtC(O)Re(CO)_5$ react with $HRe(CO)_5$, i.e., a vacant coordination site must become available on the Re bearing the propionyl ligand before the propionyl complex can be attacked by $HRe(CO)_5$ (or, presumably, by any transition-metal hydride).



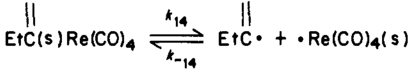
$$Et\overset{O}{\overset{\|}{C}}Re(CO)_5 + \text{excess } HRe(CO)_5 \xrightarrow[CD_3CN,\ 69.4\ °C]{k_{12}} EtCHO \qquad (12)$$



$$Et\overset{O}{\overset{\|}{C}}Re(CO)_5 \xrightarrow[CD_3CN,\ 69.4\ °C]{k_{13}} CO + \begin{array}{c} EtRe(CO)_5 \\ \downarrow\uparrow \text{ equilibrium mixture} \\ EtC(O)(CD_3CN)Re(CO)_4 \end{array} \qquad (13)$$

Discussion

A mechanism for the $EtC(O)(s)Re(CO)_4/HRe(CO)_5$ reaction which involves rhenium-acyl bond homolysis (like that found for $p\text{-}CH_3OC_6H_4CH_2Mn(CO)_4[P(p\text{-}C_6H_4OCH_3)_3]/HMn(CO)_4[P(p\text{-}C_6H_4OCH_3)_3]$[3]) can be ruled out for several reasons. Such a mechanism can only give the observed second-order kinetics if recombination (k_{-14}) competes effectively with hydrogen atom transfer to the acyl radical, and therefore if the homolysis



$$Et\overset{O}{\overset{\|}{C}}(s)Re(CO)_4 \underset{k_{-14}}{\overset{k_{14}}{\rightleftharpoons}} Et\overset{O}{\overset{\|}{C}}\cdot + \cdot Re(CO)_4(s) \qquad (14)$$

$$Et\overset{O}{\overset{\|}{C}}\cdot + HRe(CO)_5 \xrightarrow{k_{15}} EtCHO + \cdot Re(CO)_5 \qquad (15)$$

$$\cdot Re(CO)_4(s) + \cdot Re(CO)_5 \longrightarrow Re_2(CO)_9(s) \qquad (16)$$

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(11) The data in Table V were obtained on an FX-100 spectrometer, whereas the data in Table IV (and Table VII below) were obtained on a WP-200 spectrometer which become available toward the end of this work. Although both temperature controllers were carefully calibrated (see footnotes to Tables IV and V),[42] there appears to be a small systematic difference between rates measured on the two spectrometers at the same "temperature". As a result, no data points from Table IV have been included in Table V.

(12) (a) Edidin, R. T.; Longato, B.; Martin, B. D.; Matchett, S. A.; Norton, J. R. In "Organometallic Compounds: Synthesis, Structure, Theory"; Shapiro, B. L., Ed.; Texas A&M University Press: College Station, Texas, 1983; pp 260–80. (b) Edidin, R. T.; Sullivan, J. M.; Norton, J. R., submitted for publication.

(13) (a) Jordan, R. F.; Norton, J. R. *J. Am. Chem. Soc.* **1982**, *104*, 1255. (b) Jordan, R. F.; Norton, J. R. *ACS Symp. Ser.* **1982**, *198*, 403. (c) Moore, E. J.; Sullivan, J. M.; Norton, J. R., submitted for publication.

(14) This result imples that the propionyl solvate has a HM/H_2 selectivity considerably greater than that (12:1) shown by $EtO_2CCo(CO)_4$ for $HCo(CO)_4$ over H_2[15a] and probably as large as that (130:1) shown by $EtO_2CCH_2Co(CO)_4$ for $HCo(CO)_4$ over H_2.[15b] Such comparative data strengthen the case for dinuclear elimination as the terminal step in catalytic hydroformylation.[1-3,15-17] Mirbach,[18] however, has reported evidence that, under catalytic conditions, hydrogenolysis is favored over $HCo(CO)_4$ cleavage by 8:1 (cyclohexene as substrate) and even by 37:1 (1-octene as substrate).

(15) (a) Ungváry, F.; Markó, L. *Organometallics*, **1983**, *2*, 1608. (b) Hoff, C. D.; Ungváry, F.; King, R. B.; Markó, L. *J. Am. Chem. Soc.* **1985**, *107*, 666.

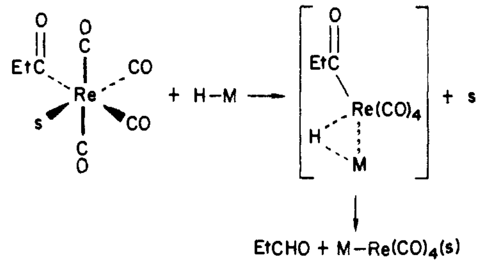
(16) Alemdaroglu, N. H.; Penninger, J. L. M.; Oltay, E. *Monatsh. Chem.* **1976**, *107*, 1153.

(17) Collman, J. P.; Belmont, J. A.; Brauman, J. I. *J. Am. Chem. Soc.* **1983**, *105*, 7288.

(18) Mirbach, M. F. *J. Organomet. Chem.* **1984**, *265*, 205.

equilibrium 14 is rapidly maintained at 25 °C and below. However, as shown above, $EtC(O)Re(CO)_5$ undergoes slow CO dissociation at 69.4 °C, with no sign of Re/acyl bond homolysis even at that temperature; facile homolysis below 25 °C of the Re/acyl bond in $EtC(O)(s)Re(CO)_4$ is therefore extremely improbable, and the propionyl solvate is stable indefinitely under those conditions. Furthermore, the hydrides most reactive (see Table VI) toward $EtC(O)(s)Re(CO)_4$ are those with the strongest M–H bonds,[19–23] contrary to the prediction of eq 14–16. Finally, no reasonable estimate of the Re–C bond strength in compounds of this type[24] is consistent with their facile homolysis below 25 °C.

We believe that our results indicate that $EtC(O)(s)Re(CO)_4$ (and by extension other acyls with a readily available vacant coordination site) undergoes nucleophilic attack at Re by the pair of electrons in the H–M bond, forming a species with a three-center, 2-electron bond. Such structures are common for stable



(17)

polynuclear hydrides, and indeed nucleophilic attack by transition-metal hydrides on coordinatively unsaturated or loosely solvated complexes has become an established method for the synthesis of polynuclear hydrides.[25–32] It is not clear whether the $Re(\mu\text{-}H)M$ species is an intermediate or a transition state; it is also not clear whether the H–M bond is completely broken (corresponding to complete oxidative addition of H–M across $EtC(O)(s)Re(CO)_4$)[33] before aldehyde elimination occurs. The small isotope effect[34–36] suggests a transition state (either before or after formation of the $Re(\mu\text{-}H)M$ species) in which the hydrogen is still primarily attached to one or both metals and no significant C–H bond formation has yet occurred.

Table VII. Observed Rate Constants for Approach to Equilibrium of Free and Coordinated CH_3CN in Solutions of $EtC(O)(CH_3CN)Re(CO)_4$ in CH_3CN/CD_3CN Mixtures[a]

T,[b] °C	10^4k_{obsd},[c] s^{-1}
−11.4	0.65 (2)
−6.1	1.23 (3)
−1.4	2.58 (11)
4.6	4.83 (20)
8.6	7.21 (37)

[a] In solutions of 10% to 33% CH_3CN and 66% to 90% CD_3CN, with initial concentrations of $EtC(O)(CH_3CN)Re(CO)_4$ from 0.2 to 0.4 M. The $EtC(O)(CH_3CN)Re(CO)_4$ was generated by heating CH_3CN solutions of $EtRe(CO)_5$ to 60 °C for 3.5 h and cooling them to −196 °C before adding the CD_3CN. The McKay equation factor relating k_{obsd} to the dissociation rate constant (see text) is negligibly different from unity (1.002). [b] These reactions were monitored in the IBM WP-200SY NMR probe, and their temperature was therefore subject to its temperature fluctuations. The temperature was determined before and after each run by use of the methanol thermometer: Van Geet, A. L. *Anal. Chem.* **1970**, *42*, 679. [c] Numbers in parentheses are the estimated standard deviations in the least significant figure.

Detailed Mechanism of Reaction 9. The data thus far presented do not establish whether the reaction of $EtC(O)(s)Re(CO)_4$ with hydrides occurs by a dissociative (rapid reversible loss of CH_3CN followed by attack of H–M on the unsolvated species) or an associative (direct displacement of coordinated CH_3CN by H–M) mechanism. However, measurement of the rate of dissociation of coordinated acetonitrile from $EtC(O)(CH_3CN)Re(CO)_4$ has enabled us to distinguish between these two mechanisms. $EtC(O)(CH_3CN)Re(CO)_4$ and $EtC(O)(CD_3CN)Re(CO)_4$ were formed by establishing equilibrium 1 in CH_3CN or CD_3CN (heating $EtRe(CO)_5$ to 60 °C for a few hours in either solvent). The isotopic composition of the solvent was then changed (by adding CD_3CN or CH_3CN) and the rate of approach to equilibrium at various temperatures (Table VII) monitored by observing the intensity of the peak at δ 2.37[5] due to coordinated CH_3CN in $EtC(O)(CH_3CN)Re(CO)_4$.

If a dissociative mechanism (eq 18) is assumed for solvent exchange, the McKay equation[37] gives the relation in eq 19, where

$$EtC(O)(s)Re(CO)_4 \underset{k_{-18}}{\overset{k_{18}}{\rightleftharpoons}} EtC(O)Re(CO)_4 + s \qquad (18)$$

[s] is the total concentration of CH_3CN and CD_3CN. As [s] ≫

$$k_{obsd} = \frac{\{[EtC(O)(s)Re(CO)_4] + [s]\}k_{18}}{[s]} \qquad (19)$$

$[EtC(O)(s)Re(CO)_4]$ during all these experiments, k_{obsd} is effectively equal to k_{18}, the rate constant for acetonitrile dissociation from $EtC(O)(s)Re(CO)_4$. The data in Table VII therefore yield activation parameters for k_{18}: $\Delta H^\ddagger = 17.4$ (7) kcal/mol, and $\Delta S^\ddagger$

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(19) It is generally believed that the M–H bond strength in a third-row hydride (e.g., $HRe(CO)_5$, $HW(CO)_3Cp$) is greater than that in the corresponding first-row hydrides (e.g., $HMn(CO)_5$, $HCr(CO)_3Cp$).[20] There is scattered evidence in support of this belief: relative rates of H· transfer to α-methylstyrene suggest a lower H–M bond strength in $HMo(CO)_3Cp$ than in $HW(CO)_3Cp$,[21] and substitution on $HMn(CO)_5$—which proceeds to a significant extent by a radical chain process involving H· abstraction—is faster than substitution on $HRe(CO)_5$.[22] Halpern, however, has commented that "transition-metal hydrogen bond dissociation energies ... do not appear to exhibit a significant increasing trend in going from the first transition series to the second and third".[23]

(20) Moore, D. S.; Robinson, S. D. *Chem. Soc. Rev.* **1983**, *12*, 415.

(21) Sweany, R. L.; Comberrel, D. S.; Dombourian, M. F.; Peters, N. A. *J. Organomet. Chem.* **1981**, *216*, 57. Other data suggesting that the W–H bond strength is greater than the Mo–H bond strength are quoted therein.

(22) Byers, B. H.; Brown, T. L. *J. Am. Chem. Soc.* **1977**, *99*, 2527.

(23) Halpern, J. *Inorg. Chim. Acta* **1985**, *100*, 41.

(24) The Re–C bond strength in $CH_3Re(CO)_5$ has been said to be 53 kcal/mol: Al-Takhin, G.; Connor, J. A.; Skinner, H. A. *J. Organomet. Chem.* **1983**, *259*, 313.

(25) For a review see: Venanzi, L. M. *Coord. Chem. Rev.* **1982**, *43*, 251. Recent examples include (a) $Ph_3PAuCl + TlPF_6 + HCr(CO)_5^- \rightarrow Ph_3PAu(\mu\text{-}H)Cr(CO)_5$;[26] (b) $Ph_3PAu(THF)^+ + H_3Ir(PPh_3)_3 \rightarrow Ph_3PAu(\mu\text{-}H)IrH_2(PPh_3)_3^+$;[27] (c) $Cp_2WH_2 + PtPh(acetone)(PEt_3)_2^+ \rightarrow Cp_2HW(\mu\text{-}H)PtPh(PEt_3)_2^+$;[28] (d) $Cu(MeCN)_4PF_6 + 2H_5Re(PMePh_2)_3 \rightarrow [H_2(MePh_2P)_3Re(\mu\text{-}H)_3]_2Cu^+$;[29] (e) $W(CO)_5(THF) + HTa(CO)Cp_2 \rightarrow W(CO)_5(\mu\text{-}H)Ta(CO)Cp_2$;[30] (f) $(Ph_2PCH_2CH_2PPh_2)Rh(acetone)_2^+ + HIr(PEt_3)_3Cl_2 \rightarrow (Ph_2PCH_2CH_2PPh_2)Rh(\mu\text{-}H)(\mu\text{-}Cl)Ir(PEt_3)_3Cl$;[31] (g) $CpMo(CO)_3^+ + HMo(CO)_3Cp \rightarrow Cp(CO)_3Mo(\mu\text{-}H)Mo(CO)_3Cp^+$.[32]

(26) Green, M.; Orpen, A. G.; Salter, I. D.; Stone, F. G. A. *J. Chem. Soc., Dalton Trans.* **1984**, 2497.

(27) Lehner, H.; Matt, D.; Pregosin, P. S.; Venanzi, L. M.; Albinati, A. *J. Am. Chem. Soc.* **1982**, *104*, 6825.

(28) Albinati, A.; Naegeli, R.; Togni, A.; Venanzi, L. *Organometallics* **1983**, *2*, 926.

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(30) Leblanc, J. C.; Reynoud, J. F.; Moise, C. *J. Organomet. Chem.* **1983**, *244*, C24.

(31) Lehner, H.; Matt, D.; Togni, A.; Thouvenot, R.; Venanzi, L. M.; Albinati, A. *Inorg. Chem.* **1984**, *23*, 4254.

(32) Markham, J.; Cutler, A. *Organometallics* **1984**, *3*, 736.

(33) Such a mechanism has been proposed for closely related elimination reactions: Humphries, A. P.; Kaesz, H. D. *Prog. Inorg. Chem.* **1979**, *25*, 145.

(34) A proton-transfer mechanism, with the proton midway between the metals in a linear transition state, would be expected to show a large kinetic isotope effect; the observed small isotope effect is thus an additional argument against a proton-transfer mechanism.

(35) In cases involving bonds between H and C or other first-row elements, nonlinearity of a transition state significantly decreases k_H/k_D. However, consideration of the usual explanation[36] for this result shows that the effect of transition-state nonlinearity on k_H/k_D should decrease for heavier terminal atoms, and for an H between a pair of third-row transition elements the effect of transition-state nonlinearity on k_H/k_D should be very small.

(36) (a) Melander, L.; Saunders, W. H., Jr. "Reaction Rate of Isotopic Molecules"; Wiley: New York, 1980; p 154. (b) More O'Ferrall, R. A. *J. Chem. Soc. B* **1970**, 785. The decrease in the effect of nonlinearity on k_H/k_D as first-row terminal atoms are replaced by second-row ones can be seen in Table IV in this reference.

(37) Espenson, J. H. "Chemical Kinetics and Reaction Mechanisms"; McGraw-Hill: New York, 1981; pp 50–53.

= −11 (2) eu. Extrapolation to 25 °C gives k_{18} (25 °C) as 4.4 (5) × 10^{-3} s^{-1}, and extrapolation to 10.7 °C gives k_{18} (10.7 °C) as 9.6 (6) × 10^{-4} s^{-1}. The latter extrapolation permits comparison of k_{18} with the data in Table IV. Clearly, the rate of disappearance of EtC(O)(s)Re(CO)$_4$ by reaction with HRe(CO)$_5$ is always less than the rate of solvent dissociation from EtC(O)(s)Re(CO)$_4$—even when [HRe(CO)$_5$] is 2.03 M. This fact strongly suggests that EtC(O)(s)Re(CO)$_4$ reacts with HeRe(CO)$_5$ (and by implication with other transition-metal hydrides HM) by the dissociative mechanism given by eq 18 and 20. Such a mechanism implies the rate law in eq 21 (assuming we describe solvent re-coordination by a first-order rate constant k_{-18}).

$$\mathrm{EtC(O)(s)Re(CO)_4} \underset{k_{-18}}{\overset{k_{18}}{\rightleftharpoons}} \mathrm{EtC(O)Re(CO)_4} + \mathrm{(s)} \quad (18)$$

$$\mathrm{EtC(O)Re(CO)_4} + \mathrm{HM} \xrightarrow[\mathrm{s}]{k_{20}} \mathrm{EtCHO} + \mathrm{MRe(CO)_4(s)} \quad (20)$$

$$\frac{-\mathrm{d[EtC(O)(s)Re(CO)_4]}}{\mathrm{d}t} = \frac{k_{18}k_{20}\mathrm{[EtC(O)(s)Re(CO)_4][HM]}}{k_{-18} + k_{20}\mathrm{[HM]}} \quad (21)$$

This rate law predicts saturation behavior, i.e., if [HRe(CO)$_5$] becomes sufficiently high that k_{20}[HRe(CO)$_5$] exceeds k_{-18}, the observed rate constant for the disappearance of EtC(O)(s)Re(CO)$_4$ will cease being linear with [HRe(CO)$_5$] and level off at k_{18}. Figure 2 (the dashed line represents k_{18}) is consistent with such behavior, but k_{20}/k_{-18} is apparently too small to permit the unambiguous observation of saturation at any meaningful [HRe(CO)$_5$]; the highest [HRe(CO)$_5$] used, 2.03 M, corresponds to a solution 39% hydride by volume. The data plotted in Figure 2 nevertheless make a dissociative mechanism far more likely than an associative one for the reaction of EtC(O)(s)Re(CO)$_4$ with HRe(CO)$_5$, and Halpern and co-workers[38] have just convincingly proven that the closely related reaction of p-CH$_3$OC$_6$H$_4$CH$_2$C(O)(Ph$_3$P=O)-Mn(CO)$_4$ with cis-HMn(CO)$_4$(PMe$_2$Ph) occurs by a dissociative mechanism. At concentrations of HRe(CO)$_5$ ≤ 1.43 M, and at *all* concentrations employed for the other, less nucleophilic, transition-metal hydrides, the rate law in eq 21 clearly reduces to that in eq 22, i.e., k_9 is actually $k_{20}k_{18}/k_{-18}$.

$$\frac{-\mathrm{d[EtC(O)(s)Re(CO)_4]}}{\mathrm{d}t} = \frac{k_{18}k_{20}\mathrm{[EtC(O)(s)Re(CO)_4][HM]}}{k_{-18}} \quad (22)$$

The values of k_{18} and k_{-18} are, of course, independent of the nature of the hydride involved, so the relative values of k_9 for the various hydrides in Table VI reflect the relative values of k_{20} for these hydrides—i.e., their relative nucleophilicities toward the coordinatively unsaturated EtC(O)Re(CO)$_4$. The data in Table VI represent the first quantitative measurement of the relative nucleophilicity of these neutral transition-metal hydrides. Kao, Darensbourg, and co-workers[39] have measured the relative nucleophilicities of a series of hydride metal *anions* toward n-BuBr, and Shriver and co-workers[40] have reported qualitative data (reactivity toward boron and aluminum Lewis acids) implying that Lewis basicity increases in the order HCo(CO)$_4$ < HMn(CO)$_5$ < HMn(CO)$_4$PPh$_3$ < HRe(CO)$_5$. We believe that knowledge of these nucleophilicities will be a valuable mechanistic tool, permitting the identification of other mechanisms involving nucleophilic attack by H–M bonds. In contrast to our series of relative kinetic acidities,[12] however, relative nucleophilicities are likely to vary significantly from system to system: steric interactions between the two complexes will be much greater in a triangular Re(μ-H)M species than in a linear proton-tranfer transition state.[41]

Experimental Section

CD$_3$CN was dried at room temperature over P$_4$O$_{10}$ and transferred on a vacuum line before use. CH$_3$CN was predried over molecular sieves and distilled under N$_2$ from CaH$_2$. Infrared spectra were obtained on a Beckman 12 or a Perkin-Elmer 983 equipped with a data station; Os$_3$(CO)$_{12}$ and DCl were used as calibrants, and wavenumber values are within 1 cm^{-1}. Low-temperature kinetics were carried out within the variable-temperature probe of either a JEOL FX-100 or an IBM WP-200SY. High-temperature kinetics were carried out in sealed NMR tubes in constant temperature baths; at appropriate intervals the tubes were removed and placed in the FX-100 or an IBM WP-270SY at ambient probe temperature (or below) so that the progress of the reaction could be determined. Residual solvent proton shifts were used as secondary chemical shifts standards. The methods used for preparation of the hydrides and EtRe(CO)$_5$, and the characterization of the products of these reactions, have already been reported.[5]

Determination of the Equilibrium Constant for Reaction 1. The equilibrium constant, K_1, was measured in CD$_3$CN solution from the heights of the methyl signal of EtRe(CO)$_5$ (H$_a$, δ 1.73) and the methyl signal of EtC(O)(CD$_3$CN)Re(CO)$_4$ (H$_b$, δ 0.80). K_1 was then H$_b$/H$_a$.

On a vacuum line, a solution of EtRe(CO)$_5$ in CD$_3$CN (generally around 7 × 10^{-2} M) was syringed into an NMR tube under N$_2$, frozen, and degassed (3×); the tube was then sealed. The tube was placed in a constant temperature bath and removed periodically and cooled in an ice bath to quench the reaction. Its NMR spectrum was then recorded at 0 °C.

As EtC(O)(CD$_3$CN)Re(CO)$_4$ slowly decomposes under the reaction conditions, and its decomposition products have NMR signals near that of H$_b$, the reported values of K_1 are time averages of the H$_b$/H$_a$ ratio after the H$_b$ signal intensity reaches a plateau. Values derived from later reaction times give artificially high apparent values of K_1.

Several tubes at equilibrium, when examined by high-field NMR (360 MHz), confirmed the accuracy of the values of K_1 already measured at 100 MHz.

Kinetic Analysis of Reaction 1. The rate of approach to equilibrium (k_{app}) in CD$_3$CN of reaction 1 was measured by monitoring the disappearance of the methyl resonance of EtRe(CO)$_5$ at δ 1.73, as described above for the determination of K_1. Due to the decomposition of EtC(O)(CD$_3$CN)Re(CO)$_4$ under the reaction conditions (above), experimental infinity points proved unreliable. Therefore, infinity points were calculated from K_1 and [H$_a$]$_0$ (the line height of the δ 1.73 resonance at zero time) according to $[\mathrm{H_a}]_\infty = [\mathrm{H_a}]_0/(K_1 + 1)$. The forward rate constant, k_1, was calculated from K_1 and k_{app} according to $k_1 = K_1k_{app}/(K_1 + 1)$.

By using identical methods, the equilibrium constant and rate of approach to equilibrium for the reaction i-BuRe(CO)$_5$ ⇌ i-BuC(O)-(CD$_3$CN)Re(CO)$_4$ were measured by monitoring the methyl signals of i-BuRe(CO)$_5$ at δ 0.98.[7]

Kinetic Analysis of Reaction 3. The rate of disappearance of EtRe(CO)$_5$ in the presence of an excess of PPh$_3$ in CH$_3$CN solution was determined by monitoring the disappearance of the IR absorption at 2010 cm^{-1}. A solution of EtRe(CO)$_5$ in CH$_3$CN (generally around 0.01 M) and excess PPh$_3$ was mixed in a 25 mL vacuum line bulb. After freezing and degassing, the bulb was filled with N$_2$, closed, and placed in a constant temperature bath. It was removed at appropriate intervals and cooled in ice water in order to quench the reaction. Aliquots were then removed under a flow of N$_2$ and their IR spectra recorded. The isolation and characterization of the product, cis-EtC(O)(Ph$_3$P)Re(CO)$_4$, have been reported elsewhere.[5]

Kinetic Analysis of Reactions 4–6. The rate of disappearance of EtRe(CO)$_5$ in the presence of an excess of various hydrides (see Table III) was measured in CD$_3$CN solution by monitoring the disappearance of the methyl resonance of EtRe(CO)$_5$ at δ 1.73. If the hydride to be used was volatile, a solution of EtRe(CO)$_5$ in CD$_3$CN (generally around 6.5 × 10^{-2} M) was syringed into an NMR tube under N$_2$ and frozen and degassed (3×) on a vacuum line; the appropriate amount of hydride was then vacuum transferred into the tube. If the hydride was nonvolatile (e.g., HWCp(CO)$_3$), it was placed in an NMR tube inside an inert atmosphere box; the tube then was attached to a vacuum line and cooled to −196 °C. The appropriate amount of EtRe(CO)$_5$ in CD$_3$CN was then syringed into the tube under a flow of N$_2$ (this procedure froze the EtRe(CO)$_5$ solution before it came into contact with the hydride and kept

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[38] Webb, S. L.; Giandomenico, C. M.; Halpern, J., submitted for publication.

[39] Kao, S. C.; Spillett, C. T.; Ash, C.; Lusk, R.; Park, Y. K.; Darensbourg, M. Y. *Organometallics* **1985**, *4*, 83 and references therein.

[40] Richmond, T. G.; Basolo, F.; Shriver, D. F. *Organometallics* **1982**, *1*, 1624.

[41] Note that the effective concentration for an intramolecular proton transfer is about 10^6 times less than that for a "tighter" intramolecular hydride transfer: Davis, A. M.; Page, M. I.; Mason, S. C.; Watt, I. *J. Chem. Soc., Chem. Commun.* **1984**, 1671.

the reaction from beginning before the tube was sealed).

After the tube, prepared by either method, was sealed under vacuum, it was placed in a constant-temperature bath. It was removed at appropriate time intervals and cooled in ice water to quench the reaction, and its NMR spectrum was recorded at 0 °C. In some cases the rate of appearance of product (EtCHO) was measured by monitoring the resonance due to the methyl group of EtCHO at δ 1.02. The rates so calculated were in good agreement with those calculated from the disappearance of $EtRe(CO)_5$.

Kinetic Analysis of Reaction 9. The rate of disappearance (k_{obsd}) of $EtC(O)(CD_3CN)Re(CO)_4$ in the presence of an excess of hydride or PEt_3 (see Tables IV and V) was measured in CD_3CN solution by monitoring the disappearance of the methylene resonance of the propionyl solvate at δ 2.60. For volatile hydrides and PEt_3, a solution of $EtRe(CO)_5$ (generally around 7×10^{-2} M) was syringed into an NMR tube under a flow of N_2. The tube was closed with a Teflon stopcock and placed in a 60 °C bath for 3 to 3.5 h (producing an approximate concentration of $EtC(O)(CD_3CN)Re(CO)_4$ of 4.7×10^{-2} M). The tube was replaced on the vacuum line, the contents frozen and degassed (3×), and the appropriate amounts of hydride vacuum transferred into the tube. The tube was then sealed under vacuum.

If the hydride was nonvolatile, it was placed in an NMR tube inside an inert atmosphere box; the tube was then connected to a vacuum line and cooled to −196 °C. Next, a solution of $EtRe(CO)_5$ and $EtC(O)(CD_3CN)Re(CO)_4$ in CD_3CN (previously equilibrated, as described above, in a 25-mL vacuum-line bulb) was syringed into the cold NMR tube under N_2 flow (this procedure prevented any reaction from occurring during sample preparation). The tube was then evacuated and sealed under vacuum (samples were stored at −196 °C until immediately before use).

The tube, prepared by either method, was removed from the −196 °C bath, quickly thawed, and placed directly in the NMR probe, which had been previously equilibriated at the appropriate temperature. The temperature of the NMR probe was measured directly before and after each run via a methanol thermometer;[42] the uncertainty in the temperatures was ±0.5 °C. Spectrum acquisition was started at appropriate time intervals and completed rapidly compared to the time scale of the reaction. In a few cases, the rate of appearance of product, EtCHO, was calculated from the increase in height of the methyl resonance of EtCHO at δ 1.02. The rates so calculated were in satisfactory agreement with those calculated from the disappearance of $EtC(O)(CD_3CN)Re(CO)_4$.

Propionylpentacarbonylrhenium was prepared by a procedure like that of Lukehart and co-workers for isobutyrylpentacarbonylrhenium.[43] A 5.0×10^{-4} M solution (1.58 mL, 0.79 mmol) of degassed propionyl chloride (previously distilled at 80 °C from PCl_5) in THF was added dropwise over 5 min to a stirred solution of 285 mg (0.816 mmol) of $Na[Re(CO)_5]$ in 10 mL of THF under N_2 at −72 °C. An additional 10 mL of THF was then added, and the reaction was stirred for 2 h at −72 °C and for an additional hour as the flask was warmed to 25 °C. Removal of solvent left a light orange residue. This was dissolved in hexanes, filtered, reduced in volume, and cooled to −25 °C. The yellow crystals thereby obtained (the first crop was 40 mg, 13%) were washed with cold hexanes and pumped to dryness. IR (hexanes) 2131 (w), 2057 (w), 2015 (s), 1999 (m), 1977 (w), 1626 (w) cm^{-1}; ^1H NMR ($CDCl_3$) δ 2.71 (q, J = 7.3 Hz, 2 H), 0.88 (t, J = 7.2 Hz, 3 H); ^1H NMR (CD_3CN) δ 2.71 (q, J = 7.0 Hz, 2 H), 0.80 (t, J = 7.2 Hz, 3 H). Anal. Calcd for $C_8H_5O_6Re$: C, 25.07; H, 1.31. Found: C, 24.87; H, 1.25.

Kinetics of the Thermal Decarbonylation of $EtC(O)Re(CO)_5$. CD_3CN (0.392 g, 1.11 mL) was added to 7.8 mg (0.0203 mmol) of $EtC(O)Re(CO)_5$ by vacuum transfer. This 18.3 mM solution (0.479 g, 0.570 mL, 0.0104 mmol) was syringed under N_2 into an NMR tube. The tube was frozen, degassed, and sealed under vacuum and then placed in a constant temperature bath at 69.4 °C. At appropriate intervals the tube was removed from the bath; observation of the ratio of the methylene quartet of $EtC(O)Re(CO)_5$ at δ 2.75 to residual CD_3CN protons at δ 1.91 gave a rate constant of 1.48 (4) $\times 10^{-5}$ s^{-1}.

Kinetics of the Reaction of $EtC(O)Re(CO)_5$ with $HRe(CO)_5$. To $EtC(O)Re(CO)_5$ (7.8 mg, 0.0203 mmol) was added 0.932 g (1.11 mL) of CD_3CN by vacuum transfer. This 18.3 mM solution (285 mg, 0.307 mL, 5.61×10^{-3} mmol) was syringed under N_2 into an NMR tube. The tube was frozen and degassed, 21.7 mg (0.0663 mmol, 11.8 equiv) of $HRe(CO)_5$ (measured ρ = 2.41 g mL^{-1}) was vacuum transferred into it, and the tube was sealed. It was placed in a constant temperature bath at 69.4 °C and removed at appropriate intervals. Monitoring the ratio of the methyl triplet of $EtC(O)Re(CO)_5$ at δ 0.77 to residual solvent protons of CD_3CN at δ 1.91 gave a rate constant of 1.38 (4) $\times 10^{-5}$ s^{-1}.

Carbonylation of $EtRe(CO)_5$ in CD_3CN. $EtRe(CO)_5$ (1.74 mg, 4.87×10^{-3} mmol) and 0.401 mL of CD_3CN were combined in an NMR tube and degassed. CO (4.9×10^{-3} mmol, 1.0 equiv) was added to the system and the tube was frozen in liquid N_2 and sealed. Periodic ^1H NMR monitoring (the tube was heated to 71.6 °C, removed at appropriate time intervals, and a spectrum recorded) showed the $EtRe(CO)_5/EtC(O)(CD_3CN)Re(CO)_4$ equilibrium mixture[5] through 7 h of heating. Only a trace of $EtC(O)Re(CO)_5$ was ever visible.

In another experiment, 35.8 mg (0.101 mmol) of $EtRe(CO)_5$, 1 mL of CD_3CN and 1 atm (10 equiv) of CO were combined in a 25-mL vacuum-line bulb. After 47 h at 70 °C, ^1H NMR showed over 73% of the ethyl rhenium species to be in the form of $EtC(O)Re(CO)_5$.

Approach to Equilibrium between the Coordinated Acetonitrile in $EtC(O)(CH_3CN)Re(CO)_4$ and Solvent Acetonitrile. In a typical reaction, $EtRe(CO)_5$ (22.0 mg, 0.0619 mmol) and CH_3CN (153.7 mg, 3.744 mmol, 0.1956 mL) were combined in an NMR tube by vacuum transfer. The tube was closed with a Teflon stopcock and placed in a 60 °C bath for 3.5 h (producing an approximate concentration of $EtC(O)(CH_3CN)Re(CO)_4$ of 0.22 M at this time). HMDS (hexamethyldisiloxane, 4.70 mL at 26 mmHg pressure at 23 °C, 6.6×10^{-3} mmol, internal standard) and CD_3CN (preweighed at 0.5913 g, 13.417 mmol, 0.70 mL) were then added by vacuum transfer to the frozen tube, which was flame-sealed under vacuum and kept at −196 °C until the kinetics run was begun, as described above for reaction 9. The total concentration of acylrhenium species was thus about 0.049 M. The decrease in intensity of the coordinated CH_3CN peak at δ 2.37 was used to monitor the reaction. Similar results were obtained with $EtC(O)(CD_3CN)Re(CO)_4$ in a mixture of acetonitriles, monitoring the growth of the δ 2.37 peak of $EtC(O)(CH_3CN)Re(CO)_4$.

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