Electrocatalytic Reduction of Vicinal Dibromides. Kinetics of reduction of vicinal dibromides in pH 2.3 acetonitrile–water at carbon microdisk electrodes were similar to those obtained at larger electrodes. The observed k_1 for reduction of DBB with cob(I)-alamine was 6×10^6 M^{-1} s^{-1} at glassy carbon[13] and 1.3×10^6 M^{-1} s^{-1} at carbon microdisks (Table IV) at a lower buffer concentration. The difference may be due to the use of an average diffusion coefficient in eq 16 for the latter estimate. A more exact model with separate diffusion coefficients for substrate and catalyst was used to analyze the glassy carbon data. Comparison of the $E^{\circ\prime}$ of the Co(II)/Co(I) couple to a correlation[42] of k_1 vs $E^{\circ\prime}$ of outer-sphere catalysts reacting with *t*-DBC predicts a k_1 of 0.02 M^{-1} s^{-1}, whereas the observed value is 5×10^6 M^{-1} s^{-1}. Thus, catalysis by vitamin B_{12r} is much more efficient than expected for an outer-sphere reaction, supporting an inner-sphere mechanism.

Apparent rate constants in the AOT microemulsion were about 3 orders of magnitude smaller than in acetonitrile/water. The k_1 measured in both media is for reaction of base-off cob(I)alamine with vicinal dibromide. Attenuation of rates is caused by the large unfavorable partition of the vicinal dihalides into isooctane (Table V), while vitamin B_{12} remains predominantly in water pools.

Relative k_1 values in water/MeCN for DBB:EDB:*t*-DBC were 1:2:4 as opposed to 1:4:20 in the microemulsion. The difference cannot be explained totally by partition of the substrate between isooctane and water. While the relative reactivity of EDB may increase because it partitions into water better than the other substrates, *t*-DBC is very poorly partitioned into water but has the largest relative rate. There are two possible explanations: (i) neglect of the reaction in isooctane is not justified; (ii) partition may be counterbalanced by specific interactions of the alkyl dibromides with AOT aggregates. Both factors may favor increased relative reactivity for *t*-DBC in the microemulsion since it is the most reactive in MeCN/water and also the most hydrophobic of the three substrates.

Conclusions

This work illustrates the possibilities of quantitative studies with microelectrodes in highly resistive w/o microemulsions. Analysis of diffusion coefficient data provided the microviscosity of the system and confirmation that vitamin B_{12} induces formation of larger surfactant aggregates in w/o microemulsions than in its absence. Comparisons of standard potentials with those in isotropic solutions led to identification of species involved in the electrode reactions of vitamin B_{12}. Relative reactivity for reductions of vicinal dibromides by cob(I)alamine was found to be modified in the microemulsion compared to an isotropic medium.

Acknowledgment. This work was supported by the donors of the Petroleum Research Fund, administered by the American Chemical Society, and partly by U.S. PHS Grant ES03154 awarded by the National Institute of Environmental Health Sciences. We thank Union Carbide for the carbon fibers, Alan Brown for preparing the microelectrodes, Thomas Leipert for help with NMR experiments, Dennis Evans for a preprint of ref 32a, and Shili Liu and the Environmental Research Institute, University of Connecticut, for access to electron-capture gas chromatography.

Supplementary Material Available: Details of calculations and figures showing voltammograms and plots of simulated steady-state catalytic efficiency vs log k_1 (8 pages). Ordering information is given on any current masthead page.

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Calculation of Correlation Times for the γ-Alumina-Supported Molybdenum Subcarbonyl, $Mo(CO)_3$(ads)

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Contribution from the Chemistry Department, Virginia Polytechnic Institute and State University, Blacksburg, Virginia 24061. *Received July 11, 1988*

Abstract: The theory of carbon-13 NMR line widths in the solid state for molecules with large chemical shift anisotropies is applied to the adsorbed molybdenum subcarbonyls $Mo(CO)_3$(ads) and $Mo(CO)_5$(ads). Correlation times for the rotation of the molybdenum subcarbonyl groups $Mo(CO)_3$(ads) and $Mo(CO)_5$(ads) on partially dehydroxylated alumina are calculated. Good agreement is obtained between data reported at observation frequencies of 15 to 75.5 MHz for carbon-13 for $Mo(CO)_3$(ads). The correlation time for this adsorbed species is calculated to have a lower limit of 4.6 ± 0.5 ms. The presence of broad lines in the room temperature spectra for $Mo(CO)_3$(ads) is thus explained by a slow molecular motion. An alternative explanation for the broad lines observed at room temperature is a distribution of overlapping isotropic chemical shifts for different adsorption sites. This explanation, however, does not account for the variation of line width (in Hz) with observation frequency. Data for $Mo(CO)_5$(ads) are available at observation frequencies of 15 to 90.5 MHz. A good fit to the experimental data is obtained assuming either long or short correlation times for this species. Thus literature estimates of $<10^{-6}$ s for the correlation time for this species cannot be confirmed with certainty from the analysis presented here.

After the initial detection of γ-alumina-supported molybdenum subcarbonyls by CP–MAS ^{13}C NMR, it was suggested that the surface species, $Mo(CO)_3$(ads) and $Mo(CO)_5$(ads), are involved in motional processes which average the carbonyl ligands.[1] This argument was used to explain the simple spectra in the carbonyl region under CP–MAS conditions. More recent broad-line and CP–MAS NMR studies[2,3] on the molybdenum carbonyl/alumina system have refined the understanding of the dynamic behavior of the subcarbonyls. In this manuscript we show that all the published work on these subcarbonyls and previously unpublished spectra from our laboratory can be used to obtain correlation times for $Mo(CO)_3$(ads).

The CP–MAS ^{13}C NMR work of Shirley noted that the chemical shift anisotropy (CSA) of $Mo(CO)_3$(ads) is very large (390 ± 50 ppm).[2] Thus, it was proposed that any motion involving

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[2] Shirley, W. M. *Z. Phys. Chem.* **1987**, *152*, 41.

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Table I. Data for γ-Alumina-Supported Molybdenum Subcarbonyls

					calcd correlation time				
	subcarbonyl	Larmor frequency, ω_o (MHz)	spinning rate, ω_r (Hz)	line width Δ (Hz)	slow exchange limit (s)	fast exchange limit (s)	$\frac{3\omega_o^2\delta^2}{10\omega_r^2}$	$\frac{2\omega_o^2\delta^2}{5}$ (s^{-2})	ref
1	$Mo(CO)_3$(ads)	15.0	2200	290 ± 30	0.0032	4.8×10^{-5}	0.95	6.13×10^6	1
2		22.7	3000	360 ± 30	0.0032	2.6×10^{-5}	1.17	14.0×10^6	this work
3		37.7	3700	600	0.0035	1.6×10^{-6}	2.12	38.7×10^6	2
4		75.5	4600	1300 ± 300	0.0042	0.84×10^{-6}	5.51	15.5×10^6	this work
1	$Mo(CO)_5$(ads)	15.0	2200	72 ± 6	0.013	12×10^{-6}	0.95	6.13×10^6	1
2		22.7	3000	74 ± 15	0.016	5.3×10^{-6}	1.17	14.0×10^6	this work
3		37.7	3700	84 ± 15[a]	0.025	2.2×10^{-6}	2.12	38.7×10^6	2
4		50.1	2700	120 ± 17	0.051	1.8×10^{-6}	7.04	68.4×10^6	this work[b]
5		75.5	3300	167 ± 13	0.063	1.1×10^{-6}	10.7	15.5×10^6	this work
6		90.5	2200	250	0.014	1.11×10^{-6}	34.8	22.3×10^6	3

[a] Estimated from the spectrum in ref 2. [b] Spectrum obtained for one of our samples by Dr. Mark J. Sullivan, JEOL, Inc.

the carbonyl ligands cannot occur at frequencies greater than 15 kHz. However, the observed CSA for $Mo(CO)_5$(ads) was significantly reduced to 203 ± 40 ppm. The reduction was attributed to a motional process. It was suggested that this motional process might be anisotropic since the upfield first-order spinning sideband was slightly larger than the downfield first-order spinning sideband which would be consistent with the observed powder pattern reversal.[4]

Oldfield et al.[3] have reported unique cis and trans signals for the $Mo(CO)_5$(ads) species. These were observed in the nondecoupled MAS spectrum which yielded a splitting of the downfield spinning sidebands corresponding to two centerbands at 210 and 204 ppm. The zeroth-order sidebands were not observable because of the presence of an intense $Mo(CO)_6$(phys) signal which obscured the central region of the sideband pattern. The presence of the two signals was further demonstrated by broad-line ^{13}C NMR spectra which contained two overlapping powder patterns with the predicted relative intensities, 4:1. The CSA for the cis carbonyls is considerably narrowed and reversed and was attributed to partial averaging by rapid ($\gg 10^5$ s^{-1}) anisotropic molecular motion. Variable-temperature broad-line ^{13}C NMR spectra demonstrated that the signal for the cis carbonyls broadens at lower temperatures as the rate of the anisotropic motional averaging decreases. The anisotropic motion of $Mo(CO)_5$(ads) was identified as a free rotation about the Mo–surface bond.

A theoretical relationship derived by Suwelack, Rothwell, and Waugh[5] has been shown to accurately describe slow molecular motions in solids. This technique is applicable to spin systems which are dominated by chemical shift interactions and not dipolar interactions. Thus the theory is appropriate for metal carbonyls which have very large chemical shift anisotropies. The calculation of the correlation times reported here for the carbonyl ligands in the surface species, $Mo(CO)_3$(ads) and $Mo(CO)_5$(ads), is made within the theoretical framework provided by Suwelack, Rothwell, and Waugh.[5] This allows us to test the hypothesis that motional processes are responsible for the variation in observed line widths in spectra as reported in the literature obtained at different field strengths and sample spinning rates for the adsorbed subcarbonyls.

Experimental Section

Methods of sample preparation and 15-MHz CP-MAS measurements are described in ref 1. The 22.6-MHz CP-MAS spectra were recorded with a Chemagnetics 2.1 T superconducting magnet and Chemagnetics probe interfaced to a JEOL FX60QS NMR console. Frequency conversions to operate the spectrometer at 2.1 T were done locally. The samples were loaded into Delrin rotors and sealed with Plasticine under nitrogen to prevent sample decomposition. The Delrin rotor material yields a single resonance at 89.3 ppm and was used as the chemical shift reference. The 75.5-MHz CP-MAS spectra were obtained on a Bruker MSL-300. Samples for this spectrometer were packed in aluminum oxide rotors with boron nitride end caps. The hole in the end caps was plugged with Plasticine; dry nitrogen, from liquid nitrogen boil-off, was used for the spinner and bearing gas to help prevent sample decomposition during data acquisition. A sample of adamantane was used as a chemical shift reference.

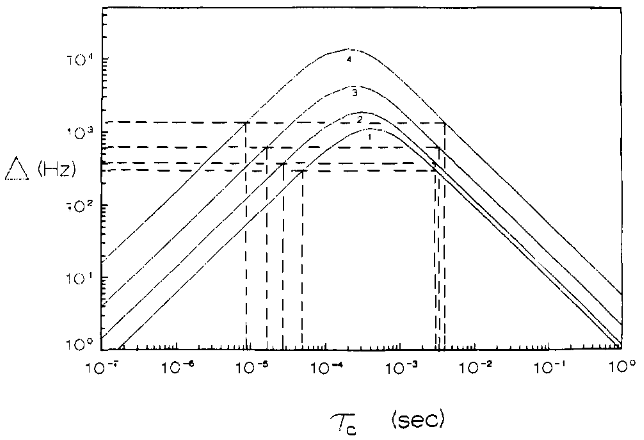

Figure 1. Line-width versus τ_c plots for $Mo(CO)_3$(ads) at field strengths and spinning rates given in Table I.

Results

The CP-MAS spectra of $Mo(CO)_3$(ads) (223 ppm) and $Mo(CO)_5$(ads) (203 ppm) measured at various field strengths have been reported in the literature.[1-3] In addition, we have also obtained spectra at carbon observation frequencies of 22.6, 50.1, and 75.5 MHz. Pertinent data obtained from all of these spectra are summarized in Table I. It is immediately apparent from these data that the line widths (in Hz) are different at various field strengths and/or spinning rates. This observation, along with the fact that the chemical shift anisotropies are reduced compared to static metal carbonyls, is evidence that the source of the line broadening is not due to simple chemical shift dispersion. Furthermore, the experimental line widths may be predicted with the assumption that the surface carbonyls are involved in motional processes.

The theoretical framework for detecting slow molecular motions in solids has been developed by Suwelack, Rothwell, and Waugh.[5] Their derived expression is given in eq 1 for isotropic motions,

$$\Delta = \frac{2}{15}\omega_0^2\delta^2\left(1 + \frac{\eta^2}{3}\right)\left(\frac{\tau_c}{1 + 4\omega_r^2\tau_c^2} + \frac{2\tau_c}{1 + \omega_r^2\tau_c^2}\right) \quad (1)$$

where ω_0 is the field strength in MHz, δ is the chemical shift anisotropy ($\sigma_{33} - \bar{\sigma}$) in ppm, η is the asymmetry parameter (($\sigma_{22} - \sigma_{11})/(\sigma_{33} - \sigma_{av}$)), ω_r is the sample spinning rate in Hz, and τ_c is the correlation time for the motion of the spins. For Lorentzian line shapes, the line width is given by, $\Delta = 2T_2^{-1}$ This equation shows the dependence of the experimentally observed line width, Δ, on the correlation time, τ_c, and the various experimental conditions of ω_0 and ω_r.

Equation 1 was used to calculate a series of line width versus correlation time curves for the $Mo(CO)_3$(ads) and $Mo(CO)_5$(ads) species. The curves for $Mo(CO)_3$(ads) are shown in Figure 1. These were calculated using the reported experimental conditions

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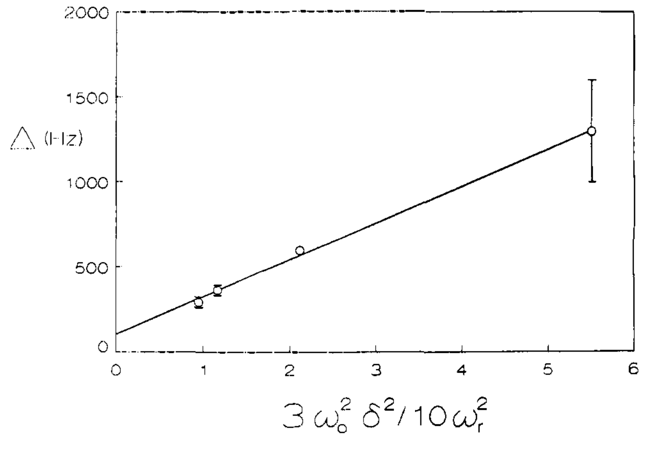

Figure 2. Plot of Δ versus $3\omega_0^2\delta^2/(10\omega_r^2)$ for $Mo(CO)_3$(ads), $\omega_r^2 \gg 1$. Least-squares slope is 4.6 ± 0.5 ms.

of ω_0 and ω_r. In our spectra of $Mo(CO)_5$(ads), as well as in the spectrum reported by Shirley,[2] apparently only the signal due to the cis carbonyl ligands was detected. However, the spectra are consistent with an anisotropic rotation about the Mo–surface bond which would average the CSA of the cis carbonyl ligands. A δ value, as defined above, $(\sigma_{33} - \bar{\sigma})$, of 260 ppm estimated by Shirley[2] for $Mo(CO)_3$(ads) was used to calculate the Δ versus τ_c curves for this species. A value of 261 ppm was used to calculate the curves for $Mo(CO)_5$(ads) which is the δ value for the cis carbonyl ligands in $Mo(CO)_5(CH_3CN)$.[3] The value of η was taken to be zero in all cases. Using the experimentally determined line widths, the calculated correlation times in the fast- and slow-exchange limits are given in Table I.

The agreement between the calculated correlation times under different experimental conditions for the carbonyl ligands in $Mo(CO)_3$(ads) is very good and suggests that a motional process, which is in the slow-exchange regime $(\omega_r^2\tau_c^2 \gg 1)$ at room temperature, may be responsible for the line-width variations. Unfortunately, the determinations of the correlation times for $Mo(CO)_5$(ads) are equally consistent with a motion in either the fast $(\omega_r^2\tau_c^2 \ll 1)$ or slow-exchange region; thus a distinction between the two regimes cannot be made.

In the slow- and fast-exchange regimes, the line width is given by eq 2 and 3, respectively. Thus, plots of Δ versus either the

$$\Delta = \frac{3}{10}\frac{\omega_0^2\delta^2}{\omega_r^2}\left(\frac{1}{\tau_c}\right),\ \omega_r^2\tau_c^2 \gg 1 \qquad (2)$$

$$\Delta = \frac{2}{5}\omega_0^2\delta^2(\tau_c),\ \omega_r^2\tau_c^2 \ll 1 \qquad (3)$$

quantity $3\omega_0^2\delta^2/(10\omega_r^2)$ or $2\omega_0^2\delta^2/5$ should yield straight lines having a slope of either τ_c^{-1} or τ_c, respectively.

As expected, for $Mo(CO)_3$(ads), the graph of the line widths in the slow-exchange regime yields a straight line which is well within the estimated error of the line-width measurements (Figure 2). However, the plot for the fast-exchange regime is not linear. The least-squares slope of the plot in the slow-exchange region is 220 ± 20 Hz which yields a τ_c value of 4.6 ± 0.5 ms.

For $Mo(CO)_5$(ads), the data plotted in both the fast-exchange and slow-exchange regime are linear within the estimated error limits. This is especially true if the point from the data of Oldfield et al.[3] is omitted. This is warranted since this spectrum was obtained without proton decoupling which would allow further broadening of the resonance over that of CSA motional averaging due to ^1H–^{13}C dipolar interactions between the carbonyls and surface hydroxyl groups. Thus using the model of isotropic motion provided by the theory of Suwelack, Rothwell, and Waugh, a distinction between exchange in the fast or slow limit cannot be made. Good evidence for a fast rotation is provided by the experiments of Oldfield et al.[3]

The dynamic behavior of $(\eta^6\text{-}C_6H_5CH_3)Mo(CO)_3$ has recently been reported.[6] Analysis of the line widths using the jump model of Suwelack, Rothwell, and Waugh yields the data given in Table II. At room temperature a correlation time of 1.83 ± 0.05 ms is calculated for tricarbonyl group rotation.

Table II. Data for $Mo(CO)_3(\eta^6\text{-}C_6H_5CH_3)$[a]

larmor frequency (MHz)	spinning rate (Hz)	temp (K)	line width (Hz)	correlation[b] time (s)	jump rate $(1/\tau_c)$ (s^{-1})
22.7	2850	298	684	0.00183	546
	2600	283	94	0.00166	60.2
	2560	273	78	0.0206	48.5
	2510	263	21.5	0.0777	12.9
	2460	243	15.6	0.112	8.93

[a] Data from ref 6. [b] Values of Δ = 261 ppm and $\eta = 0$ were used in the correlation time calculation (see text).

Discussion

The agreement between the calculated correlation times for the carbonyl ligands in the species $Mo(CO)_3$(ads) at room temperature and various field strengths and spinning rates is very good. The theoretical curves of Δ versus τ_c further show that the motional process for $Mo(CO)_3$ is in the slow-exchange regime $(\omega_r^2\tau_c^2 \gg 1)$. These results agree with previous studies. On the basis of the large chemical shift anisotropy of $Mo(CO)_3$(ads), Shirley[2] estimated that any motion involving the carbonyl ligands must be occurring at a rate less than 15 kHz. The correlation time of 4.6 ± 0.5 ms calculated for $Mo(CO)_3$(ads) is consistent with this. Oldfield et al.[3] attributed a rapid $(\gg 10^5\ s^{-1})$ anisotropic motion for the cis carbonyls in $Mo(CO)_5$(ads).

It should be noted that the likelihood of different adsorption sites for $Mo(CO)_3$(ads) and $Mo(CO)_5$(ads) is very high;[7] thus the analysis here gives the average correlation time for all sites. However, a distribution of sites cannot adequately explain the variation of line widths with field strength and spinning rate (vide infra).

The correlation time calculated for $Mo(CO)_3$(ads) is only slightly slower than the value of 1.83 ± 0.05 ms calculated for the model compound, $Mo(CO)_3(\eta^6\text{-}C_6H_5CH_3)$ (Table II). In this complex, a rotational motion of the carbonyl ligands was detected in the solid state by variable-temperature CP-MAS ^{13}C NMR.[6] The data for this complex agrees well with the jump model proposed by Suwelack, Rothwell, and Waugh and demonstrates the linear dependence of the experimental line width versus the jump rate, λ, in the slow-motion regime, i.e., $\lambda < \omega_r$.

Other model compounds studied by variable-temperature CP-MAS ^{13}C NMR [$Cr(CO)_3(\eta^6\text{-}C_6H_5CH_3)$, $Mo(CO)_3(\eta^6\text{-}C_6H_6)$, $Mo(CO)_3(CH_3CN)_3$, and $Mo(CO)_3$(diglyme) (diglyme = $CH_3OCH_2CH_2OCH_2CH_2OCH_3$)] show that tricarbonyl group rotations only occur in the solid state for the $(\eta^6\text{-arene})M(CO)_3$ complexes.[8] This is presumably due to the fact that the nondirectional character of the arene–M bond allows a very low barrier for rotation about this bond (71 kJ/mol for $Mo(CO)_3(\eta^6\text{-}C_6H_5CH_3)$).[6]

An alternative explanation for the variation of the line width as a function of field for the $Mo(CO)_3$(ads) species is that there may exist many different adsorption sites, each with a different chemical shift and magnitude of ^{27}Al–^{13}C and ^{95}Mo–^{13}C dipolar coupling. The overlapping signals would then give a broad line, and with increasing field the line width (in ppm) will narrow as the residual dipolar interactions are diminished.

The argument against this explanation is as follows. The chemical shift dispersion in ppm is field independent. As the field is increased the resolution will improve and distinct signals for the different sites should begin to emerge. For the signal to remain broad and amorphous with increasing field (as it, in fact, does) requires a fortuitous overlap of the signals from many different sites. Also the line width in ppm for $Mo(CO)_6$ narrows signifi-

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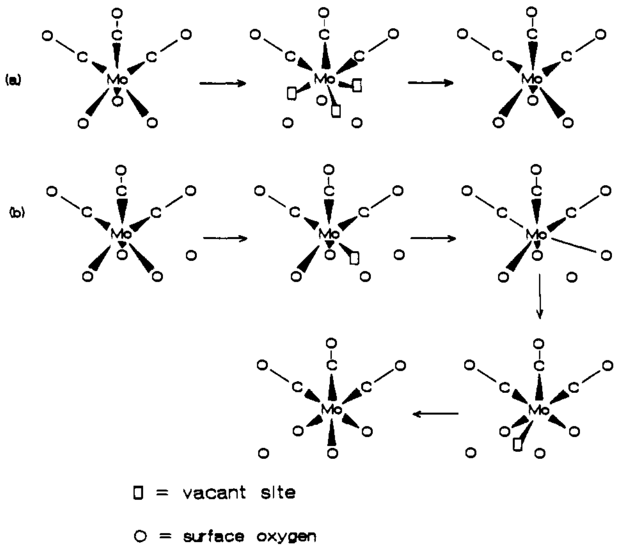

Figure 3. Schematic representations of two possible mechanisms for the motion of $Mo(CO)_3$(ads).

cantly as field increases (6 ppm at an observation frequency of 15 MHz to 2.4 ppm at 75.5 MHz), which also argues for significantly better resolution at higher field for static metal carbonyls. Since multiple sites are not observed with increasing field for $Mo(CO)_3$(ads), we feel that the best available explanation both for the broad line observed for this species at room temperature and the variation of the line width (in Hz) with field lies in the motion of the adsorbed species. Nonetheless, the possibility of a dispersion of chemical shifts means that the value of 4.6 ± 0.5 ms estimated for the correlation time represents a lower limit.

The slower correlation time calculated for $Mo(CO)_3$(ads) indicates a somewhat higher barrier for this motion compared to the rotational motion of the $-Mo(CO)_3$ fragment about the Mo–(η^6-$C_6H_5CH_3$) bond. This may reflect the directional nature of the Mo–O surface bonds. In order for the $-Mo(CO)_3$ fragment to rotate, these surface Mo–O bonds must break and re-form. Assuming that the carbonyl ligands are not exchanged in a pairwise fashion similar to the axial–equatorial exchange postulated in $Fe(CO)_5$,[9] there are two types of motion which could cause motional averaging. The first mechanism is a concerted 3-fold jump as detected in the complex, $Mo(CO)_3(\eta^6$-$C_6H_5CH_3)$.[6] This is shown schematically in Figure 3a. The second mechanism would be a stepwise motion among neighboring oxygen surface ligands as shown in Figure 3b. The fact that the $-Mo(CO)_3$ group is static in $Mo(CO)_3$(diglyme), where a concerted 3-fold jump would be possible but not a stepwise migration, favors the second mechanism.

This surface motion suggests that a coordination site at molybdenum may be obtained by breaking a surface O–Mo bond. The activity of the $Mo(CO)_3$(ads) group as a precursor to olefin metathesis may be due to its ability to coordinate substrates at the expense of surface–Mo bonds.

The turnover number for propylene metathesis calculated for $Mo(CO)_3$(ads) is 0.013 s^{-1} at 53 °C.[10] This indicates that the motion of $Mo(CO)_3$(ads), and thus the availability of open coordination sites, is not the rate-determining step for the metathesis reaction (the jump rate for $Mo(CO)_3$(ads) is ca. 20 s^{-1} at 25 °C and would be even faster at 53 °C).

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Supplementary Material Available: Correlation time versus line-width plots and least-squares line plots for $Mo(CO)_5$(ads) and (η^6-$C_6H_5CH_3$)$Mo(CO)_3$ (5 pages). Ordering information is given on any current masthead page.

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