Matrix Photochemistry of Methyltrioxorhenium(VII), CH_3ReO_3: Formation of the Methylidene Tautomer $H_2C{=}Re(O)_2OH$ and Its Potential Relevance to Olefin Metathesis

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IR spectroscopic measurements have been used to chart the reactions activated by irradiating argon matrices doped with methyltrioxorhenium, CH_3ReO_3 (**1**), first with light at wavelengths near 254 nm and subsequently with broad-band UV−visible light ($200 \leq \lambda \leq 800$ nm). Assignments of the IR absorption bands are made and their carriers identified on the basis of experiments with CD_3ReO_3 or $^{13}CH_3ReO_3$ and by comparison either with the vibrational properties forecast by density functional theory (DFT) calculations or with those of related molecules. Photoexcitation at $\lambda =$ ca. 254 nm results in tautomerization of CH_3ReO_3 to the methylidene derivative $H_2C{=}Re(O)_2OH$ (**2**), the properties of which have been determined, partly by experiment and partly by DFT calculations. The mechanism of the change is discussed, as is the relevance of the tautomeric product to the catalytic action of CH_3ReO_3 in olefin metathesis. Broad-band UV−visible radiation leads to the formation of a rhenium carbonyl, **3**, possibly the Re(V) compound $H_2Re(CO)(O)OH$.

1. Introduction

With the development of an efficient method of synthesizing methyltrioxorhenium(VII), CH_3ReO_3 (**1**),[1] the role of the compound in promoting and catalyzing numerous organic reactions has attracted much attention.[2,3] Indeed, **1** is probably the most versatile organometallic catalyst reported to date. There are two main areas of activity, namely (i) oxidation reactions such as olefin epoxidation, Baeyer−Villiger reactions, and aromatic oxidation[3−6] and (ii) olefin isomerization and metathesis.[7] The peroxo derivatives $CH_3Re(O)_2(O_2)$ and $CH_3Re(O)(O_2)_2(OH_2)$ are thought to be the active intermediates in the oxidation reactions catalyzed by **1**, a view upheld by the isolation and structural and spectroscopic characterization of these compounds.[8,9] In contrast, little or no direct evidence has come to light regarding the intermediate or intermediates responsible for activating olefin metathesis and isomerization reactions, although a species containing an $H_2C{=}Re$ unit has been proposed as the active agent.[2,10]

The potential of complexes containing rhenium−carbon multiple bonds to catalyze reactions of alkenes and alkynes has stimulated no small amount of research, but few of the compounds described to date feature rhenium in the oxidation state +7 and still fewer feature oxorhenium units.[10,11] A rare example of a structurally authenticated alkylidene rhenium(VII) ox-

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ide is $Me_3CCH_2Re[C(H)CMe_3]O_2$, as reported by Hoffman et al.;[12] this is produced with neopentane by photolysis of a pyridine solution of $(Me_3CCH_2)_3ReO_2$.

Matrix isolation has proved to be a highly informative device for detecting and identifying reactive intermediates, usually generated in situ by photolysis.[13] The optical spectrum of **1** dissolved in *n*-hexane displays three bands in the UV centered at 205, 231, and 260 nm,[14] and studies of such a solution suggest that the primary photoprocess induced by UV irradiation is homolysis of the Re−C bond and subsequent interaction of the photoproducts with the solvent molecules of nonaqueous media, ultimately yielding CH_4 and ReO_3. On the other hand, exploratory experiments carried out in Oxford and at the University of Giessen[15] revealed significantly different behavior on the part of **1** when isolated in a solid argon matrix at low temperatures.

Here we elaborate on a preliminary report[16] of the detailed and systematic study we have carried out on the matrix photochemistry of **1**. Individual molecules have been monitored and identified by their IR spectra, the conclusions being endorsed (i) by the response to D or ^{13}C substitution, (ii) by comparison of the frequencies and intensities in IR absorption with those deduced by density functional theory (DFT) calculations, and (iii) by analogies with the spectra of related carbene and Re═O derivatives, e.g. MCH_2 (M = Cr, Mn, Co, Ni, Cu)[17] and ReO_2F_3.[18] Hence, the primary reaction brought about by irradiation into the UV absorption near 260 nm will be shown to involve tautomerization of **1** to the methylidene hydroxo derivative $H_2C{=}Re(O)_2OH$ (**2**). In addition to a discussion of the mechanism of this change, the properties of **2** are discussed with particular reference to ways in which hydrogen transfer, with the formation of an $H_2C{=}Re$ unit, might be promoted by the action of a silica support.[10] Under the action of broad-band UV−visible light ($200 \leq \lambda \leq 800$ nm), a further change occurs to yield the rhenium carbonyl **3**. With only a single ν(CO) IR absorption to work from, this cannot be identified positively, but the rhenium(V) dihydride $H_2Re(CO)(O)OH$ is a likely candidate.

2. Experimental Section

Methyltrioxorhenium (**1**) was prepared from Re_2O_7, $(CF_3CO)_2O$, and $Bu^n{}_3SnMe$ according to the procedure described by Herrmann et al.[19] and purified by vacuum sublimation of the crude product at 70 °C. Its purity was checked by reference both to the ^1H NMR spectrum of a toluene-d_8 solution (singlet at δ_H 2.64) and to the IR spectrum of the vapor isolated in an argon matrix (q.v.). The isotopomers CD_3ReO_3 (**1-*d*₃**) CDH_2ReO_3 (**1-*d***), and $^{13}CH_3ReO_3$ (**1-^{13}*C***) were each prepared by the same method using the appropriately substituted stannane, viz. $Bu^n{}_3SnCD_3$, $Bu^n{}_3SnCDH_2$, and $Bu^n{}_3Sn^{13}CH_3$, respectively. Argon was used as received (BOC, research grade).

The vapor over a sample of **1** held at 0 °C was co-deposited continuously with an excess of argon on a CsI window cooled normally to ca. 14 K by means of a Displex closed-cycle refrigerator (Air Products Model CS 202); fuller details of the apparatus are given elsewhere.[20] Typical deposition rates were ca. 3 mmol of matrix gas/h, continued over a period of 2 h. Following deposition and IR analysis of the resulting matrix, the sample was exposed first to UV radiation, normally with λ = ca. 254 nm. Once the effects of such photolysis had been assessed, the sample was irradiated with light of various wavelengths, e.g. $\lambda = 200-800$ or $400-800$ nm. The photolysis source was a Spectral Energy Hg−Xe arc lamp operating at 800 W, the output from which was invariably limited by a water filter to absorb IR radiation and so minimize any heating effects. A range of filters was used to transmit radiation at particular wavelengths (notably Oriel interference filters for $\lambda = 254$ or 313 nm, with fwhh = 16−17 nm in each case, and an Oriel high-energy band-pass filter for $\lambda > 400$ nm).

IR spectra of the matrix samples were recorded with either a Mattson Instruments "Galaxy" 6020 or a Nicolet "Magna" 560 FT-IR spectrometer over the range 4000−400 or 4000−225 cm^{-1}, respectively. Measurements were made typically at a resolution of 0.5 cm^{-1} and with an accuracy of ± 0.1 cm^{-1}.

Density functional theory (DFT) calculations were performed using the GAUSSIAN 98 program package.[21a] The geometries were optimized at the BPW91 level of density functional theory with the gradient correction of Becke[21b−d] for exchange and that of Perdew−Wang[21e] for correlation. A quasi-relativistic effective-core potential (ECP) and (8s6p3d)/[3s2p2d] basis from Hay and Wadt[21f,g] was used for Re in conjunction with Dunning bases[21h] on C, O, and H. This was our standard basis set and will be denoted "LANL2DZ". Additional calculations employed an f-type polarization function on Re[21i] and standard 6-31G(d,p) basis set on C, O, and H.[21j−l] This basis set combination, denoted "II", was used solely for the geometry optimizations and frequency calculations of compounds **1**−**3**, since the BPW91/II calculations showed better agreement between the experimental and calculated frequencies than did

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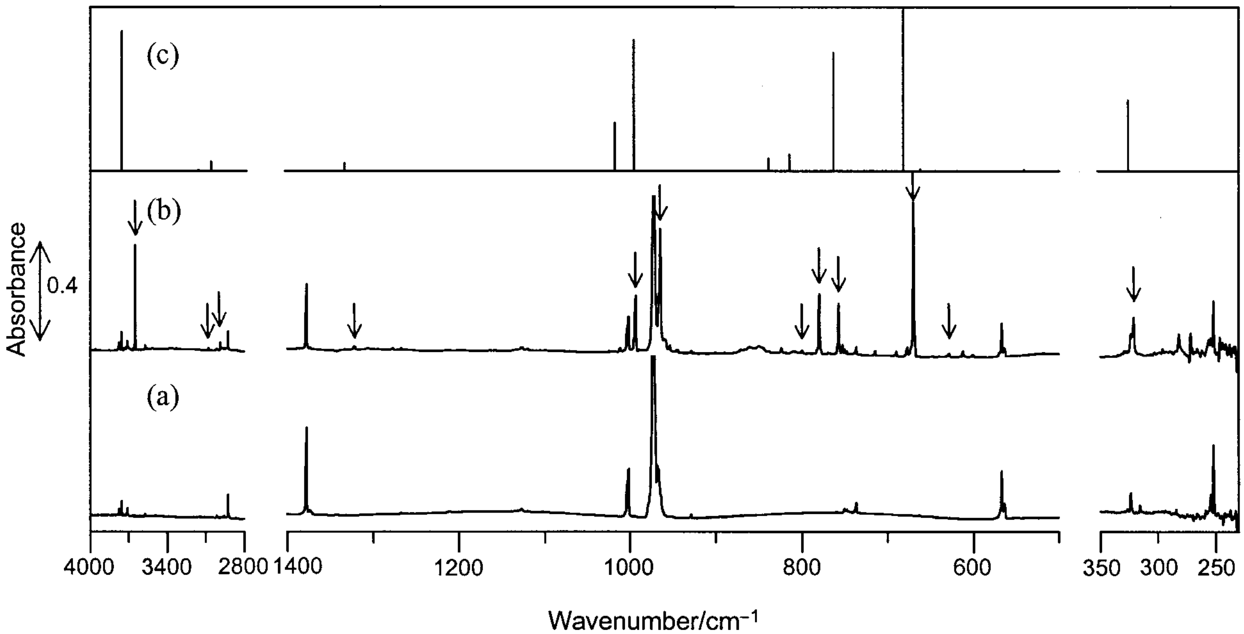

Figure 1. IR spectra of CH_3ReO_3 (**1**) isolated in an Ar matrix at ca. 14 K (a) after deposition and (b) following photolysis at λ = ca. 254 nm for 15 min. (c) IR spectrum calculated for the methylidene tautomer $H_2C{=}Re(O)_2OH$ (**2**). The arrows indicate bands assigned to **2**.

Table 1. Observed and Calculated Fundamental Vibrational Frequencies for CH_3ReO_3 Isolated in an Argon Matrix at 14 K[a]

CH_3ReO_3		$^{13}CH_3ReO_3$		CD_3ReO_3		
obsd	calcd[b]	obsd	calcd[b]	obsd	calcd[b]	mode
3012.8 (0.5)	3097.5 (0.05)	3005.3 (0.4)	3086.3 (0.04)	2255.5 (0.5)	2293.9 (0.1)	$\nu_{as}(CH_3)$, ν_7
2925.5 (4)	2994.5 (5)	2920.7 (3)	2992.1 (4)	2123.7 (2)	2144.2 (4)	$\nu_s(CH_3)$, ν_1
1966.9	2028.8	1965.8	2028.7	1965.8	2026.6	$\nu_2 + \nu_8$
1376.8 (11)	1393.3 (8)	1373.5 (8)	1390.7 (8)	1013.2 (3)	1009.3 (3)	$\delta_{as}(CH_3)$, ν_9
1210.4 (0.1)	1219.1 (1)	1201.5 (0.2)	1211.1 (1)	926.3 (0.3)	944.4 (3)	$\delta_s(CH_3)$, ν_4
1000.7 (7)	1027.2 (14)	1000.8 (7)	1027.2 (14)	1001.3 (7)	1027.5 (15)	$\nu_s(ReO_3)$, ν_2
970.3 (100)	1001.6 (100)	970.2 (100)	1001.5 (100)	969.5 (100)	999.1 (100)	$\nu_{as}(ReO_3)$, ν_8
735.4 (1)	739.1 (2)	730.5 (3)	733.8 (2)	567.8 (0.4)	567.7 (0.7)	$\rho(CH_3)$, ν_{10}
564.9 (8)	562.9 (13)	550.0 (6)	546.3 (13)	513.7 (6)	512.9 (11)	$\nu(Re{-}C)$, ν_3
323.7 (2)	325.2 (2)	323.5 (3)	325.2 (2)	323.5 (3)	325.1 (2)	$\delta_s(ReO_3)$, ν_5
253.0 (7)	265.0 (9)	251.5 (10)	264.8 (9)	252.7 (11)	264.0 (9)	$\rho(ReO_3)$, ν_{12}
c	211.0 (0.2)	*c*	208.6 (4)	*c*	194.2 (0.1)	$\delta_{as}(ReO_3)$, ν_{11}
c	166.7 (0)	*c*	166.7 (0)	*c*	119.4 (0)	CH_3 torsion, ν_6

[a] Frequencies in cm^{-1}; intensities (in parentheses) normalized to that of the most intense band set equal to 100. [b] DFT calculations were carried out on CH_3ReO_3 and its isotopomers in Gaussian 98 at the BPW91/II level of theory. [c] Below the limit of detection.

the BPW91/LANL2DZ calculations. Initial optimizations of the molecules **1**–**3**, $[H_2Si(OH)]_2O$, and **7**–**9** were carried out without symmetry restrictions and started from geometries without any symmetry. Invariably, however, the optimizations on **1**, **2**, and the disilanol $[H_2Si(OH)]_2O$ converged to C_{3v}, C_s and C_2 symmetry, respectively. The DFT Cartesian force constants and Cartesian dipole moments were determined at the theoretical equilibrium geometries. The vibrational frequencies calculated for the optimum geometries and cited hereafter differ from those in ref 16 in being unscaled. The different degrees of anharmonicity displayed by the individual vibrational modes make inappropriate the use of a single scaling factor.

3. Results

The IR spectrum of CH_3ReO_3 (**1**), isolated in an argon matrix at ca. 14 K, is depicted in Figure 1a. As revealed by electron-diffraction studies of the vapor[22] and neutron-diffraction studies of the crystalline powder,[23] the CH_3ReO_3 molecule has a staggered structure with C_{3v} symmetry, so that the 18 vibrational fundamentals are distributed over the representations $5a_1 + 1a_2 + 6e$. With reference to an earlier vibrational analysis,[24] the main features of the spectrum may be assigned as detailed in Table 1. The most prominent band, occurring at 970.3 cm^{-1}, arises from the $\nu_{as}(ReO_3)$ mode, with an appreciably weaker band to high frequency (1000.7 cm^{-1}) due to $\nu_s(ReO_3)$. Other noteworthy aspects are the weak absorptions associated with the ν(CH) fundamentals and located at 3012.8 ($\nu_{as}(CH_3)$) and 2925.5 cm^{-1} ($\nu_s(CH_3)$), and a rather stronger absorption at 564.9 cm^{-1} attributable to the ν(ReC) mode. Table 1 lists in addition the frequencies and relative intensities for the

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Table 2. Observed and Calculated Fundamental Vibrational Frequencies for $H_2C{=}Re(O)_2OH$ (2) Isolated in an Argon Matrix at 14 K[a]

$H_2{}^{12}CRe(O)_2OH$		$H_2{}^{13}CRe(O)_2OH$		$D_2{}^{12}CRe(O)_2OD$		
obsd	calcd[b]	obsd	calcd[b]	obsd	calcd[b]	mode
						a′
3650.2 (100)	3767.6 (87)	3650.4 (100)	3767.6 (87)	2694.2 (73)	2743.6 (63)	ν(O−H)
2985.8 (3)	3074.3 (5)	2980.2 (4)	3068.8 (5)	2195.1 (5)	2229.4 (6)	$\nu_s(CH_2)$
1320.9 (2)	1329.6 (5)	1311.8 (2)	1321.0 (5)	1009.9 (2)	1045.9 (6)	$\delta(CH_2)$
992.2 (25)	1014.8 (30)	991.9 (26)	1014.7 (30)	992.2 (31)	1013.5 (42)	$\nu_s(ReO_2)$
799.2 (2)	837.2 (8)	798.7 (3)	834.1 (9)	622.6 (3)	647.8 (3)	δ(Re−O−H) +
778.8 (34)	813.1 (10)	768.3 (53)	791.0 (14)	578.9 (43)	571.7 (81)	$\rho(CH_2)$ +
756.4 (30)	761.7 (73)	739.6 (19)	756.2 (67)	685.9 (10)	716.8 (6)	ν(Re═C)
668.4 (83)	681.9 (100)	668.8 (87)	681.9 (100)	666.2 (69)	682.5 (75)	ν(Re−OH)
[c]	294.0 (2)	[c]	294.0 (2)	[c]	293.6 (2)	ReO_2 wag
[c]	262.4 (1)	[c]	262.2 (1)	[c]	259.4 (2)	ReO_2 scissor
[c]	246.2 (3)	[c]	242.2 (3)	[c]	223.4 (3)	δ(CReOH)
						a″
3079.6 (3)	3174.4 (0.6)	3068.4 (1)	3161.7 (0.6)	2315.2 (1)	2360.4 (0.3)	$\nu_{as}(CH_2)$
963.3 (64)	993.0 (81)	963.4 (80)	992.9 (81)	961.8 (100)	990.8 (100)	$\nu_{as}(ReO_2)$
627.9 (3)	661.4 (1)	625.7 (5)	656.4 (2)	500.2 (2)	517.6 (0.3)	CH_2 scissor
[c]	540.5 (0.2)	[c]	539.8 (0.2)	[c]	396.4 (0.01)	CH_2 wag
321.2 (33)	324.3 (42)	320.7 (38)	323.6 (43)	239.3 (19)	260.2 (6)	δ(Re−O−H)
[c]	274.0 (15)	[c]	271.1 (15)	[c]	243.6 (15)	$\delta(CReO_2)$
[c]	239.4 (0.03)	[c]	239.4 (0.03)	[c]	214.1 (16)	$\delta(CReO_2)$

[a] Frequencies in cm^{-1}; intensities (in parentheses) normalized to that of the most intense band set equal to 100. [b] DFT calculations were carried out for species **2** in Gaussian 98 at the BPW91/II level of theory. [c] Feature too weak to be observed, or below the limit of detection.

corresponding features of the isotopomers CD_3ReO_3 (**1-*d*₃**) and $^{13}CH_3ReO_3$ (**1-¹³*C***). All the assignments are consistent not only with those proposed earlier[24] but also with the observed isotopic shifts and with the results of our DFT calculations. How well these calculations reproduce the geometry of the CH_3ReO_3 molecule in its electronic ground state, as determined by electron-diffraction measurements,[22] is demonstrated by the following comparison (distances in Å, angles in deg; calculated dimensions first (r_e, $\angle_e$), followed by experimentally determined values (r_a, $\angle_a$)): r(Re═O), 1.704, 1.709(3); r(Re−C), 2.067, 2.060(9); r(C−H), 1.101, 1.105(12); ∠O═Re═O 112.6, 113.0(3); ∠C−Re═O 106.2, 106.0(2); ∠Re−C−H 109.3, 112(3). Taken with the close agreement between the observed and calculated vibrational properties for **1**, **1-*d*₃**, and **1-¹³*C***, with an rms deviation for 30 frequencies of 2.24%, this gives us considerable confidence in the ability of the DFT methods we have used to model the properties not only of **1** but also of related organorhenium compounds.

Exposure of the argon matrix to UV radiation having λ = ca. 254 nm for several minutes resulted in the decay of the IR absorptions due to **1** with the simultaneous appearance of new absorptions. Continued photolysis at this wavelength for a period of 60 min led to the uniform growth of the new bands, thereby identifying a common origin **2**; such growth was at the further expense of the bands due to the parent molecule (Figure 1b). Hence, we find that **2** absorbs at 3650.2, 3079.6, 2985.8, 1320.9, 992.2, 963.3, 799.2, 778.8, 756.4, 668.4, 627.9, and 321.2 cm^{-1} (see Table 2), with the most prominent and distinctive features being those at 3650.2, 992.2, 963.3, and 668.4 cm^{-1}.

The matrix was then irradiated with broad-band UV−visible light ($200 \le \lambda \le 800$ nm). The IR spectrum then witnessed further growth of the bands associated with **2** and, in addition, a disproportionately larger increase in the intensity of a hitherto weak band at 2051.2 cm^{-1}, which must therefore belong to a different photoproduct **3**. **3** was the sole additional product that could be detected under these conditions, but it could be produced only in relatively low yield and then only in the presence of an abundance of both **1** and **2**. Despite repeated attempts to build up the concentration of **3**, it could never be identified by more than the single IR transition at 2051.2 cm^{-1}.

Subsequent experiments sought to investigate how the concentrations of **2** and **3** varied with the conditions of photolysis. Hence, both photoproducts were shown to be stable under visible irradiation ($400 \le \lambda \le 800$ nm), while initial photolysis at wavelengths near 208 or 313 nm reproduced the results of photolysis at λ = ca. 254 nm, albeit with a much reduced yield of **2**. Selective UV photolysis of **2** using a number of different narrow-band interference filters failed to enhance the yield of the second photoproduct **3**, the maximum concentration of which was realized only on protracted broad-band UV irradiation of the deposit.

To facilitate the identification of **2** and **3**, the experiments were repeated with different isotopic versions of **1**, viz. CD_3ReO_3 (**1-*d*₃**) and $^{13}CH_3ReO_3$ (**1-¹³*C***). The effects of photolysis at λ = ca. 254 nm on the IR spectra of the matrices are illustrated in Figures 2 and 3, respectively, and the IR characteristics of the appropriate versions of the photoproduct **2** are recorded in Table 2. Experiments were also carried out with the partially deuterated compound CDH_2ReO_3 (**1-*d***), with more complicated results clearly implying the presence of *more than one* isotopomer of **2**. The IR band at 2051.2 cm^{-1} characterizing the product **3** suffered no significant change of frequency in experiments with **1-*d*₃** or **1-*d*** but shifted to 2003.8 cm^{-1} when **1-¹³*C*** was the source.

4. Discussion

Identification of the Primary Photoproduct 2. The main IR features observed to develop under the action of UV irradiation of matrix-isolated methyltrioxorhenium (**1**) will be shown to arise from the tautomeric carbene derivative $H_2C{=}Re(O)_2OH$ (**2**). The as-

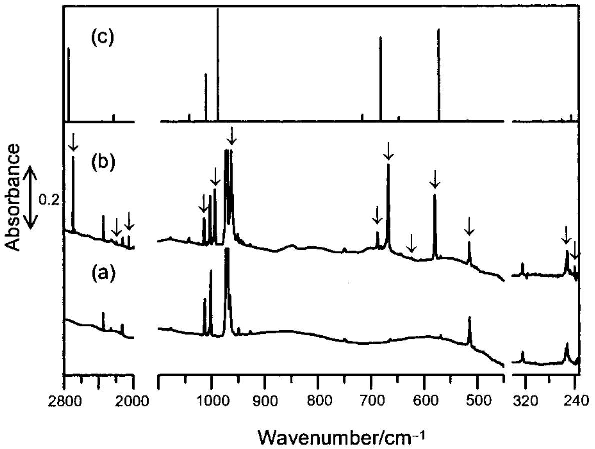

Figure 2. IR spectra of CD_3ReO_3 (**1-*d*$_3$**) isolated in an Ar matrix at ca. 14 K (a) after deposition and (b) following photolysis at λ = ca. 254 nm for 15 min. (c) IR spectrum calculated for the methylidene tautomer $D_2C{=}Re(O)_2OD$ (**2-*d*$_3$**). The arrows indicate bands assigned to **2-*d*$_3$**.

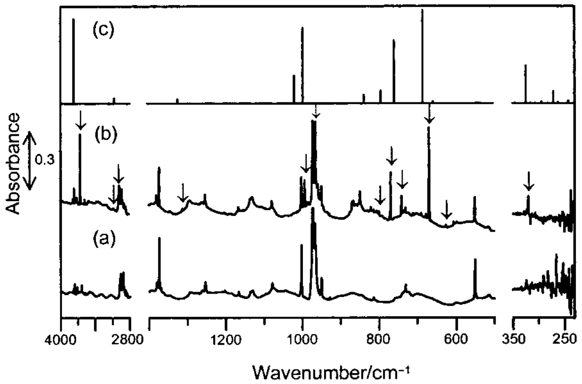

Figure 3. IR spectra of $^{13}CH_3ReO_3$ (**1-^{13}*C***) isolated in an Ar matrix at ca. 14 K (a) after deposition and (b) following photolysis at λ = ca. 254 nm for 15 min. (c) IR spectrum calculated for the methylidene tautomer $H_2{}^{13}C{=}Re(O)_2OH$ (**2-^{13}*C***). The arrows indicate bands assigned to **2-^{13}*C***.

signments will be justified by consideration of the frequencies and D or ^{13}C isotopic shifts of the observed bands, by reference to the vibrational properties anticipated for this molecule by DFT calculations, and by analogy with the vibrational properties of known, related species.

Perhaps the most immediately distinctive feature of **2** is the intense IR absorption at 3650.2 cm^{-1}. This occurs in a region typically associated with ν(OH) vibrations.[25] That it can indeed be assigned to such a mode is supported by the shift to 2694.2 cm^{-1} when **1-*d*$_3$** is the precursor, giving an H/D ratio of 1.3548:1. Photolysis of **1-*d*** was observed to give not one but two bands, one at 3649.5 and the other at 2693.4 cm^{-1}, a result implying that **2** contains just a single OH group. As expected, substitution of ^{13}C causes virtually no change in the frequency of this mode. The presumption that the OH group is bound to the metal center is supported by analogy (i) with the spectrum of gaseous $HOReO_3$ ($DOReO_3$) where ν[O−H(D)] is reported[26] to occur at 3651 (2695) cm^{-1}, so that H/D = 1.3547:1 and (ii) with the frequencies attributed to the ν(OH) mode in other compounds containing an Re−OH fragment, e.g. $Re(OH)(EtC{\equiv}CEt)_3$ (3630 cm^{-1})[27] and Tp*Re(O)(OH)Cl (3500 cm^{-1}; Tp* = hydrotris(3,5-dimethylpyrazol-1-yl)borate).[28]

Three more vibrational fundamentals are expected for an Re−OH fragment, namely, the two δ(OH) modes and the ν(ReO) mode. The intense absorption at 668.4 cm^{-1} is the obvious candidate for the ν(ReO) mode of **2**, its position being little affected by D or ^{13}C substitution (see Table 2). Such a frequency is also close to that reported (682 cm^{-1}) for the analogous mode of $HOReO_3$.[26]

2 appears also to contain an ReO_2 group, as evidenced by the strong IR absorptions appearing at 992.2 and 963.3 cm^{-1}, which show little response to D or ^{13}C substitution and are most plausibly identified with the symmetric and antisymmetric stretching vibrations of such a unit, i.e., $\nu_s(ReO_2)$ and $\nu_{as}(ReO_2)$, respectively. A very similar frequency and intensity pattern is displayed, for example, by the corresponding modes of the following molecules ($\nu_s(ReO_2)$, $\nu_{as}(ReO_2)$ in cm^{-1}): (i) ReO_2F_3, 1024.2, 988.4;[18] (ii) $(CH_3)_3ReO_2$ 1004, 966.[29] The O=Re=O bond angle θ can be estimated roughly from the relative intensities in IR absorption of the two $\nu(ReO_2)$ modes, provided that these can be realistically factored out from the vibrational secular equation.[30] A ratio I_{asym}/I_{sym} of 2.616:1 derived from the measured spectrum implies through eq 1 that θ is about 115°.

$$\frac{I_{asym}}{I_{sym}} = \left(\tan^2\frac{\theta}{2}\right)\frac{m_{Re} + 2m_O\sin^2\frac{\theta}{2}}{m_{Re} + 2m_O\cos^2\frac{\theta}{2}} \qquad (1)$$

Some indication of the reliability of this estimate may be gained from the results of similar calculations as applied to the O=Re=O bond angle in the molecules **1** and $(CH_3)_3ReO_2$. In fact, the values of 114° for **1** and 117° for $(CH_3)_3ReO_2$[29] calculated in this way agree quite well with the best experimental estimates of 113.0(3)[22] and 123(2)°,[29] respectively, afforded by electron-diffraction measurements.

In addition, the presence of an $Re{=}CH_2$ unit is signaled by the bands at 3079.6, 2985.8, 1320.9, and 627.9 cm^{-1}, which we associate with the modes detailed in Table 2. Guidance in the interpretation of these features is to be found in the spectra reported by Margrave et al. for the simple methylene derivatives $M{=}CH_2$, where M = Cr,[17a] Mn,[17b] Co,[17c] Ni,[17d] Cu,[17e] which have been trapped in solid argon matrices following the reaction of the appropriate metal atoms M with diazomethane. By analogy with the corresponding modes of $Co{=}CH_2$,[17c] for example, the bands of **2** at 3079.6 and 2985.8 cm^{-1} can be identified with $\nu_{as}(CH_2)$ and $\nu_s(CH_2)$, respectively (cf. 2979.7 and 2918.0 cm^{-1} for $Co{=}CH_2$[17c]). Confirmation of these assignments is

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(25) Nakamoto, K. *Infrared and Raman Spectra of Inorganic and Coordination Compounds*, 5th ed.; Wiley-Interscience: New York, 1997; Part B.

(26) Beattie, I. R.; Gilson, T. R.; Jones, P. J. *Inorg. Chem.* **1996**, *35*, 1301.

(27) Tahmassebi, S. K.; Conry, R. R.; Mayer, J. M. *J. Am. Chem. Soc.* **1993**, *115*, 7553.

(28) Matano, Y.; Brown, S. N.; Northcutt, T. O.; Mayer, J. M. *Organometallics* **1998**, *17*, 2939.

(29) Haaland, A.; Scherer, W.; Volden, H. V.; Verne, H. P.; Gropen, O.; McGrady, G. S.; Downs, A. J.; Dierker, G.; Herrmann, W. A.; Roesky, P. W.; Geisberger, M. R. *Organometallics* **2000**, *19*, 22.

(30) See, for example: Himmel, H.-J.; Downs, A. J.; Greene, T. M. *J. Am. Chem. Soc.* **2000**, *122*, 922.

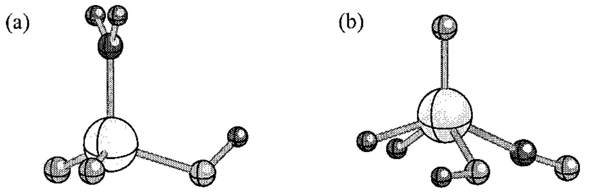
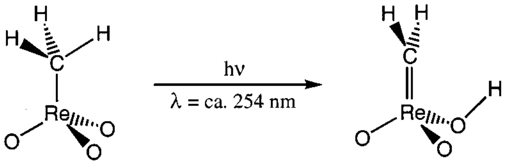


Figure 4. Structures calculated in DFT at the BPW91/LANL2DZ level of theory (a) for $H_2C{=}Re(O)_2OH$ (**2**) and (b) for $H_2Re(CO)(O)OH$ (**3**). The dimensions are as follows (distances in Å, angles in deg): (a) r(Re=C) 1.873, r(Re=O) 1.706, r(Re−O) 1.886, r(C−H) 1.096, r(O−H) 0.972, ∠H−C−H 115.7, ∠O=Re=O 118.5; (b) r(Re−C) 1.977, r(Re−H) 1.664/1.670, r(Re=O) 1.679, r(Re−O) 1.941, r(C−O) 1.164, r(O−H) 0.976, ∠H−Re−H 71.1, ∠O=Re−C 111.3, ∠O=Re−H 107.2, 112.4, ∠O=Re−O 123.8.

provided by the responses to isotopic change. Thus, deuteration causes the first band to shift to 2315.2 cm^{-1} (H/D = 1.3302:1) and the second to 2195.1 cm^{-1} (H/D = 1.3602:1), while the corresponding shifts resulting from replacement of ^{12}C by ^{13}C are −11.2 and −5.6 cm^{-1}. Similarly, the absorption at 1320.9 cm^{-1} can be attributed to the $\delta(CH_2)$ mode of an $Re{=}CH_2$ fragment on the evidence of the effects of deuteration (H/D = 1.3080:1) or enrichment in ^{13}C (giving a shift of −9.1 cm^{-1}). With an H/D ratio of 1.2553:1 and a ^{13}C shift of −2.2 cm^{-1}, the weak band at 627.9 cm^{-1} has all the hallmarks of a CH_2 scissoring motion.

The preceding analysis gives good grounds, therefore, for believing that **2** is the methylidene complex $H_2C{=}Re(O)_2OH$ formed by tautomerization of CH_3ReO_3 (eq 2), there being no other detectable product that tracks its formation. DFT calculations find an equilibrium geometry for such a complex conforming to C_s symmetry (see Figure 4a), with a C=Re−O−H unit defining a plane that bisects the ReO_2 group while being orthogonal to the $Re{=}CH_2$ plane. Rotation of the OH group by 180° afforded another energy minimum but one that lay approximately 15 kJ mol^{-1} higher than **2**. Comparison of the frequencies calculated for the δ(Re−O−H) modes of this higher energy conformer displayed a much poorer agreement with the observed frequencies than did those calculated for **2** (vide infra). Accordingly, this conformer may be discounted. The ∠O=Re=O value of **2** is predicted to be 118.5°, in good agreement with our rough experimental estimate. This isomer lies ca. 89 kJ mol^{-1} higher in energy than **1** and so would appear to be inaccessible under normal thermal conditions. The vibrational frequencies computed from the DFT-based force field for the three isotopomers $H_2{}^{12}C{=}Re(O)_2OH$ (**2**), $D_2{}^{12}C{=}Re(O)_2OD$ (**2-*d*$_3$**), and $H_2{}^{13}C{=}Re(O)_2OH$ (**2-^{13}*C***) are listed, together with the predicted IR intensities, in Table 2. The frequencies, isotopic shifts, and relative intensities simulated in this way are thus found to be in generally excellent agreement with the experimental results. For example, the 36 frequencies measured for the three isotopomers can be matched by calculation with an rms deviation of only 3.16%. With the guidance of the calculated properties, we have succeeded in locating and assigning all but one of the fundamental transitions expected in the range 300−4000 cm^{-1}, the one absentee being predicted to have an intensity no greater than 0.2% of that associated with the strongest band in the spectrum.



1 **2** (2)

It is now possible to account for the four bands observed in the IR spectrum of each isotopomer of **2** that have not been assigned hitherto. For example, the low-frequency transition at 321.2 cm^{-1} can be satisfactorily ascribed to the a″ δ(OH) vibration on the basis of both the frequency (324.3 cm^{-1}) and intensity imputed to this feature by the DFT calculations and of the response to deuteration, which causes a shift to 239.3 cm^{-1} (H/D = 1.3422:1) and to ^{13}C enrichment, which has minimal effect. Assignment of the second δ(OH) mode is rendered difficult by the appearance of no less than three bands in the region 600−800 cm^{-1}. The calculations reveal in fact that there is extensive mixing of the a′ modes δ(OH), $\rho(CH_2)$, and ν(Re=C), reflecting in part the low symmetry of the $H_2C{=}Re(O)_2OH$ molecule. For this reason, the calculations are unable to reproduce well the observed intensity pattern, and no single group vibration—including ν(Re=C)—can be identified with any one of the three bands. The five fundamentals that have then escaped detection (expected near 520 cm^{-1} or in the range 200−300 cm^{-1}) are all predicted to be weak in IR absorption, the problem being compounded in practice by the reduced sensitivity of detection at frequencies <400 cm^{-1}.

As noted previously, photolysis of the partially deuterated molecule **1-*d*** gives rise to not one but two isotopic forms of **2**, which can now be identified by the IR features appearing at 3649.5 and 2693.4 cm^{-1} as $H(D)C{=}Re(O)_2OH$ and $H_2C{=}Re(O)_2OD$, respectively. In the first of these the ν(CH) fundamental is likely to be effectively isolated from the other modes of the molecule and from the effects of Fermi resonance. The resulting frequency of 3033.2 cm^{-1} associated with this isolated mode, ν^{is}(CH), is in fact very close to the mean $\nu(CH_2)$ frequency (3032.7 cm^{-1}), so that Fermi resonance appears to pose little or no problem in this case.[31] In principle, ν^{is}(CH) gives access to relatively precise estimates of the dimensions of the CH_2 group. For example, McKean[31] has established a close linear correlation (eq 3) between ν^{is}(CH) and the C−H bond

$$r_0(\mathrm{C{-}H})\ (\text{Å}) = 1.3982 - 0.0001023[\nu^{is}(\mathrm{CH})]\ (\mathrm{cm}^{-1}) \tag{3}$$

distance r_0(C−H) for a wide range of organic species, including a number of organometallic compounds.[32] In addition, Duncan[33] has observed that a number of compounds containing a $C{=}CH_2$ or $N{=}CH_2$ group conform to approximate relationships (i) between the mean $\nu(CH_2)$ frequency and r_0(C−H) and (ii) between

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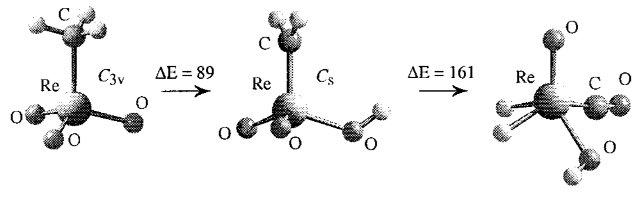
[31] McKean, D. C. *Chem. Soc. Rev.* **1978**, *7*, 399; *Croat. Chem. Acta* **1988**, *61*, 447.

[32] See, for example: McGrady, G. S.; Downs, A. J.; Hamblin, J. M.; McKean, D. C. *Organometallics* **1995**, *14*, 3783. McGrady, G. S.; Downs, A. J.; Bednall, N. C.; McKean, D. C.; Thiel, W.; Jonas, V.; Frenking, G.; Scherer, W. *J. Phys. Chem. A* **1997**, *101*, 1951.

[33] Duncan, J. L. *Spectrochim. Acta* **1970**, *26A*, 429.

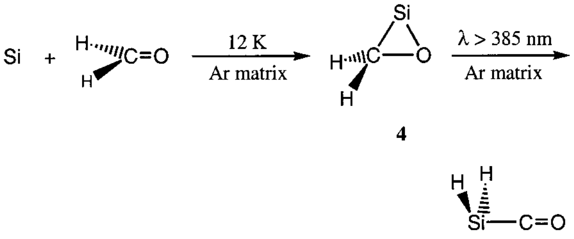
Scheme 1. Interconversion of CH_3ReO_3 (1) to $H_2C{=}Re(O)_2OH$ (2) and Thence to the Possible Carbonyl Derivative $H_2Re(CO)(O)OH$ (3)



1 **2** **3**

the frequency difference $\Delta\nu = \nu_{as}(CH_2) - \nu_s(CH_2)$ and the H−C−H bond angle. Both treatments imply that r_0(C−H) in **2** is 1.088 Å, in fair agreement with the DFT-calculated r_e value of 1.096 Å. With $\Delta\nu = 93.8$ cm^{-1} for **2**, Duncan's correlation[33] leads to an estimate of 122° for ∠H−C−H, although the reliability of this value must be diminished by the nonlinear relationship between $\Delta\nu$ and ∠H−C−H and by the comparative dearth of data points. Other functions of ∠H−C−H include the frequency ratios $\nu_{as}(CH_2)/\nu_{as}(CD_2)$ and $\nu_{as}(^{12}CH_2)/\nu_{as}(^{13}CH_2)$. These give upper and lower limits to the angle in **2** of 140.8 and 104.6°, respectively, reflecting the effects of anharmonicity; in cases such as this, the mean—here 123°—has often been found[34] to approximate closely the true magnitude of the relevant bond angle. These rough experimental estimates may be compared with the value of 115.7° found in the optimum DFT-based geometry.

Identification of the Secondary Photoproduct 3. Although the methylidene derivative $H_2C{=}Re(O)_2OH$ (**2**) is formed almost exclusively when matrix-isolated **1** is photolyzed at wavelengths near 254 nm, exposure to broad-band UV−visible light gives rise to a secondary change. The sole detectable product **3**, formed in relatively low yield under these conditions, could be recognized by no more than a single IR signal at 2051.2 cm^{-1}. The position of this band suggests that **3** contains an Re−CO fragment, an inference substantiated by the minimal change of frequency when **3** is generated from **1-*d*$_3$** or **1-*d*** but by a shift of −47.4 cm^{-1} when it is generated from **1-^{13}*C***. The circumstances clearly preclude positive identification of **3**, but with no sign of any other product it is tempting to conclude that **3** is yet another isomer of **1** formed by a second tautomeric shift. The relatively high frequency of the ν(CO) vibration argues for coordination of the CO to Re in quite a high positive oxidation state (cf. the ν(CO) frequencies (in cm^{-1} and averaged where necessary) for the following Re(I) and Re(III) compounds: $[HRe(CO)_2(\eta^5\text{-}C_5H_5)]^-$ ca. 1810;[35a] $ReH_3(CO)(PMe_2Ph)_3$ 1831;[35b] $ReCl_3(CO)(PMe_2Ph)_3$ 1862[35c]). A possible candidate is then the novel rhenium(V) hydride $H_2Re(CO)(O)OH$, although we cannot of course exclude $Re(CO)(O)OH + H_2$ or $Re(CO)(OH)_2 + H^\bullet$ as alternative products. The formation of $H_2Re(CO)(O)OH$ from $H_2C{=}Re(O)_2OH$ finds an appealing parallel in the matrix photochemistry of siloxiranylidene (**4**): under the action of light having $\lambda > 385$ nm, this rearranges to the carbonyl derivative H_2SiCO (**5**) (eq 4).[36] **2** may well be the precursor to **3**, but it must be stressed that our matrix experiments do not prove this point, in that the conditions affording **3** invariably result in a continued buildup of **2**.



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5 (4)

Further support for the belief that **3** is $H_2Re(CO)(O)OH$ comes from the results of DFT calculations on this system. Hence, a potential energy minimum is found for the molecule at an energy 161 kJ mol^{-1} above the minimum of $H_2C{=}Re(O)_2OH$ (see Scheme 1).

The structure, as illustrated in Figure 4b, approximates to a square-based pyramid with the unique oxide ligand at the apex. The vibrational properties of the molecule are noteworthy on two counts. First, the ν(CO) frequency is calculated to be 2037.6 cm^{-1} and to suffer a ^{13}C shift of −44.5 cm^{-1}, in pleasingly close agreement with the IR properties of **3** (ν(CO) 2051.2 cm^{-1} and ^{13}C shift −47.4 cm^{-1}). Second, the ν(CO) mode is expected to give an IR absorption with an intensity more than 5 times greater than that of any other fundamental. A combination of low concentration, low intensity, and masking by stronger absorptions due to **1** and **2** could then account plausibly enough for the failure to detect any IR bands beyond the one associated with ν(CO).

Reaction Mechanism. The parent molecule **1** being isolated in solid argon at high dilution, the methylidene isomer $H_2C{=}Re(O)_2OH$ (**2**), formed by UV photolysis, must be presumed to originate in a single molecule of **1**. There exist, in principle, three possible routes leading from **1** to **2**, as set out in Scheme 2.

(i) The first pathway involves fission of one of the C−H bonds in the methyl group of **1** with the formation of an $H^\bullet$ atom and the radical $^\bullet CH_2ReO_3$. Recombination of the $H^\bullet$ atom with an oxygen atom of $^\bullet CH_2ReO_3$ could then yield the hydroxo tautomer **2**. Quite apart from the improbability of causing cleavage of a C−H bond under the conditions of our experiments (λ = ca. 254 nm), it is unlikely that the $H^\bullet$ atoms thus formed would be retained exclusively by the matrix cage. On the evidence of previous studies,[37] they are quite mobile in argon matrices and might be expected therefore in large part to migrate away from the site of their formation.

(ii) An alternative requires extraction of one of the hydrogens of the methyl group in **1** by an oxygen atom of the ReO_3 fragment via a four-centered transition state. On the other hand, the structure and spectroscopic properties give no hint of a close H···O approach (shortest distance 3.28(3) Å[22]) or significant vibrational pliability of the parent CH_3ReO_3 molecule, at least in its electronic ground state.[22−24] Although there may be

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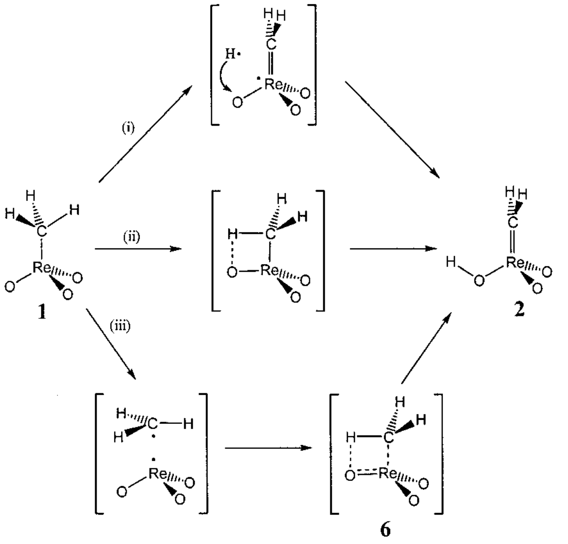
[34] See, for example: Green, D. W.; Ervin, K. M. *J. Mol. Spectrosc.* **1981**, *88*, 51. Kohlmiller, C. K.; Andrews, L. *Inorg. Chem.* **1982**, *21*, 1519.

[35] (a) Yang, G. K.; Bergman, R. G. *J. Am. Chem. Soc.* **1983**, *105*, 6500. (b) Luo, X.-L.; Crabtree, R. H. *J. Am. Chem. Soc.* **1990**, *112*, 6912. (c) Douglas, P. G.; Shaw, B. L. *J. Chem. Soc. A* **1969**, 1491.

[36] Maier, G.; Reisenauer, H. P.; Egenolf, H. *Organometallics* **1999**, *18*, 2155.

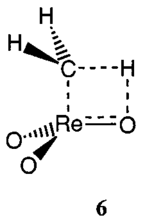
[37] Bondybey, V. E.; Räsänen, M.; Lammers, A. *Annu. Rep. Prog. Chem., Sect. C* **1999**, *95*, 331.

Scheme 2. Possible Mechanisms for the UV Photoconversion of 1 to 2 in an Ar Matrix at ca. 14 K



a significant change of geometry in one or more of its excited states, the relative lack of selectivity with regard to the wavelength of the photolyzing radiation tends to argue against such an *intra*molecular mechanism.

(iii) The most likely route to **2** would therefore seem to involve homolysis of the Re−CH_3 bond, as is reported[14] to be the primary photoprocess occurring on UV irradiation of **1** in solution. The solution studies have indeed shown that the UV absorption of **1** centered at 260 nm corresponds to the lowest energy $a_1 \rightarrow e^*$ LMCT transition and that this leads not only to rupture of the Re−CH_3 bond but also to a weakening of the remaining Re═O bonds. It seems highly probable therefore that photolysis at λ = ca. 254 nm results in the same primary event, namely the formation of $CH_3^\bullet$ and $^\bullet ReO_3$ radicals, irrespective of whether **1** is entrained in a liquid solution or in a solid argon matrix. Rather, is it the subsequent fate of these fragments that changes from one medium to the other. The greater freedom of a liquid solvent enables the photoproducts to migrate away from each other and to interact with the more abundant solvent molecules. In contrast, the rigid cage of argon atoms quenches any surplus energy the photoproducts may possess and opposes their escape. The greater size of the $CH_3^\bullet$ radical makes it much less mobile than the $H^\bullet$ atom under these conditions, so that it is effectively trapped, together with its coproduct $^\bullet ReO_3$, at its matrix birthplace. Recombination then occurs, not to regenerate CH_3ReO_3, but presumably first through coordination of the $CH_3^\bullet$ radical to the $^\bullet ReO_3$ molecule, possibly forming the four-center intermediate **6**, which rearranges with C−H cleavage and H atom transfer to an oxygen atom of the ReO_3 unit, to yield the observed photoproduct H_2C═$Re(O)_2OH$ (**2**).



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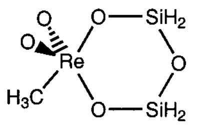
If such a mechanism is correct, there exists the possibility that some of the methyl radicals may escape the matrix cage and so be detectable. Close examination of the infrared spectrum of the deposit following photolysis does reveal a weak band at 611.4 cm^{-1} which is found to have ^{13}C and perdeutero counterparts at 605.7 and 460.1 cm^{-1}, respectively. It is possible that these arise from methyl radicals which are perturbed by the close presence of the ReO_3 fragment. When isolated in an argon matrix, the methyl radical is reported to give rise to bands at 617.4 ($CH_3^\bullet$), 612.5 ($^{13}CH_3^\bullet$) and 452.7 cm^{-1} ($CD_3^\bullet$).[38] It is not surprising that the ReO_3 fragment cannot be detected, as its frequencies would fall close to those of the parent molecule and so are likely to be obscured.

Our experiments therefore provide another dramatic example of how the photochemistry of a compound can change according to whether it is supported in a solid matrix at low temperatures or in a fluid phase. The matrix environment confines photoproducts to the cage in which they are generated and so encourages either regeneration or isomerization of the parent molecule, according to whichever path is opposed by the lower energy barrier. We note similarities here with the chlorine oxides ClOOCl, $ClClO_2$, and ClOClO, the photochemistries of which are also highly medium-dependent.[39]

Significance of the Methylidene Complex 2: Role of 1 in Olefin Metathesis. That CH_3ReO_3 (**1**) isomerizes to H_2C═$Re(O)_2OH$ (**2**) within the constraints of an argon matrix cage at ca. 14 K is a discovery of more than passing interest. This is because (i) CH_3ReO_3 is known to have the capacity to catalyze olefin metathesis and (ii) alkylidene derivatives of transition metals are widely believed to be the key intermediates active in promoting this type of reaction.[10] On the other hand, our DFT calculations indicate that **2** lies ca. 89 kJ mol^{-1} higher in energy than **1**, making it more or less inaccessible to normal thermal activation. It is noteworthy then that **1** is effective in catalyzing olefin metathesis *only* when it is activated by a cocatalyst (e.g., $S_4N_4/AlCl_3$) or by being supported on silica or alumina.[10]

To try to simulate the effect of a silica support, we have extended our DFT calculations to the model cyclic complex $CH_3Re(O)_2[\eta^2\text{-}(OSiH_2)_2O]$ (**7**), the product formed by condensation of CH_3ReO_3 with the disilanol $[H_2Si(OH)]_2O$. These show that the tautomeric H atom transfer occurs to an Re−O−Si bridging oxygen atom, with a consequent severing of an Re−O bond and opening of the ring, in preference to a terminal Re═O unit. The resulting methylidene species H_2C═$Re(O)_2(\eta^1\text{-}OSiH_2)(\mu_2\text{-}O)SiH_2OH$ (**8**) lies at an energy of only ca. 48 kJ mol^{-1} above **7**. In contrast, the cyclic methylidene species H_2C═$Re(O)(OH)[\eta^2\text{-}(OSiH_2)_2O]$ (**9**) lies at an



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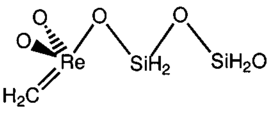

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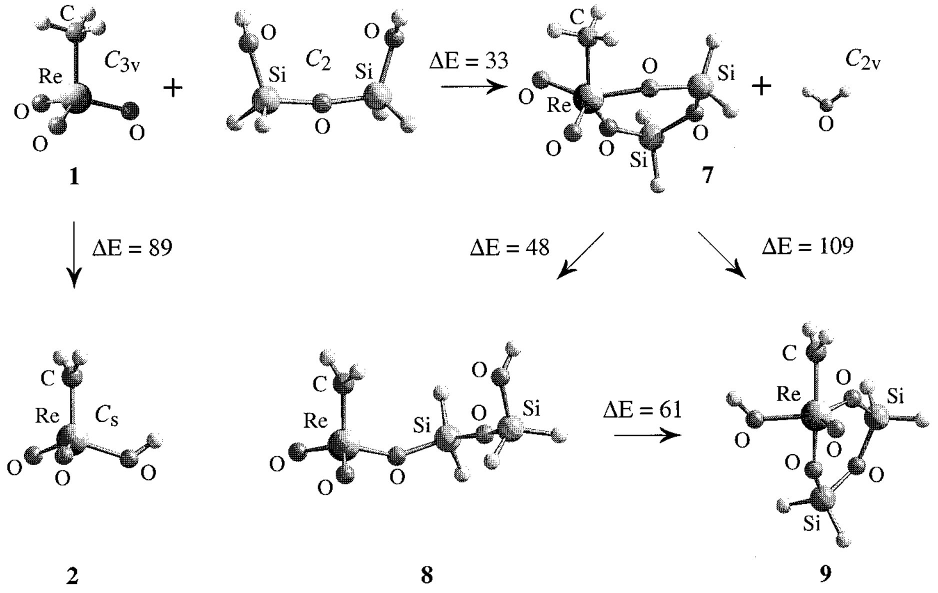
Scheme 3. Tautomerization of CH_3ReO_3 (1) to $H_2C{=}Re(O)_2OH$ (2) vs Condensation with the Disilanol $[H_2Si(OH)]_2O$ To Form $CH_3Re(O)_2[\eta^2\text{-}(OSiH_2)_2O]$ (7) and Then Tautomerization of This to either $H_2C{=}Re(O)_2(\eta^1\text{-}OSiH_2)(\mu_2\text{-}O)SiH_2OH$ (8) or $H_2C{=}Re(O)(OH)[\eta^2\text{-}(OSiH_2)_2O]$ (9)



energy of 109 kJ mol^{-1} above **7** (see Scheme 3). Hence, the thermodynamic energy barrier to tautomerization has effectively been reduced by the tethering of the CH_3ReO_3 to the siloxane fragment by ca. 41 kJ mol^{-1}. This alternative H atom transfer to the Re−O−Si bridge is likely to afford a more realistic mechanism for formation of a methylidene intermediate and hence for catalysis of olefin metathesis, when CH_3ReO_3 is supported on silica. In other words, it appears to be the function of the support or the cocatalyst to offer a site for H atom transfer that is energetically more attractive than one of the oxide ligands of unsupported CH_3ReO_3.

The molecule **8** corresponds to a global minimum on the potential surface with no imaginary vibrational frequencies; no local minima were found for alternative configurations involving, for example, an internal O−H···O bond. In fact, a literature search suggests that such units are not favored in −Si(OH)−O−Si(OH)− fragments, since the relatively large Si−O−Si angle sets the relevant oxygen atoms too far apart. All disilanols of the type $R_2(HO)Si{-}O{-}Si(OH)R_2$ investigated so far with small ligands R (= Et, Pr, Ph, etc.) exhibit O−Si···Si−O angles near 60°; for systems with larger R groups (e.g., substituted phenyl substituents) angles near 180 or 0° are observed.[40] Further studies are needed to investigate the effects of replacing the hydrogen ligands in **8** by other ligands which may help to simulate more closely the properties of a silica surface where the OH groups are known to be much more acidic than those in simple silanols. Preliminary calculations indicate that replacing hydrogen by OMe makes little difference to the energies of the reactions represented by Scheme 3. Other calculations are in progress to explore the condensation products of more elaborate silanols, but these are demanding of computer time and still leave open numerous questions: e.g., the effects of operating in the condensed as opposed to the gas phase, or just how many Si−O−Re bridges it is realistic to budget for.[40]

Extending these studies to the UV matrix photochemistry of other alkyloxorhenium compounds, viz. $(CH_3)_3ReO_2$, $(CH_3)_4ReO$, and $C_2H_5ReO_3$, has shown that formation of an alkylidene derivative of rhenium is a common, but not necessarily exclusive, feature. It can be brought about, moreover, in ways other than isomerization, as will be revealed in future reports.[42]

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